THE SOL-GEL SYNTHESIS OF ANTI-STOKES LUMINESCENT GLASS MATERIALS

ANNE CHRISTINE NEWPORT

A thesis submitted in partial fulfilment of the
requirements of the University of Greenwich for the
degree of Doctor of Philosophy

October 2000

Abstract:

The materials commonly used and the synthetic problems that arise in the field of transparent glass materials with anti-Stokes luminescent properties are described. The literature has shown that rare earth doped oxide glasses, whilst chemically durable and relatively easy to manufacture, have weak anti-Stokes emissions, whereas rare earth doped fluoride materials have considerably improved anti-Stokes luminescence but are less chemically stable and highly reactive. Recent interest in glass ceramics has proposed alternative matrices with the advantages of both fluoride and oxide host materials. These materials consist of rare earth doped fluoride crystallites in an oxide glass matrix giving the emission characteristics of a fluoride crystal protected in the stable surroundings of an oxide matrix. The work in this thesis initially set out to build on these lattices but broadened in the light of the findings outlined below.

The synthesis of silica based glasses using sol-gel techniques is covered thoroughly in this work and the incorporation of various cations into these matrices has been investigated. Amongst the cations added to silica sol-gel reactions are titania, alumina and yttrium. Their reactions and the factors that promote transparent and crystallite-free samples have been reported and discussed. Several advances in this field have been made including a detailed investigation into the synthesis and properties of yttrium based sol-gel reactions which have not been previously reported.

The incorporation of fluorine into these materials has also been described and the various problems encountered have been examined. Several novel methods of incorporating fluoride ions into silica lattices are proposed and examined. It was found that in the presence of fluoride ions, the rare earth dopants form crystallites within the glass matrix. In a similar way, it was found that glass ceramics also formed when a titanium alkoxide is incorporated with fluoride ions during the sol-gel synthesis of these lattices. In these cases it was shown that TiO_2 in the form of anatase or rutile crystallites can be grown in the glass matrix. Moreover the phase of TiO_2 grown can be easily controlled by choice of annealing temperature and firing times. Distinct anti-Stokes emissions are produced depending upon the form of titania present. These new materials are reported and discussed.

Contents

Chapter 1: Introduction

Chapter 2: Experimental methodology, techniques and analysis

Chapter 3: Synthesis of standard samples

3a – Basic silica matrices

3b – Synthesis of anti-Stokes powder samples

4c – The incorporation of zirconium into silica matrices

Chapter 5: The synthesis of rare earth containing silica gels

Chapter 6: The incorporation of sodium, calcium and chromium ions into silica matrices

Chapter 7: The synthesis of multi-cation gels

Chapter 8: Fluorination of sol-gel matrices

Chapter 9: Luminescence studies

Chapter 10: Conclusions and further work

Chapter 1 – Introduction

1.1 Introduction to Inorganic Glasses

Inorganic glasses are amongst the most ancient of materials[1]. They were originally considered to be purely beautiful items, like the gemstones. However they were soon to be seen in the better Egyptian and Roman households in the form of bottles and drinking glasses.

Early nineteenth century science led to the study of materials and by varying the compositions required for optical properties and chemical durability many new glass compositions were discovered.

In this century due to changing developments in the electrical and electronic industries, the study of glass systems still continues. In the early part of the century, filament lamps and thermionic valves required specialist glasses. These were followed by sodium and mercury vapour street lamps. Modern research is largely concerned with glass-ceramics[2], semi-conducting glasses[3] and glass lasers[4].

Perhaps the most fundamental point about glass science is that glass formation is not completely understood. Add to this the nature of the material itself and we are faced with a vast fascinating field to be studied. Nearly any liquid will form a glass if cooled to a sufficiently low temperature without the occurrence of crystallisation[5]. The question is not whether a liquid is a glass former but how fast it must be cooled to avoid crystallisation.

Two of the most important factors to be taken into consideration when synthesising a glass are:

- The determination of the glass forming region, i.e.: the composition of a material at which it can become a glass when cooled from a significantly high temperature at a suitable cooling rate.
- The stability of the glass within this region.

Most inorganic elements and compounds, when melted, become liquids that may have a viscosity close to that of water. Upon cooling, rapid crystallisation occurs at the melting point. However some materials melt to form very viscous liquids. If such a liquid is cooled to just below its freezing point then it will slowly crystallise. However if the temperature is reduced at such a rate as to avoid crystallisation, then the liquid will become more viscous until it appears to be a solid, i.e.: a glass.

As mentioned earlier[5] most liquids are capable of glass formation. The crystallisation process needs the formation of nuclei to proceed and as most liquids can be held in a state where nucleation is suppressed, they can become glassy if only for a short time under extreme conditions. Hence glasses are regarded as thermodynamically unstable materials and will eventually change to other amorphous configurations that have lower free energies until they reach equilibrium or until crystallisation occurs[5]. This change can be very quick or may take centuries depending on the material in question.

We can expect to find that the structure of a glass is similar to that of a liquid. Indeed, the X-ray diffraction patterns of a glass show an amorphous structure with broad bands rather than the sharp peaks typical of crystalline compounds. This indicates a lack of long-range order. Often a material can only form as a glass when present in very small quantities; this is mainly due to the rate of cooling being dependent upon the volume involved.

There are many types of glasses[1]. Perhaps the most well known are the oxide glasses which are used in everyday household items such as light bulbs and kitchen ware. There are two types of metal oxides that can be used in glass synthesis: network formers and network modifiers. The elements which form network formers and conditional glass formers are shown in figure 1.1[1].

B **C** **N** O
Al Si P S
Sc **Ti** V Cr
Ga Ge As **Se**
Y Zr Nb **Mo**
In Sn Sb **Te**
RE Hf Ta **W**
Tl Pb **Bi** Po

Underlined elements: simple glass formers
Elements in bold: conditional glass formers

RE = rare earth element

Figure 1.1: Elements that form simple and conditional glass formers when in an oxidic matrix.

Network formers. These will readily form glasses and are used as the primary components of oxide glasses[1]. They are as follows: silicon dioxide, germanium dioxide, boron trioxide, phosphorus pentoxide and arsenic trioxide. Antimony trioxide is also classed as a network former but requires very rapid cooling. These metal oxides may be melted with other metal oxides to form glasses usually with a limit on the amount of additional material.

Conditional glass formers: These metal oxides will not form glasses by themselves but can do so when melted with a suitable quantity of other oxides. Their bonding is part covalent and part ionic. This group of metal oxides is larger than that of the network formers and includes tellurium dioxide, selenium dioxide, aluminium oxide and gallium oxide.

Other types of glasses include hydrogen bonded glasses which consist of salts such as potassium bisulphate and aqueous ammonium hydroxide.

Halide glasses are a type that have recently generated much interest due to their highly ionic nature[1]. Until recently the only generally accepted halide glass formers were beryllium fluoride and zinc chloride. However it has been discovered that a wide range of compositions can be synthesised based on zirconium fluoride[1].

Glass-ceramics are also very important materials covered in this field. Perhaps one of the best descriptions of glass-ceramics was by P. W. McMillan in 1964: "Many glass-ceramics are made by the controlled devitrification of glasses in which microphase separation has occurred"[6]. In these samples the formation of crystallites usually occurs during heat treatment producing fine crystallites (often so small that the final product can appear transparent) within an amorphous matrix.

Crystallisation or devitrification was a serious problem in the manufacture of glass until about 40 years ago when S. D. Stookey at Corning Glass Works discovered that glass ceramics formed by internal nucleation and crystal growth had superior mechanical properties to glass itself[7]. This lead to the manufacture of improved cooking ware and machinable materials.

The diffraction patterns of glasses often show very broad bands based where strong lines occur in the equivalent crystalline patterns. This implies that glasses are composed of linkages of small crystals or crystallites and the observed broadening of the diffraction patterns can be associated with particle size broadening[1].

1.1.1 Zachariasen's Rule (Random Network Hypothesis).

Glasses have been viewed as three dimensional arrays in which the structure is not repeated at regular intervals. In the case of oxide glasses it has been suggested that these arrays consist of networks of oxygen polyhedra, see table 1.1.

The internal energy of a glass matrix is only slightly higher than that of its crystalline form. For this to occur the glass matrix must consist of polyhedra of the same type found in the crystalline equivalent joined in a similar way. However the relative orientation is different: in a crystalline form the adjacent polyhedra are orientated in a constant manner and in a glassy matrix the orientation is random.

Table 1.1: Types of polyhedra which make up glass networks

Number of oxygens surrounding atom (A)	Type of polyhedra
3	Triangle
4	Tetrahedron
6	Octahedron

Zachariasen[8] applied several rules to account for this and the structure of glass matrices:

1. no oxygen atom may be linked to more than two atoms (A)
2. the number of oxygen atoms surrounding atoms (A) must be small
3. the oxygen polyhedra share corners with each other, not edges or faces
4. if a network is three dimensional, at least three corners of each polyhedron must be shared.

Following this it can be seen that oxides of the formula A_2O and AO cannot satisfy these rules and hence cannot form glasses. This can be seen in practice with the oxides of groups I and II not forming glasses.

A modification of Zachariasen's rules is given as[9]:

A glass is formed if:

1. the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles and
2. these share only corners with each other
3. Some oxygen bonds are linked to only two cations and do not form further bonds with any other cations.

An additional rule was proposed by Smekal in 1951[10].

If a material is to form a network it must have mixed bonding, for example:

- Inorganic materials such as SiO_2, Al_2O_3 and B_2O_3 are all network formers. This is due to their partially covalent – partially ionic bonding.
- Elements such as selenium and sulphur form network structures based on chains. This is enabled because although the chains themselves are covalently bonded, van der Waals force exist between the chains.
- Organic molecules can also form networks in a similar manner if they have van der Waals forces linking their covalently bonded molecules.

The role of the network modifier:

Network modifiers are cations that disrupt the glass network. Often they fit in between the network linkages. Cations such as the group I and II metal ions are often randomly distributed through the network, located near certain anions or groups of anions.

An example of a glass: $A_mB_nO_x$ where m and n are not generally integers. B represents a network former and A a network modifier. A could fit into the gaps in the network. For a tetrahedron based glass network: n will lie between 0.33 and 0.5.

1.1.2 Methods of Synthesising Amorphous Materials

Several methods have been developed for the synthesis of glasses and other amorphous materials. A more detailed description is given in "Physics of Amorphous Materials" by S. R. Elliot[11]. Methods include:

- Thermal Evaporation.

This is one of the most widely used methods for the synthesis of amorphous thin films. See figure 1.2.

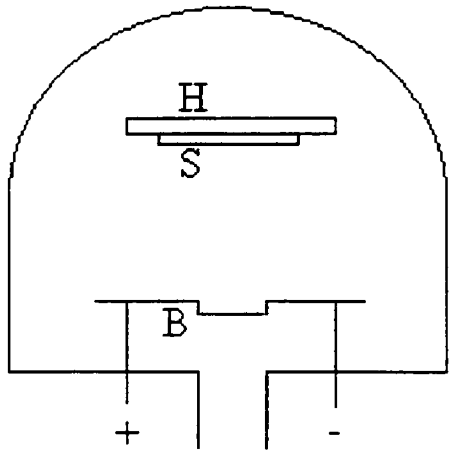


Figure 1.2: Diagram of thermal evaporation method of synthesising amorphous thin films.

The material to be heated is placed in a boat (B) through which a current is passed. The evaporated material is then collected on a substrate (S) attached to a heater (H). This takes place in a chamber under high vacuum. This method is suitable for compounds with low melting points. In the case of samples with higher melting points, vaporisation is achieved, this may be caused by bombardment with high energy electrons from an electron gun placed in the chamber.

- Sputtering

This is a more complicated method than thermal evaporation but is far more flexible. See figure 1.3.

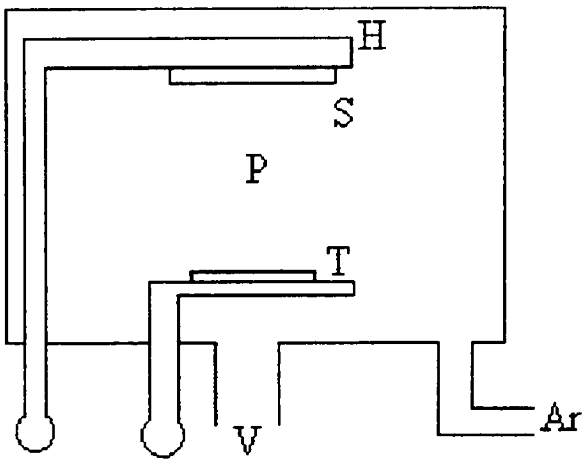


Figure 1.3: Diagram showing the set-up for the synthesis of thin films of amorphous materials using sputtering techniques.

The bombardment of a target (T) by energetic ions from a low pressure plasma (P) causes the erosion of the target material (either as indiviual atoms or as clusters of atoms) and the deposition of this material onto a substrate (S).

There are several factors that cause variations in the films produced by sputtering that are also influential in the synthesis of samples produced by thermal evaporation. These include: gas pressure, ratio of partial pressures of reactive gas to inert gas, radio frequency (RF) power applied to target and voltage applied to target or substrate.

- Glow Discharge Decomposition

This is another method for the synthesis of amorphous thin films. It was first published in 1975[12]. Like sputtering, this technique relies on the production of a plasma in a low pressure gas. However, instead of ions from the plasma ejecting material from a target, chemical decomposition of the gas occurs which leaves a solid film on a substrate placed within the plasma.

Factors which influence the film characteristics include gas pressure and temperature, ratio of reactant gas to carrier gas, gas flow rate, chamber geometry, method of producing plasma and substrate charge and temperature.

- Chemical Vapour Deposition

This is a similar method to gas discharge. Both depend on the decomposition of a gas. However chemical vapour deposition relies on thermal energy for decomposition. A RF field (if required) is used to heat the substrate upon which the vapour decomposes. Temperatures in the order of 700°C are used.

- Melt Quenching

This is the oldest method of synthesising glasses and amorphous materials. It involves the cooling of a molten material or melt very quickly. As the melt is rapidly cooled the viscosity of the liquid increases until it hardens completely. It is essential that the rate of cooling must be fast enough so that crystallisation will not occur. Crystallisation is more thermodynamically stable than the formation of an amorphous phase and hence will dominate if allowed to occur.

Perhaps the simplest description of a glass is given by Elliott[11]: "A glass is simply a supercooled liquid in which no time for crystal growth has been allowed". Modern views do not accept the description of a glass as a supercooled liquid and the process of glass formation is complicated. A detailed examination of the formation of a glass is given by Elliott[11].

The cooling rate and the composition of a material are two of the most important factors involved in the synthesis of glassy materials by melt quenching. Certain materials produce glasses readily whereas others prove more difficult to change to the glassy state. Methods of melt quenching[11]:

1. A common method for producing glasses from materials which readily form glasses (for example: B_2O_3) involves placing the material to be melted in a sealed ampoule under vacuum (10^{-6} Torr). The ampoule is then placed in an oven where it is rocked or rotated at a sufficient temperature for the components to melt and interact. The ampoule is then cooled (or quenched) by either turning the oven off or, should a faster rate be required, placing the ampoule in a liquid such that the heat is conducted away from the ampoule as fast as possible. Factors influencing this method include: temperature of oven, rate of cooling, volume and thickness of the wall of the ampoule.
2. Certain materials require faster cooling rates. For example: metals. Faster cooling rates require more dramatic methods of dealing with materials:
   - Small droplets of molten material are projected at a copper sheet. The copper sheet takes the heat away from the melt at a rate in the region of 10^5 Ks^{-1} which is considerably quicker than the methods employed above. This method is known as "splat cooling".

  - A related technique involves the hammering of small droplets of the melt between a metal hammer and a copper sheet. This gives slightly faster rates but produces samples of very thin pieces of glass with irregular areas.
  - Both of the above described methods are not suitable for producing usable samples. However there are variations that do. These are "melt spinning" and "melt extraction" techniques. Both involve a spinning copper disc. The former uses a jet of molten material hitting the disc to produce ribbons of amorphous material. The latter involves the removal of molten material from a reservoir by the disc producing fine wires of material. In both cases cooling rates of between 10^6 and 10^8 Ks^{-1} can be achieved.

- Desiccation of gels formed by sol-gel methods.

This method is covered in the following section and forms the major part of this thesis. See section 1.2.

- Electrolytic deposition[11]

Certain materials can be deposited on a cathode in an amorphous film. For example: amorphous germanium films can be produced by the electrolysis of germanium chloride in glycol. This method has drawbacks of contamination by the solution and the reaction products.

- Chemical Reaction[11]

There are a few limited situations where a precipitate can be formed from a chemical reaction which has amorphous properties. For example: when hydrogen sulphide gas is passed through a solution of As_2O_3 in diluted hydrochloric acid, the product, As_2S_3, is amorphous.

- Irradiation[11]

When a crystalline solid is bombarded with high energy ionising particles, it can sometimes cause enough structural damage to make it amorphous. Sometimes this can be localised in the case of the neutron bombardment of silica or the complete transformation of whole crystals as in the case of select organic materials.

- Shock Waves[11]

When exposed to an explosive shock wave with pressures of the order of 600 kbar and temperatures of the order of 1200°C some structures can be rendered amorphous. This is often put down to localised melting.

- Shear[11]

Vigorous grinding can render certain crystalline materials amorphous. For example: quartz and the arsenic chalcogenides.

1.2 Sol-gel Synthesis

1.2.1 General Introduction to Sol-gel Synthesis

A thorough review of sol-gel synthesis has been detailed by C. J. Brinker and G. W. Shearer[13] which covers all aspects and reactions involved in the methodolgy and their uses. Other useful reviews are by E. J. A. Pope et al[14] and in "Structure and Bonding" Volume 77[15]. Most of the information in this section is from these references unless otherwise noted.

The sol-gel technique is a methodology used to synthesize materials with greater homogeneity than that expected by other methods. Materials produced by this method can usually be sintered and densified at lower temperatures than normally used in the conventional processing of these same materials. The method can be used to produce powders and films of crystalline and amorphous materials and also of monoliths of amorphous material (monoliths are generally defined as single pieces of materials where the smallest dimension is greater than a few millimeters[13]).

It is now necessary to present a few definitions applicable to sol-gel science:

- **Colloid**: A suspension of particles which are small enough for gravitational forces to be negligible. Sizes range from 1-1000nm and the particles exhibit Brownian Motion. Any interaction between the particles is due to surface charges.
- **Sol**: A colloid of solid particles in a liquid medium.
- **Hydrolysis**: In the case of sol-gel chemistry, hydrolysis is a substitution reaction where a cation exchanges a ligand for a hydroxyl group. This often results in the liberation of an alcohol.
- **Condensation**: In the sol-gel reaction scheme this occurs when the particulates of a sol react together to liberate a solvent molecule or a water molecule and link themselves together to form a larger molecule. When this continues to occur, the process is known as polymerisation. This in turn will lead to gelation where the polymers spread throughout the whole system and a solid matrix develops with the liquid held in it.

See figure 1.4 for an overview of the sol-gel process showing the various products that can be synthesised by this methodology.

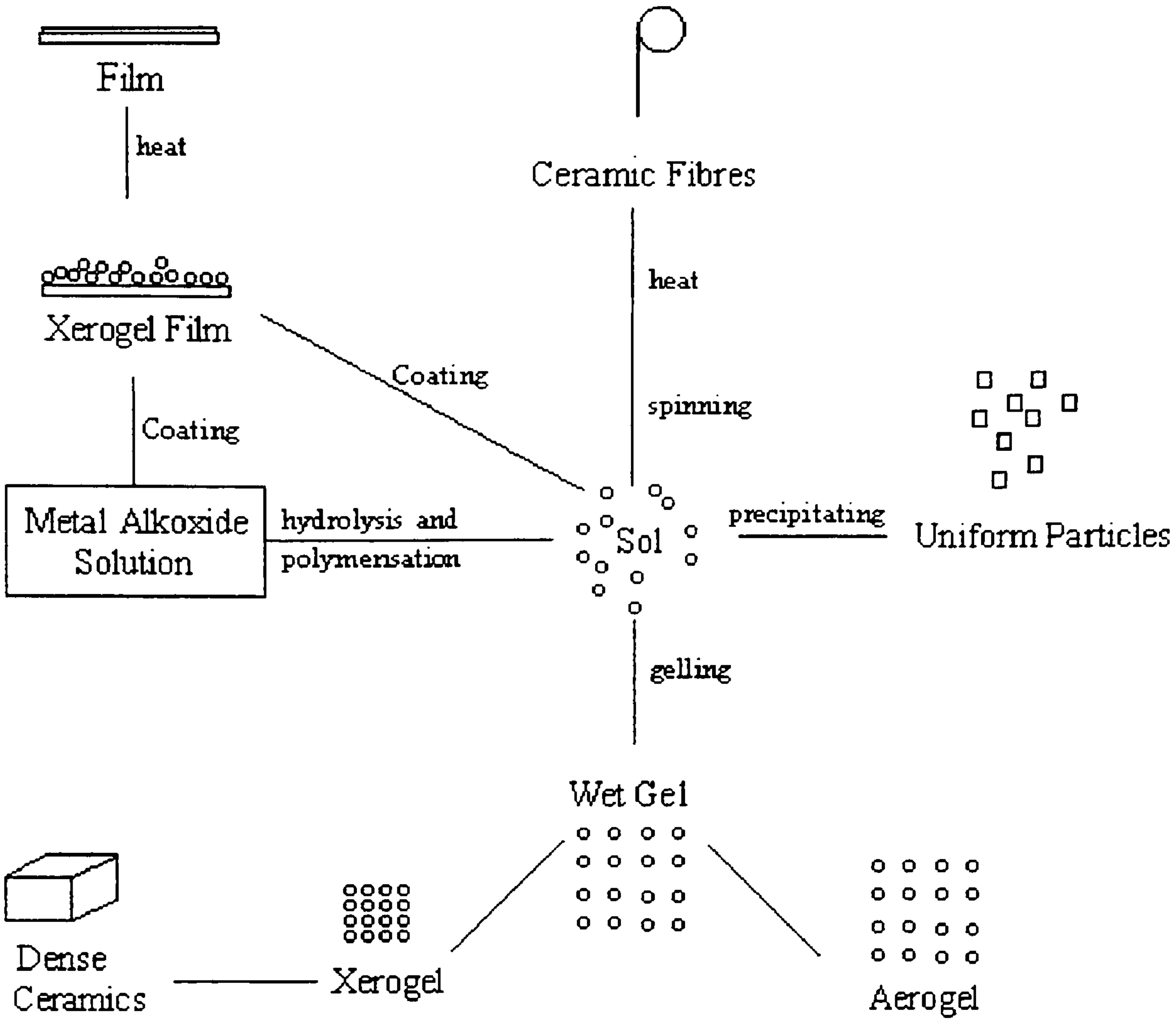
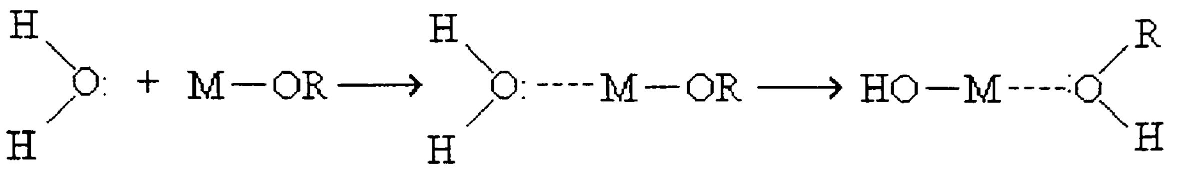


Figure 1.4: An overview of the sol-gel process[14].

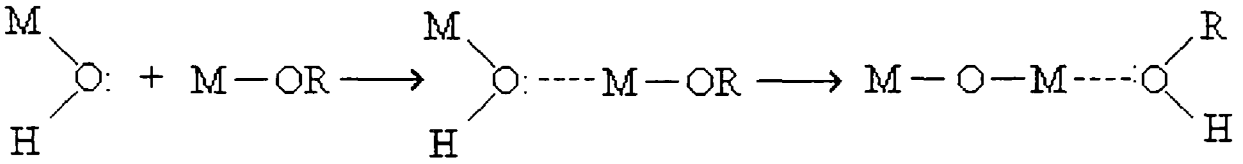
Sol-gel processes generally involve metal alkoxides. This is due to their reactivity which can be controlled using suitable reagents and also to the alkoxide ligand being a good leaving group. Early studies involved the SiO_2-Al_2O_3 system and considerable work has been done with this system especially with silica as its chemistry is ideal for sol-gel type reactions. Silicon alkoxides react slowly producing strong matrices without requiring additional reagents to prolong the hydrolysis[13]. The reactions which generally take place in the sol-gel chemistry of silicon are summarised in equations 1.1 and 1.2.

Equation 1.1 shows the general reaction scheme for the hydrolysis of silicon alkoxide.



$$\longrightarrow \mathrm{MOH} + \mathrm{ROH}$$ Eqn 1.1

Equation 1.2 shows the condensation process of partially hydrolysed molecules.



$$\longrightarrow \mathrm{MOM} + \mathrm{ROH}$$ Eqn 1.2

This condensation can continue until a network is formed.

Metal alkoxides are very reactive with water due the electronegative character of the alkoxide groups. This is especially the case for transition metal alkoxides such as titanium and zirconium. These examples are stabilised in their highest oxidation states by the alkoxide groups and make the metal very susceptible to nucleophilic attack from the water. Hence sol-gel reactions involving transition metal alkoxides require great control over the addition of water, otherwise they react too quickly and become completely hydrolysed. If this occurs it will produce oxide precipitates rather than stable sols.

Particulate sols, which will form particulate gels consisting of individual species, will form in a predominantly aqueous enviroment, whereas polymeric sols will form in a non aqueous solvent such as ethanol. Under extreme conditions, such as a high pH or in the presence of a high fluoride concentration, particulate gels will also be formed in organic solvents. However particulate gels may be redispersed as they are only held together by van der Waals forces and may be induced to polymerise depending on the conditions.

1.2.2 Catalysis of Sol-gel Reactions[13]

Acids and bases can be introduced to the initial mixture to catalyse the hydrolysis and condensation reactions. When basic conditions are present more complete hydrolysis can occur and hence increase the likelihood of a particulate gel being produced[16]. However in the presence of acid, polymeric gels will be produced. Under very low pH this has one drawback: long chains will be formed with little crosslinking between them due to limited hydrolysis promoted by the acidic conditions. This leads to a network of tangled chains rather than a three dimensional network which would be stronger. For example: a pH of 2-3 is best for gelation of silicon alkoxides as at higher values the condensation reaction becomes reversible. At lower pH values the network formation becomes more linear due to the lower water content – under these conditions cross linking does not occur.

1.2.3 Influences on Sol-gel Reactions[13]

Steric effects may also play a part in determining the rate of the hydrolysis reaction. As the alkyl group of the alkoxide increases in size the rate of hydrolysis will be slowed and gelation times will increase. Alcohol exchange is something else that can occur depending on the alkoxide groups present and on the alcohol solvent used. Although little is known about this process, it seems that a large primary alkoxide group will exchange for a small alcohol group; this is thought to be based on steric effects. This will have an effect throughout the entire reaction. The choice of alkyl group can also influence whether a particulate gel will form or not. For example: the addition of aluminium tri-sec-butoxide to ethanol will result in a particulate gel whereas the addition of this alkoxide to 2-methylbutan-2-ol will give a transparent gel.

Gelation time also decreases with increasing alkoxide to solvent ratio due to the increasing reaction rate as more molecules are able to come into contact with each other and link up. Additionally the choice of solvent must also be determined by the nature of the precursor. Silicon alkoxides, for example: tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS), are not miscible with water. Hence a solvent is required that is both miscible with water and TEOS. This is normally an alcohol such as ethanol

The physical nature of the resulting materials will also be affected by the size of the substituents involved. As the size increases then the pore size will increase but the pore size will decrease as the polarisability of the ageing solvent decreases.

1.2.4 Drying Control Chemical Additives[13]

Addition of drying control chemical additives (DCCAs) can have an effect on the rate of the hydrolysis of the precursors. Most commonly used DCCAs include dimethylformamide (DMF) and glycerol. These additives may also have an effect on the pore network of the gels. However they can sometimes be difficult to remove especially in the case of glycerol as its decomposition temperature is a little too high in comparison with the sintering temperature of the sample and the final product may contain trapped carbon and organic molecules. It is always ideal to have non-network forming compounds that are easy to remove from the finished product, hence sometimes it is preferable to use an inorganic salt such as a nitrate rather than a bulky alkoxide group as a starting material for the same reason.

1.2.5 Order of Precursor Addition[13]

When synthesising multicomponent gels, the order of addition is important, for example: when synthesising a gel consisting of silicon and titanium ions, it is necessary to hydrolyse the silicon alkoxide prior to the addition of the titanium alkoxide as its rate of hydrolysis is much slower than that of the titanium alkoxide. This gives greater homogeneity in the final product.

1.2.6 Ageing and the Processes That Occur During Ageing[13]

Ageing is the process that occurs when a gel is left to stand in its mother liquor after gelation for a considerable time. It is sometimes ideal to age samples at slightly elevated temperatures such as 120°C. Several processes may occur during ageing:

Condensation can still occur between polymers even though the initial network is set up as small areas. These may condense as they move closer together. There is always some remaining sol caught up within the network which can attach itself to the network.

Other processes include dissolution of the gel into the solvent and reprecipitation of particulates. Phase transformations may occur within the solids and liquid phases. Generally leaving a gel to age for a week or two will strengthen the network. In the case of certain systems ageing will bring about the formation of undesired phases.

Syneresis will also occur during ageing. This is where the gel begins to shrink expelling its pore liquids. It arises from the attraction between the neighbouring polymers and the formation of bonds across the pores. It may be controlled by the addition of electrolytes.

Syneresis may also occur during firing as the gel shrinks due to capillary forces pulling the pores together promoting bond formation within the pores. A gel that has been aged for a considerable period of time will become quite strong and as a result will not shrink as much as a gel that has not been aged. Sometimes unaged gels will collapse under the pressure of the capillary forces and become fine powders. The smaller the pores in a gel the greater the capillary forces. Ageing can also be beneficial here due to the coarsening processes which is where parts of the gel are dissolved leaving large pores and eliminating the pores by bond formation within them.

1.2.7 Drying of Gel Samples[13]

At a certain stage during the drying process and in the absence of crystallisation the gels may appear opaque. It is believed that this is due to the pores scattering light, although no definite explanation has been proposed for this. These gels become transparent again upon sintering.

With certain systems crystallisation can occur upon drying. Carbonates can be formed from atmospheric carbon dioxide; this is quite common in the case of sodium containing gels. Upon sintering the carbonates may not decompose prior to closure and this causes bloating and blackening due to residual carbon.

DCCAs are useful when drying a sample as they link with the surface of the gel via hydrogen bonding and protect it from attack. However they do have drawbacks. The use of formamide as a DCCA will attract water from the atmosphere causing cracking to occur in the final product. Glycerol will also produce its own carbonates upon heating. Both DCCAs are also difficult to remove from the final matrix when heated.

The dried product that is of most interest in the synthesis of glasses is the xerogel. This is simply a gel that has been dried by allowing its pore liquid to evaporate slowly, leaving behind a porous transparent matrix. Other products can be produced such as aerogels which consist of a high percentage of air or other gases. The xerogel is the simplest monolith and leads to glass formation.

1.2.8 Sintering of Gel Products[13]

After drying the gels may be heated. This will remove any residual organics trapped within the network. If a pore free sample is required the sample must be sintered, that is heated to a sufficient temperature to collapse the pores by increasing the surface energy. Some gels may crystallise upon heating. In amorphous systems, atoms may transport themselves around the matrix, in this case the process is called viscous sintering.

To produce glasses by sol-gel it is often necessary to heat the samples to just above the glass transition temperature and hence not melt the sample. This eliminated any problems associated with contamination from crucibles etc. which would normally occur with high temperature firings. For example: silica glass formation normally takes place at 1300-1400°C, but with sol-gel methods, silica glass samples can be fired at temperatures between 600 and 800°C.

As temperature control is important, it is often necessary to increase the furnace temperature at a very slow rate to allow residual organics to evaporate off and to allow the pores to close slowly. It is also advisable to allow the furnace to remain at set temperatures for long periods of time to allow by-products to escape before raising the temperature. The temperatures at which different organic residues and other substances evaporate off can be determined by thermal analysis.

1.2.9 Sol-gel Chemistry of Metal Cations[13]

Transition metals are hydrolysed by a similar mechanism to that of silicon but as mentioned above require greater control in the hydrolysis step. This can be achieved by chemical modification using alcohol, acid, base or a chelating agent to retard the reaction rates. The modified ligand should be less easily removed than the alkoxide ligand during the hydrolysis and hence it reduces the number of sites available for hydrolysis. Steric inhibition of hydrolysis also occurs due to the presence of the chelating ligand. This will promote the formation of polymers rather than monomers and promote gelation. Common ligands used for this purpose are alcohol, chloride, acetate, acetylacetonate and diethylenetriamine. If a mixed system is required, for example: zirconia-silica, then a chelating agent can be used to slow down the reactivity of the zirconium alkoxide to match that of the silicon alkoxide, and hence promote the formation of the Zr-O-Si bonds.

Hydrolysis of metal cations involves setting up certain equilibria depending on the pH of the system. In water the following equilibria occur:

$$[M(OH)_2]^{z+} \leftrightarrow [M\text{-}OH]^{(z-1)+} + H^+ \leftrightarrow [M{=}O]^{(z-2)+} + 2H^+$$

Aquo ligand   Hydroxo ligand   Oxo ligand

Eqn 1.3

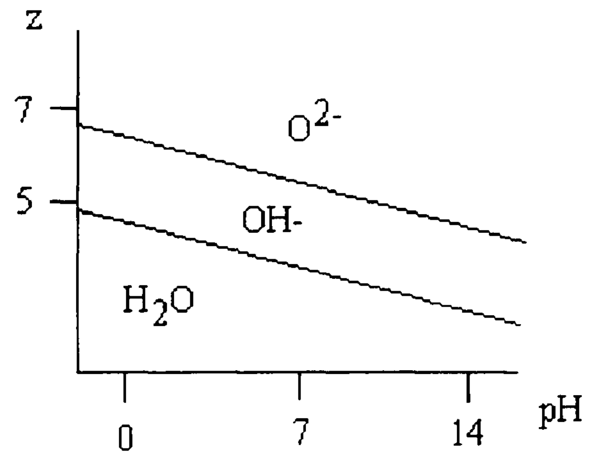


Figure1.5: Diagram showing relationship between pH and charge for metal cations[17]

The nature of the metal cations depends on the charge *z* on the metal ion, the co-ordination number N, the electronegativity of the metal and the pH of the solution. Typical effects of pH and charge can be demonstrated by the pH/charge relationship diagram[17] shown in figure 1.5. It should be noted that there are exceptions that do not fit into this diagram, for example: Fe^{3+} and Mn^{7+} and that this model does not allow for precise electronic structures and changes in co-ordination of reactant species. Further details are given by J. Livage et al[17] and C. J. Brinker and G. W. Scherer[13].

The sol-gel chemistry of transition metal alkoxides has not been studied as thoroughly as silicon and hence there is not an exclusive knowledge of it. Transition metals do behave very differently to silicon as they have a variety of co-ordination numbers and lower electronegativities. Therefore they are much more reactive toward hydrolysis. Precipitation of hydroxide and oxohydroxide species will readily occur upon hydrolysis unless some form of chemical control is used. A review of hydrolysis kinetics is given by Bartlett et al[16].

1.2.10 Sol-gel Chemistry of Zirconium

With zirconium use of chelating agents has become standard methodology with respect to sol-gel chemistry. Use of acetylacetonate (acac) appears to be a popular method of controlling the hydrolysis and is employed by many authors[19,20]. Organic acids have also been chosen such as acetic[21] and formic acid. Zirconium can be stabilised by using 2-methoxyethanol[22] as a solvent requiring no additional hydrolysis control. If DMF, which has a high pH, is used as a DCCA then it is necessary to use acac or some other form of hydrolysis control[23] to prevent precipitation unless 2-methoxyethanol is used as a solvent. If a multi-component gel is required containing silicon and the silicon alkoxide precursor is prehydrolysed properly then a stabilising agent is not required. However the ratio of silicon to water in the prehydrolysis stage will affect the outcome greatly[24]. The addition of a small percentage (about 5 molar %) zirconium to a silica based system will increase the hydrolysis rate of the silica slightly as well[16].

When heating above 400°C, samples containing a high percentage of zirconium will often crystallise to form tetragonal or cubic zirconia phases. At temperatures above 750°C monoclinic zirconia formation occurs. Gels containing small percentages (less than 20molar %) zirconia will form tetragonal zirconia at temperatures around 850 °C[19]. Hence as yet completely amorphous glasses containing zirconia have not been synthesised by this route. Sol-gel does allow for the successful synthesis of zirconia-containing glass-ceramics which can contain a large number of nucleation sites[20]. A review of the kinetics of the crystallisation of such samples is given by Sanchez-Soto[25].

It has also been noted by several authors that upon firing samples containing zirconium they turn black[26]. Explanations suggest that residual organics are being trapped within the matrix; however this problem has not been mentioned by other authors, indeed some claim to have never encountered the problem[22].

1.2.11 Sol-gel Chemistry of Titanium

Titanium containing materials synthesised by sol-gel methods have many applications including optical waveguides and colouration. Barium titanate ceramics, which have useful ferroelectric properties, may also be sucessfully synthesised by sol-gel techniques[16]. The addition of up to 0.3molar % barium oxide to a titanate sample may cause it to change its electronic character to become superconducting. Introduction of 0.2 molar percent of a lanthanide to titanate samples inhibits crystallisation, lowers the refractive index and increases porosity[27].

The titanium cation is of a similar reactivity compared to the zirconium cation and also has a similar chemistry although it has a smaller co-ordination number. When an amorphous gel of titanium oxide is made by sol-gel methods and heated, it crystallises to produce anatase and rutile which are the two readily formed phases of titania. The phase produced depends on the pH of the system prior to gelation.

Combination of up to 30 molar % titania with silica will result in an amorphous and continuous phase up to 850°C; at higher temperatures bloating will occur along with crystallisation[28]. The resulting glass will have a higher refractive index than that of a pure silica sample.

1.2.12 Sol-gel Chemistry of Aluminium

Along with silicon, aluminium has been studied in great detail. Similar techniques used in zirconium sol-gel chemistry can be adopted for aluminium reactions, for example, use of chelating agents and organic acids to stabilise the hydrolysis of the alkoxides.

Formation of glasses containing aluminium is difficult in both standard and sol-gel techniques as there are many stable phases of aluminates, alumino-silicates and silicates making samples prone to phase separation[29]. However there are many applications for these glasses predominantly in optics, dielectrics and catalysis.

The commonly used precursor for aluminium sol-gel is aluminium tri-sec-butoxide with isopropanol as a solvent. Chelating agents most regularly used are acetic acid[29], acac, and EAA[30]. Reaction conditions affect the final product quite strongly: pH, solvent, precursor concentrations and water concentration all affect which phases will be present in the sintered gel, whether the starting material is an alkoxide or an inorganic salt or whether a multi-component gel is required[30]. Glycolethers such as isopropylalcohol can also be used as stabilising agents[31].

As aluminium alkoxides are very reactive towards hydrolysis, when combined with silicates, the silicon alkoxide must always be prehydrolysed or an opaque gel will result[29].

One of the most satisfactory methods of synthesising aluminate gels was developed by Yoldas, involving the hydrolysis of aluminium alkoxide in alcohol with a large excess of water. Addition of a mineral acid produces a stable sol which could easily be gelled by evaporation of the solvents given transparent xerogels.

When aged, aluminate sols tend to yield precipitates of aluminium oxide especially bayerite rich phases.

1.2.13 Sol-gel Chemistry of Sodium

Sodium is one of the most difficult elements to work with in sol-gel chemistry. When in combination with silicon alkoxides upon drying sodium carbonates are formed with atmospheric carbon dioxide. In addition it will form sodium rich phases prior to drying[16]. Being univalent it is not a network former and hence its incorporation into a matrix will be limited if a strong glass is required.

It is well known that sodium ions complex with the crown ether 18C6 ($C_{12}H_{24}O_6$) in a very stable way giving a species that is more stable than the uncomplexed ion in alcohol. As the sodium ion is highly soluble in alcoholic solvents it does not always join up with the matrix and when drying occurs it can precipitate out in the pores in the form of a salt.

The use of the crown ether enables some bonding between the complex and the other components of the matrix due to the attractive forces[32].

1.2.14 Sol-gel Chemistry of Rare Earth Metal Cations

As a large proportion of this thesis has been dedicated to the sol-gel chemistry of the rare earth metal cations, it is appropriate to introduce these here. Quantities greater than 5-7 molar % rare earth oxide cannot be incorporated into a sol-gel system if a transparent glass is to be synthesised[33]. This is normally acceptable as dopant quantities of rare earth metal cations are often much lower than this value for luminescent materials.

The rare earth elements are often added to a matrix as nitrates[34], acetates[35], chlorides[36] and alkoxides[37]. The alkoxides have to be synthesised in situ as once they have precipitated out they become insoluble in alcohol and other organic solvents. Addition of nitrates will bring about phase separation but with small quantities such as a few molar percent it does not severely effect the overall structure and can only be detected if the sample is analysed thoroughly.

Yttrium and the rare earth elements may be stabilised against segregation using chelating agents such as acac, diethylenetriamine (DETA)[38] and ethylacetoacetate (EAA)[39]. Rapid hydrolysis may also be slowed using these reagents. Films and powders of the superconductors $YBa_2Cu_3O_7$ using EAA as a stabiliser have been successfully made by Katayama and Sekine[40]. The solubility of alkoxides and acetates may also be improved by reaction with the above mentioned reagents to produce a soluble complex.

In the literature to date there has only been one reference to a gel synthesised using sol-gel methods that contains rare earth ions as the sole cations[38]. This utilises DETA as a chelating agent and 2-methoxyethanol as a solvent where yttrium will react with both through a proposed elaborate reaction mechanism and produce a gel matrix. Unfortunately the authors make no mention of any work carried out on the system post-gelation such as drying and sintering. It is known that yttrium acetate has a low solubility in 2-methoxyethanol at room temperature and the authors have shown that by addition of DETA it will dissolve more readily. By comparison, in the synthesis of multi-component gels, Walck and Pantano[43] dissolved yttrium acetate in boiling 2-methoxyethanol to form a stable complex which could be successfully used as a precursor in a sol-gel reaction.

1.2.15 Fluoridation of Sol-gel Products

Fluoridation of sol-gel products can take several forms:

- Introduction of fluorine into the matrix upon initial mixing of the gels, either as hydrogen fluoride or another fluoride salt such as ammonium fluoride.
- Introduction of fluorine after gelation by allowing the gel to absorb fluoride ions present in its surrounding environment.

The introduction of fluoride into the matrix prior to gelation generally speeds up the hydrolysis of alkoxides present often to an unacceptable rate, producing opaque gels or even precipitates with silica[42]. The use of stabilising agents is necessary here sometimes even when using silicon alkoxides.

Post-gelation introduction of fluoride ions has been attempted by various routes depending on the size and nature of the sample. A semi-dried xerogel may be placed in an alcoholic solution containing fluoride ions. The gel will generally soak up the solution and the fluoride ions can become bonded to the surface of the gel. As changes can be made to the syneresis of gels when they are placed in a different solvent to their mother liquor this method has to be considered carefully. However it is the safer and cheaper option of the post-gelation treatments.

The second method involves the firing of the dried gels in an atmosphere containing ammonium bifluoride and other gases. Control here is limited as complete fluorination of the oxide gel usually results and hence require revitrification to produce a glass as in the general synthesis of fluoride glasses.

Rabinovich[43] covered the incorporation of fluoride ions into a silica matrix in his 1988 patent. He set an upper limit on the fluoride concentration at 5% body weight due to the limited solubility of fluoride ions in the silica matrix. However he states that percentages greater than 0.01% would have an effect on the final sintered product. The main aim of the patent is to demonstrate that the incorporation of fluoride ions into a silica matrix prevents bubbling and bloating of monoliths during heating, hence producing glasses of high optical purity.

Introduction to Anti-Stokes Luminescence

1.3.1 What is Luminescence?

Luminescence is defined as the absorption of electromagnetic energy followed by the subsequent emission of energy of a different wavelength. The emission is usually at a lower energy than that absorbed, i.e.: at a longer wavelength. This is known as a Stokes' process from Stokes' law which states that the emission of light from a luminophore is at a lower energy than that which is absorbed[44].

The absorption of a specific amount of energy by an ion will cause it to be promoted to an excited state, from which it will lose a small amount of energy to the host body and fall to a lower state from which it can radiate the rest of its energy as light.

Generally the absorbing ion, which is referred to as an activator, gains its energy in one of two ways: either by absorbing the radiation directly itself or by absorbing it by transfer from the host.

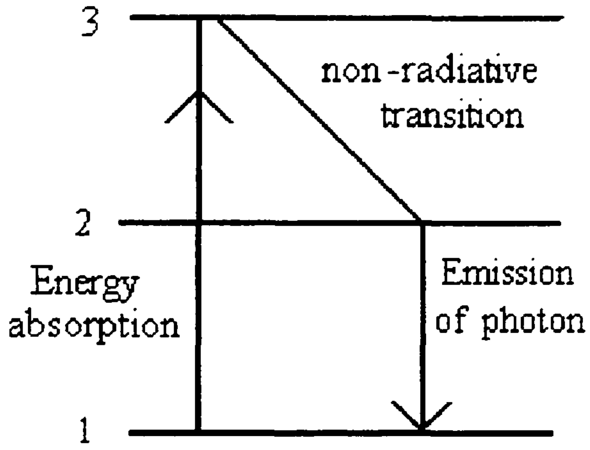


Figure 1.6. General mechanism Scheme for a Luminescent Process

Anti-Stokes, or upconversion, processes are possible where the emitted radiation is of a higher energy than that absorbed. Many mechanisms have been proposed for this type of luminescence and are dependant upon many factors. In general, however, several photons are absorbed for each one emitted.

Perhaps the simplest way of regarding an anti-Stokes' process is to consider an ion having a series of energy levels which are fairly evenly spaced. As the ion absorbs a photon it enters an intermediate excited state, and will enter further excited states upon each absorption until it can absorb no more and the energy is released as a single photon of higher energy than those absorbed.

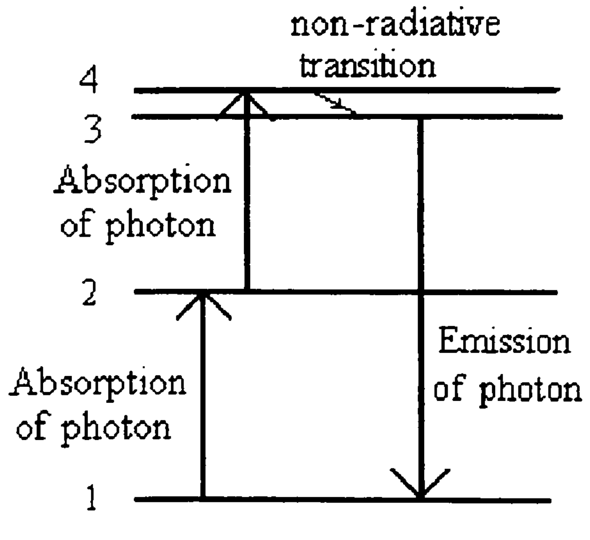


Figure 1.7. General Mechanism for Anti-Stokes Process

1.3.2 Luminescent Processes in Glass

Although other ions have luminescent properties, the rare earths have advantages for optoelectrical uses, because their 4f electrons are partly shielded from perturbation by electromagnetic fields. This makes their absorption and emission spectra less affected by external influence, ie: from surrounding atoms[45]. In glasses two effects generally influence the spectra of the rare earths:

- Stark splitting where any degeneracy is removed by the influence of non-uniform distribution of electric fields caused by the bonding of the host atoms around the activator ions.
- Broadening of the energy levels which can be caused by temperature dependant phonon broadening. The latter occurs throughout the glass and causes perturbation of the energy levels by the host lattice electric fields which are independent of temperature and is an inhomogenous effect.

1.3.3. Applications of Multi-Photon Rare Earth Processes in Glasses

There are many applications of multi-photon rare earth processes in glass matrices. The main ones are as follows:

Fibre Optics[46,47]
Optical waveguides[46]
Optical amplifiers[46]
Lasers[48,49,50]

A three dimensional imaging system has also been demonstrated[51].

1.3.4 Influences on Anti-Stokes Processes:

The intermediate excited states must have long enough lifetimes so that while the ion is absorbing another photon the energy is not lost to the host lattice or as Stokes' luminescence[52]. The host matrix has a large influence on the lifetime of the activators excited states - if the bonding around the activator is covalent then the lifetimes will be short as the ion readily loses energy to the host. Hence a highly ionic system is preferable due to its limited host-activator interaction[52]. This has been demonstrated by many authors, who have shown that the ideal host is based on fluorides[5354]. Rare earth based fluorides are the best as these cations can be easily substituted by rare earth activators due to the latter atoms having similar chemical and physical properties such as size and charge.

Heavy metal fluoride glasses have been studied in considerable depth and are ideal hosts for anti-Stokes processes[55]. It has been shown that they can be as efficient as crystalline fluoride powders and they have a good solubility for rare earth ions[56]. Normally they are based around zirconium and barium fluorides and require many components to produce a suitable glassy network as fluoride materials are very poor glass formers[57]. The influence of different network modifiers such as alkali earth ions can have a noticeable effect on the luminescence efficiency due to the changing symmetry of the fluoride ions around the rare earth[58]. Trivalent europium is often used as a probe to determine the environment which is influencing the rare earth, for example: analysis using Raman spectroscopy[57] and luminescent emission[60,61].

Table 1.2 Lifetimes Of Intermediate Energy States in Various Glass Hosts[58]:

	lifetimes:(ms)		
Glass	thulium $^3H_4$	thulium $^3F_4$	holmium $^5I_7$
aluminate	4.84	0.16	8.21
gallate	6.0	0.21	7.23
silicate	0.41	0.04	0.32
germanate	1.18	0.17	0.36
fluorophosphate	1.46	0.39	5.60
fluoride	18.3	1.38	26.7

Table 1.3. Phonon Energies of Various Glass Hosts[58]. The smaller the value the less interaction between host and activator.

Glass host	phonon energy (cm^{-1})
fluoride	540
gallate	660
aluminate	800
germanate	820
vanadate	850
fluorophosphate	1050
silicate	1050
phosphate	1300
borate	1350

Other factors that influence the emission of anti-Stoke luminescence include the intensity of the incident radiation, the presence of any auxiliary radiation and the energy gap between the transitions. Whether a pulsed source or a continuous wave source is used will also influence the resulting mechanism.

1.3.5 Anti-Stokes Mechanisms

Upconversion may occur with quite a few activators. It has been most studied in erbium[62], thulium[63], holmium[64] and praseodymium[65], and it has also been successfully demonstrated in neodymium[66], chromium[67], samarium[68] and gadolinium[69] doped systems. Erbium is probably the most useful rare earth ion for fibre optic doping as it has a strong absorption around 1550nm which falls within an important telecommunications window. This makes it also suitable for amplification. Additionally it can emit energy from this absorption as visible light. Erbium doped materials can have laser properties and are now very much comparable to neodymium doped glass laser systems[50]. The upconversion luminescence of these glasses is widely studied because of the availability of high powered laser diodes with emission wavelengths of 800nm and 980nm which may be used as excitation sources.

Not only do erbium doped systems have good practical uses, they are also of great academic interest because of the many mechanisms that can occur within these systems. However several of these mechanisms can be mistaken for each other as they have many similarities and it has been shown that several processes can occur simultaneously[70].

In erbium doped systems optimum concentrations will vary depending on the excitation wavelength employed and the mechanism involved. For example, if a quantum counter scheme is in use which involves the sequential absorption of infrared photons of 1550nm by a single ion to a state where it can emit visible light then if the concentration of erbium ions exceeds 1 mole % then concentration quenching will occur[62]. By comparison, a second process involving migration of excitation through the matrix until it collects at a single ion and hence becomes converted to visible light will become optimum at 10 mole percent[62].

Quantum counting or excited state absorption (ESA) is a common mechanism in erbium doped systems where the ions absorb energy to reach an excited state from which point, after a non radiative transition to a slightly lower level, they absorb further quanta of energy and are prompted to the higher energy states[71], see figure 1.7. This is often regarded as the simplest example of an anti-Stokes luminescence mechanism. Direct step-wise absorptions rarely occur as some of the energy is always lost to the matrix in non radiative processes. With its complicated energy level system there are many proposed mechanisms of this type for erbium ions and there are many papers published on the subject.

A second common mechanism is energy transfer where two separate ions in the ground state absorb a photon of energy each and are both excited to the next excited state[72]. By transfer of energy, one ion will become excited further to another level after the deexcitation of the other which will return to the ground state, see figure 1.8. This is sometimes referred to as the APTE effect (Addition de photon par Transferts d'Energie)[72,73]. However it can often be mistaken for other effects due to similarities and simultaneous existence within the same system.

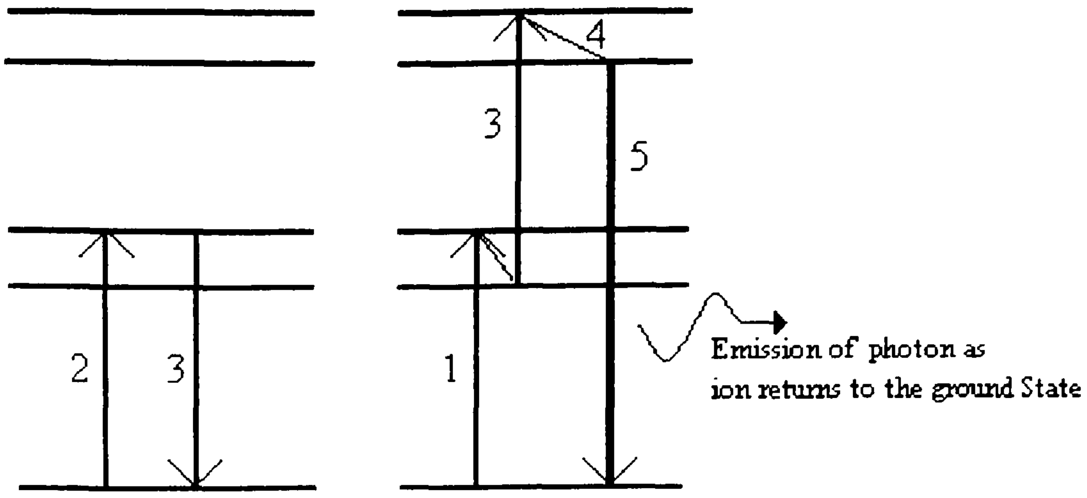


Figure 1.8. Scheme showing energy transfer between two ions to produce anti-Stokes luminescence. A photon is absorbed by both ions (1 and 2). Energy is transferred from one ion to another (3) leaving one ion in an excited state and the other in its ground state. The ion in the excited state loses a small amount of energy in a non-radiative transition (4) followed by the emission of a photon as the ion returns to its ground state (5).

Photon Avalanche effects have been shown in erbium doped fluoride glasses[74]. This process was first discovered in Pr^{3+} doped crystals in 1979[75]. A laser source is selected to match the energy of a transition which is not from the ground state although a small amount of absorption from the ground state is necessary for the process to begin. This will produce a population in the second metastable state from which the laser excitation may promote the ion into the emitting state from which the energy may be exchanged with a second ion which is in the ground state promoting it to its second state. A second energy transfer can occur from the third energy level to excite a ground state ions to its second level as well. With both processes possible, the initial excitation of one ion can cause two others to become excited to a level where they can absorb the incident radiation effectively and reach the higher radiative level resulting in a total of three ions in this state. Naturally these three can then go on and excite other ions in a similar manner. See figure 1.9

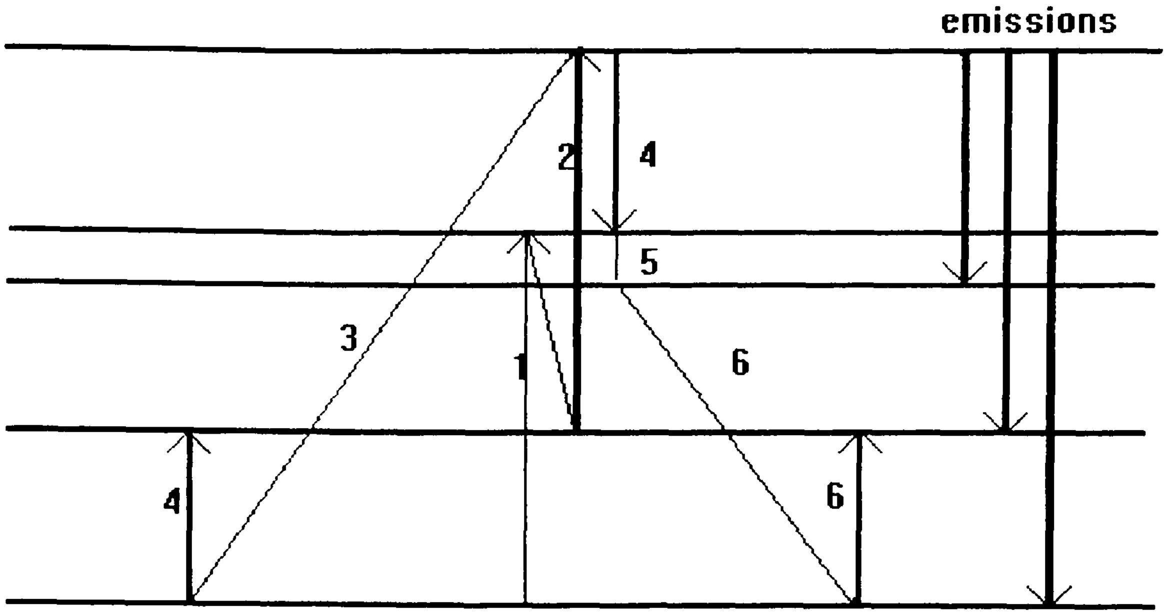


Figure 1.9. Scheme showing photon avalanche process involving three ions. 1)Weak excitation to 4th energy level followed by relaxation to the 2nd level. 2) Laser excitation to 5th level. 3)Energy transfer to second ion in ground state promoting it to 2nd level where it can be excited from the laser excitation. 4) The first ion falls to the 4th level. 5)Then it relaxes to the 3rd level. 6) It transfers energy with a third ion which is then promoted to the second level, leaving the initial ion in the second level.

The incident radiation must exceed a certain limit for emission to occur, otherwise the population of the second level may fall to the ground state through the natural decay of that energy level. For the erbium system, a laser of 579.2nm pumps the transition between $^4S_{3/2}$ and $^4F_{9/2}$, from which point they can reach the $^4I_{11/2}$ level by cross-relaxation and non-radiative decay. As the $^4I_{11/2}$ to $^2G_{9/2}$ absorption coincides with the laser frequency, the ion is promoted into this upper state from which the photon avalanche can occur.

In several anti-Stokes systems a sensitiser may be used in addition to the activator[72, 76]. It's role is to absorb energy of the correct wavelength and transfer it efficiently to the activator. Ytterbium may be used as sensitiser for erbium and this may be demonstrated using the Successive Energy Transfer Model. This is demonstrated in figure 1.10.

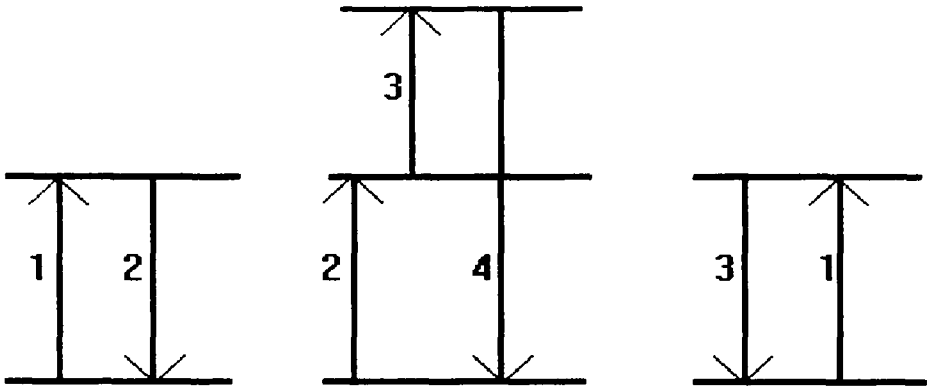


Figure 1.10. Scheme showing the successive energy transfer model between ytterbium and erbium. Two sensitiser ions absorb photons of energy (1). These are transferred to the activatot ion causing the sensitisers to return to the ground state and promoting the activator up two excited states (2 and 3). The activator then releases the energy as a photon (4). There are often non-radiative transitions in a mechanism of this type but are omitted in this schematic for simplification.

Certain conditions are required for efficient sensitisation:

- The sensitiser S should have a large absorption cross-section (or line strength) for IR radiation, hence having a large concentration of excited ions available.
- The probability of S to activator A transfer should be reasonably high, but not too efficient or all the energy will be transferred and a necessary second transfer will not occur. In fluoride glasses the lifetime of the ytterbium ion is much more reduced than in oxide glasses and hence the efficiency is increased.
- The highest level should have a high radiative efficiency.
- The activator concentration should be large enough to get a visible emission but small enough to prevent concentration quenching.
- Transitions must agree with the selection rules
- For a more efficient process the energy levels of S and A should match so the transfer of energy may be considered resonant.

The use of ytterbium as a sensitiser for erbium was first reported in 1966 by Auzel for the $NaWO_3$:Er^{3+},Yb^{3+} system[72] and the energy level diagram is shown in figure 1.11. As the concentration of ytterbium is increased relative to the host material (for example YF_3)[77], more photons are transferred to the erbium ions causing an increase in the green emission. At between 20 and 40 % ytterbium the intensity reaches a maximum. If the concentration is increased beyond this maximum then this intensity will begin to decrease hence ytterbium fluoride alone is unsuitable as a host, see figures 1.12 and 1.13 (the erbium concentration is fixed at 3 mole % in this example). This is due to interaction between the ytterbium and erbium ions which causes the Er^{3+} to give part of its energy to ytterbium and lose its emission[78].

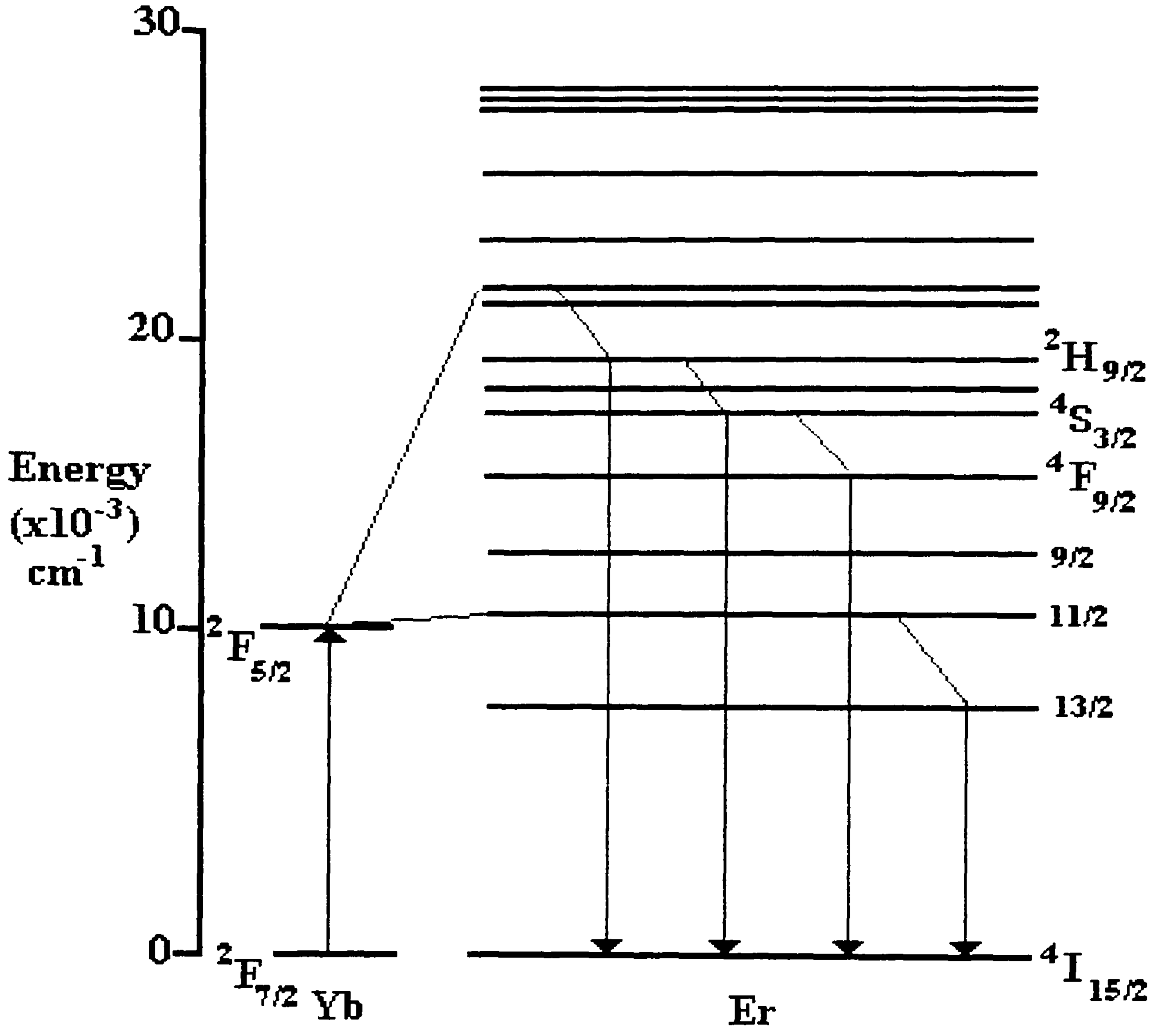


Figure 1.11: Energy level diagram of trivalent ytterbium and erbium ions showing examples of excitation mechanisms which produce anti-Stokes' luminescence.

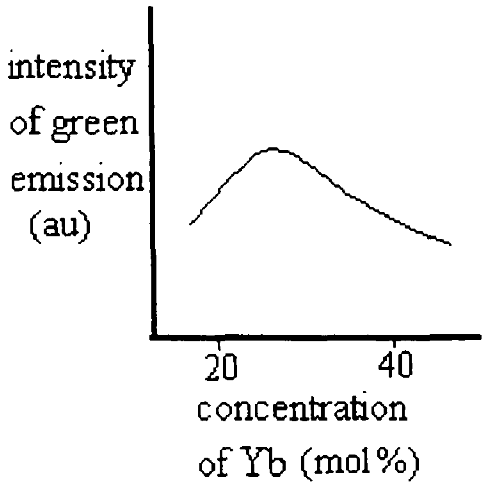


Figure 1.12. Variation of Intensity with Ytterbium concentration

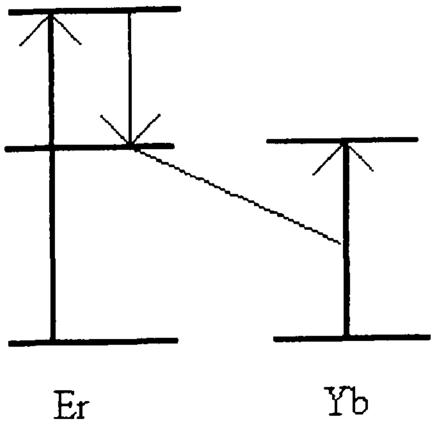


Figure 1.13. Energy Level Scheme Showing Energy loss from Er^{3+} to Yb^{3+}

A similar study of the erbium ion concentration has been carried out[72]. If the erbium concentration is increased from zero the number of luminescent centres will also increase. Maximum green luminescence is reached at between 2 and 4 % followed by a sharp decrease, see figures 1.14 and 1.15 (in this example the ytterbium concentration is fixed at 20 mole percent). This is caused by nearby ions interacting with each other. As the ions get closer the strength and the number of interactions increases very quickly[77].

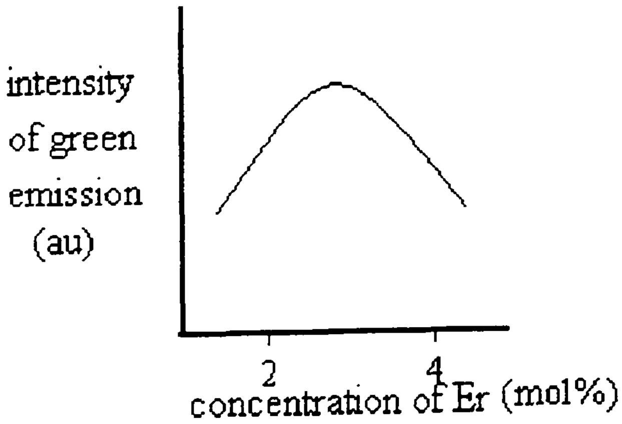


Figure 1.14. Variation of Intensity with Erbium Concentration:

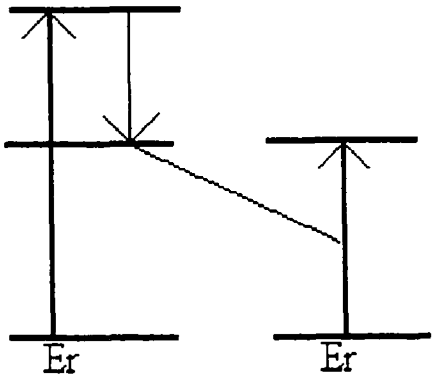


Figure 1.15. Energy Level Diagram Showing Energy Loss From Er^{3+} to Er^{3+}:

For red emission such interactions are much weaker and as ytterbium and erbium concentrations increase then the red/green ratio will increase.

A similar effect is caused by the type of host matrix chosen. In highly ionic systems the green emission is dominant, this will decrease as the system becomes more covalent due to increased interactions between the activator ions. This can be demonstrated by the fact that yttrium oxide doped with ytterbium and erbium will have a red emission[79], whereas with yttrium fluoride the emission will be green[77]. In this system the intensity of the green emission is dependant on the square of the infrared pump power which implies that it is a two stage process. Under pulsed excitation the intensity will remain evident after the diode is switched off. The red luminescent process depends directly upon the pump power. Further three and four photon processes will produce blue and UV emission. Hence if a high pump power is used a green overall emission will be observed, and a low power will give a red emission.

Trivalent erbium may be combined with chromium as a sensitiser which gives a positive effect on the emission of 550nm light[80]. Cr^{3+} has a wide absorption between 600 and 800nm, with a peak at 680nm and when its concentration is 0.5 molar percent combined with 1% erbium it can have a four-fold increase over singly doped erbium emission. The presence of chromium ions in a matrix can also have a positive effect on the lasing properties of the erbium ion[81]. In addition the presence of chromium may improve the properties of ytterbium sensitised erbium doped laser glasses[50]. This system involves the chromium ions acting as sensitisers for the ytterbium ions which in turn sensitise the erbium ions. This system would not be possible if it were not for the long lifetime of the erbium $^4I_{13/2}$ transition.

Thulium may also be used a sensitiser[62, 82]. However it only sensitises the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition under 790nm and 1500nm excitation. The other transitions are quenched, reducing the green and blue emissions and hence enhancing the red emission. Like erbium, thulium[83] and holmium[64, 84] may be sensitised by ytterbium, producing an increase in anti-Stokes emission. There are no additional process that occur here that are not seen in the erbium based systems although thulium may be sensitised by terbium ions and emits in the blue and ultraviolet region of the electromagnetic spectrum[85].

Rare earth ion	Mechanism	absorption wavelength (nm)	emission wavelength (nm)	reference
Sm^{3+}	single photon followed by double photon	1060	560 595 640	68
Er^{3+}	ESA + energy transfer	797	855, 662, 410	86
Er^{3+}	photon avalanche	579.2	550	74
Pr^{3+}	photon avalanche	677	644	87
Sm^{3+}	photon avalanche	IR + 593.2	644.2	88
Ho^{3+}	photon avalanche	585	545	89
Tm^{3+}	photon avalanche	630-650	450-480	90
Er^{3+}	ESA	1.13µm and 1.5µm	410, 524, 546, 660 and 850	91
Nd^{3+}	ESA	805	360, 385, 415, 433, 480, 520, 532, 575, 592, 650, 665	92

Table 1.3. Rare Earth Ions that Exhibit Upconversion and Examples of their Mechanisms, Absorptions and Emissions.

Praseodymium may also be excited by two laser sources of different energies to obtain an excited state absorption process[51]. This can also occur in thulium and erbium-doped systems. A glass matrix doped with erbium, thulium and praseodymium has been demonstrated as a three dimensional display utilising 6 different infrared lasers as excitation sources[93].

Of recent interest has been the upconversion of samarium in glass. A novel mechanism has been proposed where a single photon absorption has been followed by a double photon absorption producing an overall emission[68]. This is demonstrated in figure 1.16

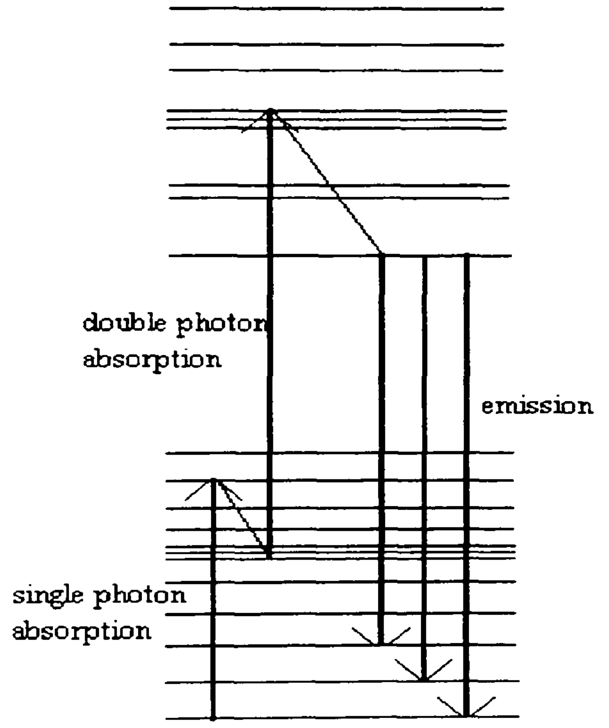


Figure 1.16. Energy Level Diagram of Sm^{3+} Showing Upconversion Mechanism Involving a Single Photon Followed by a Double Photon Absorption.

References:

1. H. Rawson, "Inorganic Glass Forming Systems", Academic Press, London, 1967.
2. M. Dejneka, MRS Bull. 23(11) (1998) 57
3. E. P. Denton, H. Rawson and J. E. Stanworth, Nature, 173 (1954), 1030
4. R. Reisfeld, D. Brusilovsky, M. Eyal, E. Miron, Z. Burstein and J. Ivri, Chem. Phys. Lett. 160 (1989) 43.
5. "A Treatise on Solid State Chemistry: Volume 3: Crystalline and non-crystalline solids", Ed. R. Hannay, (1976).
6. P. W. McMillan, "Glass Ceramics" p. 229, 1964, Academic Press, London
7. S. D. Stookey, Glastech. Ber. , 32 (1959) 1 and Ind. Eng. Chem., 51(7) (1959) 805.
8. H. Zachariasen, J. Am. Ceram. Soc. 54 (1932) 3841..
9. H. Rawson, "Inorganic Glass Forming Systems", Academic Press, London, 1967.W.
10. A. Smekal, J. Soc. Glass Technol. 35 (1951) 411 T
11. S. R. Elliott, "Physics of Amorphous Materials", Longman Group Ltd., New York 1983.
12. W. E. Spear and P. G. LeComber, Sol. State Comm. 17 (1975) 1193.
13. C. J. Brinker and G. W. Shearer, "Sol-gel Science: The Physics and Chemistry of Sol-gel Processing". Academic Press, London, 1990.
14. E. J. A. Pope, S. Sakka and L. C. Klein (editors), "Sol-gel Science and Technology", Ceramic Transactions, Volume 55, 1995.
15. "Structure and Bonding", Volume 77, "Chemistry, Spectroscopy and Applications of Sol-gel Glasses", Springer Verlag, New York, 1992.

16. C. Harrison, "Principles and Applications of Sol-gel Chemistry", Sira course notes, 1995.

17. J. Livage, M. Henry and C. Sanchez, "Sol-gel Chemistry of Transition Metal Oxides" in "Progress in Solid State Chemistry", volume 18, p. 259, 1993.

18. J. R. Bartlett, I. Woolfrey, M. Percy, L. Spiccia and B. O. West, J. Sol-gel Sci. & Tech. 2, (1994), 215.

19. I. M. Miranda-Salvado et al, J. non Cryst. Solids, 87, (1986), 185.

20. A. Aronne, P. Pernice and A Marotta, J. Mat. Sci. Lett. 10, (1991),1136.

21. J. Mendez-Vivar and C. J. Brinker, J. Sol-gel Sci & Tech. 2, (1994), 393.

22. J. P. Pirard, P. Petit, A. Mohsine, B. Michaux, F. Noville and A. J. LeCloux, J. Sol-gel Sci & Tech., 2, (1994), 875.

23. J. Ray, M. Chatterjee and D. Ganguli, J. Mat. Sci. Lett., 11, (1992), 968.

24. K. T. Miller and Ko, J. Cat. 153 (1995) 194.

25. P. J. Sanchez-Soto, M. Macias, M. A. Aviles, G. Colon and J. A. Navio, J. Sol-gel Sci. & Tech. 2 (1994) 353

26. Shingo Katayama and Masahiro Sekine, J. Mat. Chem. 1(6) (1991) 1031

27. M. Gartner, G. Parlog and P. Osiceanu, Thin Solid Films, 234 (1993) 561.

28. I. M. Miranda-Salvado and J. M. Fernandez-Navarro, J. Mat. Sci. Lett., 9 (1990) 173

29. G. Pozarnsky, E. Westenberg, O. Zarembowitch and A. McCormick, J. Sol-gel Sci. & Tech., 2 (1994) 7

30. Yun-Fa Chen and S. Vilminot, J. Sol-gel Sci. & Tech. 2 (1994) 525

31. W. Glaubitt, D. Sporn and R. Jahn, J. Sol-gel Sci & Tech. 2 (1994) 525

32. J. Eamsiri, A. Elyamani and R. E. Riman, J. non Cryst. Solids, 163 (1993) 133

33. Kang Sun, Wook-Hwan Lee and W. M. Risen, J. non Cryst. Solids, 92 (1987) 145

34. W. Xu, S. Dai, L. M. Toth, G. D. Del Cul and J. R. Peterson, J. Phys. Chem. 99 (1995) 4447

35. G. Gowda, J. Mat. Sci. Lett. 5 (1986) 1029

36. Osamu Yamaguchi et al, J. Mat. Sci. Lett., 10 (1990) 101

37. R. S. Hay, J. Mat. Res. 8(3) (1993) 578

38. Wenjian Weng, Juan Yang and Zishang Ding, J. non Cryst. Solids, 169 (1&2) (1994) 177

39. Shingo Katayama and Masahiro Sekine, Mat. Res. Soc. Symp. Proc. 180 (1990) 897

40. Shingo Katayama and Masahiro Sekine, J. Mat. Chem. 1(6) (1991) 1031

41. J. C. Walck and C. G. Pantano, J. non Cryst. Solids, 124 (1990) 145

42. E. Pope and J. D. Mackenzie, J. non Cryst. Solids, 87 (1986) 185

43. E. Rabinovich, EP 0281282 (1988)

44. G. Q. Stokes, Phil. Trans. 142 (II) 463 (1852).

45. J. L. Sommerdijk and A. Bril, Phillips Tech. Rev. 34 (1), (1971), 24 .

46. P. Urquhart, IEE Proc. 135 pt. J, no. 6, (1983) 385

47. Robinson in "Halide Glass Fibre Optics", Ed. Almeida.

48. J. Y. Allain, M. Le Flohic, M. Monerie and H. Poignant, J. non Cryst. Solids, 161 (1993) 222

49. J. Fernandez, R. Balda and M. A. Arriandiaga, Opt. Mater. 4 (1994) 91

50. B. G. Potter Jr., and A. J. Bruce (Eds), "Synthesis and Application of Lanthanide-Doped Materials", Ceramic Transactions, Volume 67, 1996, p.33, J. D. Myers, "Evolutionary Developments in Laser Glass".

51. E. A Downing, L. Hesselink, R. M. Macfarlane and C. P. J. Barty, CLEO 94, paper CMB1, (1994); E. A. Downing, L. Hesselink, J. Ralston, R. M. Macfarlane, Science 273 (5279), (1996), 1185.

52. S. Bergh and G. Dean, "LED's", (1976), chapter 4 "Upconverters (Infrared to Visible)", Oxford: Clarendon Press.

53. R. A. Hewes and J. F. Sarver, Phys. Rev. 182 (1969) 427.

54. J. L. Somerdijk, J. Lum. 4 (1971) 441

55. X. L. Zou and L. Izumitani, J. non Cryst. Solids, 162 (1993) 58

56. R. E. Riman in "Sol-gel Optics", Ed. L. C. Klein, 1994, Kluwer Academic Press, Holland.

57. H. Bach and N. Neuroth (Eds.) "The Properties of Optical Glasses", P. 128 –132, Springer-Verlag, 1995.

58. M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe and K. Hirao, J. non Cryst. Solids, 168 (1994) 137.

59. Setsuhisa Tanabe, Kazuyuki Hirao and Naohiro Soga, J. non Cryst. Solids, 113 (1989) 178.

60. R. Reisfeld, J. non Cryst. Solids, 121 (1990) 254

61. C. Brecher and L. A. Reisberg, Phys. Rev. B, 13(1) (1976) 81

62. J. P. van der Ziel, L. G. van Uitert, W. H. Grodkiewicz and R. M. Mikulak, J. Appl. Phys. 60 (12) (1986) 4262.

63. J. P. Jouart, M. Bouffard, G. Klein and G. Mary, J. Lum. 60&61 (1994) 93

64. L. Esterowitz, J. Noonan and J. Bahler, Appl. Phys. Lett., 10 (4) (1987) 126

65. J. L. Sommerdijk, A. Bril and A. W. de Jager, J. Lum. 8 (1974) 341

67. S. G. Demos, V. Petricevic and P. R. Actano, Phys. Rev. B. 52(3) (1995) 1544

68. Chen Xiao Bo and Chen Jin Kai, Opt. Commun. 97 (1993) 69

69. R. Mahiou, J. Metin and J. C. Cousseins, J. Lum. 45 (1990) 363

70. F. Auzel, J. Lum. 45 (1990) 341

71. N. Bloembergen, Phys. Rev. Lett., 2 (1959) 84

72. F. Auzel, C.R. Acad. Sci. (Paris) 262 (1966) 1016

73. F. Auzel, C.R. Acad. Sci. (Paris) 263 (1966) 819

74. F. Auzel, Yihong Chen and D. Meichenin, J. Lum. 60&61 (1994) 692

75. J. S. Chivian, W. E, Case and D. D. Eden, Appl. Phys. Lett., 35 (1979) 124

76. L. G. van Uitert, Appl. Phys. Lett., 15 (2) (1969) 53

77. J. L. Sommerdijk and A. Bril, Philips Tech. Rev. 34 (1) (1974) 24

78. R. Case et al, J. Mat., 45 (1990) 45

79. J. P. Wittke, I. Ladany and P. N. Yocom, J. Appl. Phys. 43(2) (1972) 595

80. S. Parke and S. Gomolka, Phys. Chem. Glasses, 23(3) (1982) 88

81. Weiji Jia, Ki-Soo Lim, Huimin Liu, Yanyun Wang, F. Fernandez and W. M. Yen, J. Lum., 66&67 (1996) 228

82. J. P. Jouart, J. Lum. 46 (1990) 39

83. J. L. Somerdijk, J. Lum. 8 (1973) 126

84. L. F. Johnson, J. E. Geusic, H. J. Guggenheim, T. Kushida, S. Singh and L. G. Van Uitert, Appl. Phys. Lett., 15 (2) (1969) 48

85. T. Riedener, H. U. Gudel, G. C. Valley and R. A. McFarlane, J. Lum., 63 (1995) 327

86. Z. Pan, K. Dyer, A. Loper and S. H. Morgan, "Infrared to visible upconversion in Er^{3+} doped lead germanate glasses", p. 55, Ceramic Transactions, volume 67, 1996, Edited by B. G. Potter Jr., and A. J. Bruce.

87. W. E. Case, M. E. Koch, and A. W. Kueny, J. Lum., 45 (1990) 351

88. N. J. Kratsutsky, J. Appl. Phys. 54 (1983) 1261

89. G. K. Lui, Y. H. Chen and J. V. Beitz, J. Lum., 81 (1999) 7.

90. S. Guy, D. P. Shepherd, M. F. Joubert, B. Jacquier and H. Poignant, J. Opt. Soc. Am., 14 (1997) 926

91. S. C. Goh, J. non Cryst. Solids, 161 (1993) 227

92. Takashi Tsuneoka, Kazuo Kojima and Sreedhar Bojja, J. non Cryst. Solids, 202 (1996) 297

93. L. Kodar, Adv. Mater., 9(1) (1997) 83

Chapter 2: Experimental Methodology, Techniques and Analysis

As demonstrated in tables 1.2 and 1.3 and also section 1.3.4, fluorides are the most efficient hosts for anti-Stokes processes. However due to the nature of the processing, fluoride glasses may not be produced directly by sol-gel methods (see section 8.1.3). Sol-gel methodology forms the major part of this project due to its safer, more cost effective and efficient nature. After due consideration, an oxide host with added fluoride ions incorporated was chosen to be synthesised.

2.1 Chemicals used

Most chemicals used in this study were purchased from Aldrich Chemical Company with the exception of the solvents which were obtained from BDH.

2.2 Synthesis of Precursors

Standard reflux equipment was used with additional N_2 gas lines added if needed. Careful control of the heating mantle was required to enable correct temperatures to be used in the synthesis of the precursors. This was used with an overhead stirrer. When heating was not required synthesis was done in a beaker over a magnetic stirrer. When low temperatures were required a round bottomed flask was suspended over a beaker of liquid nitrogen. Additionally a pH meter was used to determine the acidity of the solutions. This was calibrated using buffers of pH 4.2 and 7. A stop watch was used as well when taking pH measurements over a set period of time. Details of sol-gel methods for the synthesis of glasses, powders and thin films are given by C. J. Brinker and G. W. Scherer[1].

2.3 Mixing of sol-gel systems

Generally the mixing of sol-gel systems did not require heating as mixing at room temperature gave a greater degree of control over the reaction rates than if the mixtures were heated. Hence a beaker and a magnetic stirrer was used. Certain precursors are highly reactive to water in the atmosphere and were introduced to the mixture using hypodermic needles and syringes. A nitrogen gas line was also needed for similar reasons. Equipment was also purged with nitrogen prior to addition of any highly reactive reagents. Again a pH meter and a stop watch were also used for measurements.

2.4 Gelation and Ageing of Gels

Thin pieces of gel were produced by pouring gel mixtures into plastic petri dishes with vented lids. Plastic was chosen as it has a very smooth surface which the gel does not stick to and hence fairly large pieces of gel could be made. Larger pieces of gel such as monoliths were produced from plastic pots. To dry these gels cling film was placed over the top of the pot to allow a controlled escape of the solvents – slow drying is beneficial in these cases, as if the process is too quick the gel can break up under capillary forces. Ageing in petri dishes was achieved by wrapping the dishes in parafilm and cling film, several layers thick to ensure that only a minimum of solvent could escape. Drying generally took place in an oven set between 40 and 50°C. For ageing at higher temperatures where plastic pots and petri dishes would melt, eg 120°C, the gel mixtures were placed in clean glass containers, but were not allowed to gel in them. Certain samples were gelled at room temperature in sealed containers and then the whole mixture including pore liquid was transferred to a glass container and put at a higher temperature to age.

2.5 Sintering

Sintering was carried out primarily in a programmable muffle furnace. The temperature was increased from room temperature until a specific temperature was reached. Depending on the sample being fired, this temperature was maintained for a prolonged period of time, and the sample was cooled in the furnace at a controlled rate or removed and allowed to cool to room temperature without any external influences. Firing tempertures and times were determined from the literature and from studying the different systems. These firings were carried out using programmable Carbolite muffle furnaces. Certain firings were performed in a tube furnace under nitrogen. Unfortunately these could not be programmed as extensively as with the muffle furnace.

2.6 Analysis

The objective of the analysis in this study was to determine structural information about the glass samples produced and to determine the presence and identity of any crystalline phases produced.

2.6.1 Principle Methods of Analysis

Various types of spectroscopic and elemental analysis was carried out:

- UV/visible/NIR absorption – Kontron UVkon 860[2].
- Infrared (FTIR) – Perkin Elmer Paragon 1000 and ATI Unicam Genesis[2].

- X-ray diffraction – Phillips Powder Diffractometer 7600[5]. Pieces of glass were held in the sample holders using BluTack ensuring that the X-ray beam passes over an area of sample which is flat with the surface of the sample holder.
- Elemental detemination analysis by x-ray (EDAX) Link AN10 Beryllium Window Detector[4]
- Transmission Electron Microscopy (TEM) JEOL 200CX operating at 200kV.
- Scanning Electron Microscopy (SEM) – Cambridge Instruments Stereoscan 90[4].

2.6.2 Fluoride analysis

Glasses were ground in a pestle and mortar then weighed. Approximately 0.5g of sample was mixed with 5g sodium carbonate and placed in a platinum crucible. This was then heated using a Meker burner until the mixture melted and fused – usually after about 40 minutes. The fusion was then allowed to cool and was dissolved in a small amount of de-ionised water. For samples not containing rare earth or any other cations that may form insoluble fluorides the solution was placed in a volumetric flask and made up to the mark. Fluoride content was determined using the ion selective electrode.

For samples containing rare earth and fluoride ions, a precipitate of rare earth fluoride resulted. This was filtered off and weighed. A comparison with the initial concentrations of starting materials was then possible.

2.6.3 Anti-Stokes Luminescence Analysis

Luminescence and Raman spectra were obtained using a Labram Raman spectrometer equipped with an 1800g/mm holographic grating, using a holographic supernotch filter and a peltier-cooled CCD detector. Samples were excited using a helium-neon laser with an output of 8mW of power at the sample on the 632.8nm line unless an attenuation filter was used. Luminance observed using infrared excitation using a Spex Triplemate Raman spectrometer equipped with an intensified photodiode array detector. The infrared excitation was provided by a 3900 titanium-sapphire laser (Spectra Physics) pumped by an intracavity frequency doubles Nd:YAG laser (Spectra Physics); the laser power varied between 20mW and 50Mw at the sample.

References

1. C. J. Brinker and G. W. Scherer, "Sol-gel Science: The Physics and Chemistry of Sol-gel processing". Academic Press, London, 1990.
2. C. N. Banwell, "Fundamentals of Molecular Spectroscopy", McGraw-Hill Book Company (UK) Ltd., Maidenhead, 1983.
3. J. B. Cohen, "Diffraction Methods in Materials Science", MacMillan, New York, 1966.
4. J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. Fiori and E. Lifshin, "Scanning Electron Microscopy and X-ray Microanalysis", Plenum Press, New York, 1981.

Chapter 3 Synthesis of Standard Samples

3a – Basic Silica Matrices

3a.1 Introduction to the Synthesis of Basic Silica Matrices

The aim of this section of work is to study the synthesis of basic silica matrices, i.e.: those containing silica cations only, to gain an understanding of the roles of the various components involved in sol-gel processing and how they influence the outcome of the final product. Estimates for reaction and gelation times, drying conditions and firing temperatures can also be determined from studying these basic syntheses and could be applied to the synthesis of high-content silica materials. Although most of the work discussed here has been documented in the literature (see section 1.2) it has been included to give an insight into the versatility of the silica sol-gel system and because the majority of materials prepared in this work are silica based.

3a.1.1 Main components required.

The main components required for the synthesis of basic silica matrices are as follows:

1. Silicon precursor. The silicon alkoxides have the ideal chemistry for sol-gel reactions having hydrolysis rates that are slow and hence easily controlled. These compounds are quite stable if not over-exposed to air and are easily handled. Tetraethylorthosilicate (TEOS) was chosen for this study over tetramethylorthosilicate (TMOS) because it is less expensive and less reactive, hence making its chemistry easier to control (see section 1.2).

2. Water. This hydrolyses the silicon alkoxide.
3. Solvent. As TEOS and water are not readily miscible, a suitable solvent is required to facilitate their thorough mixing and hence reaction. There is a wide range of suitable solvents, although the most commonly used are alcohols. As the solvent can have an influence on the reaction rates and the quality of the final product, there are limitations on the choice (see section 1.2). When combining other cations into the system, their solubility and reactivity with the chosen solvent must also be taken into account.
4. Catalyst. This controls the rates of hydrolysis and condensation. It can be either in the form of an acid or a base. The choice affects the type of gel produced and influences the quality of the final product; –generally acid catalysed systems are used to produce glassy products and base catalysed are used to produce fine powders (see section 1.2)

3a.2 Synthesis of Silica Matrices

3a.2.1 Acid Catalysed Synthesis

The following components were mixed to produce a silicon based xerogel:

40ml deionised water
17g concentrated hydrochloric acid
150ml absolute ethanol
35g 98% tetraethylorthosilicate (TEOS)

These components were mixed thoroughly and in some cases heated whilst mixing. As this combination utilises an acid catalyst, this reaction yields a glassy material.

Using the above mixture, a number of samples were made up. Volumes were divided into smaller amounts (for example: 10ml) to reduce the gelation and drying times. It was found that with larger volumes (usually larger than 25ml), greater care had to be taken whilst drying. To produce a large sample that was intact and not cracked slower evaporation of the solvent was required. Various lids and other methods of sealing the vessels containing the samples were investigated (see section 3a.3.2). The influence of temperature upon gelation and drying times was also studied (see section 3a.3.2).

To reduce gelation and drying, samples were left in an oven at 40°C. Additionally the gelation and drying times were reduced by using smaller quantities of solvent (for example 50ml instead of 150ml).

When TEOS is mixed with water in the absence of a suitable amount of solvent, the two are initially immiscible. However after continuous stirring for a considerable length of time, relative to the amounts involved, complete mixing occurs. If a few drops of acid are added the mixing time is greatly reduced, likewise if a few drops of ethanol are added the mixing time is also reduced. This process was studied by simply mixing together different ratios of TEOS, water and acid and measuring the times involved. The amounts of acid used were primarily kept to drop-wise quantities (see section 3a.3.5). pH and temperature readings were also taken during the duration of the reaction between TEOS and water.

The additions of drying control chemical additives (DCCA's) were studied briefly (see section 3a.3.6). Common DCCAs include dimtheylformamide (DMF), oxalic acid, and glycerol.

Once thoroughly dried the samples were placed in a furnace at room temperature. A programmable furnace was necessary as the temperatures need to be increased at a controlled rate (from room temperature up to values as high as 1500°C with heating rates from 0.2°Cmin^{-1} to the maximum heating rate of the furnace). Samples were also put directly into the furnace at fixed temperatures and removed after short periods of time (see section 3a.3.7). Thermal analysis was also performed upon the samples to determine percentage weight loss with respect to temperature (thermal gravimetric analysis or TGA) and also to determine any crystallisation temperatures (differential thermal analysis or DTA).

3.2.2 Base Catalysed Synthesis

Repeats of the above synthesis were made using ammonium hydroxide instead of hydrochloric acid as the catalyst (see section 3a.3.1).

3a.3 Results and Discussion

3a.3.1 Effect of Different Catalysts on the TEOS Reaction:

It was found that the synthesis of silica matrices utilising TEOS was facile if the above acid catalysed recipe was followed and variations kept to within the components involved. In the majority of cases a transparent xerogel was produced. However when ammonium hydroxide was substituted for the acid, a thick white precipitate of amorphous silicon dioxide was produced instantly.

3a.3.2 Reaction Times:

When heated in a flask under reflux the acid catalysed mixture gels in approximately 6 hours. The resulting gel was broken up into very small pieces. This is due to the stirring and bubbling of the mixture during reflux. To avoid this the above components were mixed at room temperature and then left to stand uncovered at room temperature taking approximately one week to gel. To reduce this time, the mixture was heated under reflux for four hours and then leaving the mixture to cool to room temperature and stand. Gelation then occurred within 24 hours.

Limiting the solvent evaporation during gelation and drying produced larger uncracked samples. Obviously this slowed these processes, but upon doing so made stronger matrices as the bonding within them is more extensive. The evaporation of the solvent was slowed by putting various coverings on the containers. The use of unsealed lids was perhaps the least effective as the evaporation couldn't be controlled. Covering the containers with cling film and parafilm slowed the evaporation rate, however the parafilm was prone to splitting and the cling film had too fast an evaporation rate. It was found that the best method involved using a deep petri dish with a plastic vented lid, covered in cling film. On average this doubled the gelation and drying times. Accurate comparisons could not be made as many factors are involved, including the amount of stretching of the cling film (affecting its thickness and permeability) and how tightly it is wrapped around the dish.

When samples were placed in an oven at 40°C the processing times were dramatically reduced with samples using a smaller volume of solvent in the initial reaction being ready for firing within a week. With use of lidded petri dishes and cling film the additional temperature had no detrimental effect on the quality of the final product.

3a.3.3 Effect of Vessel Composition:

It was found that the vessel itself could have an impact on the final quality of the sample. Containers made from various plastics were compared to standard glass beakers. A container with a rough surface would cause the gel to stick and as a result pull itself apart during shrinkage hence glass was rejected in favour of polystyrene petri dishes and PTFE beakers. With glass containers as the gel shrunk it developed concave sides, yet with plastic containers the gel had straight sides. One disadvantage of polystyrene was its lack of resistance to attack by TEOS itself. Although, when mixed in alcohol TEOS did not attack the dish, with certain other solvents, i.e.: 2-methoxyethanol, it did. This could cause organic impurities in the gel and the dish to leak.

3a.3.4 Effect of Solvent:

It is known that the use of ethanol is quite suitable for a TEOS based reaction (see section 1.2.3), however other solvents may be used. With n-butanol the mixture was slow to mix and once mixed it rapidly showed signs of gelation around the edges of the flask. Most small chain alcohols were tested for suitability with TEOS and were found to be satisfactory. The glycolether, 2-methoxyethanol, was found to slow the gelation time. This solvent required careful handling due to its toxicity especially when the gel was drying. As, in this work, TEOS was to be combined with other cation containing mixtures that may have specific solvent requirements, it is thus useful that this compound can be made to produce stable gels in a wide range of solvents.

3a.3.5 Drying Control Chemical Additives:

With regard to additional compounds as DCCA's, the presence of oxalic acid would be unsuitable for use in the final systems required for this study due to the presence of rare earth ions which would produce insoluble rare earth oxalates. DMF supposedly produces very strong matrices, but it is has been shown to be difficult to remove from the matrix upon firing. A little work was done with glycerol but it proved to be difficult to measure out due to its high viscosity. Removal of glycerol from the matrix during firing processes also gave problems, and many samples ended up black and cracked due to the presence of trapped organics. The addition of DCCA's was abandoned due the difficulties encountered in removing the residual compounds.

3a.3.6 Firing of Samples:

On firing the samples it was found that the slower the temperature increase the more intact the final product. In addition it was stronger and hence more optically useful. Those samples which were placed into the furnace at high temperatures without any steady temperature manifested many cracks and in some cases tiny pieces of glass were spread over the inside of the furnace.

3b: Synthesis of Anti-Stokes Powder Samples

As a luminescence comparison for the glasses produced in this study, various standard powder phosphor materials were produced. To allow comparison with commercial samples, a couple of samples were donated by Phosphor Technology Ltd.

3b.1 Synthesis of Oxide Phosphors

The method chosen for the synthesis of yttrium oxide doped with ytterbium and erbium was based on the synthesis of the standard yttrium oxide doped with europium phosphor[1]. 0.8gYttrium oxide, 0.2g ytterbium oxide and 0.06g erbium chloride were slurried together in isopropanol (IPA or propan-2-ol). These were dried and then fired initially for 2 hours at 1000°C followed by 2 hours at 1500°C. Both firings were carried out in air. All samples emitted a yellow-green luminescence when excited by a 940nm diode.

3b.2 Synthesis of Oxychloride Phosphors

General methods of synthesising oxychloride phosphors include the firing of mixed chlorides in an air/chlorine atmosphere[2,3]. The method in this study was chosen to eliminate the use of chlorine gas and the results show that the oxychloride was being formed.

Hydrated chlorides of yttrium (2g), ytterbium (0.4g) and erbium (0.1g) were mixed together in a pestle and mortar, heated to 120°C for several hours and then fired at 700°C in a platinum crucible under a nitrogen atmosphere for 1 hour. The resulting body colour of the material was grey. When the samples were fired at 900°C the body colour was a lighter shade of grey. Upon firing for 2 hours at 900°C using a lidded crucible, the body colour was considerably lighter again. The luminescence colour was green and brighter than the oxide phosphors. As the body colour became lighter the luminescence increased. A sample of this phosphor was mixed with water to determine the proportion of yttrium chloride present. As yttrium chloride is soluble and yttrium oxychloride is insoluble this is a very simple test. The results are summarised in the table 3b.1.

Mass of filter paper	0.3841g
Mass of sample	0.4862g
Mass of filter paper plus residue	0.8226g
Mass of oxychloride	0.4385g
Mass of chloride	0.0477g

Table 3b.1 Analysis of oxychloride phosphor to determine the content of yttrium chloride present in sample.

According to these results the percentage of yttrium chloride in the sample tested is 9.8%.

When zirconium chloride (1g) was added to this system replacing 1g of yttrium chloride, the luminescence became weaker and was comparable with that of the oxide samples. When a silica crucible was used in place of a platinum crucible, the crucible was blackened and the sample had a grey body colour and was very coarse.

3b.3 Synthesis of Fluoride Phosphors

1g yttrium fluoride, 0.25g ytterbium fluoride and 0.06g erbium fluoride were mixed in a pestle and mortar. These were fired at 600°C in a platinum crucible under nitrogen. The resulting body colour was white. A second sample was fired at 840°C under nitrogen.

The resulting emission was bright green when excited by 940nm light from a diode. This luminescence was considerably brighter than the oxychloride samples. The emission spectrum is given in figure 3b.1. By comparison when the sample was excited by a titanium-sapphire laser turned to 974nm the emission was considerably brighter. The spectrum of this emission shows greater detail than that obtained when the sample was excited by the infrared diode. This can be seen in figure 3b.2.

Addition of barium fluoride to the mixture prior to firing, resulted in a phosphor that had a brighter emission. The addition of 0.35g barium fluoride and 0.5g zirconium fluoride caused the final product to melt after firing at 840°C. This product also had a grey body colour but also had green luminescence when excited using infrared LED.

3b.4 Analysis of Commercial samples from Phosphor Technology Ltd.,

Two samples were donated by Phosphor Technology Limited for this project. They were simply labelled by a code and the emission colours of red and green.

From analysis by EDAX it was determined that these samples contain the following elements: Yttrium, ytterbium and erbium.

Sample	Y atom %	Yb atom %	Er Atom %
QU1 (green)	50.93	44.00	5.06
QU2 (red)	67.91	26.86	5.23

Table 3b.2 EDAX elemental analysis of commercial anti-Stokes phosphors

As all other metal cations heavier than magnesium are detectable by EDAX we can conclude that it is possible that these sample only contain the detected ions. We can also eliminate the possibility that these samples are chlorides, sulphates, phosphates etc. Fluorine and oxygen are not detectable and as fluoride hosts are known to be the ideal matrices for anti-Stokes luminescence it can be assumed that these samples are similar to the fluoride samples made in this study. It is unlikely that these samples are oxide-based hosts, although we cannot rule out the possibility of oxyfluorides.

The above EDAX results are in agreement with the literature. High ytterbium:erbium ratios yield green emissions and low ratios yield red emissions[4].

These samples had a brighter emission than our fluoride samples.

3b.5 Conclusions:

The results of the synthesis of the above samples may be summarised as follows in table 3b.3. The excitation source was an infrared LED with emission based around 950nm.

Type of powder phosphor	Emission colour
Oxide Y_2O_3:Yb,Er	Yellow-green
Oxychloride YOCl:Yb,Er	Green
Fluoride	Green

Table 3b.3: Emission of various anti-Stokes phosphors synthesised in this study (in order of increasing luminescence, weakest first).

From this we can conclude that fluoride hosts are the best for this type of luminescence process (see section 1.3.4).

The commercial samples were brighter than the above samples which are suggested to be of a similar composition. It is believed that this is due to higher purity starting materials and lower contamination in the firing process.

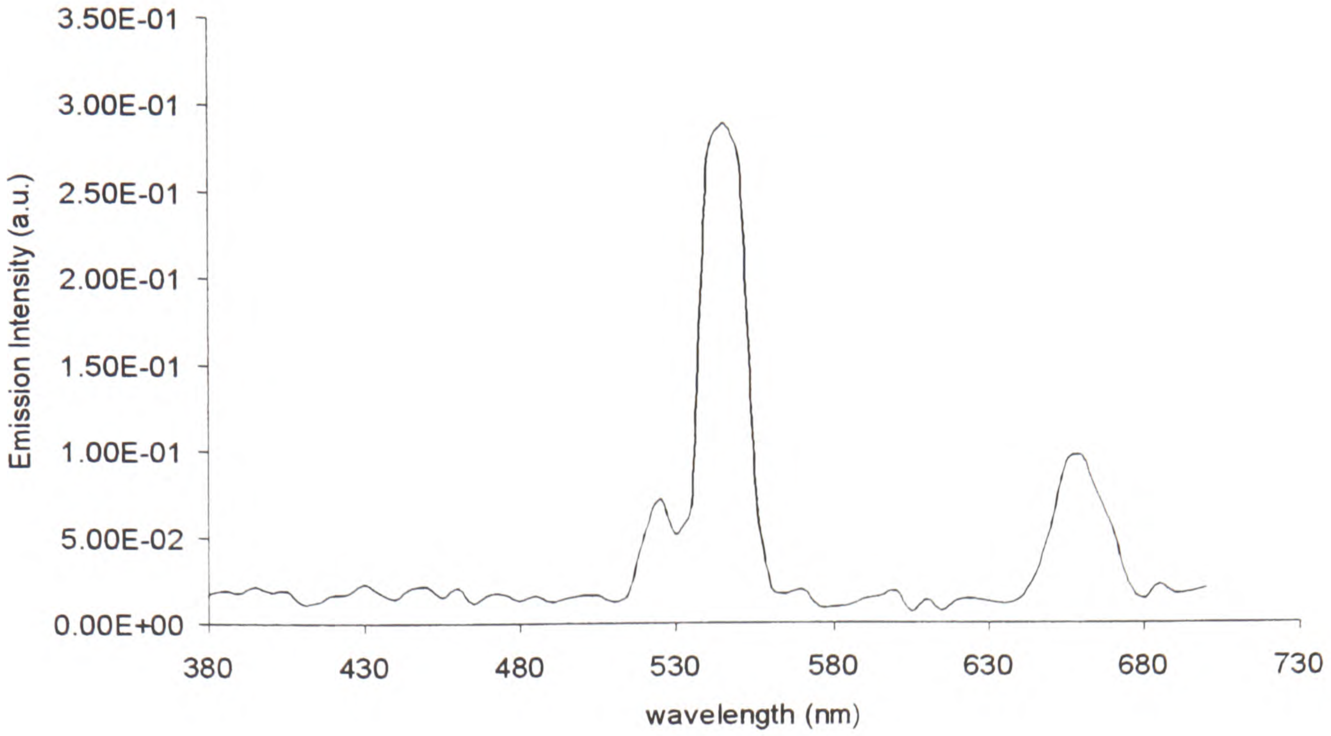


Figure 3b.1: Emission Spectrum of YF_3:Yb, Er under excitation from infrared LED based at 950nm

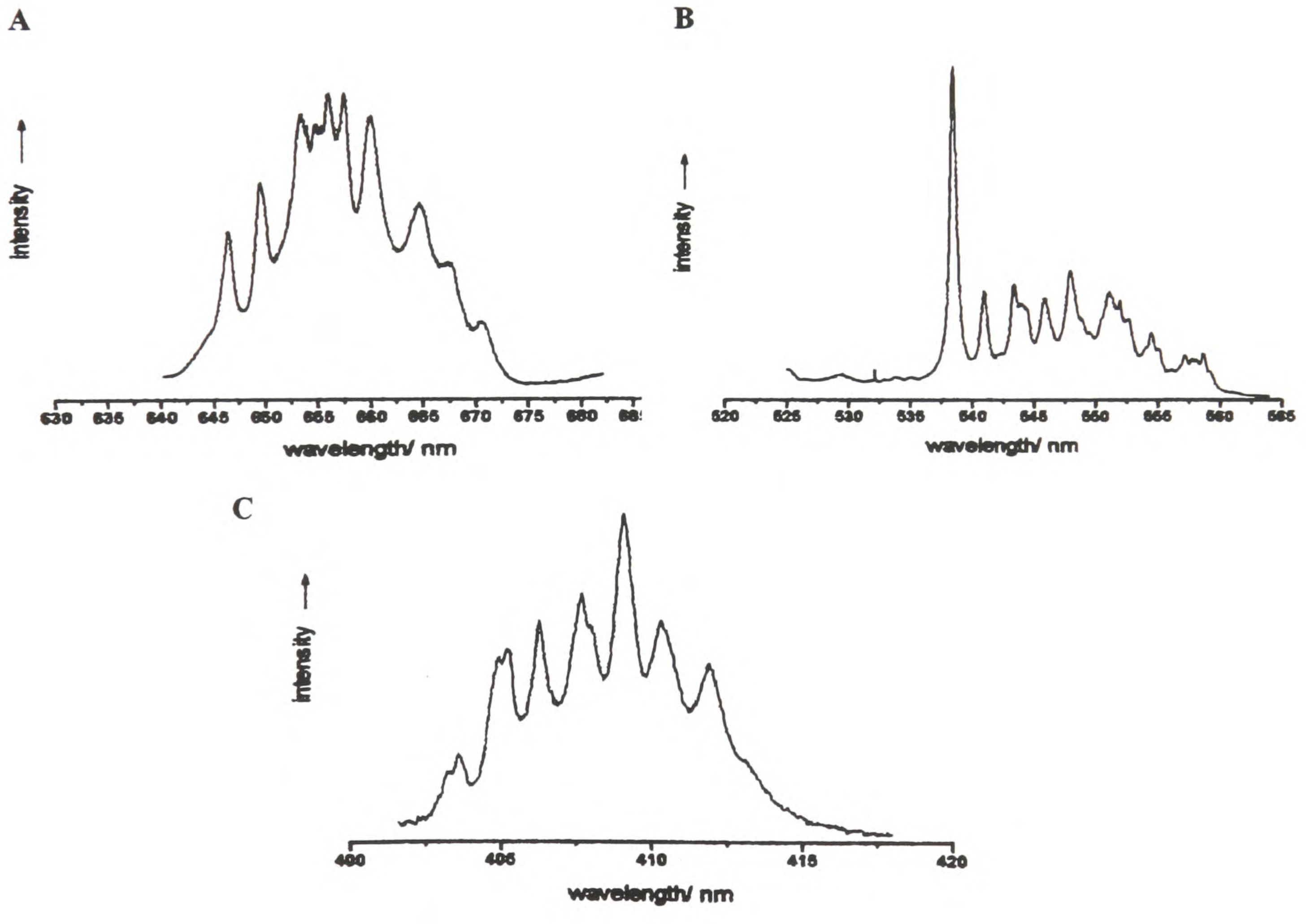


Figure 3b.2: Emission spectra of YF_3Yb,Er under 974nm excitation from titanium-sapphire laser. A) red emission, B) green emission, C) blue emission.

References:

1. J. P. Wittke, I. Ladany and P. N. Yocom, J. Appl. Phys. 43(2), (1972), 595.

2. A. Berg and G. Dean, "LEDs", Clarendon Press, Oxford, 1967 .

3. L.G.Van Uitert, App. Phys. Lett. 15(2) 53 (1969).

4. R.C.Ropp, Studies in Inorganic Chemistry 12: Luminescence in the Solid State.

Elsevier, 1991.

Chapter 4. Incorporation of Transition Metal Cations into Silica Sol-gel Matrices

According to figure 1.1 in the introduction, aluminium and titanium are classed as conditional glass formers. They will not form glasses on their own, but will do so when combined with a suitable second oxide or mixture of oxides. They are also classed as network modifiers along with zirconium. In this section we investigate methods of combining aluminium, titanium and zirconium with silica matrices.

For clarity the sol-gel chemistry of each of these metals is reported separately and each of the following sections should be considered as an individual part of this study:

Section 4a: the incorporation of aluminium into silica matrices.
Section 4b: the incorporation of titanium into silica matrices.
Section 4c: the incorporation of zirconium into silica matrices.

4a – Incorporation of Aluminium into Silica Matrices

4a.1 Introduction to the Sol-gel Chemistry of Aluminium

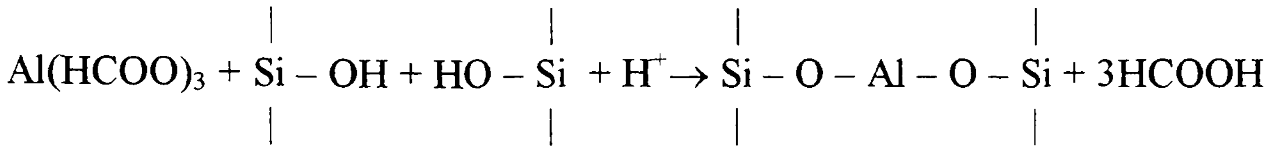
As a conditional glass former (see definition in section 1.1) aluminium does not form an oxide glass on its own. It is necessary to combine it with other suitable oxides to gain glass formation. It has been suggested[1,2] that the preferred co-ordination of aluminium in its pure crystalline oxide form is octahedral and when in a glassy matrix it is tetrahedral, hence Zachariasen's rules (see section 1.1.1) can be used to explain why aluminium oxide is not a glass former itself. It must be noted that although aluminium does not form oxide glasses on its own, stable aluminium based gels can be synthesised using sol-gel methods with the aluminium ion as the sole cation[3].

Standard methods of synthesising aluminium containing glasses usually involve heating an oxide mixture to its melting point[4,5] in a platinum crucible using high temperatures in the region of 1600°C. This is costly and carries a high risk of contamination hence the attraction of sol-gel chemistry.

There are many methods reported[6,7] for combining TEOS with various alumina precursors utilising sol-gel methodology. Perhaps the simplest method[6] uses aluminium nitrate producing octahedral and tetrahedral co-ordinated aluminium ions. It was found[4] that as the Al:Si ratio is increased, the percentage of aluminium in octahedral sites increases suggesting that a low Al:Si ratio would produce a better quality glass. Other authors have shown that the amount of aluminium that can be combined with silica to produce a transparent matrix is quite low. For a transparent gel to be successfully formed an aluminium:silicon ratio of 1:2 is ideal[8]. However for a matrix to remain transparent after firing, an aluminium content of 15 molar % is the suggested maximum in a silica matrix[9]. As the aluminium content is reduced the hydrolysis and gelation rates are reduced. The gelation rate is also slowed by decreasing the silicon:water ratio and by increasing the catalyst concentration[6].

Another method of increasing the quality of the final product involves the partial prehydrolysis of TEOS. This requires the TEOS to be mixed with an appropriate solvent and enough water to hydrolyse a fraction of the alkoxy groups attached to the silicon so that the latter is on the verge of condensation. With the comparatively fast hydrolysis rate of the aluminium, condensation of the two components can then occur relatively simultaneously increasing the likelihood of increased homogeneity and Al-O-Si bonding.

The use of aluminium formate has been described in the literature with successful combination with TEOS[7]. This is a simple method as it requires no additional acid and has a final structure that is free of formic acid. Freshly precipitated aluminium hydroxide is dissolved in 50 % formic acid solution to produce aluminium formate. This is mixed with prehydrolysed TEOS with hydrolysis and condensation occurring according to the reaction scheme shown in equation 4a.1.



$$\mathrm{Al(HCOO)_3} + \underset{|}{\overset{|}{\mathrm{Si}}} - \mathrm{OH} + \mathrm{HO} - \underset{|}{\overset{|}{\mathrm{Si}}} + \mathrm{H^+} \rightarrow \underset{|}{\overset{|}{\mathrm{Si}}} - \mathrm{O} - \mathrm{Al} - \mathrm{O} - \underset{|}{\overset{|}{\mathrm{Si}}} + 3\mathrm{HCOOH} \qquad \text{Eqn.4a.1}$$

The formic acid formed in this reaction is removed during evaporation. It should be noted that other alkali and alkaline-earth metal formates can be successfully used in this reaction with TEOS instead of aluminium[7].

A common method of synthesising aluminium based sol-gel systems has been described by T. Maki and S. Sakka [10]. Aluminium hydroxide is precipitated by adding ammonium hydroxide to aluminium chloride solution. After filtering and washing to remove ammonia, this is then peptised by adding acetic acid to form an alumina sol that can form a transparent gel after careful evaporation. The process of peptisation is defined as the process of redispersing a colloid that has become coagulated[11].

A well-known variation on this method has been developed by Gowda[11] using an aluminium alkoxide as starting material yielding alcohol as a by-product (the latter is easier to remove from the product than chloride ions). This method utilises aluminium tri-sec-butoxide, a thick, colourless liquid that is reactive with air decomposing to a white powder of aluminium oxide with the liberated alcohol evaporating. It was found that the ideal method for handling this compound is to use hypodermic needles and syringes. A large proportion of aluminium sol-gel chemistry cited in the literature[4,7,11,12] utilises this compound.

Another well-known variation is given by Yoldas[11]. Aluminium tri-sec-butoxide is hydrolysed with water to give aluminium hydroxide. This has the advantage of removing the filtering step due to the absence of ammonia. This precipitate can then be peptised with hydrochloric acid at 80°C. Alcohol and water can then be removed to produce a gel.

Other sol-gel methods using this alkoxide involve stabilising agents and chelating agents to slow the hydrolysis reaction. Chelating agents used include ethylacetoacetonate (EAA)[13,14] and acetylacetonate (acac)[15]. As the hydrolysis of aluminium tri-sec-butoxide is so fast, when combining with TEOS, it is necessary to slow the aluminium hydrolysis Stabilisation using a chelating compound is a straightforward method of doing this. The partial prehydrolysis of TEOS is also advisable[16]. However removal of the residual organic compounds in the matrix (when using additional organic compounds such as chelating agents) can often be troublesome.

There are other difficulties involved with mixing aluminium tri-sec-butoxide with TEOS. As discussed in section 1.2, ethanol is normally the solvent of choice for use with TEOS. However its use with aluminium tri-sec-butoxide is unsuitable, readily producing a gelatinous precipitate of aluminium hydroxide. This is also the case with the other primary alcohols[17]. Mixing aluminium tri-sec-butoxide with tertiary alcohols, such as 2-methyl-butan-2-ol, produces stable solutions which can be then be hydrolysed in a more controlled manner (see discussion in section 1.2).

Other solvents that can be successfully used with aluminium tri-sec-butoxide include glycolethers, for example: isopropoxyethanol[18]. These have a stabilising effect on the alkoxide producing a mixed alkoxide enabling the hydrolysis reaction to be controlled.

Alternative ways of producing precursors from aluminium alkoxides for the synthesis of matrices include reacting aluminium metal in ethanol using mercury chloride as a catalyst producing the required aluminium alkoxide[19,20]. This alkoxide, retained in its parent alcohol, can be mixed with other cation solutions with care, for example the solvents used must be water free and be suitable for use with the aluminium alkoxide. This method enables the use of alkoxides that once in their crystalline form are insoluble in most solvents. Once synthesised these solutions should be used as soon as possible otherwise they will begin to hydrolyse due to atmospheric water or water already in the alcohol. Alternatively they can be stored under argon or nitrogen once produced from dry alcohols although a complete water-free environment is difficult to maintain.

Aim

The aim of this section of the chapter is to demonstrate the limitations of aluminium precursors in sol-gel chemistry and how these may be overcome.

4a.2 Experimental

4a.2.1 General Synthetic Methods

Aluminium isopropoxide is considerably more stable to hydrolysis than aluminium tri-sec-butoxide. However, this compound is a solid and it does not dissolve in many solvents. It was found that aluminium tri-sec-butoxide was more suitable for these reactions.

It should be noted that the reactivity of aluminium tri-sec-butoxide is such that the ideal way of handling it is with a hypodermic needle and syringe otherwise it will react with the water in the air and convert to aluminium oxide which is insoluble and of no use in these reactions.

4a.2.2 Effect of Solvent on Synthesis of Aluminate based gels.

With regard to the discussion given in section 1.2, the following experiments were carried out to examine the effect of solvent on the synthesis of aluminium containing matrices.

1g of aluminium isopropoxide was added to 50ml ethanol. However it didn't dissolve. Upon adding 3ml concentrated hydrochloric acid it begins to dissolve giving gel formation around the edge of the beaker at liquid level. 6g of TEOS were added to the final solution and a stable gel was formed. Although this may appear to be a suitable method for making aluminium-containing gels, the slow dissolution and gelation of the mixture prior to total dissolution implies that the resulting gel could contain alumina-rich phases due to inhomogeneous mixing during gelation. It has been observed that this is often the case when using aluminium isopropoxide due to its slow dissolution rate in most solvents. Following the above method, to 6g of prehydrolysed TEOS was added 1g aluminium isopropoxide. 1ml of concentrated hydrochloric acid was added and the mixture was boiled until the isopropoxide dissolved. The resulting gel was transparent. Aluminium tri-sec-butoxide was added to various solvents. The results are summarised in the table 4a.2.1:

Solvent	Additional conditions	Result
2-methylbutan-2-ol	No acid present 0.5ml aluminium tri-sec-butoxide and 20ml solvent.	pH 5-6. Clear solution that gels within 2 minutes and goes opaque. Overall resulting gelatinous precipitate. Hydrolysis probably due to water in solvent.
	2 drops hydrochloric acid	pH 3: Gelatinous precipitate forms more slowly than the sample without acid, it also does not go through an obvious gelation stage.
Butan-2-ol	No acid present	10ml aluminium tri-sec-butoxide added to 50ml butan-2-ol. Appears to be stable until water added, then a fine precipitate is formed.
Ethanol	No acid present	Immediate precipitation of gelatinous white solid.
Isopropanol	No acid present	Immediate precipitation of gelatinous white solid.
2-methoxyethanol	No additional compounds added. Mixture retained in sealed container under nitrogen.	No precipitation.
	Add water	Sample gels slowly upon addition of water. As the water content increases, the gelation time decreases.
	Water-free sample consisting of 3ml aluminium tri-sec-butoxide and 20ml solvent, left in lidded petri dish in oven at 40°C.	Sample gels over period of one week. Hydrolysis caused by water in atmosphere.

Table 4a.2.1 Effect of adding aluminium tri-sec-butoxide to various solvents.

4a.2.3 The Use of Chelating Agents

Little work using chelating agents was carried in this study with aluminium. It was found that although stable gels could be synthesised using compounds such as acac and EAA, their removal from the final product during firing proved difficult. An example of the use of acac as a chelating agent is given in the following experiment:

0.5ml aluminium tri-sec-butoxide was added to 20ml methylbutanol containing 0.5ml acac. This produced a transparent gel after being left to evaporate overnight. It should be noted that in the absence of acac this system will gel within 2 minutes giving a crystalline product.

4a.2.4 Synthesis under N_2 Atmosphere

Nitrogen was bubbled through 150ml ethanol prior to the addition of 1g aluminium isopropoxide. This was heated under reflux and a gel is formed which broke up to form a gelatinous precipitate.

To 30ml isopropanol under nitrogen 1ml aluminium tri-sec-butoxide was added. An immediate precipitate was formed.

20ml IPA was flushed with nitrogen. 0.5ml aluminium tri-sec-butoxide was added producing a fine white precipitate. Upon addition of 0.5ml acac the precipitate became considerably thicker. When 3ml water were added the solids dissolved leaving a clear solution. Upon addition of 1ml TEOS the mixture began to go cloudy and the resulting gel was translucent containing fine crystals. This reaction was repeated with the acac included in the solvent during the flushing with nitrogen. In this case the addition of aluminium tri-sec-butoxide and prehydrolysed TEOS gave a clear solution. However the removal of the nitrogen supply one minute after complete mixing caused an immediate precipitate to form. By comparision, when a mixture of 20ml IPA, 0.5ml acac and 0.5ml aluminium tri-sec-butoxide was allowed to stand with nitrogen flushing through it, a gelatinous precipitate was formed after five minutes. After the addition of a further 1ml acac the precipitate became considerably thicker. The addition of water did not affect the precipitate.

4a.2.5 Effect of acetic acid on reaction:

It was noted that the presence of acetic acid can have a stabilising effect on the hydrolysis of aluminium compounds. Its effect is enhanced by the presence of hydrochloric acid. However excess amounts of acetic acid can lead to precipitation. This can be demonstrated in the following reaction: To a mixture of 30ml ethanol and 2ml acetic acid 2ml aluminium tri-sec-butoxide was added. This produced an instant precipitate which dispersed after the addition of 0.5ml hydrochloric acid.

A series of reactions following this method were performed in duplicate using 2-methoxyethanol and IPA as solvents. The results are summarised in tables 4a.2.2 and 4a.2.3.

Table 4a.2.2. The results of the addition of 1ml aluminium tri-sec-butoxide 20ml 2-methoxyethanol containing varying amounts of acetic acid and water.

Solvent	Amount acetic acid	Amount water	Immediate Result
20ml MeOEtOH	-	-	Instant transparent gel.
20ml MeOEtOH	1 drop	-	Transparent gel, formed very rapidly but not quite as fast as without acetic acid
20ml MeOEtOH	0.5ml	-	Clear liquid
20ml MeOEtOH	1ml	-	Clear liquid
20ml MeOEtOH	2ml	-	Clear liquid
20ml MeOEtOH	3ml	-	Clear liquid
20ml MeOEtOH	4ml	-	Opaque gel
20ml MeOEtOH	5ml		Opaque gel

Continuing the experiments summarised in table 4a.2.2, the following were performed: 1ml aluminium tri-sec-butoxide was added to 20ml isopropanol containing various amounts of acetic acid, hydrochloric acid and water. The results are shown in table 4a.2.3.

Table 4a.2.3 Results of the addition of 1ml aluminium tri-sec-butoxide to 20ml isopropanol containing varying amounts of acetic acid, hydrochloric acid and water.

Amount of acetic acid	Amount of hydrochloric acid	Amount of water	Immediate Result
0.5ml	2 drops		Fine precipitate
0.5ml	.5ml		Clear liquid
0.5ml	-	2 drops	Fine precipitate
0.5ml	-	0.5ml	Fine precipitate
0.5ml	2 drops	2 drops	Fine precipitate
0.5ml	0.5ml	0.5ml	Clear liquid

4a.2.6 Synthesis involving Gowda's Methods

Following the method described by Gowda[10], 4g aluminium isopropoxide were added to 100ml water. 2g of ammonium hydroxide were added dropwise whilst the mixture was stirred and heated. The resulting precipitate of aluminium hydroxide started off as solid lumps that broke down rapidly during reflux to produce a fine suspension. This precipitate was filtered off and washed with water. This procedure is difficult as the aluminium hydroxide is gelatinous and it is difficult to wash water through it. The residue is added to 100ml water and heated gently to re-disperse the hydroxide. A wet red litmus paper was used to test to see if ammonia was still given off. In the case where any residual ammonia was present, the hydroxide was filtered and washed again before proceeding with the process. 2.5ml of acetic acid were added to the suspension to peptise it under reflux. After refluxing for an hour the mixture became clear however upon cooling it took on a cloudy appearance. After adding a further 0.5ml acetic acid and refluxing for 5 hours, the liquid remained clear upon cooling although it had a slightly opalescent tinge to it. Upon placing a few drops on a microscope slide a gel-film formed.

It proved difficult to combine this aqueous aluminium sol with TEOS to form an alumino-silicate system due to the immiscibility of TEOS with water. Another draw-back with this method involved the length of time of synthesis.

By comparison aluminium tri-sec-butoxide was added to water producing a very thick white precipitate (endothermic reaction). Upon adding hydrochloric acid, the solid material began to agglomerate into a solid lump surrounded by a clear liquid. After refluxing this mixture for an hour at 80°C, a two layer system was formed. The lower layer was opaque and the upper transparent. Upon leaving this to cool after refluxing, three layers developed with the upper two transparent and the lower opaque. These layers were not identified.

4a.3 Conclusions:

The most suitable aluminium compound for this work was shown to be the tri-sec-butoxide, despite requiring careful handling as it is a thick viscous liquid and highly air sensitive and reactive.

The most influential factor upon the hydrolysis rate of the aluminium ion was found to be the choice of solvent. As discussed in Section 1.2.3 and shown in section 4a.2.2, it has been shown that the use of secondary alcohols with aluminium tri-sec-butoxide can result in transparent gel products. The choice of 2-methoxyethanol as solvent for aluminium tri-sec-butoxide was found to give superior stability compared to other solvents. This solvent has also been found to be compatible with other alkoxides which may be combined with this system.

The use of acid can aid the stability of the aluminium cation towards hydrolysis. It has been shown here that the addition of small amounts of acid can slow the hydrolysis of this cation. However if too much acid is used it can have an adverse effect and the hydrolysis rate increases again.

It was found that the stability of the aluminium could be increased by using a nitrogen atmosphere and a water-free environment. However these conditions do not improve the performance of non-suitable solvents.

It was also found that the use of chelating agents can aid the stability of the aluminium but this was not studied in great depth due to concerns with removing residual organics during firing.

Synthesis using methods described by Gowda[12] were shown to be suitable when used with aluminium isopropoxide. However, the Yoldas method cannot be sucessfully used to combine aluminium with silicon as TEOS is immiscible with water. Variations on Gowda's method could be attempted using other suitable solvents.

References:

1. J.E.Stanworth, J.Soc.Glass Technol. 32, (1948), 154-172.
2. W.Bussem and W. Eidtel, Z. Kristallogr. 95, (1936), 175-178.
3. Kiyoharu Tadanaga, Sachiko Ito, Tsutomi Minami and Noboru Tohge, J. non Cryst. Solids, 201 (1996) 231.
4. V. Saraswati, S. Raoot, K. V. S. R. Anjaneyulu and N. V. Visveswararao, J.Mat.Sci, 28, (1993), 1867.
5. J. E. Shelby, S. M. Minton, C. E. Lord and M. R. Tuzzolo, Phys. Chem. Glasses, 33(3) (1992), 93.

6. G. Pozarnsky, E. Westenburg, O. Zarembowitch and A. McCormick, J. Sol-Gel Sci. and Tech. 2, (1994), 7-10.
7. P. Pramanik and S. K. Saha, J. Mater. Sci. Lett. 11, (1992), 311.
8. M. Reese, J. Sanchez, A. V. M^{c}Cormick, Scientific Issues in Ceramic Processing, MRS Proceedings, 190, (1990), 90.
9. M. Nogami, J.non Cryst. Solids, 178, (1994), 320.
10. T. Maki and S. Sakka, J. non Cryst. Solids, 100, (1988), 303-308.
11. C.J.Brinker and G.W.Scherer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing", Academic Press, 1990.
12. G. Gowda, J. Mat. Sci. Lett. 5, (1986), 1029-1032,
13. Yasuyuki Mizushira and Makoto Hori, J.Mat.Res., 8(11) (1993), 2993
14. C. Harrison and Zubin Luo, J. Sol-gel Sci. and Tech. 2, (1994), 71-79.
15. A. G. Williams and L. V. Interrante in "Better Ceramics Through Chemistry", eds: C.J. Brinker, D. E. Clarke, D. R. Ulrich, North-Holland, New York, 1984, p. 151-156.
16. B. E. Yoldas, J.non Cryst. Solids, 63, (1984), 150.
17. C. Harrison, SIRA course 1995.
18. W. Glaubitt , D. Sporn and R. Jahn, J. sol-gel Sci and Tech. 2, (1994), 525.
19. O. Yamaguchi, K. Takeoda and A. Hayashida, J.Mat.Sci.Lett. 10, (1990), 101.
20. R.Hay, J.Mat.Res. 8(11) (1993), 2993.

Chapter 4b – Incorporation of Titanium into Silica Matrices

4b.1.1 Introduction to the Sol-gel Chemistry of Titanium

The majority of systems for microelectronics involve combining titanium, zirconium and niobium with lead, barium, strontium and bismuth. For example: lanthanum titanate ($La_2Ti_2O_7$) is used as a high temperature transducer[1]. Titanium dioxide films with dielectric properties have uses as interference filters, anti-reflective coatings, protective layers amongst others[2]. Lead zirconium titanate (PZT) is used in high frequency piezoelectric transducers and when doped with lanthanum has used in electrooptics[3]. Hence there is great interest in the sol-gel chemistry of compounds of these elements in the literature.

Titanium is a transition metal belonging to group IVB of the periodic table. It has similar properties[4] to zirconium and hafnium. It is tetravalent with an ionic radius of 0.68 angstroms, which is larger than the tetravalent silicon ion (0.40 angstroms) and smaller than Zr^{4+} (0.74 angstroms) and the trivalent rare earth ions. Ti^{4+} normally forms tetrahedral molecules and has a tendency to form predominantly covalent bonds; for example $TiCl_4$ is liquid at room temperature. It can also form complex ions in solution; for example $TiCl_6^{2-}$. It is also possible for Ti^{3+} to exist giving rise to violet coloured solutions.

At room temperature titanium dioxide is white, however when hot it becomes yellow, having similar properties to tin oxide. There are three forms of titanium dioxide: rutile, anatase and brookite. In the most common, rutile, the Ti^{4+} is in an octahedral site and is isomorphous with cassiterite - a form of tin (IV) oxide[4]. Anatase consists of slender tetragonal prisms made up of molecules of TiO_2 and brookite consists of orthorhombic flat plates[4]; both anatase and brookite have the Ti^{4+} in distorted octahedral sites.

There are several advantages to adding titanium to glasses. It increases the refractive index. It can also increase the T_g value and improve the chemical durability[5]. In silica-based glasses the Ti-O-Si bands can be detected using FTIR at $910cm^{-1}$ and when Ti^{4+} is in an octahedral environment it can be detected in the near UV as a dominant feature. When high concentrations of titanium are combined into a glass intense absorption bands occur in the UV region, which extend into the visible giving rise to a yellow colouration[5]. Along with niobium and zirconium, titanium is regarded as network-forming element that will dictate the evolution of the microstructure in the sol-gel transition[6].

It has been stated that for a completely homogenous solid solution of TiO_2-SiO_2, a concentration of 1-6.7molar % TiO_2 is required[7]. These binary oxides are used primarily as supports for catalytic reactions. However it has been reported that in silica based glasses, up to 8.3mol % Ti can be substituted directly for silica where it takes on the same tetrahedral co-ordination[8].

A method for the production of titanium based gels simply involves mixing titanium tetrabutoxide with cyclohexane[9]. This solution is left to stand in a beaker with cling film covering it. The cling film has small pinholes in it to allow moisture to reach the sample.

The sample gels at an ideal temperature of 20°C and at a relative humidity of 55%. However, upon firing this sample crystallises.

Another method for producing gelatinous titanium based solids begins with the neutralisation of an aqueous solution of titanium chloride with ammonia[10]. This produces a black precipitate that turns white when oxygen is bubbled through the mixture. This solid can be aged in water or ammonia to produce xerogel or aerogel particulates depending on the conditions used.

A slightly more complicated method of producing a titanium sol for incorporating with other systems involves taking a 0.2M solution of titanium 2-methyl-2-butoxide in 2-methylbutan-2-ol[11], stirring and adding a mixture of water and alcohol dropwise. This mixture is also slightly acidified. The whole solution is stirred for 3 hours to ensure a complete reaction. The final concentration of TiO_2 was given as 0.1 mol dm^{-3}.

As with aluminium, the use of 2-methoxyethanol as a solvent for titanium sol-gel chemistry is well recognised[6]. It has been reported that when titanium propoxide is refluxed with 2-methoxyethanol for 2 hours at a ratio of 1:12 for Ti:2-methoxyethanol, the propoxide groups are replaced by methoxyethoxide groups[6]. This solution can be distilled down to produce a viscous yellow liquid of the substituted alkoxide. It has been proposed[6] that not all propoxide groups are substituted, however the number increases with the amount of 2-methoxyethanol used (this quantity should always be in excess).

The number of substitutions also increases if the alcohols produced are distilled off. See section 1.2.3 for discussion of substitutions of alkoxy groups.

The use of chelating agents in sol-gel chemistry of titanium has also been documented in the literature[3,6,12]. Titanium isopropoxide can be reacted with acac. It is known that only mono- and bis-acetylacetonate can be successfully formed. These reactions have been followed by FTIR where unreacted acac can be detected in the mixture[6]. As bidentate ligands such as acac are difficult to remove, the hydrolysis rate of the titanium ion will depend on the nature of the remaining alkoxy ligands attached to it. For example, propoxy groups are easy to remove so that hydrolysed species may associate rapidly. If low water concentrations are used the partially hydrolysed species may undergo olation (see section 1.2), forming particles with relatively small hydrodynamic radii. By comparison, when a large volume of water is added regular condensation may occur and crystalline particles may form, for example: $Zr_2(OPr^n)_6(acac)_2$. However, by comparison with propoxy groups, methoxyethoxide groups can be replaced gradually so that no rapid association occurs and a gel is formed slowly over a long period of time.

To stabilise titanium acac complexes further, small quantities of dilute nitric acid can be added prior to the water addition[6].

To promoted further homogeneity, double metal alkoxides or heterometallic alkoxides have been used instead of two single metal alkoxides; for example: diethylsiloxaneethyltitanate copolymer with built-in Ti-O-Si linkages[8] has been hydrolysed in methanol to produce a highly homogenous aerogel.

There are also many examples in the literature of crystalline materials being synthesised using sol-gel techniques. SiO_2-TiO_2 spheres have been synthesised using prehydrolysed TEOS prior to the addition of the titanium alkoxide[13]. Titania spheres have also been synthesised by carefully controlling the hydrolysis of titanium precursors[14].

4b.1.2 Aim

The aim of the following experiments is to demonstrate the synthesis of titanium-containing gels and the factors controlling this.

4b.2 Experimental:

Although there are other titanium compounds available for use in sol-gel synthesis, this work utilises titanium isopropoxide that has been demonstrated in the literature to be the most versatile and suitable compound for these types of reactions. As with aluminium tri-sec-butoxide, this titanium alkoxide is a highly reactive liquid that must be handled using a hypodermic syringe and needle. It is not as reactive as the chosen aluminium alkoxide and is not as viscous hence a small bore needle may be used with little difficulty.

4b.3.1 General Synthesis of Silica Gels Containing Titanium

This is a simple synthesis requiring a beaker and a magnetic stirrer. 4g TEOS are added to 25ml ethanol. To this solution 2ml titanium isopropoxide is added followed by 5 drops of acetic acid. Upon gelation after two days a transparent, pale yellow gel is formed. This became black upon firing and although it remained intact it was easily broken into small pieces.

4b.3.2 Determination of the Composition of a Stable Silica-Titania Gel:

A range of mixtures was made up based on the above recipe. However the solvent was changed to isopropanol (more suited for titanium isopropoxide) and the acid was changed to hydrochloric (less complicated reaction). The mixtures are given in table 4b.1.

From these results it can be seen that there is a distinct relationship between the TEOS:titanium propoxide ratio and the amounts of acid and water used to produce a transparent gel. This relationship can be demonstrated in figure 4b.1.

Table 4b.1: Compositions of Silica-Titania gels. All samples used 30ml isopropanol

Amount of TEOS (ml)	Amount of Titanium Propoxide (ml)	Amount of acid (drops: 50drops=1ml)	Amount of water (ml)	Result
5	5	5	-	Transparent gel
3	7	5	-	Highly cracked gel
7	3	5	-	Transparent gel
5	5	10	-	Slightly cracked gel
-	5	10	-	Cracked gel
5	4	10	1	Bloated gel
6	4	20	1	Clear sol
3	7	20	1	Very rapid gelation
30	7	5	1	Clear sol
3	2	-	1	Very rapid gelation
1	9	20	1	Very rapid gelation
1	9	50	1	Very rapid gelation

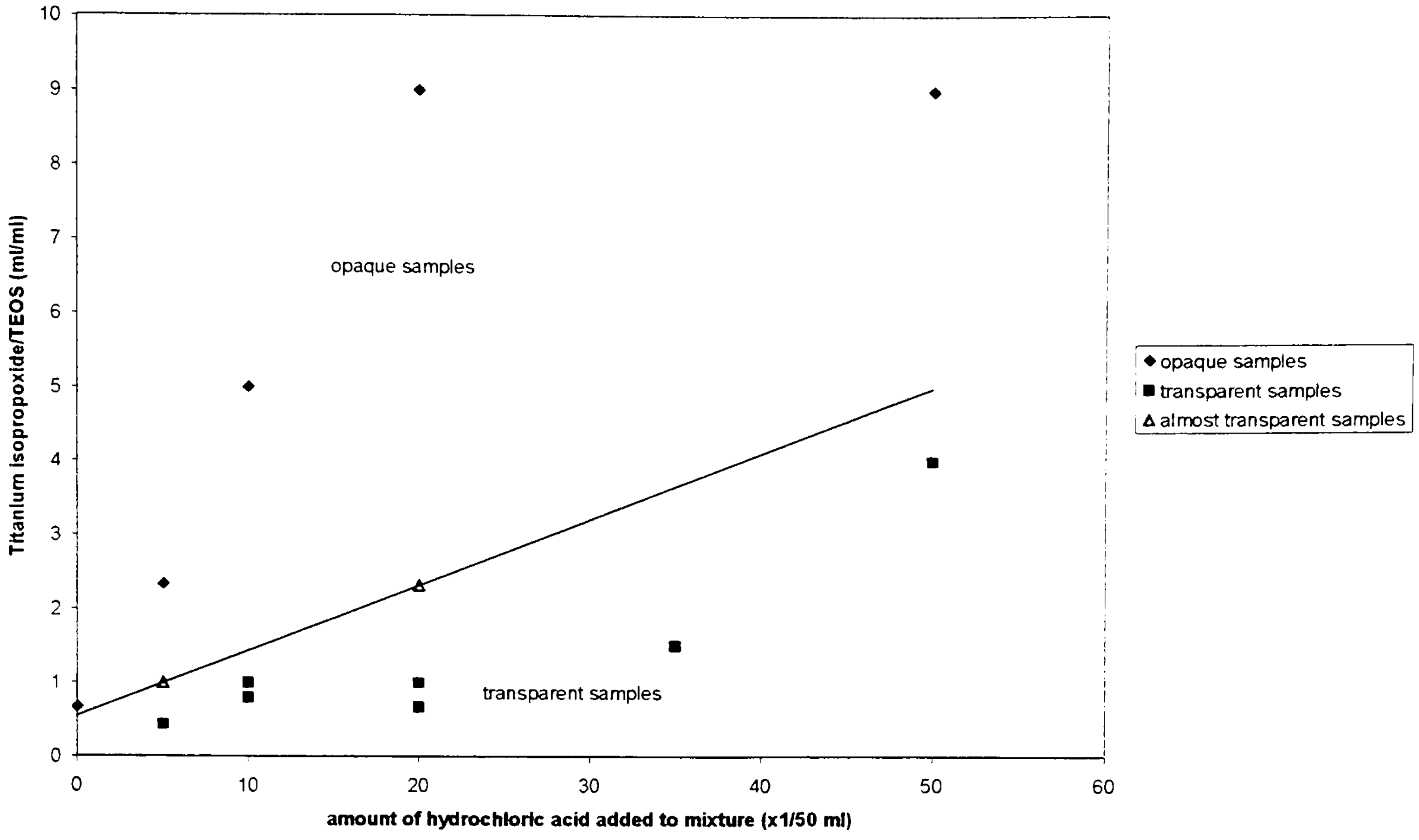


Figure 4b.1 Relationship between amount of hydrochloric acid used and ratio of titanium propoxide and TEOS.

4b.3.3 Use of 2-methoxyethanol as a Solvent in the Synthesis of Titanium containing Silica Gels

Stable gels were synthesised using 2-methoxyethanol as solvent. It was found that once the titanium alkoxide had been introduced to the solvent via a hypodermic syringe and needle it formed quite a stable solution that if left to dry at room temperature would form a solid yellow gel that broke down upon heating.

When combined with TEOS transparent gels could be synthesised which then could be fired to make transparent glasses under certain compositions. An example of such a mixture is as follows:

2.3ml TEOS is hydrolysed with excess water (2.3ml) plus a very low amount of hydrochloric acid (this was taken from a mixture of 100ml TEOS being combined with 100ml water in the presence of 1/5ml hydrochloric acid). To this 10ml 2-methoxyethanol was added followed by 0.4ml titanium isopropoxide.

Stable gels were also synthesised by simply adding the titanium isopropoxide to 2-methoxyethanol and leaving to gel and dry in lidded petri dishes at 40°C for 2 weeks. These gels remained stable for months although upon firing they became powders.

4b.4 Conclusions

From the results given in table 4b.1 and figure 4b.1 it can be seen that it is necessary to have some acid in the gel mixture to prevent the formation of precipitates when using isopropanol as a solvent for the synthesis of titanium containing silica gels and glasses. It can also be seen that as the ratio of titanium to silicon increases the probability of producing opaque and particulate samples increases unless the amount of acid added is above a certain level shown in figure 4b.1. It also implies that it is not possible to synthesise a titanium based glass by this method with titanium as the sole cation.

However it has also been shown in section 4b.3.3 that titanium containing glasses could be synthesised successfully using 2-methoxyethanol as a solvent. This solvent has been

12. K. G. Severin, J. S.. Ledford, B. A. Torgenson and K. A. Berglund, Chem. Mater. 6b (1994) 890

13. M.H.Selle, J. Sjoblom and R. Lindberg, Colloid Polym. Sci. 273, (1995), 951.

14. H.Kumazawa, H. Otsuki and E. Sada, J. Mat. Sci. Lett., 12, (1993), 839 .

demonstrated to produce very stable solutions and gels when used with titanium isopropoxide although these gels do not always form glasses when fired.

As can be seen in chapter 9, SiO_2 glasses containing nanoparticle crystallites of TiO_2 can be prepared by the above routes.

References:

1. V. Prasadarao, U. Selvaraj and S. Komarneni, J. Mater. Res., 10(3) (1995), 704.
2. M. Gartner, G. Parlog and P. Osiceanu, Thin Solid Films, 234 (1993) 561 and references therein.
3. Guanghua Yi and M. Sayer, J. Sol-gel Sci. & Tech., 6 (1996) 65.
4. R.B.Heslop and P.L.Robinson, "Inorganic Chemistry", Elsevier, 1963
5. L. E. Bausa, J. G. Sole, A. Duran and J. M. Fernandez-Navarro, J. Non Cryst. Solids, 127(3) (1991) 267
6. M. Sedlar and M. Sayer, J. Sol-gel Sci. and Tech. 5, (1995), 27.
7. T. Lopez, J. Navarro and R.Gomez, "Sol-gel Science and Technology" Ceramic Transactions number 55, Edited by E. Pope, S. Sakka and L. Klein. 1995, American Ceramics Society.
8. J. B. Miller and L. J. Mathers, J. Mater. Chem. 5(10) (1995), 1759.
9. Y. Tanaka, H. Hirakawa and M. Nogami, J. Ceram. Soc. Jpn., Int.Edn., 102, (1994), p577.
10. N. Yacoub, J. Ragai and S. A. Selim, J. Mat. Sci., 26(18) (1991) 4937 and references therein

11. G. W. Koebrugge, L. Winnubst and A. J. Burggraaf, J. Mater. Chem. 3(11), (1993), 1095

12. K. G. Severin, J. S.. Ledford, B. A. Torgenson and K. A. Berglund, Chem. Mater. 6b (1994) 890

13. M.H.Selle, J. Sjoblom and R. Lindberg, Colloid Polym. Sci. 273, (1995), 951.

14. H.Kumazawa, H. Otsuki and E. Sada, J. Mat. Sci. Lett., 12, (1993), 839 .

4c: The Incorporation of Zirconium into Silica Matrices

Introduction: An Overview of Zirconium Sol-gel Chemistry

A brief glance at the chemistry of the zirconium ion[1] shows that it can exist in different co-ordination environments. Its primary state is tetravalent and can be found in four, six, seven and eight co-ordinate sites of a range of geometries. Its ionic radius, given at 0.74 angstroms, is approximately twice that of Si^{4+} and just slightly smaller than the trivalent rare earth ions. An ionic radius of 0.75 angstroms for hafnium, due to the lanthanide contraction, leads to zirconium and hafnium having very similar properties resulting from this fact they are the two most alike elements of the periodic table. Zr^{4+}, due to a larger ionic radius than Ti^{4+}, gives rise to more ionic bonding than titanium hence $ZrCl_4$ is crystalline at room temperature[2] compared to $TiCl_4$ which is liquid at room temperature[2].

As sol-gel chemistry is primarily concerned with hydrolysis of ions, a look at the solution chemistry of zirconium reveals that no true hydroxide exists. When hydroxide ions are added to a solution of zirconium ions, a gelatinous precipitate of the hydrated oxide is produced. It should also be noted that a zirconium-based sol is less susceptible towards gelation than a titanium-based sol[3].

The incorporation of zirconium into glasses has similar benefits to the incorporation of titanium[4]. It increases the refractive index and increases the amount of fluorine that can be added to the glass[4]. Due to the resistance of zirconium oxide to acid and alkali, the addition of zirconium also gives greater chemical durability to the glass[4]. However, unlike titanium, it does not give colour to the glass unless it is exposed to X-rays, producing a grey coloration[4]. It has been used in making glass-ceramics and opaque glasses. Other advantages of the addition of zirconium include strength, toughness and oxygen conductivity[4].

Traditionally, the zirconium content in silica glasses was limited to a few molar percent due to the high melting temperatures required for conventional synthetic methods (zirconium oxide itself melts at about 2700°C). However, utilising sol-gel methods, glasses up to 50mol % zirconia can be synthesised using temperatures below 1000°C[5] and as a result the quality of glasses produced by sol-gel techniques can be greater than those produced by melt-quench techniques[4]. Because of this, there is extensive information available about the sol-gel chemistry of zirconium in the literature.

The opacity and quality of sol-gel derived zirconia-silica glasses is dependent on the percentage of zirconium incorporated into the lattice. Experiments have shown that as the zirconium content increases in a silica lattice the greater the opacity of the final fired product[6]. Surface segregation can also occur giving a powdered film of zirconium oxide across the surface of the sample[4]. In these studies, although a sample consisting of 100%zirconium was made to gel, it collapsed into a powder upon firing[6].

Upon firing a zirconia-containing gel certain changes become evident. It has been reported that opaque samples undergo a colour change from white through to grey then black as the tempreature increases to around 500°C[6]. Then, as the temperature is increased further, the samples gradually become white again at around 800°C. This was explained by Nogami[7] as the presence of unhydrolysed alkyl bonds remaining trapped in the gel structure and breaking down in the heating process to be eventually released.

As many of the sol-gel techniques described for the synthesis of aluminate and titanate containing samples apply to the synthesis of zirconate-containing samples, the following methods are those that are unique to zirconium.

It has been reported that a zirconia-based gel has been produced by dripping zirconyl chloride into water producing a precipitate[8]. This was centrifuged and dried, resulting in a gel. Upon heating to 390°C the mass and pore-volume of this gel decreased due to water being expelled from the matrix. When heated to higher temperatures the gel densifies further and begins to crystallise.

As with aluminium and titanium, the use of glycolethers has been examined[9,10]. In the case of zirconium propoxide substitution of the n-propoxide groups occurs when the starting alkoxide is reacted with 2-methoxyethanol. This reaction has also been documented more fully by Mehrohta[11]. It is believed that the reaction is a bimolecular substitution[9]. In this report the reaction was performed in a Schlenk apparatus to continuously remove the n-propyl alcohol produced by distillation.

It is known that the commercially available alkoxide, zirconium propoxide has a fast hydrolysis rate and is not suitable for sol-gel processing[9]. Many authors[6,12,13,14,15] suggest chelation of the zirconium ion to stabilise it. For example, to solutions of acetylacetone with zirconium propoxide, water and nitric acid in ethanol has been added[15]. This resulted in a yellow glassy material which crystallised upon heating. Further stability can be obtained by initially producing the methoxyethoxide substituted complex prior to reaction with acac[3].

Partially hydrolysed TEOS was mixed at room temperature with zirconium acac solution in ethanol[6]. This could be catalysed with either an acid or a base and heated at 30°C producing a gel. The gel was dried at 120°C over a period of forty eight hours to produce a transparent glass. The ideal concentration for a transparent sample was given as 10 molar % zirconium.

It has also been reported that fibres of zirconia were successfully pulled from a solution of zirconium n-propoxide and EAA (ethylacetoacetate) in ethanol[14].

Zirconia monoliths have been synthesised from zirconium n-propoxide and dimethylformamide[16]. When the dimethylformamide (DMF) is added to a solution of zirconium propoxide in 2-propanol an instant precipitate is formed due to the basic nature of the DMF. The addition of acac prior to the DMF stabilises the zirconium against rapid gelation and a stable sol is formed which can be hydrolysed in a controlled manner.

A method for the preparation of zirconia based xerogels has been proposed which does not involve the use of chelating agents.[17]. A commercially available solution of zirconium tetrapropoxide was dropped into a diluted nitric acid solution. This caused an immediate precipitate which was then peptised over a period of 3 days resulting in a clear sol with a pH of about 1. This was increased to between 4 and 7, and, after evaporation of the solvent, a xerogel was formed.

The choice of solvent has also been studied for the synthesis of stable zirconia systems. Most of the solvent requirements for titanium chemistry also applies to zirconium, however it must be noted that for the use of zirconium n-propoxide which is commercially available, cyclohexane is far more suitable than n-propanol[18]. The former allows slow hydrolysis rates and hence transparent gels may be formed and the latter produces precipitates due to fast hydrolysis rates.

Aim

The aim of this section of work is to confirm the work published prior to this investigation and to demonstrate the production of stable zirconium-containing systems.

4c.2 Experimental:

4c.2.1 Synthesis Using Zirconium Chloride

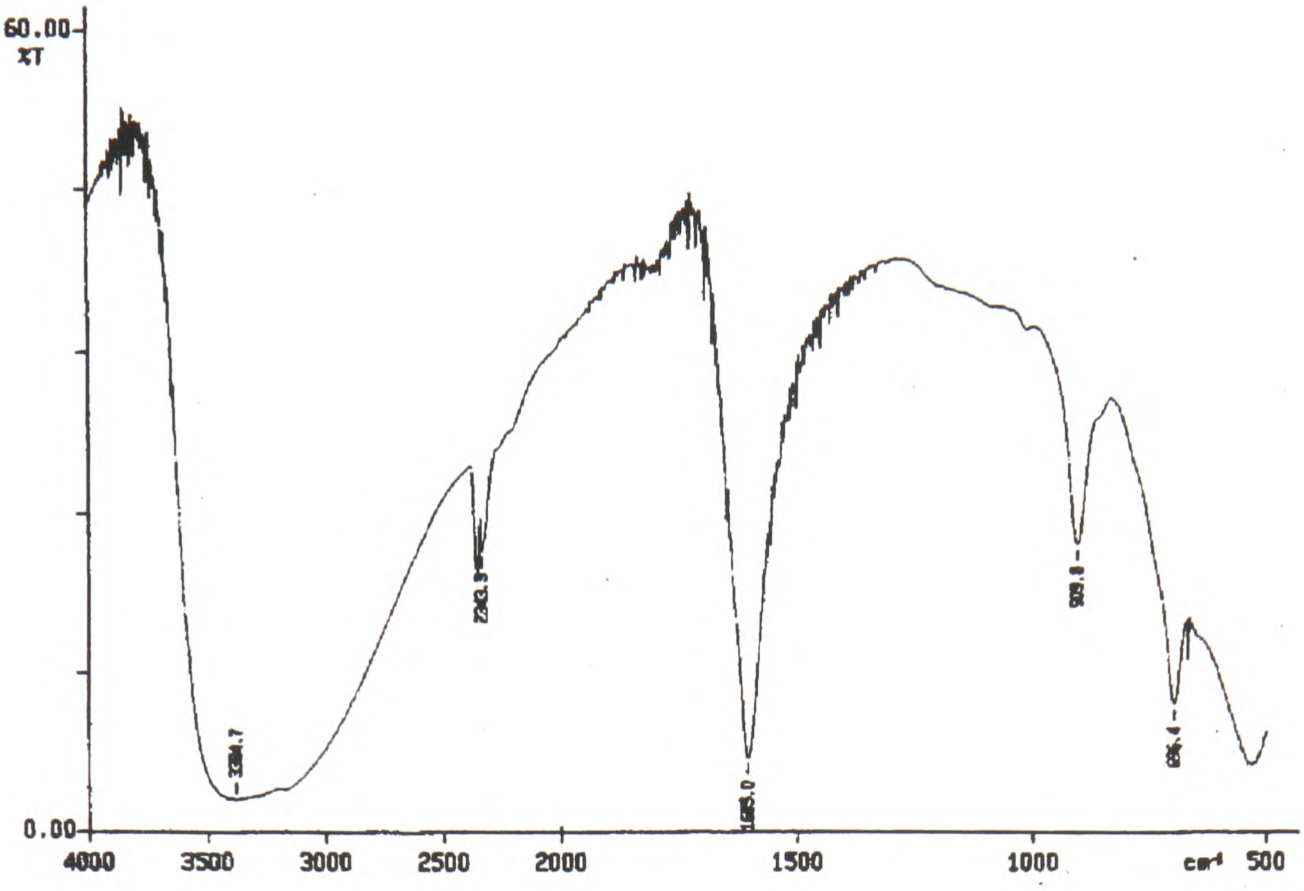
Two sources of zirconium chloride were used in this work. Initial gels were made with an old sample of zirconium chloride that was several years in the laboratory and had turned yellow. This dissolved with difficulty in several solvents, and did not dissolve as readily as it should in water. It has been suggested that zirconium tetrachloride is quite reactive and this did not seem to be the case with this sample.

A fresh sample of zirconium tetrachloride was purchased from Aldrich Chemical Company and used. This was a much more reactive and dissolved in many more solvents than the older material. FTIR analysis was performed on the two samples to compare their structure. See figures 4c.1 and 4c.2.

Gels were made up using the new sample of zirconium chloride and when combined with TEOS in low concentrations (around 20mol %) transparent gels were formed. It was noted that crystals were forming on the surface of several zirconium- containing gels. These were studied using scanning electron microscope. See figure 4c.3 and 4c.4.

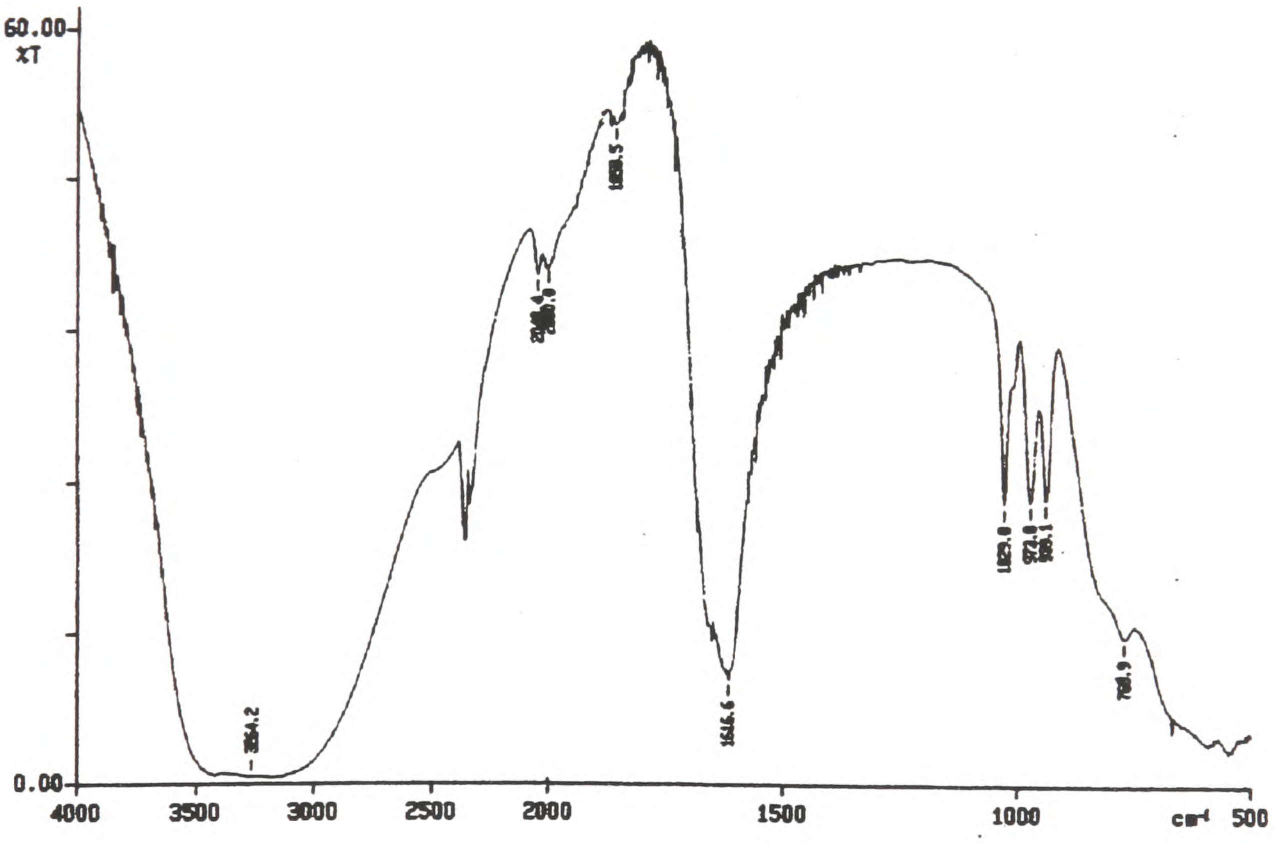
A typical method of making a zirconium-containing silica gel using zirconium chloride is as follows:

0.5g zirconium chloride was added to 50ml ethanol. This does not dissolve until the ethanol is heated producing a yellow solution. It must be noted that if some of this solution is left to stand in a shallow plastic dish, very small pieces of yellow gel are formed which crystallise after several days. 10ml water, 6g TEOS dissolved in 50ml ethanol and 3g hydrochloric acid is added to this solution.



95/02/02 12:35 UNSPECIFIED
X: 10 scans, 2.0cm-1

Figure 4c.1: FTIR analysis of fresh zirconium chloride



95/02/02 12:50 UNSPECIFIED
X: 10 scans, 2.0cm-1

Figure 4c.2: FTIR analysis of older sample of zirconium chloride

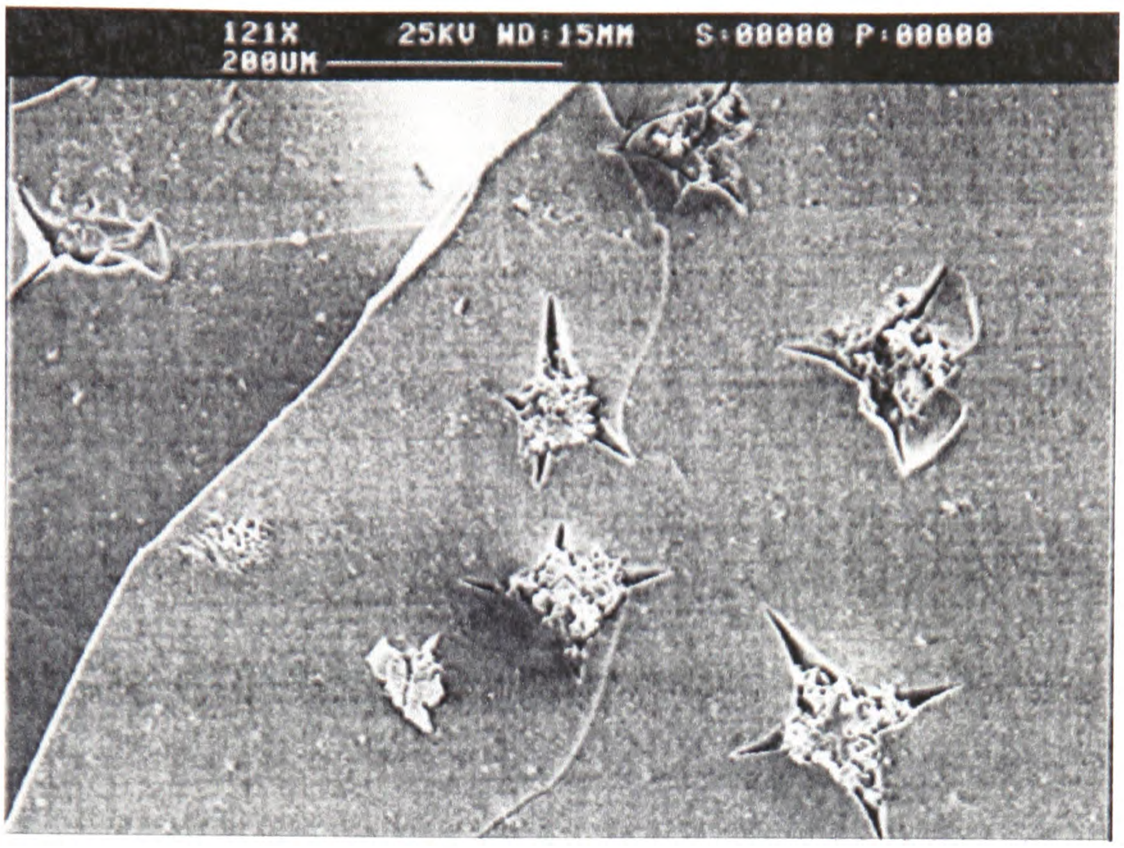


Figure 4c.3: SEM picture of silica gel containing 20mol% zirconium dioxide made from TEOS and zirconium chloride.

Figure 4c.4: SEM picture of silica gel containing 20mol% zirconium dioxide made from TEOS and zirconium chloride.

4c.2.2 Synthesis using zirconium propoxide

Although some work was performed with zirconium chloride and oxychloride, the majority of the experiments were carried out using zirconium propoxide of 70wt%Zr in propan-1-ol. This is a reactive liquid that must be handled using hypodermic needles and syringes to prevent contact with air and water. However it is not as reactive as aluminium tri-sec-butoxide and is considerably less viscous and hence easier to handle. Table 4c.1 shows the results of the addition of zirconium propoxide to various solvents, followed by the addition of TEOS, water and acid.

Table 4c.1: Additions of zirconium propoxide to various solvents.

Sample	Amount of Zrpropoxide	Solvent	Amount of TEOS	Water	Acid	Nitrogen	Result
1	10ml	ethanol	6ml	3 drops	-	yes	Gelatinous white solid
2	10ml	ethanol	6ml	3 drops	1g HCl	yes	Gelatinous white solid
3	10ml	IPA	6ml	-	0.5 acetic	no	Transparent solution, becomes particulate upon reflux or after time
4	1.3ml	IPA	6ml	-	-	no	Transparent gel
5	0.4ml	ethanol	5.5ml	1ml in 10ml IPA	-	no	Translucent gel but intact.
6	0.5ml	ethanol	5.5ml	2ml	-	no	Transparent gel
7	0.5ml	ethanol	5.5ml	10ml in 15ml IPA	0.5mlHCl	no	Cloudy after minutes
8	2ml	ethanol	5.5ml	3ml in 15ml IPA	0.5mlHCl	no	Gelatinous precipitate
9	2ml	ethanol	5.5ml	3ml in 15ml IPA	12mlHCl	no	Gelatinous precipitate

4c.2.3 Firing of samples:

Upon firing immediately after drying the samples became blackened and highly cracked. It was suggested that this was due to organics trapped within the matrix. To overcome this, the samples were fired at a lower heating rate to allow the organic molecules to escape prior to pore closure (see section 1.2). This was unsuccessful and the samples were still blackened. However after leaving samples at room temperature in lidded petri-dishes for more than two months, the majority did not go black upon firing.

4c.2.4 Use of Chelating Agents

Acetylacetonate was chosen as a stabilising agent for the zirconium propoxide. A range of samples were synthesised varying the amounts of water, solvents and acid. It was found that the presence of hydrochloric acid was not necessary for the production of a transparent gel. However it was found that the use of isopropanol as a solvent with zirconium propoxide and acac produced instant white precipitates even in the presence of TEOS. In contrast, the use of ethanol with these reagents produced stable solutions which remained transparent even when excess water was added. However the addition of excess water did cause the resulting gels to be opaque.

Example: 0.5ml zirconium propoxide added to a solution of 0.5ml acac in 30ml ethanol, which was then mixed with 5.5ml TEOS and 2ml water in 15ml ethanol produced a transparent gel. However upon mixing 5ml water instead of 2ml, the gel became opaque.

Samples made using acac as a chelating agent became blackened upon firing (see section 4c.2.3).

4c.2.5 Use of 2-methoxyethanol as a solvent

It was found that 2-methoxyethanol could be used successfully as a solvent for zirconium sol-gel chemistry. When zirconium propoxide is introduced to this solvent using a hypodermic needle and syringe a stable solution is formed which if placed in a lidded petri dish at 40°C will gel eventually. The time of gelation being inversely proportional to the concentration of the zirconium. However if this solution is made up in dry 2-methoxyethanol and placed in a sealed container under nitrogen it will remain stable for many months.

4c.3 Results and Discussion

4c.3.1 Samples made up using Zirconium chloride:

The FTIR spectra of the two samples of zirconium chloride are given in figures 4c.1 and 2. As can be seen in the region of 900-1030cm^{-1} there is a significant difference between the two samples.

It proved difficult to make a zirconium based gel using the chloride as precipitates were formed in the mixture. Samples based on TEOS and zirconium chloride sometimes had white crystalline material on the surface of the gel. Upon analysis using SEM it was shown that this material was made up of crystallites embedded in the surface of the sample. See figure 4c.3 and 4c.4.

4c.3.2 Samples made up using Zirconium Isopropoxide:

Table 4c.1 shows the results of the different combinations and compositions used to make zirconium containing silica gels. From this table we can see that the best methods are given by examples 4 and 7. This shows that use of low zirconium concentrations and minimal water addition are best in this type of synthesis.

By comparison with zirconium chloride containing samples, the majority of the samples made up using TEOS and zirconium isopropoxide (approx.20 mol%) had smooth surfaces without crystallites growing. See figure 4c.5.

By examining the EDAX spectra produced from silica-zirconia samples synthesised using zirconium chloride, it can be suggested that the crystallites formed when the chloride is used are zirconium chloride or a form of the chloride. If this is the case then it can be concluded that not all the zirconium is bonded into the silicate matrix as it must remain in solution to be precipitated out of the pores of the gel as it dries. Figure 4c.6 shows the EDAX spectrum of a silica sample made with zirconium chloride showing the presence of chloride ions on the surface of the sample, however this is not conclusive as the spectrum is a measure across the whole surface of the sample.

Alternatively, it could be proposed that there is some phase separation occurring with the zirconium-rich phases bringing about precipitation on the surface of the silica-based matrix.

Figure 4c.5: SEM picture of silica gel containing 20mol% zirconium dioxide made from TEOS and zirconium isopropoxide

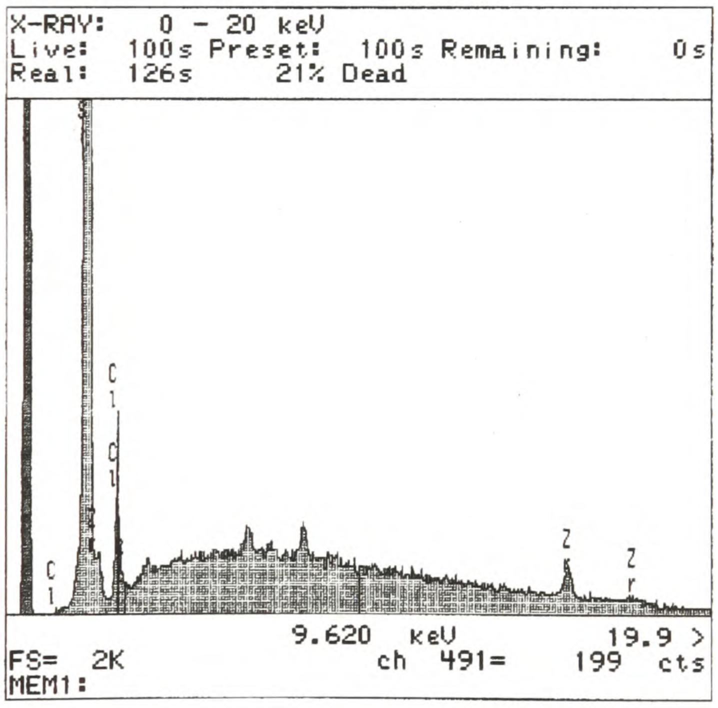


Figure 4c.6: EDAX analysis of silica gel containing 20mol% zirconium dioxide made from TEOS and zirconium chloride showing the presence of chloride ions.

4c.4 Conclusions

As with titanium and aluminium, there are many problems to be encountered when attempting to synthesise zirconium containing silica glasses. As with the other transition metals studied here, it can be seen that 2-methoxyethanol is the ideal solvent for making stable solutions for sol-gel chemistry.

References:

1. F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry", Wiley Interscience, 1988, United States.
2. R. B. Heslop and P. L. Robinson, "Inorganic Chemistry", Elsevier, Holland, 1963
3. M. Sedlar and M. Sayer, J. Sol-Gel Sci. and Tech. 5, (1995), 27.
4. "Sol-gel Technology for thin films, fibres, preforms, electronics and speciality shapes", editor: L. C. Klein. p194, Noyes Publications, United States, 1988.
5. P. J. Dirken, R. Dupree and M. E. Smith, J. Mater. Chem., 5(8) (1995) 1261
6. I. M. Miranda-Salvado, Serna, J. M. Fernandez-Navarro, J.non Cryst. Solids. 100, (1988), 330-8.
7. M. Nogami J. Non-Cryst. Solids, 178 (1994) 320-6.
8. E. Crucean and B. Rand, J. Brit. Ceram. Soc., 78(3), (1979), 58.
9. G. Antonioli, P. P. Lottici, I. Manzini, G. Gnappi, A. Montenero, F. Paloschi and P. Parent, J. Non-Cryst. Solids, 177 (1994), 179-186.
10. J. P. Pirard, P. Petit, A., Mohsine, B. Michaux, F. Noville and A. J. LeCloux, J. Sol-gel Sci. & Tech., 2, (1994), 875-880.
11. R. C. Mehrohta, J. Non-Cryst. Solids, (1988), 1001.

12. S. Sakka and K. Kamiya, J. Non-Cryst. Solids, 63 (1984), 223.

13. C. J. R. Gonzales-Olivier, P. F. James, H. Rawson, J. non-Cryst. Solids, 48 129 (1982).

14. T. H. Jung and R. V. Subramanian, J. Mater. Res. 9(4) (1994), 1007.

15. A. Aronne, P. Pernice, A. Marotta, J.Mat.Sci.Lett. 10 (1991), 1136-8.

16. J. Ray, M. Chatterjee and D. Ganguli, J. Mat.Sci.Lett., 11, (1992), 968.

17. Q. U. Xu and M. A. Anderson, J.Mater.Res. 6(5) (1991), 1073.

18. L.C.Klein, "Sol-Gel Optics". Kluwer Acramenic Press, Holland, 1994.

Chapter 5 – The Synthesis of Rare Earth-Containing Silica Gels

5.1 Introduction

5.1.1 Properties of the Rare Earth Ions

The rare earth elements consist of the lanthanides (the elements from cerium to lutetium) and yttrium and lanthanum. The chemical and physical properties of yttrium and lanthanum closely resemble those of the lanthanides and hence are grouped together with them. The dominant valency of this group is three although certain of the lanthanides can exist as divalent or tetravalent ions.

The lanthanides have a full $6s^2$ level and begin to fill the 4f level. There is an overall decrease in atomic and ionic radii from lanthanum to lutetium that is known as the Lanthanide Contraction. This is caused by the increasing nuclear charge being poorly shielded by the 4*f* electrons from the outer 6s electrons[1].

5.1.2 Rare Earth Element Gels.

Gels, where the sole cation is a rare earth element (RE), are not well documented in the literature. One source dedicated to the synthesis of yttrium based gels is authored by Wenjian Weng et al[2]. As the yttrium alkoxides are highly reactive with water and have low solubility in alcohols, these authors attempted to produce a stable concentrated yttrium alkoxide solution by the addition of yttrium acetate to 2-methoxyethanol and diethylenetriamine (DETA) giving a solution concentration of yttrium acetate of greater than 0.5M. Careful addition of water to this solution yielded a gel[2].

5.1.3 Properties and Uses of Rare Earth Ion – Doped Glasses

Some of the rare earth ions have distinctive colours and absorptions in glassy matrices as shown in table 5.1

Table 5.1: properties of the lanthanide ions (Additionally, the divalent europium ion gives a weak yellow colouration to glass[3]).

Ion	Colour of ion	Configuration	Absorption of ion in glass
La^{3+}	Colourless	$4f^{0}$	-
Ce^{3+}	Colourless	$4f^{1}$	Absorbs at 320nm
Pr^{3+}	Green	$4f^{2}$	Weak and narrow
Nd^{3+}	Lilac	$4f^{3}$	Weak and narrow
Pm^{3+}	-	$4f^{4}$	-
Sm^{3+}	Yellow	$4f^{5}$	Broad, absorbs 300-500nm
Eu^{3+}	Pale pink	$4f^{6}$	-
Gd^{3+}	Colourless	$4f^{7}$	Weak and narrow
Tb^{3+}	Pale pink	$4f^{8}$	Weak and narrow
Dy^{3+}	Yellow	$4f^{9}$	Weak and narrow
Ho^{3+}	Yellow	$4f^{10}$	Weak and narrow
Er^{3+}	Rose red	$4f^{11}$	Weak and narrow
Tm^{3+}	Pale green	$4f^{12}$	Weak and narrow
Yb^{3+}	Colourless	$4f^{13}$	-
Lu^{3+}	Colourless	$4f^{14}$	-

The addition of rare earth ions to glasses has several effects. The addition of lanthanum ions to alumino-silicate glasses increases the T_g value and an overall increase in density and refractive index is observed as the amount of rare earth ions in increased[4]. The incorporation of low concentrations of lanthanum oxide can also reduce the chance of crystallisation in the glass and the lanthanide ion has been recognised as acting as a network modifier[5]. The addition of rare earth ions to silica glass matrices also increases the amount of non-bridging oxygens in the silica forming weaker Si-O-R bonds – one definition of network modifier is that it is something that causes the formation of non-bridging oxygens[6], see section 1.1.

Europium ions have been used considerably in the literature to study the environments that the rare earth ions are in during and after undergoing sol-gel reactions with silica precursors to produce rare earth-doped silica glasses[7,8,9]. This is useful as the lifetimes, energy levels and homogenous linewidths of the trivalent europium ion are influenced by the environment that the Eu^{3+} ion is in[10]; further details are given in section 5.1.9.

The applications of rare earth doped glasses include: lasers, sensors and radiation resistant glass[11]. Although yttrium doped silica glasses have good mechanical strengths at high temperatures[12], firing the glass in an atmosphere of ammonia will partially replace oxygen atoms with nitrogen increasing the strength further[12].

5.1.4 Homogeneity of RE_2O_3-SiO_2 Glasses

There are limits to the amounts of rare earth ions that can be successfully added to silica-based glasses. At concentrations above 5 molar %[13], phase separation occurs which leads to crystalline phases of the rare earth oxides being present in the glass[4] leading to loss of transparency and the eventual production of crystalline powders.

Rare earth ion clustering in sol-gel synthesised silica glasses occurs before it becomes noticeable from the decreasing transparency of the sample. By using Eu^{3+} ions as a probe, it has been shown[14] that clustering occurs in samples containing as low as 0.5 mol %

Eu^{3+}. However, the addition of aluminium ions can have a noticeable effect on this[14] suggesting that the aluminium is effective in dispersing and isolating the europium ions. Unfortunately no detailed explanation has been given in the literature.

It has been suggested[15] that the presence of co-dopants such as Sr^{2+},Y^{3+}, Sc^{3+}, Ga^{3+} can inhibit clustering and promote better dispersion. This is probably due to the co-dopants penetrating into the europium clusters and dispersing the ions away from each other. This effect is more noticeable with cations of larger field strengths as they have a larger disruptive effect on the network[15].

5.1.5 Rare earth salts as starting materials in the synthesis of rare earth –doped silica glasses

A simple synthesis of rare earth – containing silica glass is described in the literature[12] as yttrium nitrate dissolved in a minimum amount of water that is added dropwise to a mixture of TEOS and ethanol (at a ratio of 1:3) at room temperature in an ultrasonic bath. Additional water was added until the overall amount reached 3 times that required for complete hydrolysis of the alkoxides in solution. This solution was stirred for one hour at room temperature, transferred to a Teflon beaker, covered in plastic wrap and placed in an over at 40°C. The resulting dried gels were transparent. A range of gels with varying yttrium content was reported with the concentration varying from between 5 to 30 weight %. No crystalline phases were detected using XRD analysis.

Similarly, the synthesis of rare earth doped silica glasses is described by Kang Sun et al[16] using rare earth carbonates mixed with prehydrolysed TEOS with the water content being kept to a minimum. The carbonates are initially dissolved in the minimum amount of hydrochloric acid and then added dropwise to an ethanol-TEOS mixture. Transparent glasses with a rare earth content of up to 5.2 mol% RE_2O_3 (RE=rare earth element) were reported.

Much synthesis has been reported using similar methods and starting materials[7,17,18]. It has been shown, by utilising the trivalent europium ion as a probe, that during the synthesis of these gels differences occur due to the nature of the precursor introduced[6]. A comparison between the presence of nitrate, chloride and perchlorate ions was carried out and differences were noted between their positions around the europium ions in the gels. However upon firing the gel, the Eu^{3+} ion loses water and solvent co-ordination and becomes surrounded by a rigid silica cage and any differences are eliminated.

However, another report[19] examining the differences between using neodymium nitrate, chloride and acetate as starting materials makes some conflicting statements. When using nitrate and chloride it was discovered that above 5 weight % Nd_2O_3 a single phase was not produced although with neodymium acetate added to TEOS hydrolysed with acetic acid resulted in no observable phase separation up to 10 weight % Nd_2O_3. It was also claimed that the interior of the chloride synthesised gels had a lower neodymium content that at the surface. This effect was also noticed with the acetate synthesised gels however the variation between surface and interior was less significant.

5.1.6 Rare earth alkoxides and oxy-alkoxides as starting materials in the synthesis of rare earth –doped silica glasses

As rare earth alkoxides are insoluble in most solvents, the majority of rare earth alkoxides detailed in the sol-gel literature are based on yttrium salts combined with 2-methoxyethanol.

Perhaps the simplest suggestion for the synthesis of yttrium methoxyethoxide is from the reaction of yttrium metal and 2-methoxyethanol with a mercury chloride catalyst under reflux for 24 hours[20]. Other authors[21] have used an electrochemical technique instead of utilising the mercury chloride catalyst to react rare earth metals with 2-methoxyethanol.

The general features and behaviour of yttrium derivatives of 2-methoxyethanol are described in the literature[22]. Metal alkoxides are preferred in sol-gel chemistry for several reasons: high purities can be obtained, easy transformation of the anions into volatile by-products and ability to form homogenous solutions. Heterometallic alkoxides (or multi cation alkoxides) can be formed as well and have been used in sol-gel chemistry with success[23]. However the hydrolysis of metal alkoxides is hard to control if successfully dissolved or synthesised in situ. 2-methoxyethanol is much more reactive than standard alcohols and its yttrium derivatives are more stable towards hydrolysis than standard alkoxides – this solvent is regarded as a chelating alcohol[23].

When yttrium oxoalkoxides are reacted with 2-methoxyethanol at room temperature, the trimethoxyethanolate derivative is formed[22] see equation 5.1. This compound is highly soluble in many solvents including non-polar liquids whereas the oxoalkoxides are considerably less soluble and more reactive.

$Y_5O(O^iPr)_{13} + MeOC_2H_4OH_{(xs)} \rightarrow 5/m[Y(OC_2H_4OMe)_3]_m + 13^iPrOH$ Eqn. 5.1

The ethoxide analogue of this oxoalkoxide is highly insoluble. The product of equation 5.1 has been shown[22] to be a decamer (m=10) with a cyclic structure which allows organic solvent molecules to form a layer structure and gives a high solubility. Upon solution this compound retains its solid state structure as determined by nmr studies[22].

By comparison, the dissolution of yttrium acetate in 2-methoxyethanol does not yield yttrium trimethoxyethanolate as expected even after reflux[22]. Instead a yttrium methoxyethoxyacetate derivative is produced. According to the literature the infrared spectrum of the isolated product shows absorption peaks due to uncoordinated acetate groups ($1586cm^{-1}$ and $1423cm^{-1}$)[22]. This compound is still highly soluble in many solvents and its hydrolysis leads to colloidal suspensions which in turn lead to stable and homogenous gels[22]. This modification to yttrium acetate is useful as the acetate itself has low solubility and hence is only suitable for use in systems that have a high water content[24].

There are other mentions and studies in the literature concerning the production of stable systems by dissolving yttrium acetate in 2-methoxyethanol[24,] . However the conclusions drawn assume that the final yttrium-based solution consists of yttrium methoxyethoxide.

It has been shown[24] that the addition of this product to prehydrolysed TEOS does not produce a transparent glass, however the authors do not take into account the low solubility of yttrium in silica glass systems.

5.1.7 The use of chelating agents in the synthesis of rare earth -doped silica glasses

It is a known fact that yttrium isopropoxide is highly insoluble in the majority of solvents. However it has been shown that it will dissolve in 2-methoxyethanol in the presence of ethylacetoacetate (EAA) or 2-dimethylaminoethanol producing a chelated compound[25]. A comparison of these two modifiers shows that EAA gives more homogeneity when the yttrium complex is mixed with network formers[25].

Using a chelating agent with a rare earth ion in sol-gel chemistry also has the advantage of protecting the rare earth ion from being surrounded by hydroxyl ions that quench or reduce the emission from that ion[21].

5.1.8 Other Methods of Synthesising Rare Earth Containing Glasses

An alternative method of incorporating rare earth ions into sol-gel matrices is described by G. De et al[26]. This involved introducing an amino alkoxysilane (N-(2-aminoethyl)-3-aminopropyltrimethoxysilane or DAMO) to praseodymium chloride to stabilise the Pr^{3+} ion in the minimum amount of water. This is added to prehydrolysed TEOS at a pH of 4 (this prevents precipitation upon addition of the Pr-DAMO complex).

5.1.9 Influences on the Rare Earth Luminescence in Sol-gel Derived Glasses

Clustered Eu^{3+} ions are identified from their luminescence that shows a lack of line-narrowing effect due to the energy transfer between the ions[14].

The lack of periodicity in atomic arrangement in glassy matrices causes the rare earth ions to be found in different energy environments to each other within a single glass matrix[27]. This leads to the broadening of the luminescence bands compared to those found in crystals[27]. As the luminescence of the rare earth ions is a result of the excitation of the inner 4*f* electrons which are shielded by the outer electrons, any changes in structure and composition of the host glass do not lead to large changes in the luminescent characteristics[27].

The excitation of a luminescent centre (i.e.: rare earth ion) is strongly influenced by the absorption characteristics of the glass[27].

5.2. An investigation into the Sol-gel Chemistry of the Rare Earth Elements

5.2.1 Experimental: The addition of metal salts to various solvents

Various yttrium salts (chloride, nitrate, acetate) were dissolved in different solvents and left to stand and evaporate at 40°C. Combinations of water and acids were added to these solutions. The following chelating agents were also used in conjunction with the rare earth salts: ethyl acetoacetate, acetylacetonate, and diethylenetriamine.

5.2.2 Experimental: The Addition of Rare Earth Acetates to 2-methoxyethanol

Experiment 1

Various quantities of rare earth acetates were added to different volumes of 2-methoxyethanol. As the acetates were stirred with the solvent, pH readings were taken with respect to the time of mixing.

Experiment 2

2g of yttrium acetate and 40ml 2-methoxyethanol were refluxed together at the boiling point of the 2-methoxyethanol (125°C) until the acetate had completely dissolved. This process took several days producing a pale yellow solution. Drops of this solution were placed on microscope slides and left to dry. 5ml volumes of this mixture were placed in lidded plastic petri dishes and left unsealed in an oven at 40°C for several days. Larger volumes were partially sealed plastic containers at room temperature. Both hydrous and anhydrous acetates were used in separate experiments.

Experiment 3

0.2g of hydrated yttrium acetate were added to 20ml of 2-methoxyethanol at room temperature. The acetate dissolved quite quickly and a white powder precipitated out of the solution. This was collected and analysed. Upon continued stirring and additional heating this precipitate redissolved in the 2-methoxyethanol and the mixture was treated as above. By comparison 1g of yttrium acetate was added to 20ml 2-methoxyethanol and stirred at room temperature. The dissolution of the acetate and the following precipitation were not readily observed.

To aliquots of the final mixtures from experiments 2 and 3, small amounts of water were carefully added whilst stirring.

The resulting dried samples were fired in a muffle furnace at temperatures up to 1200°C with the temperature being increased slowly from room temperature at various rates.

The various powders and products were analysed using Fourier Transform Infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

5.2.3 Results and Discussion:

Results from the addition of Rare Earth Salts to Various Solvents:

The rare earth nitrates were highly soluble in most solvents. In contrast the acetates and chlorides were soluble primarily in water. It was found that the only combination that produced a gel film on a microscope slide was when yttruim acetate was dissolved in boiling 2-methoxyethanol.

Following the literature[2] chelating agents were added to 2-methoxyethanol prior to the addition of the acetate. In this case the mixture was not heated. It was found that little success was had with EAA and dissolution only occurred after the addition of water. This did not lead to a gelatinous product but to colourless crystals.

In contrast, DETA and acac gave gel films, after addition to 2-methoxyethanol prior to the addition of acetate, when droplets of the final mixture were placed on a microscope slide. However considerably more acac was needed than DETA. By comparision, acac gave a solution when mixed with 2-methoxyethanol prior to the addition of yttrium isopropoxide, but with DETA a solution did not form. The results are given in table 5.2.

Table 5.2: Results of the addition of DETA and acac to various rare earth solutions in 20ml 2-methoxyethanol:

Yttrium salt	Amount of chelating agent	Result
0.4g yttrium acetate	82 drops acac	Acetate dissolved. Produced gel film on microscope slide
0.4g yttrium acetate	6 drops DETA	Acetate dissolved. Produced gel film on microscope slide.
0.2g yttrium isopropoxide	50 drops DETA	No dissolution.
0.2g yttrium isopropoxide	28drops acac	Isopropoxide dissolved. Large crystals formed on microscope slide.

It must be taken into consideration when handling DETA that this chelating agent will thicken and become quite gelatinous itself when left to stand on a microscope slide in the open lab. As yttrium acetate forms a gel film with 2-methoxyethanol in the absence of DETA and acac, further study of these chelating agents in this system was put aside for this project.

In experiment 1, the pH of the mixtures of acetate and 2-methoxyethanol dropped as the acetate dissolved and increased as the precipitate appeared (see figure 5.1). From this it can be concluded that the drop in pH of dissolution of the acetates is due to the decomposition of the acetates and its release of water molecules. Upon precipitation the water remains in solution hence the resulting lower pH once the system has stabilised.

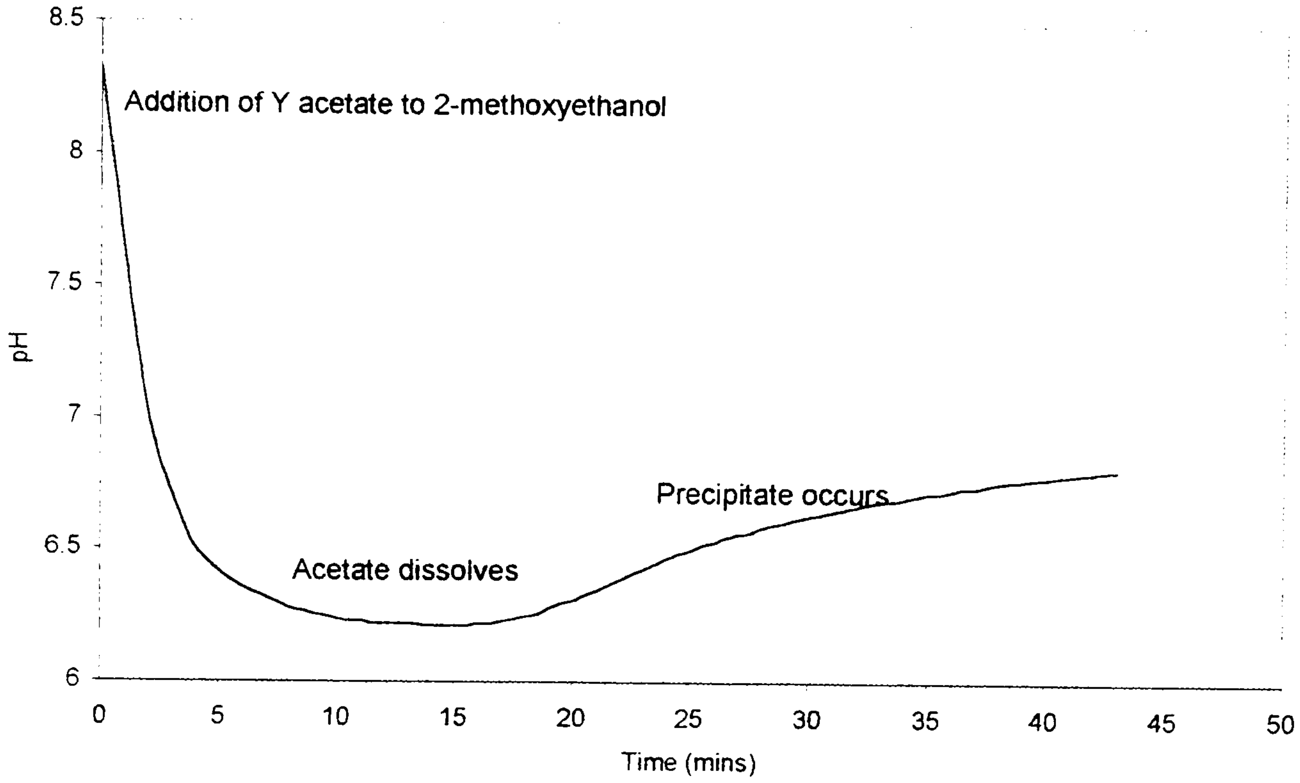


Figure 5.1 Plot of pH against time for the reaction of yttrium acetate with 2-methoxyethanol.

The room temperature reaction from experiment 3 produced similar final results to the heated mixture in experiment 2. However the acetate took longer to dissolve at room temperature. The precipitated powder did not readily dissolve in 2-methoxyethanol once collected and dried. The mixture had to be heated before dissolution occurred.

Although dissolution of the acetate was not readily observed during experiment 3 when 1g of acetate was added to 20ml 2-methoxyethanol, the pH readings of this reaction are similar to those of the reaction using the smaller amount of acetate in which dissolution was observed. This suggests that a similar process is occurring and the FTIR spectra of the collected solids after several hours also indicate that this is the case. The final product, although left to dry in an oven at 40°C for several weeks, was quite hydroscopic and absorbed water from the air at room temperature resulting in water droplets appearing on the surface which then caused the gel to be broken more easily. When the transparent gel was fired in a muffle furnace it broke down into a powder despite the slow heating rate from room temperature.

The precipitate that is produced after the initial dissolution of the acetate in the 2-methoxyethanol can be seen to be anhydrous acetate from the FTIR spectra (see figures 5.2 and 5.3). Here it can be seen that the large peak assigned to water and OH^- stretch between 3400 and 3600 cm^{-1} is significantly reduced in the spectrum of the precipitate compared with that in the hydrated acetate spectrum. It can also be seen that apart from this difference, the two spectra are very similar. This dehydration of the acetate by the 2-methoxyethanol suggests that there is a much stronger attraction of the yttrium ion for 2-methoxyethanol rather than water. This perhaps offers an explanation of the much observed stabilising effect of 2-methoxyethanol on the hydrolysis of various metal cations.

When water was added to aliquots of the mixtures from experiments 2 and 3, gelation occurred very quickly and in excess water redispersion of the gel occurred as the ions became completely hydrated. Therefore careful addition of the water was necessary to prevent this as excess would prevent gel formation.

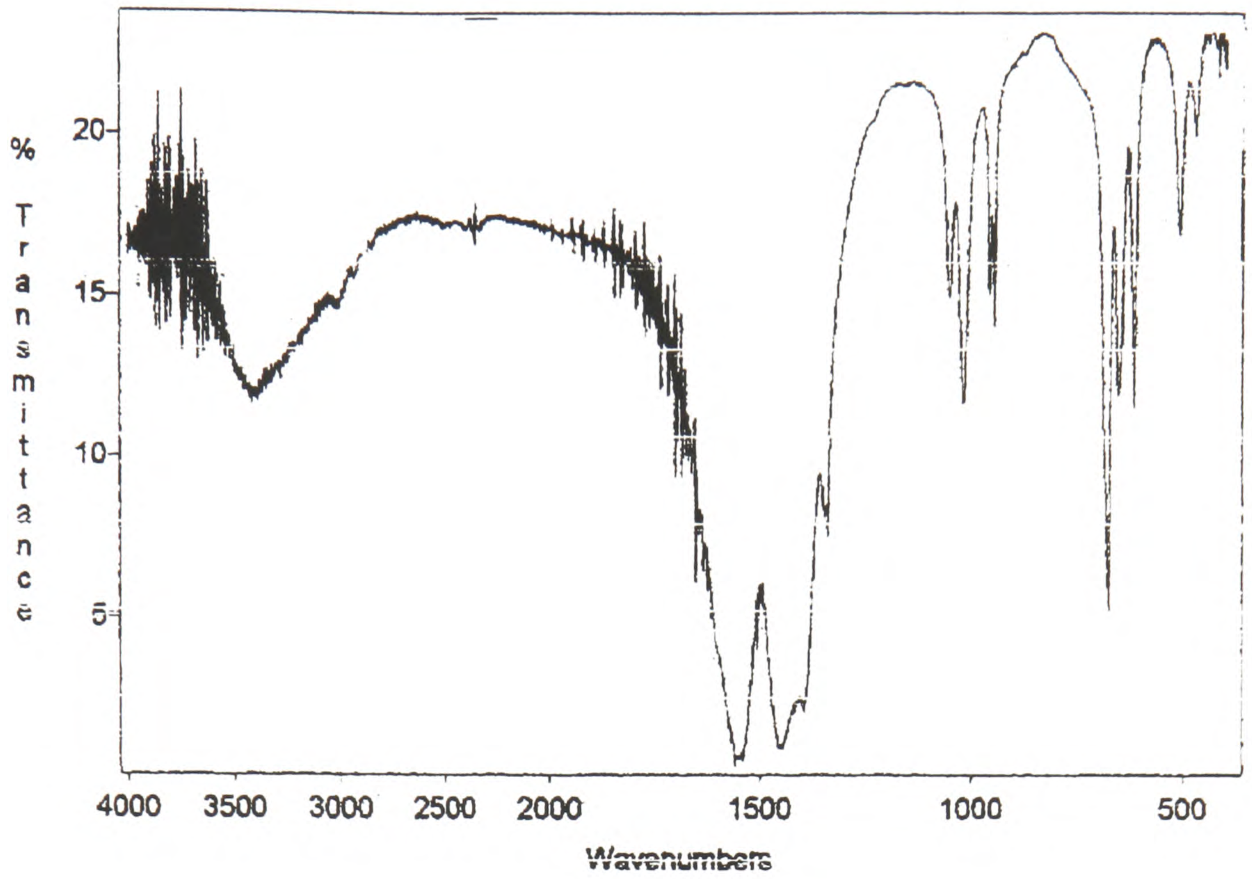


Figure 5.2: FTIR spectrum of hydrated yttrium acetate

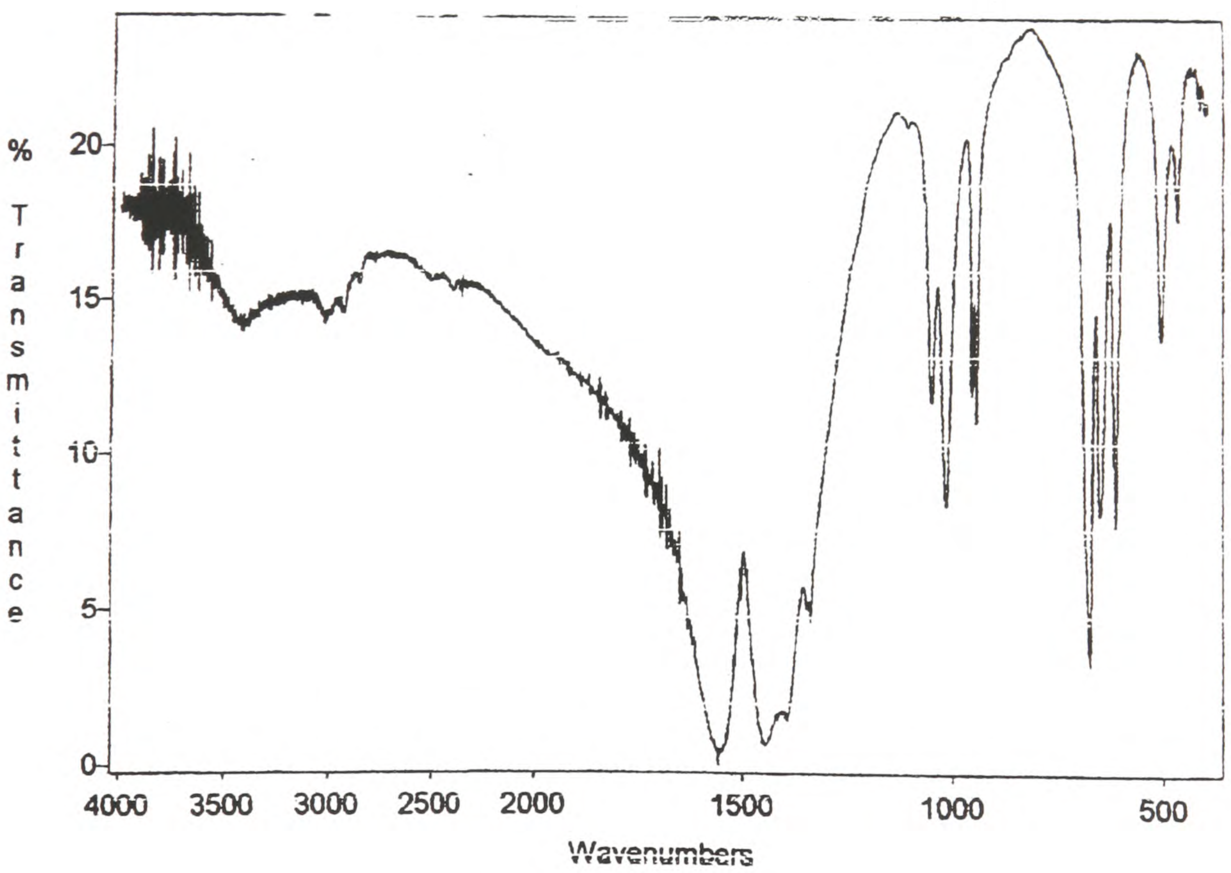


Figure 5.3 FTIR spectrum of precipitate from reaction of yttrium acetate with 2-methoxyethanol

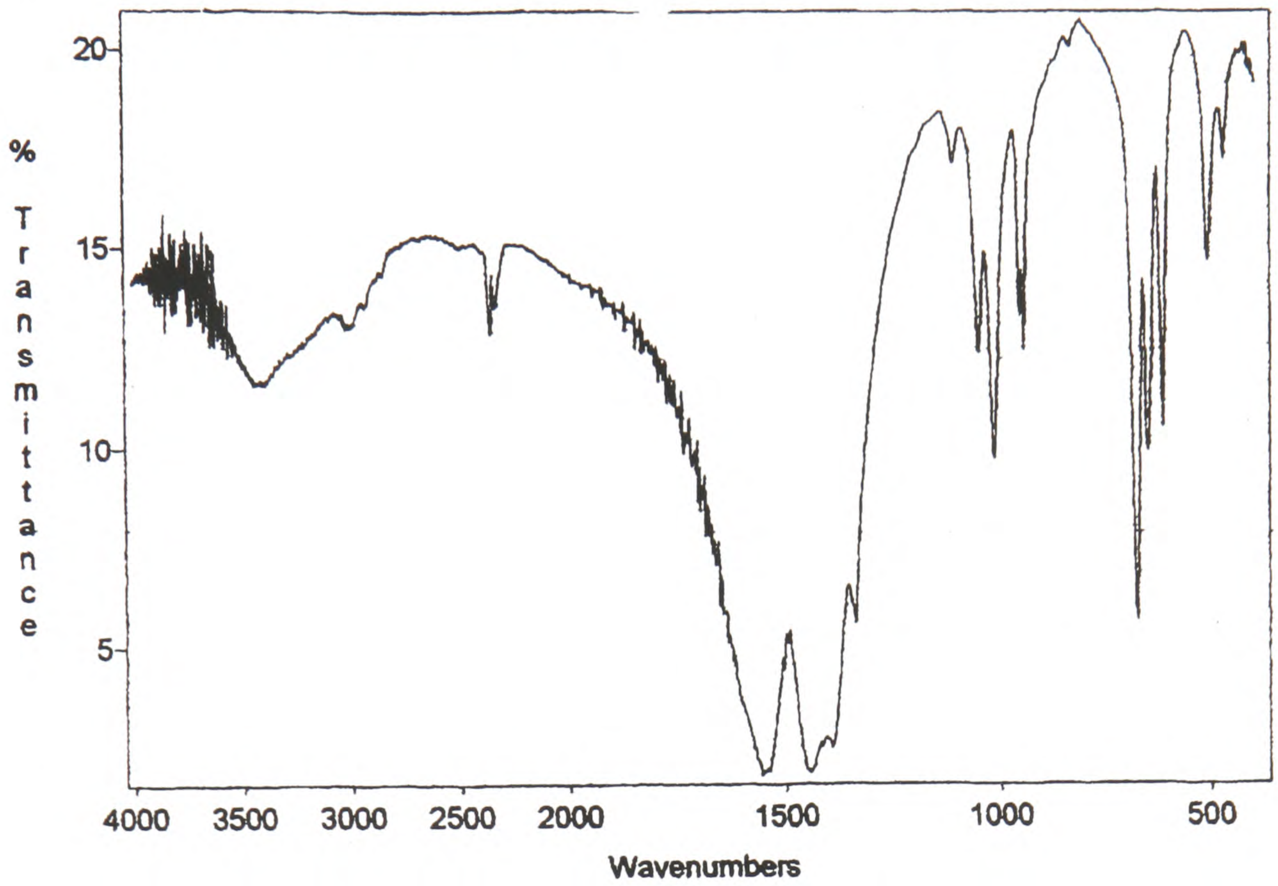


Figure 5.4 FTIR spectrum of final dried gel product from reaction of yttrium acetate with 2-methoxyethanol.

5.2.4 Conclusions on Systems where Rare Earth Ions are the Sole Cations.

Upon addition of rare earth acetate to 2-methoxyethanol a small amount of dissolution occurs where liberation of water molecules occur. This dissolution is only readily observable if the amounts of acetate are kept low with respect to the amount of 2-methoxyethanol used. The loss of water can be shown by comparison of the FTIR spectra of the hydrous acetate and the precipitate (see figure 5.2 and 5.3). It can be clearly seen that the precipitate has a anhydrous acetate structure. This conclusion is backed up by thermal gravimetric analysis (TGA) of the products and precursors (see figures5.5, 5.6 and 5.7). where the trace of the anhydrous acetate is very similar to the precipitate and does not lose water as the hydrated acetate does. The pH change over the reaction (see figure 5.1) is probably due to the gain of water by the solvent from the acetate. The FTIR of the final dried gel also shows an acetate structure (see figure 5.4). It is known that yttrium acetate has a polymeric structure[2]. This is explained by the yttrium trivalent ion normally requiring a co-ordination number of 8 and the acetate ligands only providing six oxygen ligands to the ion in a nominal yttrium acetate molecule[2]. Hence some acetate ligands have bidentate and bridging forms of co-ordination[2]. It has been proposed that as the methoxyethoxide anion ($CH_3OC_2H_5O^-$) is quite nucleophilic and will attack the Y^{3+} ion and substitute bridging acetate ligands from other yttrium acetate molecules, it will therefore break down the polymeric structure of the acetate and form a stable complex[2], see equation 5.2.

$$Y(OAc)_{3\,(solid)} + 2\ CH_3OC_2H_5O^- \rightarrow [Y(OAc)_3(CH_3OC_2H_5O)_2]^{2-} \qquad \text{Eqn. 5.2}$$

The results in this project do not concur with those of other authors[2,22] who propose that the reaction of yttrium acetate and 2-methoxyethanol produce various compounds and complexes. The two suggested structures: yttrium methoxyethoxide and yttrium methoxyethoxyacetate complex do not fit with the FTIR spectra presented here which clearly show the acetate structure.

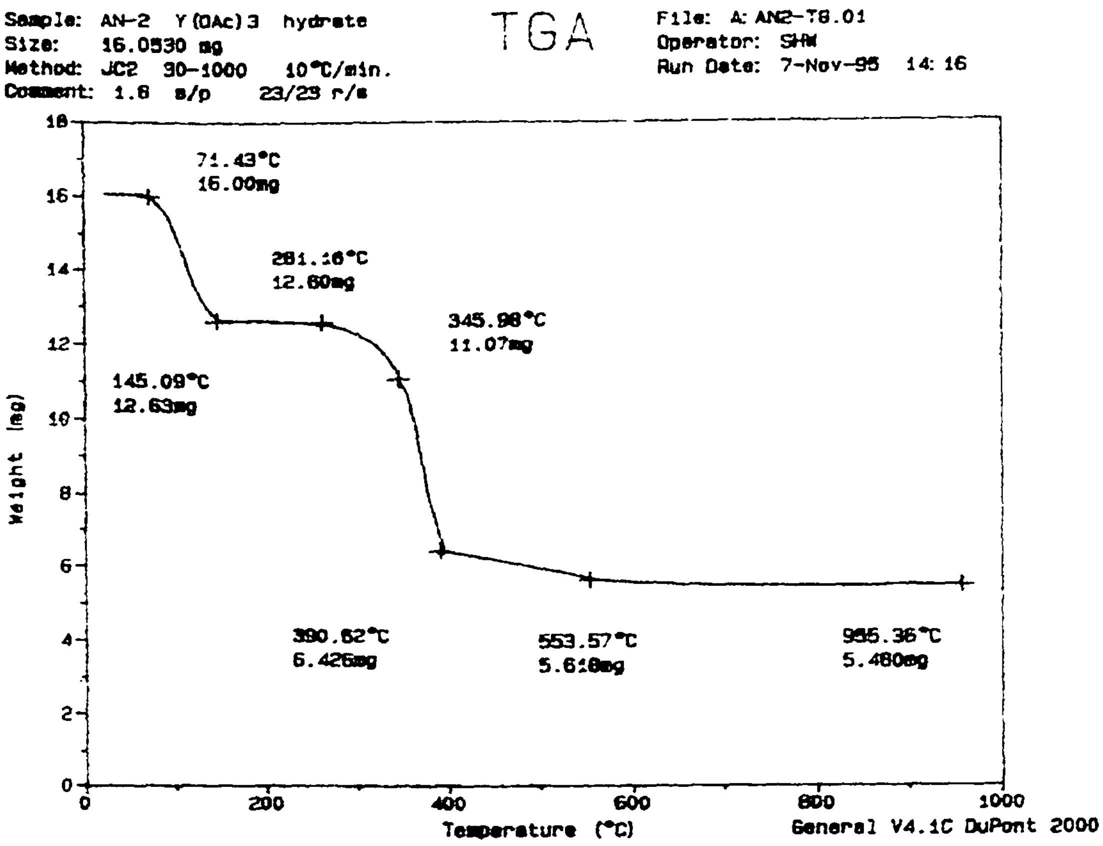


Figure 5.5: TGA results of hydrated yttrium acetate

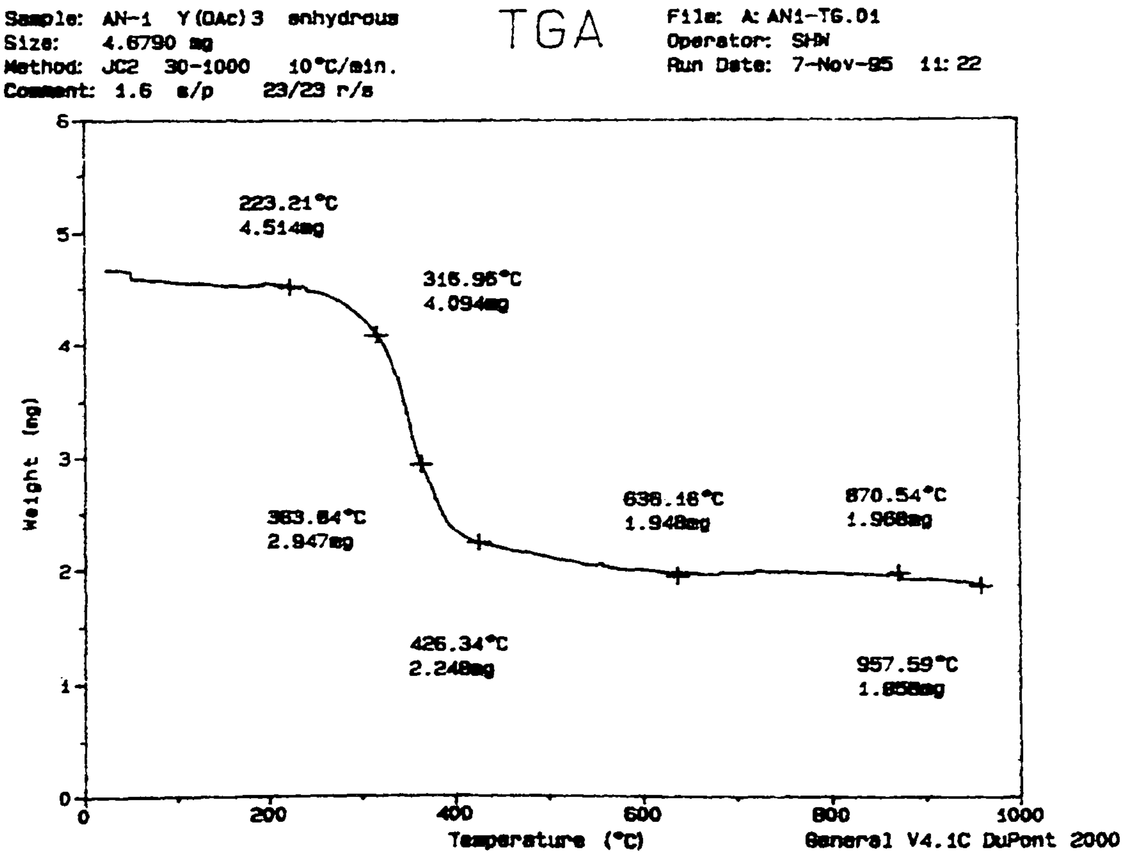


Figure 5.6 TGA results of anhydrous yttrium acetate

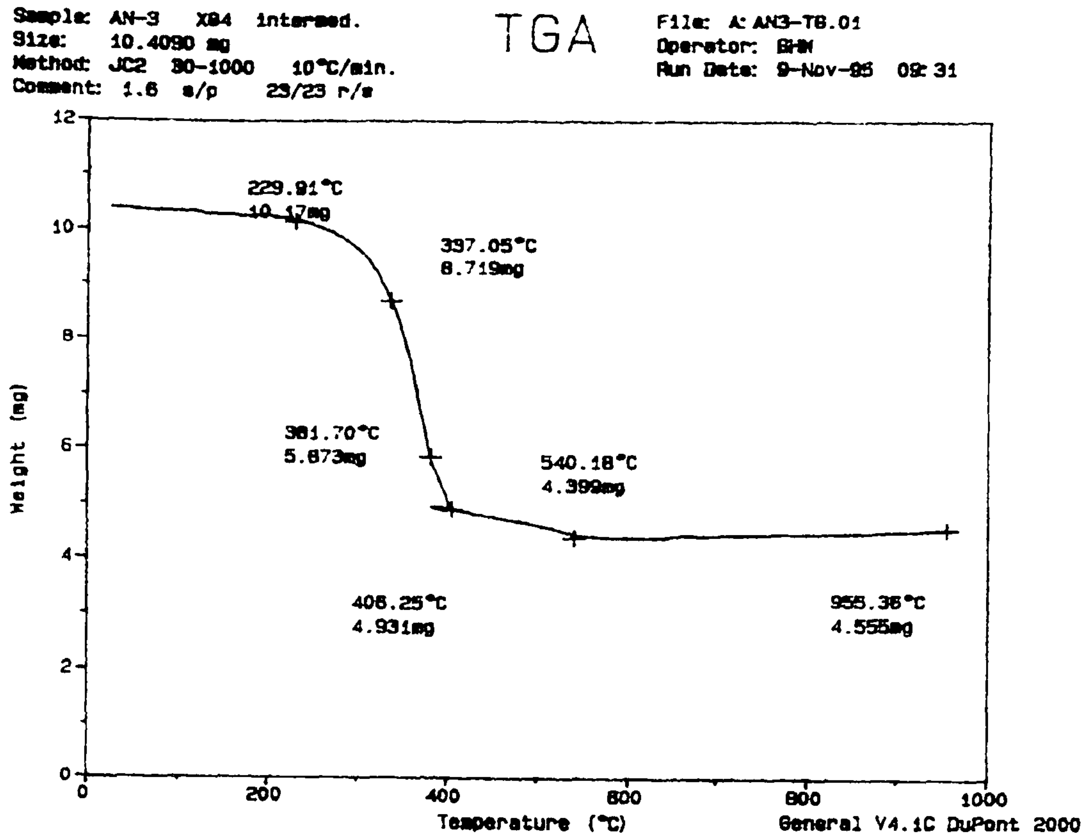


Figure 5.7 TGA results of precipitate produced from reaction of yttrium acetate with 2-methoxyethanol.

5.3 Addition of rare earth solutions to TEOS-based sol-gel systems

5.3.1 Experimental:

Yttrium nitrate solutions were added to a mixture of TEOS and different solvents along with various amounts of water and acids. Amounts of yttrium nitrate were added to 10ml of either 2-methoxyethanol or 10ml ethanol. These two solvents were chosen as the most suitable for both components. It can be seen from the above experiments that 2-methoxyethanol is more suitable of the two for the rare earth but due to its toxic nature, the next most suitable alternative must be considered. To these solutions 10ml TEOS, 2ml hydrochloric acid and 5ml water were added.

5.3.2 Results

For both ethanol and 2-methoxyethanol transparent gels and glasses were formed with yttrium oxide (Y_2O_3) concentrations below 5 mol %. At concentrations above this the glasses become opaque and begin to break up upon firing. Apart from the gels containing 2-methoxyethanol taking a little longer to dry, there was very little difference found between the two groups of samples.

FTIR analysis of the dried, unfired samples show peaks associated with silica matrices and yttrium nitrate. These results also concur with the spectra and results from a similar study described in the literature[12]. The spectra of the fired samples are described as showing a shoulder at 950cm^{-1} which is related to Si-O-Y bonding[12]. This is not obvious in the spectra of the nitrate samples produced in this part of the study.

5.4 The Reaction of Yttrium Alkoxides with Hydrochloric Acid and the Incorporation of the Products into TEOS-Based Sol-gel Systems

Yttrium ethoxide ethanol complex and yttrium isopropoxide are highly insoluble in the majority of solvents. However they react with concentrated hydrochloric acid and the products are added to a TEOS based sol-gel system.

5.4.1 Experimental

1g yttrium isopropoxide was added to 6g concentrated hydrochloric acid. This gave off a lot of heat, a pungent odour and produced an oily brown residue. Upon completion of the reaction and cooling, this was mixed with 12g TEOS in 50ml ethanol. After leaving to stand at 40°C for several days in petri dishes, a golden yellow gel was formed. This gel becomes dull and cloudy upon drying. After firing the sample becomes transparent and colourless.

Higher concentrations of yttrium were also mixed with this system.

5.4.2 Results

Upon initial addition of the yttrium isopropoxide to the acid an orange colour is produced which gets darker as the reaction continues. This results in an amber-brown oily substance that settles on the surface of the liquid after stirring is ceased and the system is allowed to settle. A pungent smell is also given off which is similar to that of an olefin. It is believed that the oily substance is polypropene from polymerisation of the isopropyl groups of the yttrium isopropoxide.

The gels were golden yellow with a shiny appearance when wet. However, as they dry, the colour becomes darker reaching a brown colour. The gels also lose their shiny appearance and become dull. This was found to give a good indication as to when the gels are dry and ready to be fired. The organics in this system were also easily removed in the firing process.

At yttrium concentrations higher than 5 mol % the resulting glasses were white, opaque and easily broken.

5.5 The Use of Drying Control Chemical Additives (DCCAs) in the Synthesis of Rare Earth Containing Silica Sol-gel Systems

Suggested DCCAs in the literature[28] include glycerol, dimethylformamide (DMF) and oxalic acid.

5.5.1 Experimental

Yttrium nitrate was dissolved in ethanol. TEOS, water and hydrochloric acid were added. A small amount of one of the following DCCAs were added: glycerol, DMF and oxalic acid. The resulting gels were dried and fired as described in section 2.4.

5.5.2 Results

It was found that none of the DCCAs used were suitable for this system. The amount of glycerol was very difficult to measure accurately due to its highly viscous nature. It was also difficult to remove upon firing leaving black residues in the glass from trapped organics in the matrix. This also caused the sample to crack. Being basic DMF was unsuitable as it increased the pH of the gel and influenced the gelation process. Upon addition of oxalic acid a fine white precipitate was formed. This was believed to be the insoluble yttrium oxalate salt. This was backed up by the precipitation of a pink solid when erbium nitrate was substituted for yttrium nitrate.

5.6 Conclusions

It was found that a stable gel could be formed by simply mixing yttrium acetate in 2-methoxyethanol and heating until it is completely dissolved. This gel has an acetate structure and becomes powder upon sintering. If the acetate is added to 2-methoxyethanol and not heated, it initially dissolves and then a precipitate occurs which has the structure of anhydrous acetate.

It was found that silica gels containing yttrium synthesised from solutions of yttrium acetate in 2-methoxyethanol were similar to those synthesised using other sources of yttrium.

The reaction of yttrium isopropoxide with hydrochloric acid produced a brown oily compound that when combined into a gel matrix with TEOS gave an indication of the dryness of the gel and hence when it was ready for firing. It was also found that the use of standard DCCA's are unsuitable for these gels.

References:

1. F. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", p.955-6, Wiley Interscience, London, 1988.
2. Wenjian Weng, Juan Yang and Zishang Ding, J. Non-Cryst. Solids, 169, (1994), 177.
3. Gu Zhenan, J. Non-Cryst. Solids, 170, 3(1982), 37
4. J. Coon and J. E. Shelby, Phys. Chem. Glasses, 35(2), (1994), 47
5. F. Busi, Phys. Chem. Glasses 23, (1982), 37

21. B. Viana, N. Koslova, P. Aschekong and C. Sanchez, J. Mat. Chem. 5(5) (1995), 719 and references therein.
22. L. G. Hubert-Pfalzgraf, O. Poncelet, R. Papiernik, S. Boulmaaz and C. Sirio, Eurogel '91, p. 293. Elsevier Science Publications B.V., Holland, 1992.
23. R. C. Mehrotra, "Structure and Bonding: Chemistry, Spectroscopy and Applications of Sol-gel Glasses", Volume 77, Edited by R. Reisfeld and C. K. Jorgensen, Springer Verlag, Berlin, 1992. P.1-36.
24. J. C. Walck and C. G. Pantano, J. Non Cryst. Solids, 124, (1990), 145
25. S. Katayama and M. Sekine, J. Mater. Chem. 1(6) (1991), 1031
26. G. De, A. Licciulli, and M. Nacucchi, J. non Cryst. Solids, 201, (1996), 153
27. G. E. Rindone, "Luminescence in the Glassy State", chapter 8 in "Luminescence in the Solid State", edited by P. Goldberg.
28. C. J. Brinker and G. W. Scherer, "Sol-gel Science: The Physics and Chemistry of Sol-gel Processing", Academic Press, London, 1990.

22. L. G. Hubert-Pfalzgraf, O. Poncelet, R. Papiernik, S. Boulmaaz and C. Sirio, Eurogel '91, p. 293.

23. R. C. Mehrotra, "Structure and Bonding: Chemistry, Spectroscopy and Applications of Sol-gel Glasses", Volume 77, Edited by R. Reisfeld and C. K. Jorgensen, Springer Verlag, Berlin, 1992. P.1-36.

24. J. C. Walck and C. G. Pantano, J. non Cryst. Solids, 124, 145 (1990).

25. S. Katayama and M. Sekine, J. Mater. Chem. 1(6) 1031 (1991).

26. G. De, A. Licciulli, and M. Nacucchi, J. non Cryst. Solids, 201, 153 (1996).

27. G. E. Rindone, "Luminescence in the Glassy State", chapter 8 in "Luminescence in the Solid State", edited by Goldberg.

28. C. J. Brinker and G. W. Scherer, "Sol-gel Science: The Physics and Chemistry of Sol-gel Processing", Academic Press, London, 1990.

Chapter 6 – The Incorporation of Sodium, Calcium and Chromium Ions into Silica Matrices.

Metal ions from groups I and II can be mixed into silica based lattices along with the transition metals and the rare earths. These metals do not act as glass formers but as modifiers.

As chromium has been used a sensitiser for the luminescence of erbium ions[1], for this work its sol-gel chemistry needed studying. This enables the possiblity of making chromium and erbium doped gels at a later date should the need arise.

The aim of this section of work was therefore to study the addition of sodium, calcium and chromium ions to silica based sol-gel systems.

6.1 The Incorporation of Sodium Ions into Silica Matrices

Sodium salts are highly soluble in most solvents. During the formation of silica matrices these salts tend to remain in solution. As a result, when the well-established network is dried, soluble salts precipitate in the pores of the gel, leading to segregation. The phases produced are a similar size to the pores in the gel[2].

Sodium ions complex very stably with the crown ether 18C6 in the molar ratio 1:1[3]. As the size of these molecules are ideal to accommodate sodium ions, this is more stable in the gels than sodium ions alone[3]. Comparisons of sodium-18C6 complex in methanol and sodium methoxide dissolved in methanol show that the complex produces more stable gels with less phase separation[3].

6.1.1 Experimental

Following the literature[3] 0.12g sodium methoxide powder was added to 0.59g 18C6 in 10ml ethanol. This was heated gently and then added to prehydrolysed TEOS. Water and hydrochloric acid was added.

This was repeated using 2-methoxyethanol instead of ethanol. The sodium alkoxide took longer to dissolve in 2-methoxyethanol than in ethanol. This was added to prehydrolysed TEOS, water and hydrochloric acid.

For comparison, sodium methoxide was added to ethanol and stirred until dissolved. This solution was added to TEOS, ethanol, water and hydrochloric acid.

6.1.2 Results

It was found that these samples containing sodium ions produced precipitates to varying degrees upon drying. The crystalline precipitation that occurred in the samples containing 18C6 could be due to the use of hydrochloric acid which perhaps causes the breakdown of complexation between the sodium ion and 18C6 crown ether. As hydrochloric acid is necessary in the sol-gel chemistry of many other cations that may need to be incorporated with sodium, its use could not be ruled out. In the case of the samples made up without 18C6 the precipitation appears in the form of fine hair-like crystals growing out of the pores in the gel (Figure 6.1 shows an SEM picture of this precipitate). This is where a highly soluble sodium salt comes out of solution in the pores of the gel as it dries.

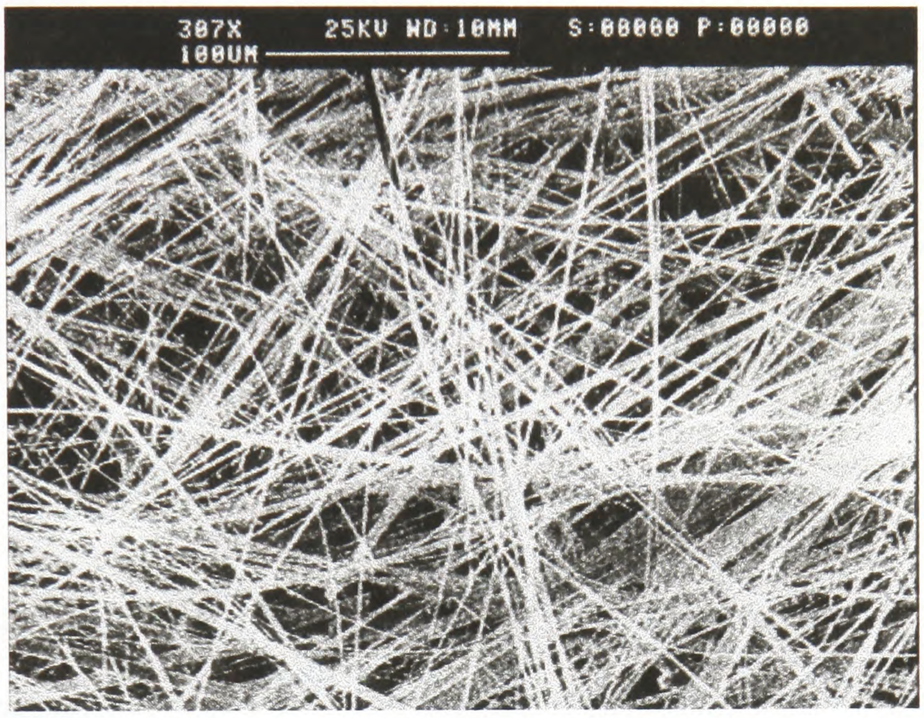


Figure 6.1 SEM picture of crystal growth on the surface of a silica gel containing sodium.

6.2 The Incorporation of Calcium into Silica Matrices

6.2.1 Experimental

Samples were synthesised using TEOS with ethanol containing calcium chloride ions. Although transparent gels could be made containing high concentrations of calcium they powered upon firing. A typical mixture is based on the following:

1.5g calcium chloride dissolved in 50ml ethanol. To this 12g TEOS are added along with 3g hydrochloric acid and 10ml water. These samples were dried at 40°C in air and then fired in a muffle furnace at temperatures up to 1000°C at heating rates ranging from 2°C min^{-1} down to 0.25°C min^{-1}. However, despite great care over the drying and firing processes, all samples became powders upon firing although as xerogels they were transparent and strong.

6.2.2. Results

All samples synthesised with calcium chloride were unstable and formed powders when fired. Some with very low calcium (0.1g calcium chloride) contents resulted in highly cracked samples after firing. In these cases however white particulates appeared on the surface of the gels.

6.3 The Incorporation of Chromium Ions into Silica Matrices

6.3.1 Experimental

Two methods were investigated:

1) 0.06g chromium nitrate were dissolved in 40ml ethanol. To this 20ml TEOS were added along with 5ml water and 1ml hydrochloric acid. The chromium nitrate was a little slow to dissolve but upon the addition of water and acid it dissolved rapidly.
2) 1g chromium acetate was refluxed with 100ml 2-methoxyethanol for 6 hours. This was based on the method for the incorporation of rare earths in section 5.2.2. Initially the mixture appeared as a black suspension which then developed into a green solution. Aliquots of this mixture were added to mixtures of prehydrolysed TEOS.

6.3.2 Results

Stable samples were made using both methods. In method 1, the reluctance of the chromium nitrate to dissolve in ethanol is not ideal for this system as ethanol is the ideal solvent for TEOS.

Using method 2, glasses with chromium contents up to 0.5g chromium acetate in 5g TEOS were synthesised. The chromium solution appeared purple during synthesis becoming green when introduced to the other components of the gel. It was found that these samples changed from a green colour to a deep amber colour upon firing. Thick samples (those thicker than 5mm) appeared almost black due to the presence of chromium ions.

Conclusions:

It has been seen that further work is required to successfully incorporate sodium and calcium ions into the sol-gel systems under investigation in this work. As the incorporation of these ions is not particularly important here, additional studies were not performed.

Successful addition of chromium ions into a sol-gel silica lattice has been demonstrated in this study.

<u>References:</u>

1. Weiji Jia, Ki-Soo Lim, Huimin Liu, Yanyun Wang, F. Fernandez and W. M. Yen, J. Lum. 66&67, (1996) 228.
2. S. P. Szu, M. Greenblatt and L. C. Klein, J. Non Cryst. Solids, 124 (1990) 91.
3. J. Eamsiri, A. Elyamani and R. E. Riman, J. Non Cryst. Solids, 163 (1993) 133-147.

Chapter 7 – The Synthesis of Multi-Cation Gels

7.1 Introduction to the synthesis of multi-cation gel systems

There are many materials which can be made by sol-gel methods which consist of three or more metal cations and are documented in the literature. In general it is accepted that for multi-metal cation systems careful hydrolysis is required to prevent inhomogeneities occuring. Some of the main problems associated with the sol-gel synthesis of multi-component systems is the different degrees in solubility of the precursors and the varying rates of hydrolysis[1]. Care must be taken to overcome problems associated with solubility and ideally a single solvent should be used for the whole system if possible.

Often the order of addition of the precursors to the reaction mixture is important in overcoming inhomogeneity caused by the different hydrolysis rates[2,3]. This method involves the addition of the precursor alkoxides in the order with respect to their hydrolysis rates, ie: the least reactive is added first and partially hydrolysed prior to the addition of the next alkoxide. The newly added unhydrolysed precursors will then condense with partially hydrolysed species and form multi-component polymers rather than with themselves[3].

Another method of synthesising multi-component systems is to use multi-cation precursors - usually starting from the single alkoxides. The alkoxides are mixed and condensed via an alcolation process to form a complex containing all the cations in the correct stoichiometry[4,5]. The complex is then hydrolysed in much the same manner as a single alkoxide to form an oxide matrix. Up to 8 membered systems have been investigated by this method[3,4,5].

Many questions have been raised about the homogeneity of these systems made by these methods[3]. However a study using ^{17}O NMR to determine the reaction pathway has shown that the different alkoxide precursors combine to create a homogenous matrix[6]. A second study using ^{13}O NMR has also shown that multi-cation complexes are formed using a citric acid chelate method[7] based on a method known as the Pechini process[8].

Examples of multi-component systems synthesised by sol-gel methodology given in the literature are as follows:

- $YBa_2Cu_3O_{7-x}$ superconducting powder[9,10,11]. This material has been synthesised by the careful combination and hydrolysis of the precursor alkoxides to make a multi-cation alkoxide which is then condensed to soley form the required phase[9]. It has been shown that simply mixing the component alkoxides and hydrolysing does not only produce this material but also other crystalline phases with it[9].
- Phosphors, for example: $Ca_4Y_6(SiO_4)_6O{:}A$ (A=Pb^{2+}, Eu^{3+}, Tb^{3+}, Dy^{3+})[12]. This method differs from those given above. Calcium carbonate, yttrium oxide and the dopant oxide were dissolved in nitric acid then combined with ethanol and tetraethylorthosilicate (TEOS) to produce a gel. This was dried, ground and then fired as a normal phosphor mixture. Although this method does not claim the homogeneity described in the methods above it does give better homogeneity than that of the

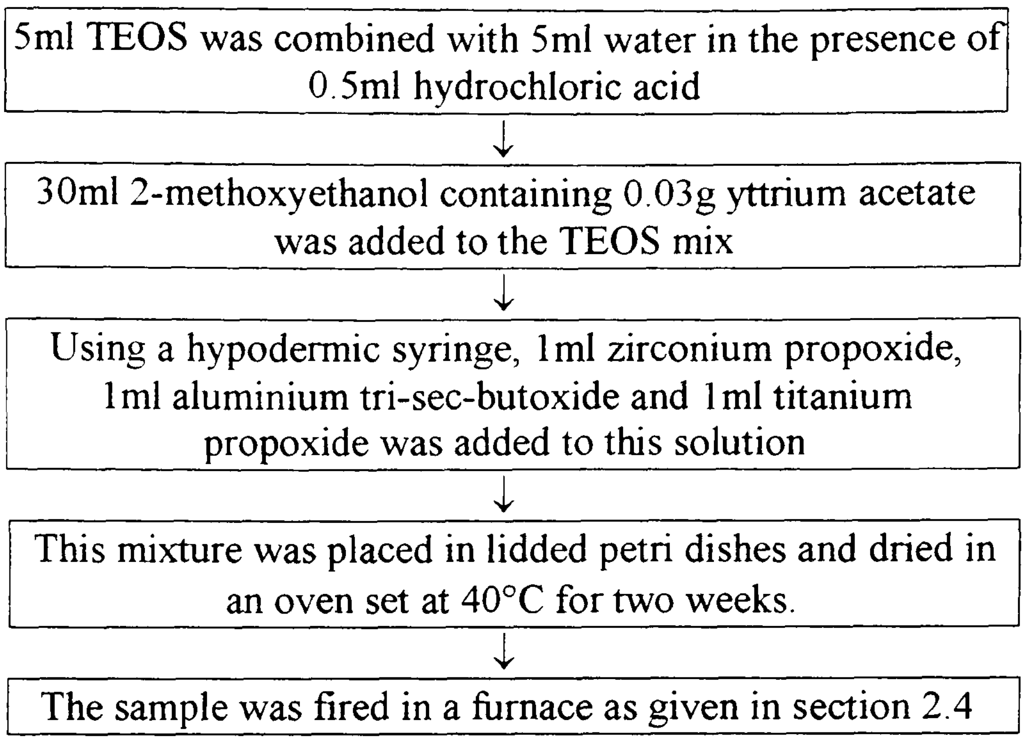
material synthesised by the standard dry mixing of the precursor carbonates and oxides. This can be seen in the improved properties of the phosphor.

- PZT (lead zirconium titanate dielectric powder). This has been synthesised by the co-precipitation of the alkoxide precursors and by careful control of conditions improved properties can be obtained[13].
- ZBLAN fluoride glasses. This synthesis is detailed in sections 1.3.4 and 8.1.3. Fluoride glasses usually are composed of many cations. They have many uses in the optoelectronic industry due to their broad IR transmission range, low scattering, low refractive index, and other properties. A homogenous oxide gel is formed by the careful order of addition of the precursor alkoxides which is the fluorinated and then sintered to form a fluoride glass[14].

7.2 Experimental

TEOS was mixed with various other cations where TEOS was kept as the major consituent. With the transition metal alkoxides this proved difficult as they are hydrolysed very rapidly in ethanol which is the ideal solvent for TEOS. The addition of zirconium propoxide to an mixture of ethanol and TEOS resulted in a white precipitate of zirconium hydroxide.

2-methoxyethanol was used as a solvent for the synthesis of multi-metal cation systems as it has been shown that this is suitable for most of the precursors used in this study (see sections 4a.3, 4b.4, 4c.4 and 5.6). Figure 7.1 shows the method used for synthesising gels using 2-methoxyethanol as sole solvent and for the prehydrolysis of TEOS. The solvent contains yttrium acetate which has been dissolved by refluxing over three hours as described in section 5.2.3.



5ml TEOS was combined with 5ml water in the presence of 0.5ml hydrochloric acid

↓

30ml 2-methoxyethanol containing 0.03g yttrium acetate was added to the TEOS mix

↓

Using a hypodermic syringe, 1ml zirconium propoxide, 1ml aluminium tri-sec-butoxide and 1ml titanium propoxide was added to this solution

↓

This mixture was placed in lidded petri dishes and dried in an oven set at 40°C for two weeks.

↓

The sample was fired in a furnace as given in section 2.4

Figure 7.1 Flow chart showing the method of synthesising multi-metal cation gels.

7.3 Results and Conclusions

The incorporation of sodium ions into these systems was omitted due to unsuccessful results in synthesis of silica gels incorporating sodium ions as shown in section 6.1.

Zirconium, titanium and aluminium were successfully incorporated into systems containing silica using 2-methoxyethanol as solvent using the method shown in fugure 7.1.

References

1. A. S. Rizkalla, D. W. Jones, G. C. Hall and E. J. Sutow, Br. Ceram. Trans. J., 90, (1991), 81.
2. I. M. Thomas, U.S. Patent 3791808, February 12th 1974.
3. C. J. Brinker and G. W. Scherer, "Sol-gel Science – The Physics and Chemistry of Sol-gel processing", Academic Press, London 1990.
4. H. Dislich, Angew Chem. Int. Ed. Engl., 10, (1971), 363.
5. H. Dislich in "Transformation of Organometallics into Common and Exotic Materials", Ed. R. Laine, NATO ASI Series E, No. 141, (Nijhof, Dordrecht, 1988), p. 236-249.
6. F. Babonneau, J. Maquet and J. Livage, "Sol-gel Science and Technology", Ceramic Transactions, Volume 55, p.53 (1995), Eds: E. J. A. Pope, S. Sakka and L. C. Klein.
7. M. Kakihana, M. Arima, M. Yashima, M. Yoshimura, Y. Nakamura, H. Mazaki and H. Yasuoka, "Sol-gel Science and Technology", Ceramic Transactions, Volume 55, p. 65, (1995) Eds: E. J. A. Pope, S. Sakka and L. C. Klein.
8. M. P. Pechini, U.S. Patent 3330697, July 1967.
9. Shingo Katayama and Masahiro Sekine, J. Mater. Chem., 1(6) (1991), 1031.
10. F. J. Gotor, P. Odier, M. Gervais and J. Choisnet, J. Sol-gel Sci. and Tech. 2, (1994), 427
11. G. Kordas, G. A. Moore, M. B. Salamon and J. B. Hayter, J. Mater. Chem., 1(2), (1991), 181
12. Jun Lin and Qiang Su, J. Mater. Chem. 5(4) (1995), 603
13. R. C. Buchanan and J. Boy, J. Electrochem. Soc. 132(7) (1985), 1671

14. J. Eamsiri, A. Elyamani and R. E. Riman, J. non Cryst. Solids, 163, (1993), 133

Chapter 8 – Fluorination of Sol-gel Matrices

8.1 Introduction:

As established in section 1.3.4, fluoride matrices are perhaps the most ideal hosts for anti-Stokes luminescence. The synthesis of fluoride glasses using sol-gel methods have been covered in the literature. The interaction of fluoride ions with silicon complexes has also been detailed by several authors[1,2,3].

The object of the work in this chapter is to prepare sol-gel systems incorporating fluoride ions. When incorporated in silica glass matrices, fluoride ions can have several effects on the properties of the glass (these are set out below). Fluoride ions are regarded as a popular dopant for lowering the refractive index of silica for optical fibres[4].

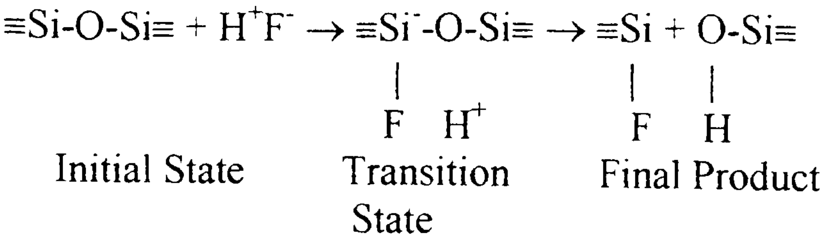
8.1.1 Effect of fluoride ions on silica based glasses.

A. Silica (SiO_2) is severely attacked by fluoride ions. It causes depolymerisation reactions to occur[2] as demonstrated in equation 8.1.

$$\equiv Si\text{-}O\text{-}Si\equiv + HF \rightarrow \equiv Si\text{-}OH + \equiv SiF \qquad \text{Eqn. 8.1}$$

Although the silicon-oxygen bond is strong it is polar and hence attacked by nucleophiles such as fluoride and hydroxide ions[2].

A detailed reaction scheme[2] is given in equation 8.2.



$$\equiv\text{Si-O-Si}\equiv + \text{H}^+\text{F}^- \rightarrow \equiv\underset{\underset{\text{F}}{|}}{\text{Si}^-}\text{-}\underset{\text{H}^+}{\text{O}}\text{-Si}\equiv \rightarrow \equiv\underset{\underset{\text{F}}{|}}{\text{Si}} + \underset{\underset{\text{H}}{|}}{\text{O}}\text{-Si}\equiv$$

Eqn.8.2

B. When incorporating fluoride ions in silicate lattices produced from the melt, the fluoride ion replaces oxygen in the lattice, preferably taking bridging over non-bridging positions[5]. At higher temperatures larger amounts of fluoride ions can be incorporated into the network than at lower temperatures where free ions are favoured resulting in the precipitation of insoluble fluoride compounds[5]. Additionally it has been shown[6] that if the melt has greater than 55-60 molar % metal oxide the fluoride ion is present as predominantly a free ion[6]. The conclusion that can be drawn from this is that the state of the fluoride ions in a silica matrix depends on the temperature and composition used[5].

C. If sodium ions are present in the melt, they prefer to be located near fluoride ions rather than an oxygen ion[5]. The reverse is true for silicon. This is due to the silicon ions having shielding around them due to the doubly charged oxygens[5] resulting in the Si-F attraction being lower than Na-F.

In sol-gel systems the above must be considered when the samples are fired.

8.1.2 Incorporation of fluoride ions into silica sol-gel systems

Traces of fluoride ions have a marked effect on the sol-gel reaction of silica at low pH[1] with the fluoride ion causing a marked acceleration of the hydrolysis and polymerisation reactions. Above pH 2 the polymerisation is catalysed mainly by hydroxyl ions and at lower pH it is catalysed by HF. The rate of hydrolysis is proportional to the hydrogen ion concentration and the fluoride ion concentration[5]. This can be retarded by the addition of traces of aluminium ions, as well as iron, thorium, and beryllium ions. These form complex fluorides which take the fluoride out of the silica reaction. It has been reported that in silicic acid solutions of very high purity, as little as 1ppm fluoride can have a marked effect on the rate of polymerisation. However it should be noted that at pH 7 fluoride ions have no effect on the sol-gel reaction[1]. Table 1 shows a comparison between various acids and bases as catalysts on the gelation reaction of TEOS.

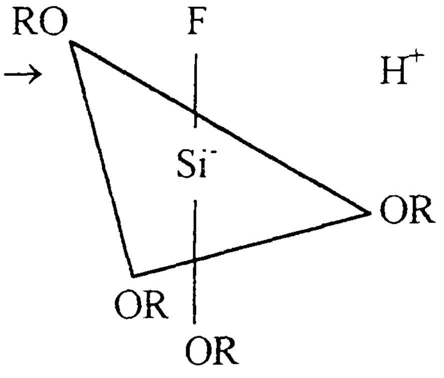
Table 8.1: a comparison of the various catalysts on the gelation of TEOS[7].

Catalyst	Concentration Mol:TEOS	Initial pH of solution	Gelation time (hours)
HF	0.05	1.90	12
HCl	0.05	0.05	92
Acetic acid	0.05	3.70	72
HNO_3	0.05	0.05	100
H_2SO_4	0.05	0.05	106
NH_4OH	0.05	9.95	107
No catalyst	-	5.00	1000

A possible mechanism for the increased rate of gelation has been suggested due to the similarity in size of the F^- ion to that of the O^{2-} ion and hence they can substitute each other in the network[8]. The OH^- ion is also almost the same size as the F^-ion and it is possible for the F^- to substitute for OH^- on the surface of the gel with the fluoride effectively driving the hydroxyl group out[8]. The fluoride ion is regarded as the most effective catalyst for speeding up the gelation process[3].

The fluoride ion acts in a similar fashion to the hydroxyl ion when interacting with silica precusors in sol-gel chemistry. The resulting gel that has been catalysed by fluoride also has similarities to that catalysed by a base. For example: high porosity and low density. The hydroxyl group causes hydrolysis to proceed via nucleophilic substitution of the hydroxyl group for the alkoxy group. It has been demonstrated[3] that the F^- ion attacks the $Si(OR)_4$ groups by nucleophilic substitution as well. This involves the expansion of the co-ordination number of silicon from 4 to 5 which is also the case of the hydrolysis catalysed by hydroxyl ions[3]. This increase in the co-ordinate number of the silicon leads to a more reactive species that can interact with other silanol groups via electrophilic attack. This increases the polymerisation reactions[3].See Equation 8.3.

$Si(OR)_4 + HF \rightarrow$



$H^+ \rightarrow Si(OR)_3F + HOR$ Eqn. 8.3

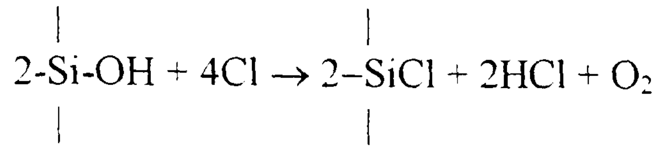
The fluoride ions effectiveness in the reaction has been put down its ionic radius being slightly smaller than that of the hydroxyl ion[1]. It has also been suggested that the dried gels which contain fluoride ions absorb less water compared with fluoride-free gels as the gel surface is less hydrophilic due to the presence of the fluoride ions and hence the bloating due to the loss of water upon firing is substantially reduced[3]. It has also been shown that the presence of low amounts of fluoride (>1 molar %) in silica glasses produced by sol-gel methods reduces bloating of the glass during firing[8].

It has been suggested that the pentavalent silica species shown in equation 8.3 decomposes rapidly to form a partially fluorinated silicon alkoxide[9]. This yields by products of water and alcohol under continued reaction. It is also suggested that additionally another species will also decompose into partially hydrated silicon alkoxide and regenerated fluoride ions[9] although little information is available about this species.

It has been noted that the addition of fluoride ions in the presence of hydrochloric acid decreases the gelation times less dramatically than in its absence[10]. In the presence of hydrochloric acid the pore sizes, the surface area and the measured nitrogen BET surface area are also greatly decreased[10].

An additional reason for incorporating fluoride and other halide ions into sol-gel systems other than the modification of the optical properties include chemical dehydroxylation of the gel surface[11,12]. Heating in a furnace in air brings about dehydroxylation of the surface of a fluoride-free gel, however this does not reduce the levels of hydroxyl groups to parts per billion levels which are necessary for good optical properties (hydroxyl groups have strong absortions that influence optical and other properties of the glass). An example given in the literature[12] has the gel heated in oxygen to remove any residual organics at 800°C followed by treatment with chlorine gas at 800°C for 30 minutes to remove the hydroxyl groups. This sample is then fired in oxygen at 1100°C and finally in helium at 1300°C. It has been found that the residual hydroxyl content is only reduced if the temperature of the furnace is above 700°C[12]. This temperature corresponds to the decomposition of chlorine to chlorine atoms which is the rate determining step of this process as shown in equations 4 and 5.

$$2Cl_2 \rightarrow 4Cl$$ Eqn. 8.4



$$2\text{-}\overset{|}{\underset{|}{\mathrm{Si}}}\text{-}OH + 4Cl \rightarrow 2\text{-}\overset{|}{\underset{|}{\mathrm{Si}}}Cl + 2HCl + O_2$$ Eqn. 8.5

Although almost complete dehydrolysis occurs in this process, the glasses tend to foam during the latter heating treatments due to the evolution of hydrochloric acid gas and sometimes chlorine gas[11]. This occurs around the softening point of the glass[13]. This problem can be eliminated by using fluorine instead although this is generally less preferable than chlorine due to safety reasons. The fluorine can be introduced as HF, NH_4F or SiF_4 gases. The prevention of foaming is due to the Si-F bonds being much stronger than the Si-Cl bonds.

Dehydroxylation can also be accomplised by introducing the fluoride ions into the matrix in solution[14]. It is proposed that the fluoride ions are retained in the matrix by reaction with the silicon hydroxide producing strong Si-F bonding[12, 14]. Evidence for this comes from testing the liquid that is expelled from the gel during syneresis for the presence of fluoride[1]. However loss of fluoride starts to occur at temperatures as low as 400°C[15]. This is in the form of gaseous SiF_4[15].

The presence of fluoride ions in a silica glass matrix has the effect of decreasing the refractive index of the glass[15]. This is a property useful in the application of fibre optics.

A simple method of incorporating fluoride ions into silica sol-gel systems has been described utilising a fluorinated silicon ethoxide[4]. A silica sol is formed into which fluorinated silicon ethoxide ($Si(OC_2H_5)_3F$) is titrated at 3°C. It is reported that this mixture can be gelled and sucessfully consolidated into transparent glass by firing in an atmosphere of He + 5-10% O_2 + 5-10% Cl_2. It is proposed that Si-F bonds are generated on the surface of silica particles of the initial sol. After firing Si-F bonds stay in the silica glass.

8.1.3 Methods of synthesising fluoride glasses by sol-gel methods

The sol-gel synthesis of fluoride glasses is described by several authors[16,17]. Generally methods involve the synthesis of an oxide matrix based on the correct stoichiometry of the cations involved in the glass. With correct order of addition this enables these cations to be mixed on a highly homogenous level. After the resulting gel has been dried it is fired in a dry fluoride atmosphere to produce a fluoride glass at a temperature above the glass transition point of the glass. The advantage of this method, as mentioned previously, is that the cations involved get mixed on a highly homogenous, even molecular, level. The disadvantages are that the samples are full of hydroxyl, water and other groups that reduce the efficiency of any optical processes that the samples are intended for. Even careful elimination of water and oxygen in the firing processes can not always guarantee the complete loss of these hydroxyl groups etc.

The synthesis of ZBLAN (zirconium barium lanthanum aluminium sodium fluoride glass) (see section1.3.4) is given in figure 8.1[17]:

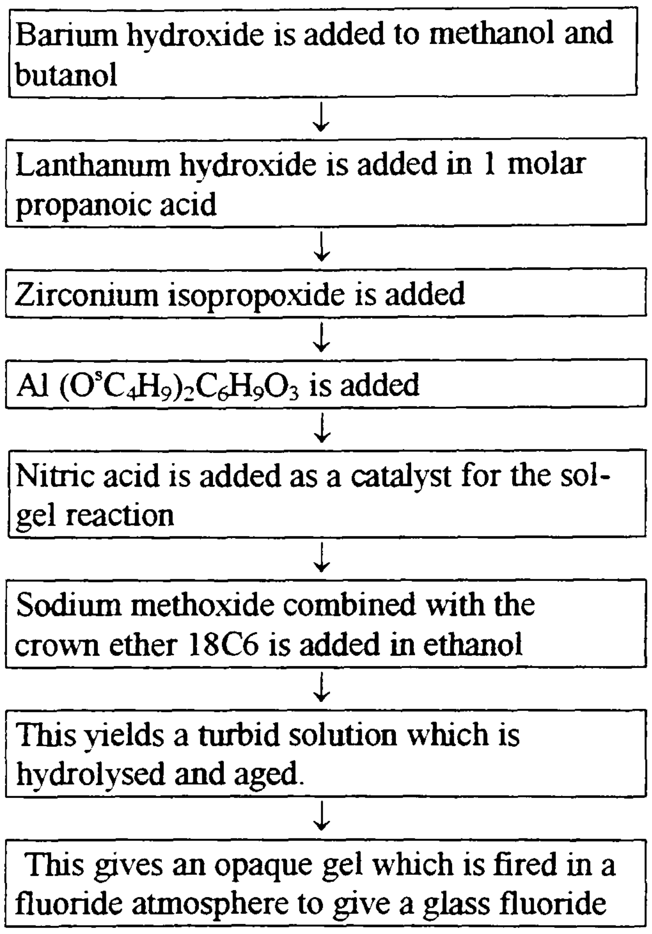


Figure 8.1: The synthesis of fluoride glass using sol-gel methods

Rare earth doped ZBLAN has been widely studied over the past decade and is regarded as being suitable for many optical and optoelectronic uses. It is the most well-known of the glass systems based on zirconium and barium fluorides.

Fluorination of the unreacted hydroxides and alkoxide ligands involves simple reactions with good leaving groups[17]. The fluorination temperature is determined after a series of experiments. It must be low enough to prevent hydrolysis and crystallisation, yet must be high enough to complete fluorination within a short time[2]. A typical fluorination time for a batch of 10g ZBLAN as described above is 1 hour at 200°C[16]. The temperature at which crystallisation occurs is in the region of 350-400°C[2] and the melting point for ZBLAN samples are in the region of 525°C[17].

It should be noted that the water content in the oxide gel can limit the efficiency of the fluorination process[16] – this is demonstrated in equation 8.6

$$\text{Oxide} + 2HF \rightarrow 2F^{-} + H_20 \qquad \text{Eqn. 8.6}$$

This reaction is controlled by the presence of HF and H_2O, and hence any water present will reduce the effect of the HF.

Other methods of fluorination have involved the use of BrF_3[18]. This method has been proved to be less effective and is not conventional because of safety reasons.

8.1.4 Glass Ceramics

Recent interest in new materials for optics applications has shown that for efficient optical properties fluoride glasses are suitable host materials. However they are toxic, expensive to manufacture, corrosive, unstable and must be processed in a dry oxygen-free atmosphere[19]. Oxide glasses do not have these drawbacks. However they are unsuitable for optical uses as they have poor luminescence efficiency which is required for optical materials[19].

Oxyfluoride glass ceramics have been developed which overcome this dilemma[19]. They consist of fluoride crystallites of less than 40nm held close together within an oxide matrix, hence resulting in a material that has the optical properties of a fluoride but the strength and stability of an oxide. These materials are a recent addition to the science of luminescence of glassy materials and were first mentioned in this field in 1993[20].

8.2 Experimental

8.2.1 The influence of fluoride ions on the sol-gel reaction of TEOS .

A range of samples were synthesised using TEOS, ethanol, water and hydrofluoric acid. Ammonium fluoride was also used and the resulting samples were compared with those made using hydrofluoric acid. The order of addition is given in figure 8.2.

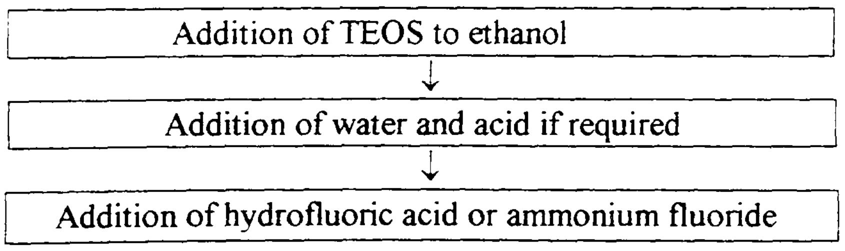


Figure 8.2; the synthesis of fluoride containing silica gels, these samples were stirred thoroughly throughout the procedure.

The gelation time was measured after the addition of the fluoride source and compared for each sample and its composition. pH readings were also taken during the addition of each component.

Infrared analysis of the gels was performed to identify the Si-OH and Si-F bonds in the matrices.

8.2.2 Sol-gel synthesis of glasses containing rare earth ions and fluoride ions.

An extensive range of samples were synthesised using hydrofluoric acid, rare earth compounds and TEOS. The rare earth metal (RE) and fluoride contents were varied with respect to each other and several different ways of introducing the RE^{3+} ions into the mix were investigated. Different solvents and the use of chelated RE^{3+} ions were also investigated. Samples of prehydrolysed and non-prehydrolysed TEOS were also compared. A summary of the experiments is given in table 8.2.

Table 8.2: A summary of a range of experiments to compare the gelation and final state of samples made with TEOS, fluoride ions and RE^{3+} ions.

Solvent	TEOS	Water	Rare earth	Hydrofluoric acid	Hydrochloric acid	Additional notes
10ml 2-methoxyethanol	10ml	10ml	-	0.5-5ml solution	2ml	
10ml 2-methoxyethanol	10ml	10ml	0.3g erbium acetate	0.5-5ml solution	2ml	
10ml 2-methoxyethanol	10ml	10ml	0.3g erbium nitrate	0.5-5ml solution	2ml	
10ml 2-methoxyethanol	10ml	10ml	0.3g erbium acetate	0.5-5ml solution	2ml	TEOS not prehydrolysed
10ml ethanol	10ml	10ml	0.3g erbium nitrate	0.5-5ml solution	2ml	
10ml ethanol	10ml	10ml	0.3g erbium nitrate	0.5-5ml solution	2ml	TEOS not prehydrolysed
10ml 2-methoxyethanol	10ml	10ml	0.3g erbium acetate	1ml HF solution	2ml	Additional solvent is added
10ml 2-methoxyethanol	10ml	10ml	0.3g erbium acetate	0.5-5ml solution	2ml	DETA is present as a chelating agent

The hydrofluoric acid was added as a solution of 0.5ml 48% hydrofluoric acid in 10ml water and this was added in increasing amounts of 0.5ml to the mixtures. In the case of the TEOS being prehydrolysed, this was carried out by adding water to TEOS in a ratio of 1:1 and stirring vigorously until complete mixing occured. This mixture was added to the RE^{3+} solution in the specified solvent. In the case of the acetate, it was refluxed with the 2-methoxyethanol to give a stable solution as described in section 5.2.2. It should be noted that erbium acetate does not dissolve in ethanol and hence this factor was not studied.

All samples were dried at 40°C and then fired at temperatures up to 800°C starting at room temperature and increasing the temperature slowly at a rate of 1°C min^{-1}.

From these results a further range of samples were synthesised to identify the compositional region in which transparent materials may be formed.

8.2.3 Absorption of fluoride ions into silica matrices

Several different types of experiment were performed.

- Wet gels placed in various solution and left to stand.
- Wet gels placed in a dish and having various solutions poured over them
- Various solutions injected into the centres of the wet gels using a fine hypodermic needle and syringe.
- Dried gels fired with small quantities of ammonium fluoride. See figure 8.3.

The solutions used in these experiments were as follows:

- Cobalt: this was chosen so that the deep blue colour could be observed readily spreading through the gel.
- Europium: this was chosen as it is luminescent under 366nm ultraviolet excitation in solution and as a rare earth its interaction with various gels is of great importance.
- Hydrofluoric acid: this was chosen as ammonium fluoride is unsuitable due to many of the gels containing hydrochloric acid (see section 8.3.1). However due to the hydroxyl groups on the surface of the gels giving an overall negative charge it is not expected that the fluoride ion will be easily absorbed. It was also expected that the hydrofluoric acid would attack the gel.

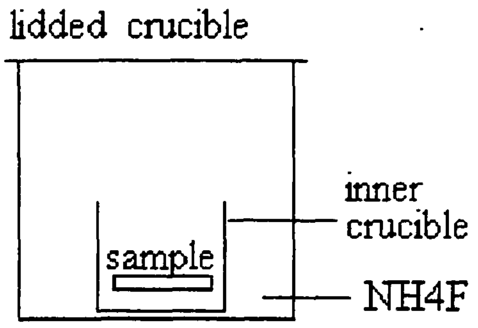


Figure 8.3: Arrangement for firing gel samples in an air-ammonium fluoride atmosphere.

8.2.4 Microwave experiments

Mixtures which had been determined to produce good transparent samples were placed in sealed Teflon vessels and placed in an CEM MDS2100 microwave cavity. To one of the vessels temperature and pressure probes were connected. Under these conditions the mixture undergoing synthesis was exposed to microwave energy. As the samples were held in sealed vessels temperature and pressure effects were caused by the microwave interaction.

8.2.5 The interaction of fluoride ions with RE ions.

Hydrofluoric acid was added to solutions of erbium acetate and erbium nitrate in 2-methoxyethanol and ethanol respectively. The hydrofluoric acid was added dropwise .

An example of the quantities used is given:

0.5g erbium nitrate in 20ml ethanol. To this 10ml HF solution is added.

8.2.6 The synthesis of RE^{3+} and fluoride doped silica glasses containing titanium, zirconium and aluminium

Samples containing ytterbium, erbium and fluoride ions based on the results of the experiments described in section 8.2.2 were synthesised incorporating titanium, zirconium and aluminium ions.

For the titanium and aluminium containing samples, two ranges were made up, one containing 2 molar % of the transition metal and the other containing 10 molar %.

Zirconium containing samples were made up based on the results from the titanium and aluminium.

Alkoxides of titanium, zirconium and aluminium were dissolved in the RE^{3+} acetate solution in 2-methoxyethanol as described in section 5.2.2. To this mixture was added prehydrolysed TEOS, water and hydrochloric acid followed by hydrofluoric acid solution.

8.2.7 Sintering and Annealing of Glasses

Glass samples were placed in a programmable muffle furnace on a silica tray and heated at a rate of 1°min^{-1} from room temperature to 1100°C. Certain of these samples were removed from the furnace at this temperature and allowed to cool in air. The rest of the samples were cooled in the furnace at a rate of 10°Cmin^{-1} to 400°C where they were held for 10 hours before being cooled to room temperature. A selection of these samples were then returned to the furnace and heated to 800°C where they were held at this temperature for a further 10 hours. X-ray diffraction anaylsis was performed on samples having undergone each of these three firing processes.

8.3 Results and Discussion

8.3.1 The influence of fluoride ions on the sol-gel reaction of TEOS

In agreement with the literature it was found that the presence of fluoride ions dramatically decreased the gelation times. A summary is given in table 8.3.

Table 8.3: Composition and gelation times of a selection of silica gels reacted with ammonium fluoride. The chosen samples were all synthesised with 45ml ethanol.

Amount of TEOS (ml)	Amount of water (ml)	Amount of hydrochloric acid (ml)	Amount of ammonium fluoride (g)	Gelation time (minutes)
7	2	-	0.07	Instant
7	2	-	0.05	1
7	2	-	0.02	5
7	2	2	0.06	10

It was found (see table 8.3) that the presence of hydrochloric acid slowed the gelation of the samples. The resulting gels were more transparent when made with hydrochloric acid than without. When acetic acid was substituted for hydrochloric acid in the above mixture gelation was almost instant. It was also found that by increasing the solvent content the gelation time could be reduced.

The pH readings for this experiment are shown in table 8.4.

Table 8.4: pH readings taken during the mixing of TEOS solution with hydrochloric acid and ammonium fluoride

mV (reading)	pH (calculation)	Solution
-133	3.40	40ml ethanol
-101	2.85	+20ml TEOS
-30	1.50	+0.1ml HCl
-35	1.65	+0.1ml HCl
-290	6.35	+0.35g NH_4F + 20ml ethanol
-311	6.95	gelation

The pH values were calculated from buffer solutions:

pH 4 = -165mV

pH 7 = -322mV

It was found that the gels synthesised with ammonium fluoride and hydrochloric acid produced white particulates at the base of the dried sample. From the FTIR spectra of this material, it was found that these particulates were ammonium chloride (see figures 8.4 and 8.5) showing strong agreement in the overall shape of the spectra and major peaks at 1400, 2805, 3040 and 3130 cm^{-1}. As the rapid gelation can be controlled by using hydrochloric acid, it was decided that the use of ammonium fluoride should be stopped and hydrofluoric acid used instead. With the use of hydrofluoric acid the precipitation did not occur.

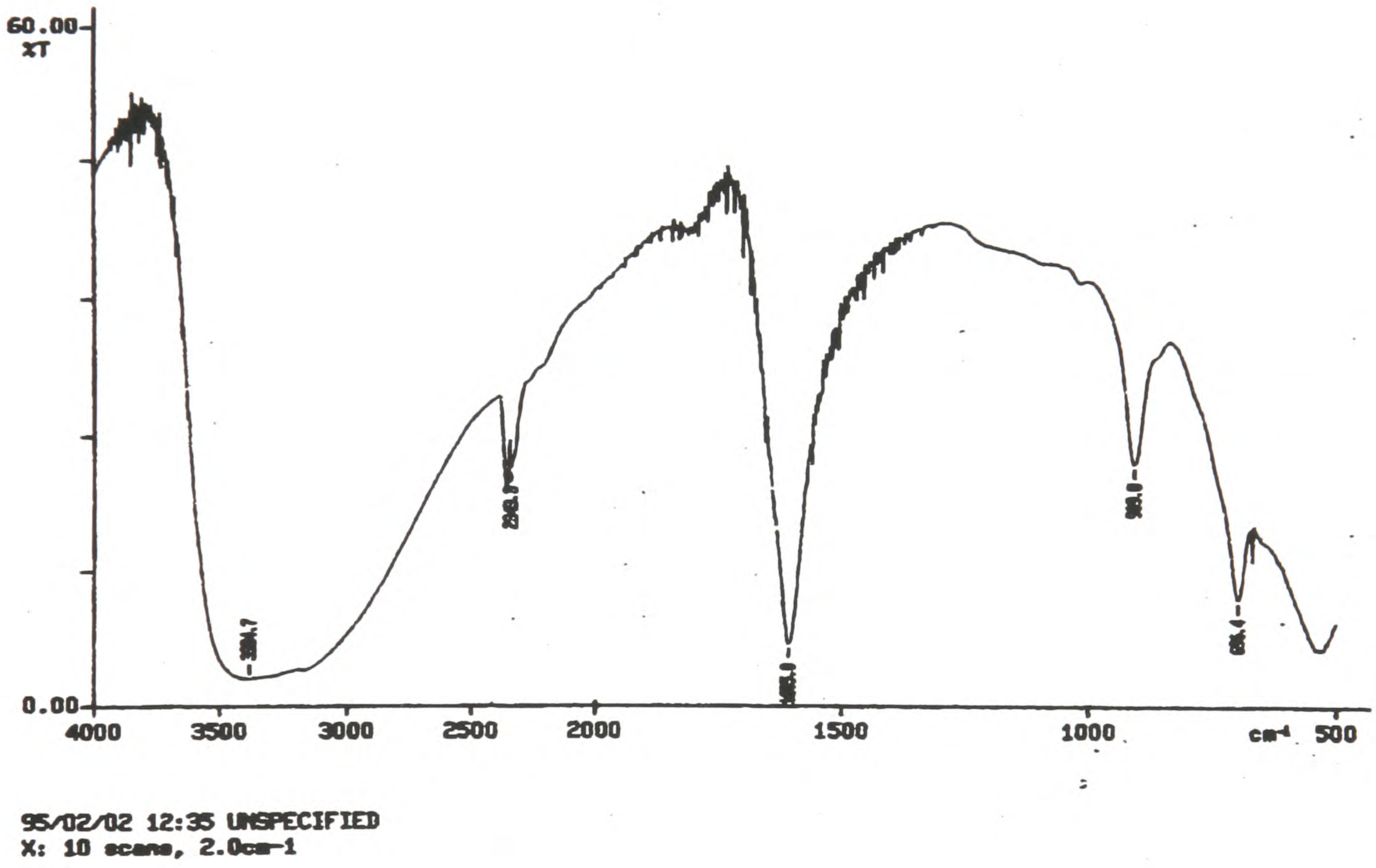


Figure 8.4: FTIR spectrum of particulates found on the surface of gels synthesised with ammonium fluoride and hydrochloric acid.

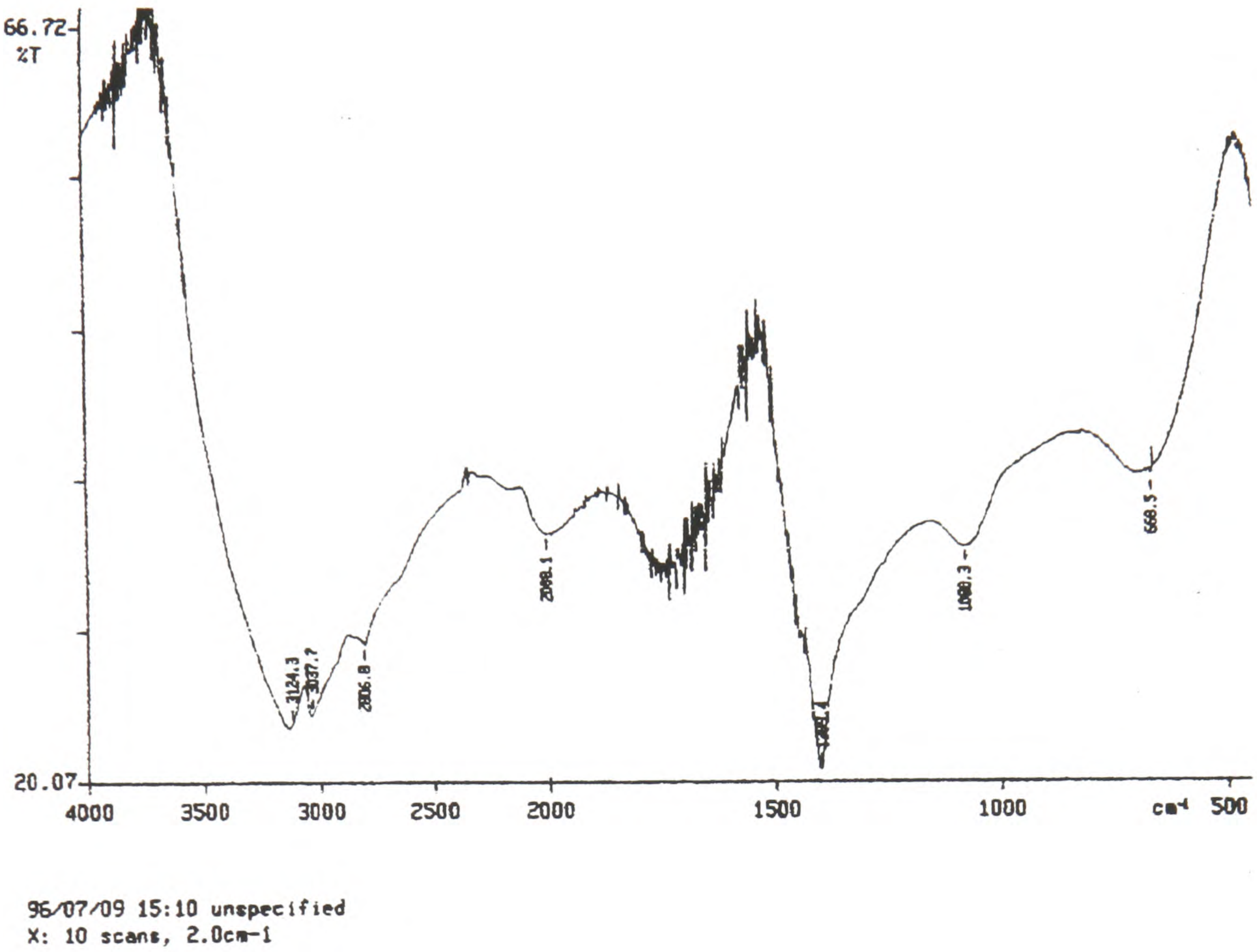


Figure 8.5 FTIR spectrum of ammonium chloride.

FTIR spectra of the silica samples containing fluoride ions show that when dry the xerogels have Si-F and Si-OH bonds present (the Si-F bond has an absorption in the region of 937cm^{-1} which creates a "shoulder" on the Si-OH absorption peak at 975cm^{-1} - see figure 8.6). After firing however only a single peak remains in the spectrum. It has been suggested[1] that this peak is due to Si-F not Si-OH yet the presence of hydroxyl groups is still observed in the 3500cm^{-1} region of the spectra and, from the spectra generated in this study, it is clear that the Si-OH peak not the Si-F remains (see figure 8.7).

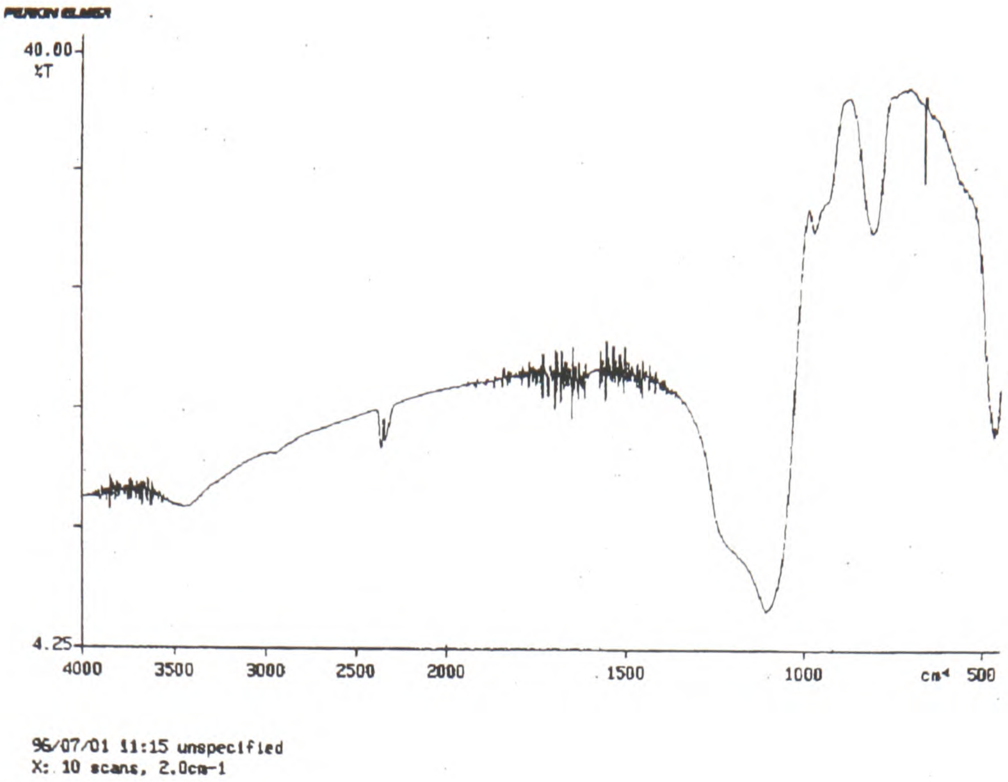


Figure 8.6 FTIR spectrum of dried silica gel synthesised with hydrofluoric acid

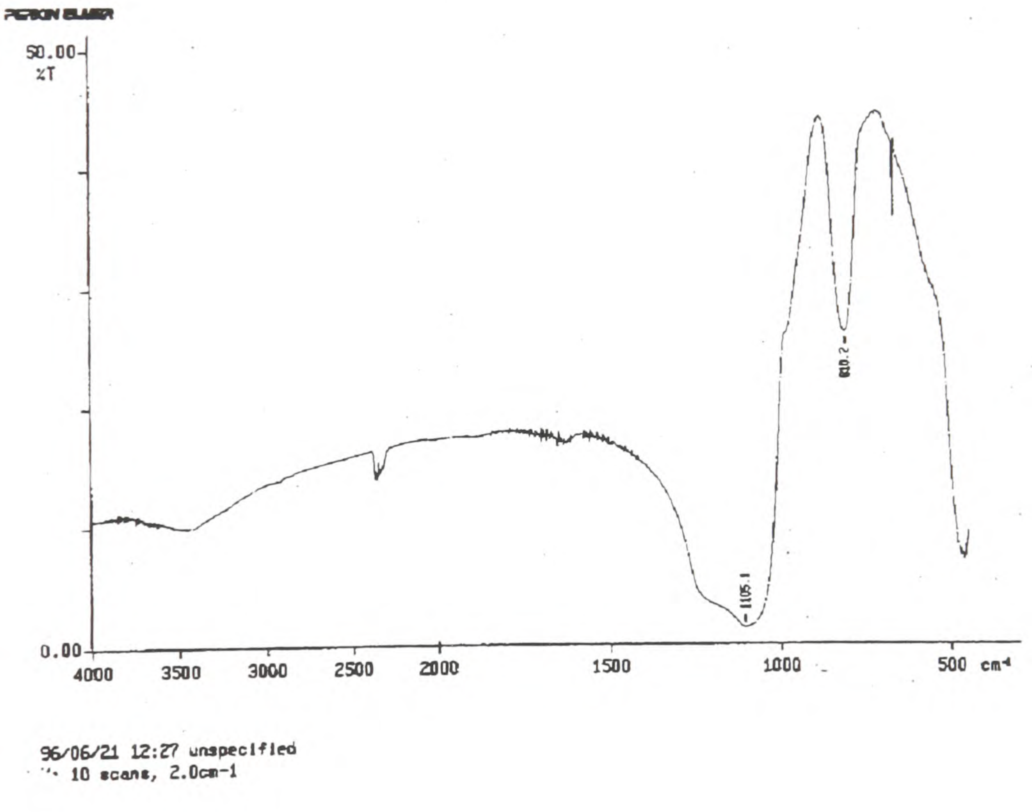


Figure 8.7 FTIR spectrum of fired silica gel synthesised with hydrofluoric acid.

8.3.2 Sol-gel synthesis of glasses containing rare earth ions and fluoride ions

After extensive study of the mixing of TEOS, rare earth ions and fluoride ions the following conslusions were drawn. These are shown in table 8.5.

Table 8.5 Summary of experiments to study the effect of mixing hydrofluoric acid with RE^{3+} and TEOS in solution.

Experiment	Result
Increasing HF content without RE present	Fired sample gets cloudy at the addition of 5ml HF solution
Increasing HF content with the presence of RE acetate	Fired samples start to get cloudy after the addition of 4ml HF solution
Increasing HF content with the presence of RE nitrate	Fired samples start to go cloudy after the addition of 2.5ml HF solution
Non-prehydrolysed TEOS, HF content increased with the presence of RE acetate	Fired samples start to go cloudy after the addition of 3 ml HF solution
HF content increased with the presence of RE nitrate in ethanol	Fired samples start to go cloudy after the addition of 1.5ml HF solution.
Non-prehydrolysed TEOS, HF content increased with the presence of RE nitrate and ethanol	Fired samples start to go cloudy after the addition of 2.5ml HF solution.
Increasing 2-methoxyethanol	All samples were transparent. The gelation time was increased with the solvent content
HF content increased with the presence of RE acetate and DETA	All samples cracked badly and were unsuitable for firing

Unless stated otherwise the samples represented in this table were made with 2-methoxyethanol. For exact details of this series of experiments see table 8.2.

It is clear from these results that several factors need to be taken into account when making a good transparent glass matrix by these methods:

- Less fluoride must used when incorporated into a gel system containing rare earths than when rare earths are omitted.
- Rare earth acetate reacted with 2-methoxyethanol is the best rare earth precursor with 2-methoxyethanol as the best solvent.
- TEOS should be prehydrolysed.
- The presence of DETA is unsuitable for these reactions.

From these results a further range of samples were synthesised to identify the combinations of rare earth and fluoride that produce transparent and opaque samples. The results of this study is given in figure 8.8.

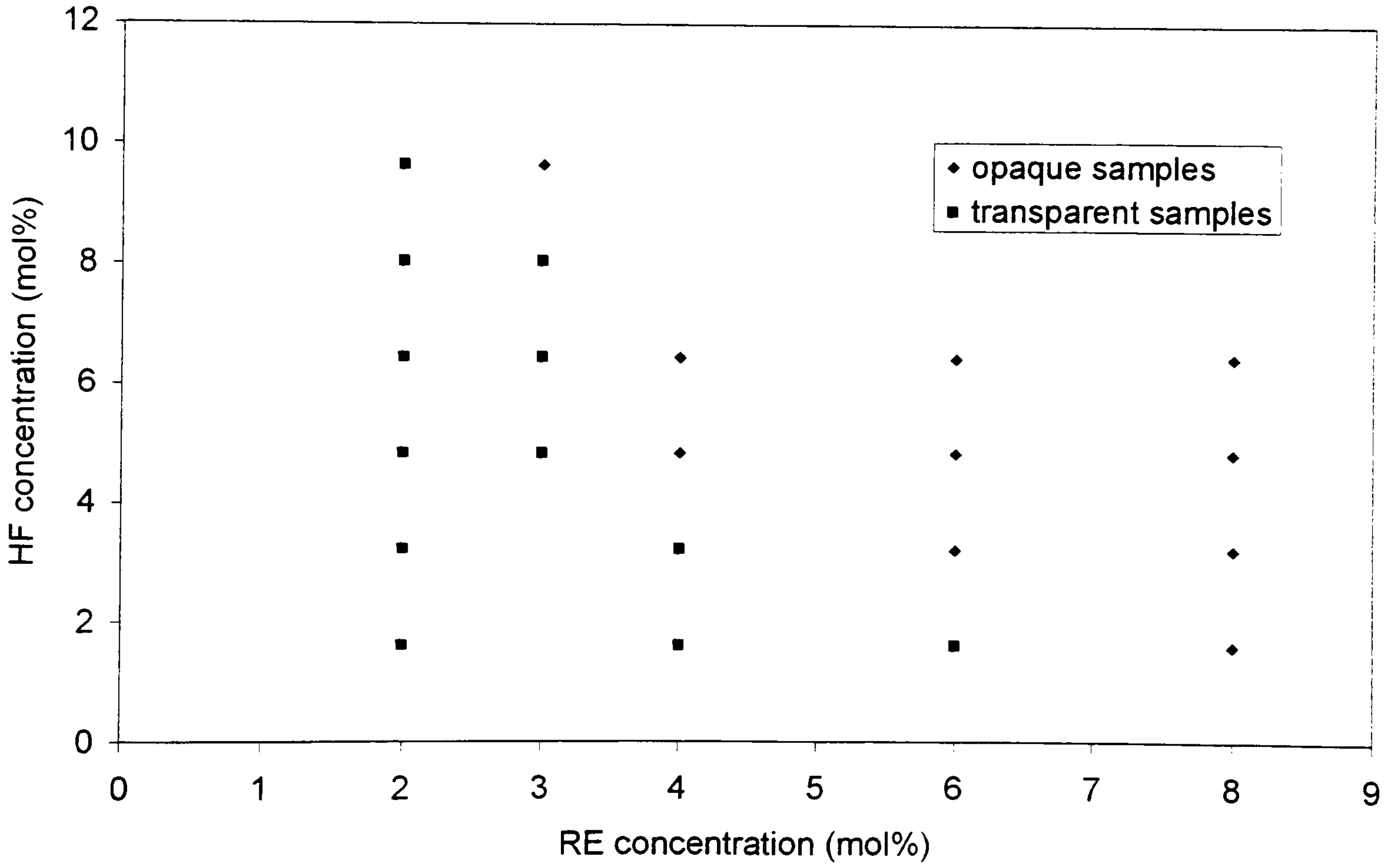


Figure8.8 Plot of rare earth element content against fluoride content of silica glasses.

Detail of the surface of a sample synthesised by the method described above and fired in air is given in figures 8.9. Evidence for crystallites in the sample can be seen in this SEM picture. Pores on the surface of these samples can be seen in figure 8.10.

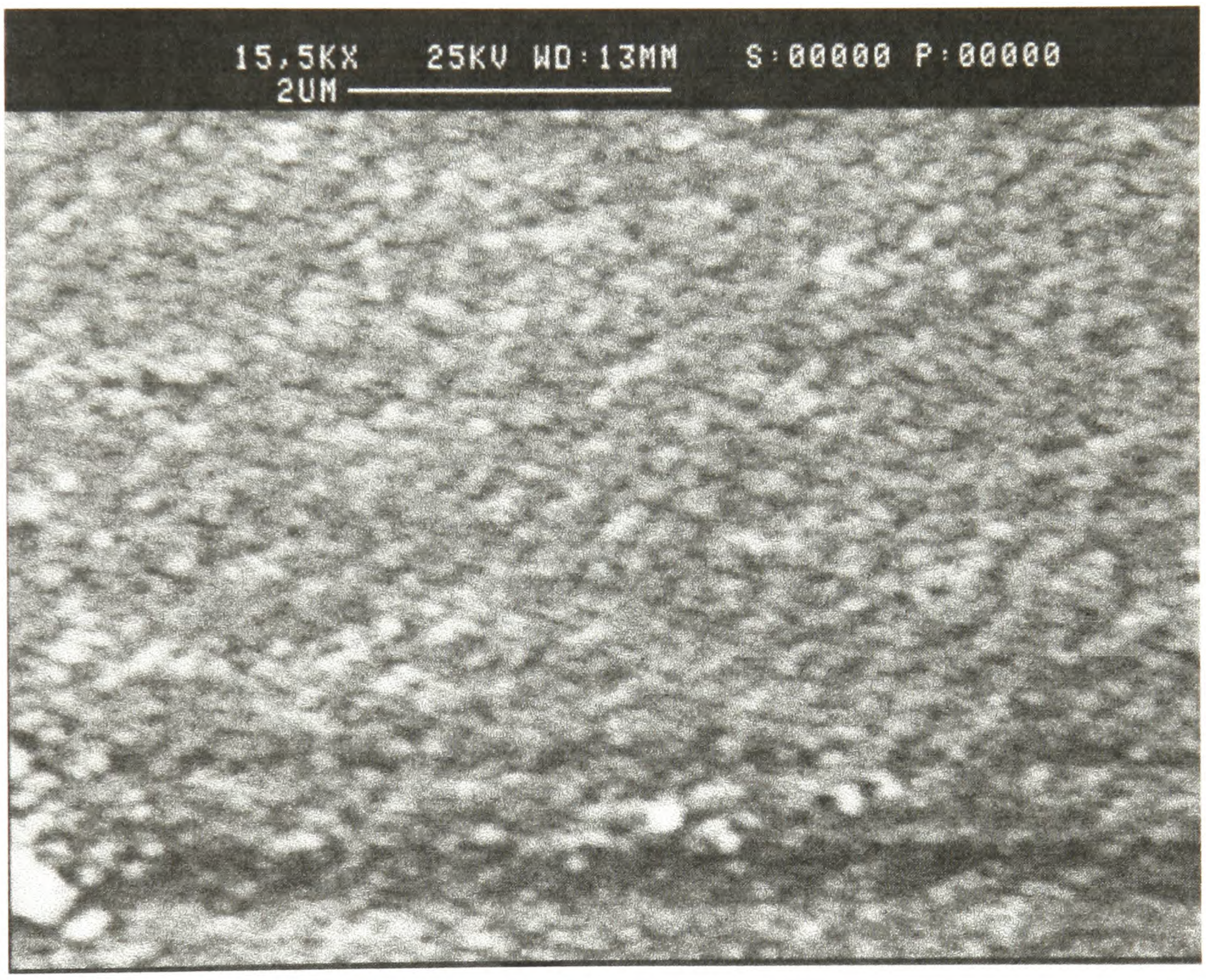


Figure 8.9 SEM picture of the surface of a gel sample produced by the method described above.

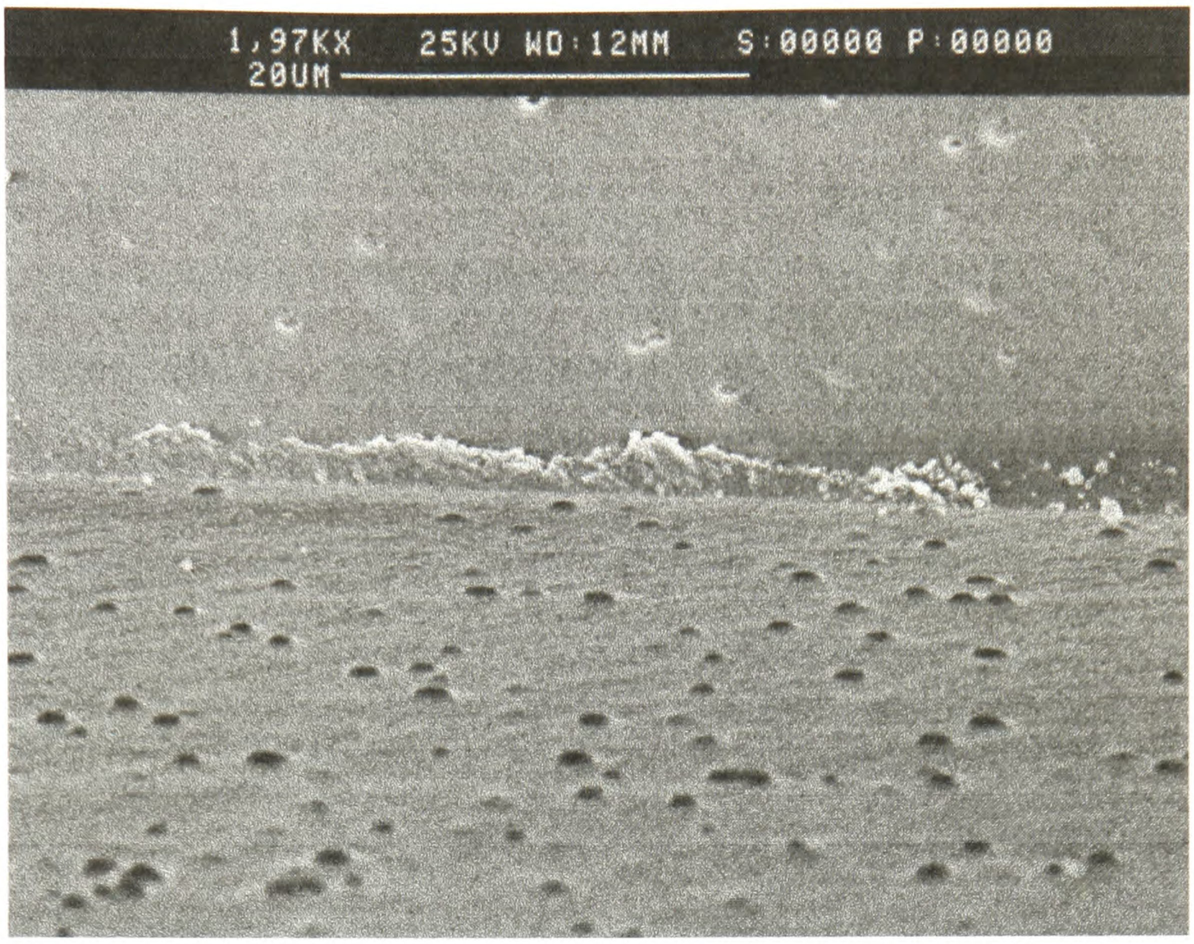


Figure 8.10: SEM picture showing pores in the surface of a sample produced by the method described above.

8.3.3 Absorption of fluoride ions

In most cases the positively charge ions were readily absorbed into plain silica matrices. This could be observed by the colour of the cobalt absorbed samples and the luminescence of the europium absorbed samples. In some cases where the samples were particularly large and the europium solution quite dilute it was quite difficult to observe the luminescence.

In the case of the addition of europium solution to fluoride containing silica lattices, instant precipitates started coming out of the gel. This suggests that the fluoride is not all bonded to the silica and is being precipitated as europium fluoride.

However, in the case of the addition of fluoride ions to rare earth containing silica gels no precipitate was observed. This implies that the rare earth ions are bound into the lattice. When low concentrations of fluoride were used the outer parts of the gels absorbed them nore than the inner as expected. These gels were tested using a fluoride ion selective electrode, see table 8.6. When more concentrated solutions were used the gels began to dissolve.

Table 8.6 Results of analysis of silica gels using fluoride ion selective electrode.

Sample	Area of sample tested	Amount of fluoride
A	Top surface	1.574 ppm
	Lower edge under liquid level	1.14×10^{1} ppm
	Centre of gel	1.82×10^{-1} ppm
B	Centre of gel	level too low
	Outer edge	22.26 ppm
C	Centre of gel	level too low
	Outer edge	2.61 ppm

When dried gels were fired with ammonium fluoride they lost small amounts of weight. The loss of mass is directly proportional to the amount of ammonium fluoride used (see figure 8.11). In some cases where the amount of ammonium fluoride is large the gels lost their transparency and became opaque and were easily broken. It is assumed that this is due to the attack of F^- on the gel. SEM micrographs showing surface detail of a sample containing rare earth ions fired in ammonium fluoride are given in figures 8.12. Damage to the surface of the material is evident in the form of crystallisation occuring on the surface.

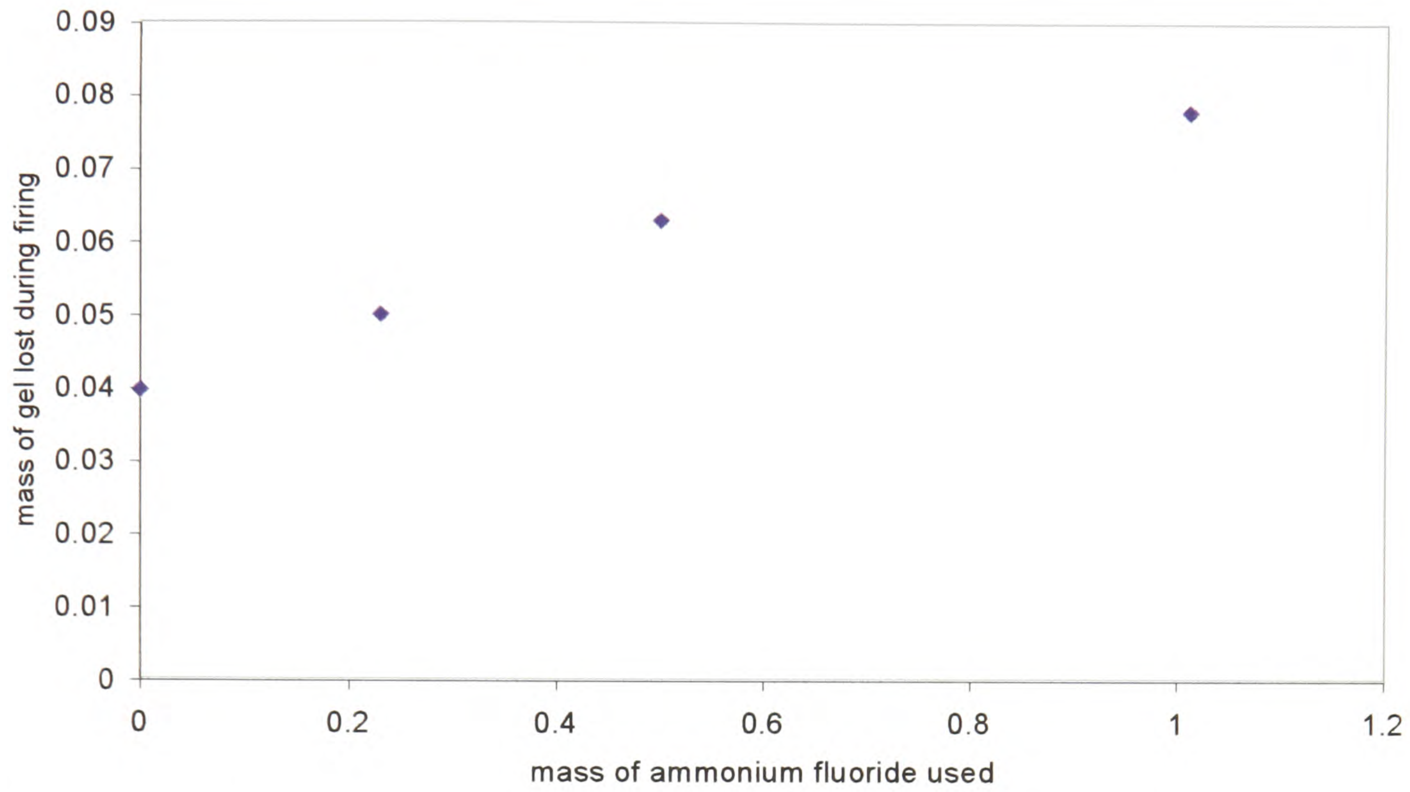


Figure 8.11 Plot of mass of ammonium fluoride used in firing process against mass of gel lost during firing.

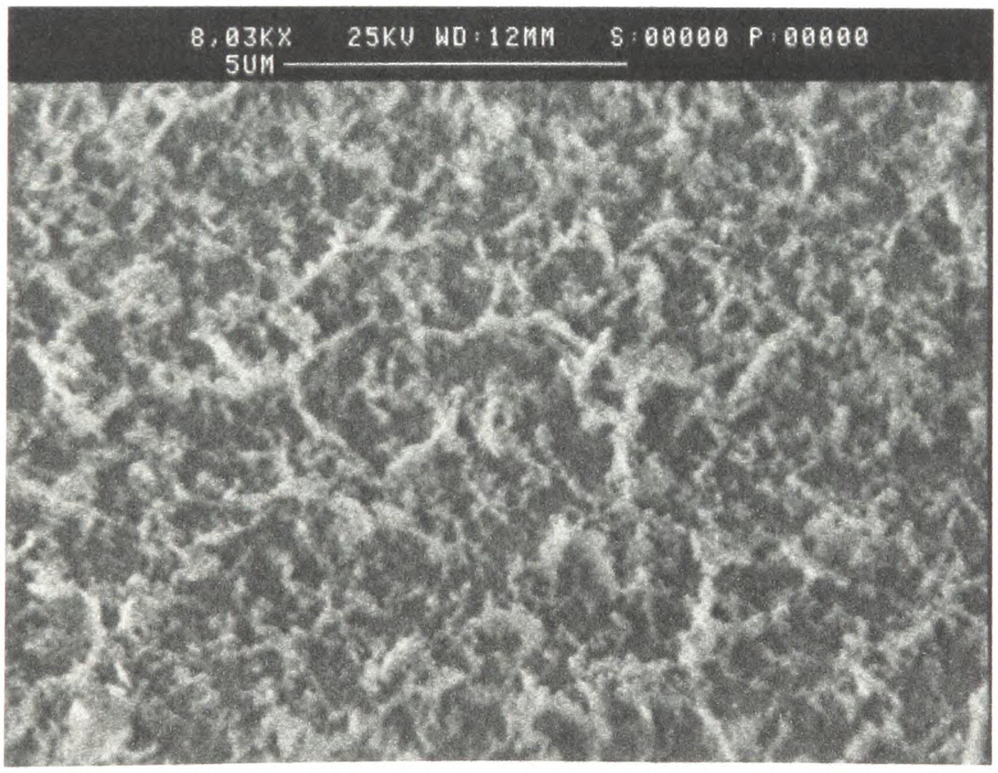


Figure 8.12 SEM picture of surface detail of a sample fired with ammonium fluoride.

8.3.4 Microwave experiments

As expected samples produced in the microwave were more easily broken and more opaque than samples produced conventionally in the lab. This is due to the microwave interaction and the resulting elevated pressures causing the hydrolysis and gelation processes to be accelerated and therefore producing poor samples where the bonding is incomplete.

8.3.5 The interaction of fluoride ions with rare earth ions

In the case of 0.3g erbium acetate solution in 10ml 2-methoxyethanol gelation is observed after the addition of 0.5ml HF solution. Upon the addition of further HF solution however the gelation dissipates and eventually a pale pink precipitate is observed.

Upon addition of 0.5ml HF solution to 0.5g erbium nitrate in 10ml ethanol turbidity is observed. No precipitation readily occurs and when the liquid is tested with sodium carbonate solution, very little reaction is evident suggesting that the fluoride is bound to the rare earth.

8.3.6 The synthesis of rare earth and fluoride doped glasses containing titanium, zirconium and aluminium

The 2 molar % titanium containing samples were found to be similar to the samples that were synthesised without the titanium. A diagram showing the range of compositions and the state of the resulting glasses is shown in figure 8.13. By comparison, samples containing 10 molar % titanium were nearly all opaque and in some circumstances became powder upon firing. Only samples of low concentration rare earth or of no fluoride content were transparent after firing. The up-converting properties of some of these titanium-containing ceramics are discussed in the next chapter.

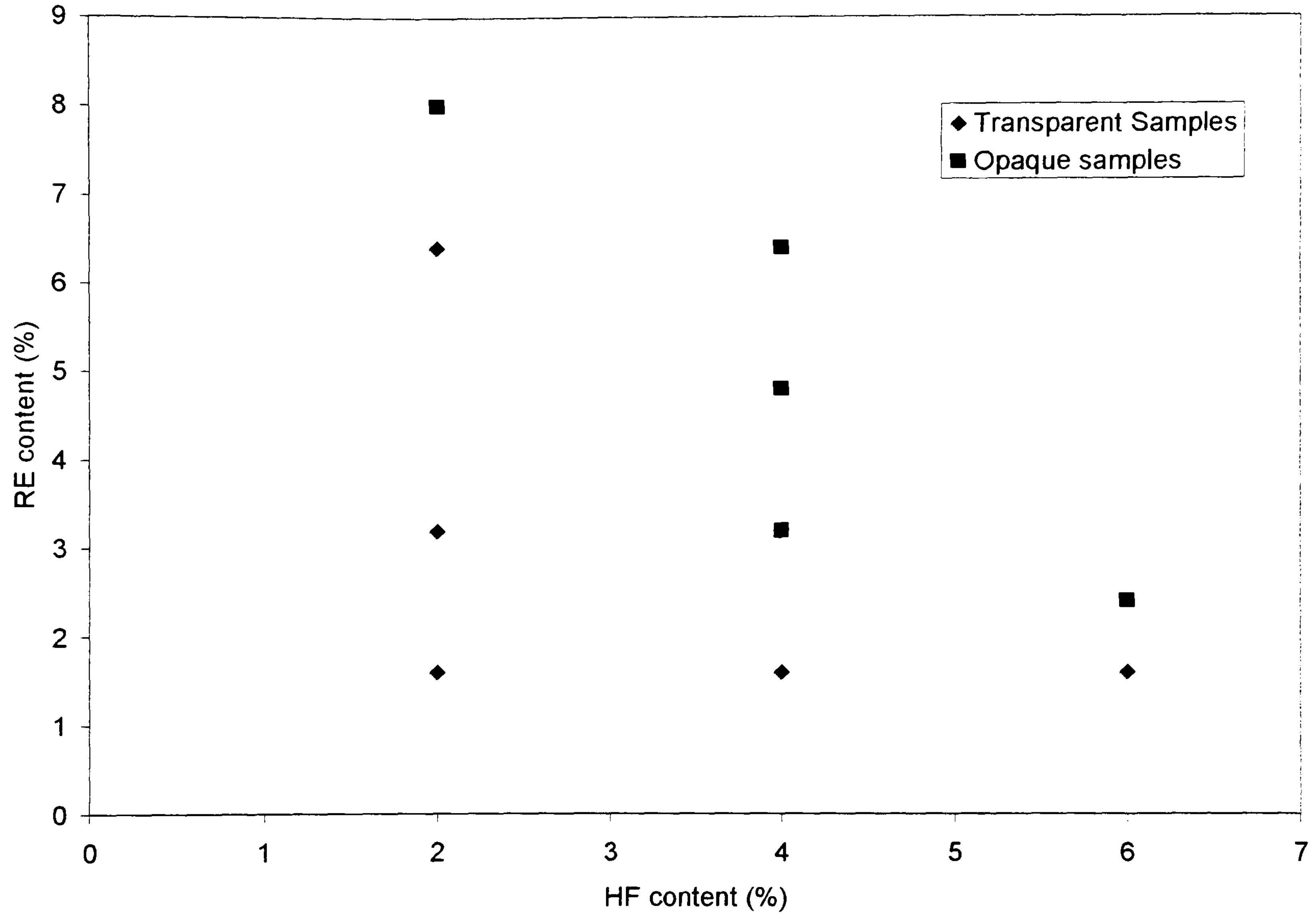


Figure 8.13 Plot of rare earth element concentration against fluoride content for silica glass samples containing 2mol% titanium.

The 2 molar % aluminium containing samples reflected the results of the 2 molar % titanium samples. These results are shown in figure 8.11. However these samples fit a little less easily into the sort of diagram shown in figure 8.10. Again with the 10 molar % aluminium containing samples the resulting glasses were much the same as the 10 molar % titanium samples. Again the up-converting properties of the aluminium-containing ceramics are discussed in chapter 9.

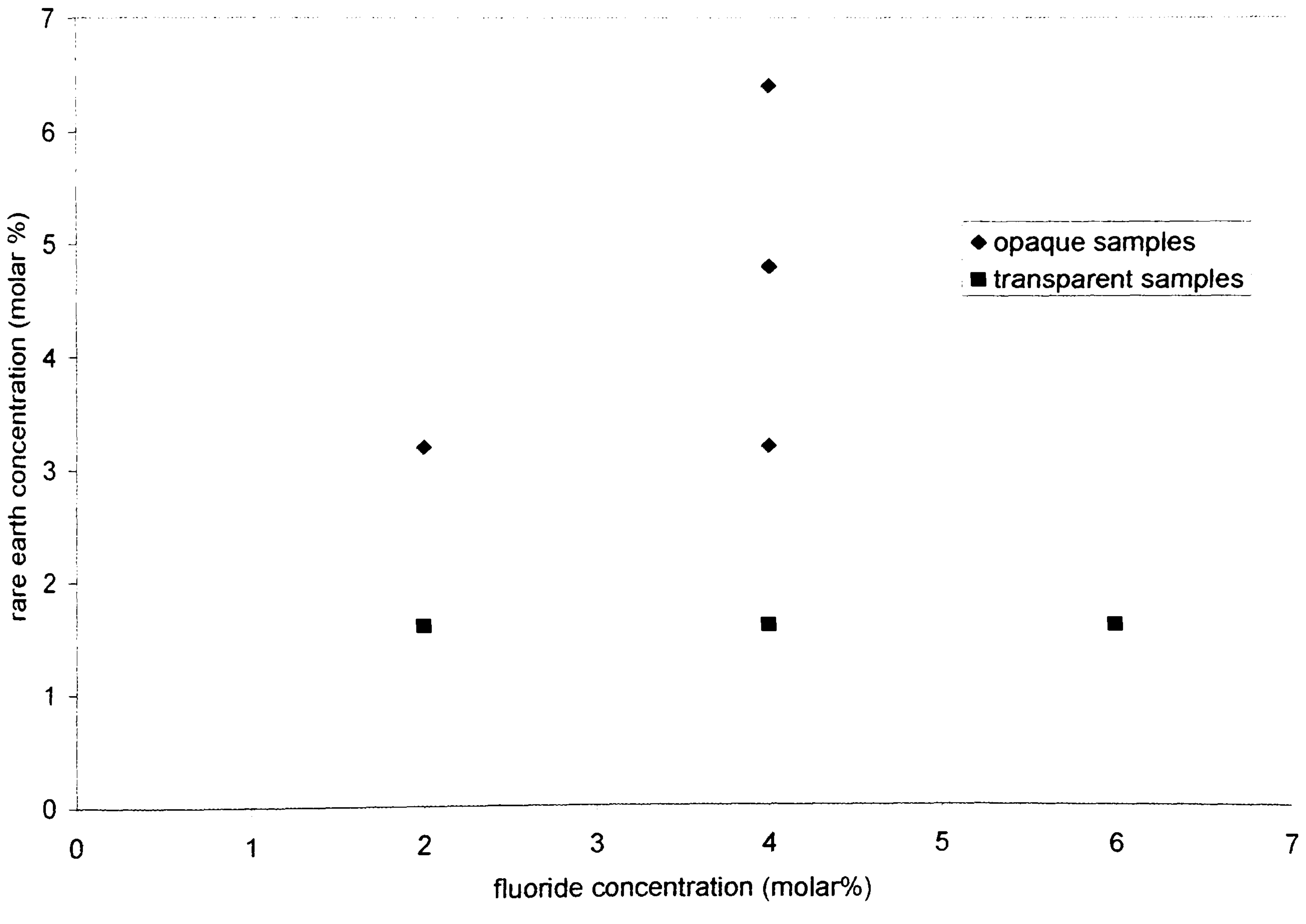


Figure 8.14 Plot of rare earth element concentration against fluoride content in samples containing 2mol% aluminium.

Samples containing 2 molar % zirconium based on the transparent samples produced by the titanium and aluminium compositions were synthesised. These samples were transparent as expected.

8.3.7 X-Ray Diffraction Analysis Results

It was found that the unfired gels were amorphous from the XRD results. The samples fired to 1100°C and then removed from the furnace also had an amorphous structure. The samples that were held at 400°C for 10 hours showed the presence of crystalline structure although this was not as structured as that of the samples held at 800°C. Additionally the samples containing titanium had a different diffraction pattern at 400°C compared to the samples at 800°C.

8.4 Conclusions

From the above experiments the following conclusions can be drawn:

- For transparent samples containing fluoride and rare earth ions, concentrations in the range shown in figure 8.9 should be adhered to when synthesising gels by putting fluoride into the matrix as a catalyst during mixing;
- The presence of hydrochloric acid is necessary to control the increased sol-gel processes caused by the presence of fluoride ions;
- As hydrochloric acid is necessary, ammonium fluoride cannot be used as it causes the precipitation of ammonium chloride in the pores of the sample. Hydrofluoric acid should be used instead;

- The use of prehydrolysed TEOS is necessary for the production of a good gel matrix and
- The best precursor for the RE^{3+} solution is the RE^{3+} acetate reacted with 2-methoxyethanol.
- Wet gels do not readily absorb fluoride ions due to their negative surface charge. Absorption of fluoride ions in the gaseous phase is also unsuitable due to loss of mass as silicon tetrafluoride.
- The fluoride ions bind to the RE^{3+} ions present in the matrices during the solution phase of the reactions.
- The fluoride ions do not bind to the silica matrices.
- The higher temperature the samples containing erbium, ytterbium and fluoride ions are fired at, the better crystalline structure is formed.
- SiO_2 ceramics contain either titania or aluminia as well as rare earth element ions can readily be prepared (the properties of these ceramics are discussed in the next chapter).

References

1. S. Shibata, T. Kitagawa and M. Horiguchi, J. Non Cryst. Solids, 100 (1988) 269-273.
2. M. Saad and M. Poulain, J. Non Cryst. Solids, 184 (1995) 352.
3. R. E. Riman, M. Dejneka, J. Eamsiri, E. Snitzer, A. Mailhot and A. Leaustic, J. Sol-gel Sci. & Tech., 2 (1994) 849
4. P. J. Melling and M. A. Thomson, J. Mat. Res. 5(5) (1990) 1092.
5. A. Thompson and J. M. Parker, "The Structure of non crystalline materials 1982". P305, Taylor and Francis Ltd., London, 1983.
6. D. Kumar, R.G. Ward and D. J. Williams, Discussions of the Faraday Society, 32 (1961) 147.
7. R. Iler, "The Chemistry of Silica" and references therein, Wiley, New York, 1979.
8. A. Paul, Chemisty of Glasses, Chapman and Hall, London, 1982.
9. L.C.Klein, "Sol-gel Optics" and references therein.
10. C. J. Brinker and G. W. Scherer, "Sol-gel Science – The Physics and Chemistry of Sol-gel Processing", Academic Press, London, 1990.
11. Matsuyama, Suza, Satoh and Suganuma, Ceram. Bull. 63(1984) 1408
12. Suza, Matsuyama, Satoh and Suganuma, J. Non Cryst. Solids, 79(1986) 165
13. E. M. Rabinovich, Wood, D. W. Johnson, Fleming, Vincent and J. B. MacChesney, J. Non Cryst. Solids, 82(1986) 42.
14. Tsunehiro Tsukada, Masahiro Shinmei and Toshiro Yokokawa, J.Non Cryst. Solids, 100(1998) 435.
15. R. Winter, J.-B. Chan, R. Frattini and J. Jonas, J. Non Cryst. Solids, 105 (1988) 214
16. E. J. A. Pope and J. D. Mackenzie, J. Non Cryst. Solids, 87 (1986) 185

17. R. Rodriguez, M. Flores, J. Gomez and V. M. Castano, Mater. Lett. 15 (1992) 242.

18. P. B. Malla, S. Komarnenim, H. Taguchi and H. Kido, J. Am. Ceram. Soc., 74(12) (1991) 2988.

19. M. Dejneka, Mat. Res. Bull. 23(11) (1998) 57

20. Yuhu Wang and Junichi Ohwaki, Appl. Phys. Lett., 63(12), (1993), 3268.

Chapter 9 – Luminescence Studies

9.1 Introduction

As explained in section 1.3.4 Anti-Stokes' luminescent processes or upconversion in glass have been shown to be more efficient in fluoride-based glasses than in oxide-based glasses[1,2]. However it is also known that crystalline materials have better properties as hosts for anti-Stokes processes than covalent glasses[3]. Recent studies have suggested that oxyfluoride glass ceramics have better properties compared to fluoride glasses[4]. This is due to the existence of very small luminescent fluoride crystallites embedded in an oxide matrix, hence combining the high luminescent efficiency of a fluoride with the stability and durability of an oxide glass[5,6,7]. This is shown in table 9.1. The phonon energy of a material is inversely proportional to the efficiency of the dopant in the material.

Glass Family	Highest energy phonon (cm^{-1})	Quantum efficiency of Pr^{3+} in this host
Glasses:		
Borate	1250	0
Silicate	1100	0
Heavy metal oxide	800	1
Fluorozirconate	580	3
Fluoroindate	520	5
Oxyfluoride glass ceramics:		
LaF_3	350	8
$Pb_{1-x}Cd_xF_2$	250	7

Table 9.1 Phonon energy and quantum efficiency of Pr^{3+} of a selection of glasses and glass ceramics[4].

9.2 Initial Studies

The spectra of yttrium fluoride doped with ytterbium and erbium was obtained under infrared excitation using infrared diodes with an emission centred on 950nm and a broad spectrum emission. This was detected with a Bentham spectrometer and can be seen in figure 3b.1. A more detailed spectrum was obtained using a tuneable titanium-sapphire laser obtained through a grant from the EPSRC. The sample gave its maximum emission when excited by 974nm and the spectrum is given in figure 3b.2.

Glass samples synthesised as described in section 8.2.2 were placed in the titanium-sapphire laser beam tuned to wavelengths in the region of 970-985nm and no luminescence was observed in these samples.

As the titanium-sapphire laser was on loan for this project for a short time no further investigations could be performed using it.

9.3 Further Studies

9.3.1 Analysis of Anti-Stokes Powder Phosphors

Yttrium fluoride doped with ytterbium and erbium was analysed using a red laser at 660nm and a spectrum was obtained. By comparison, yttrium oxide doped with ytterbium and erbium was also excited using the 660nm source and spectra were also collected. These can be seen in figures 9.1 and 9.2.

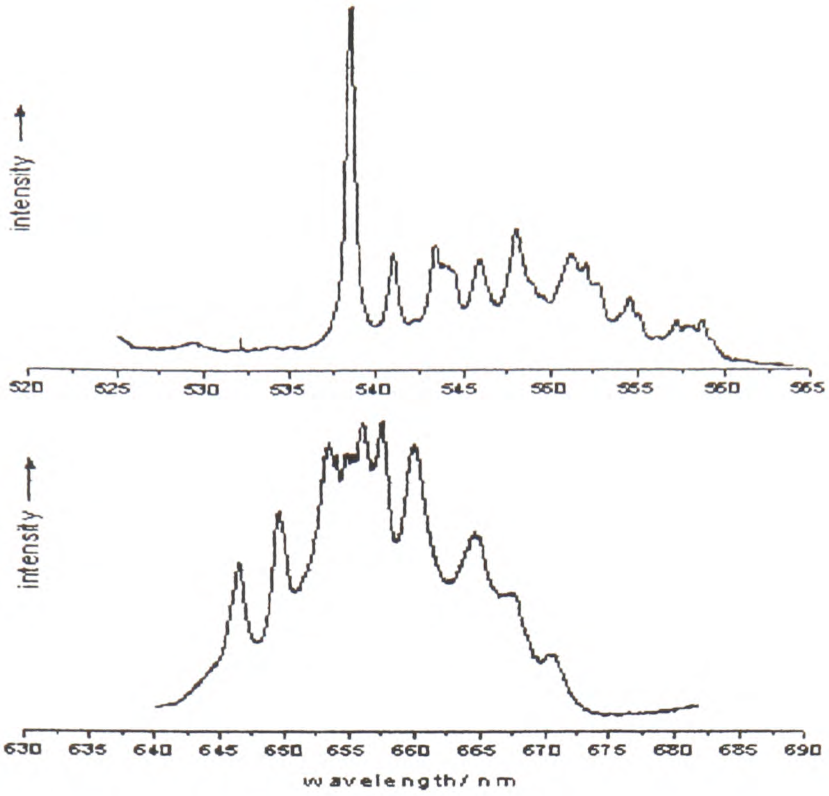


Figure 9.1 Anti-Stokes emission spectra of yttrium fluoride doped with ytterbium and erbium. Upper spectrum – green emission, lower spectrum – red emission.

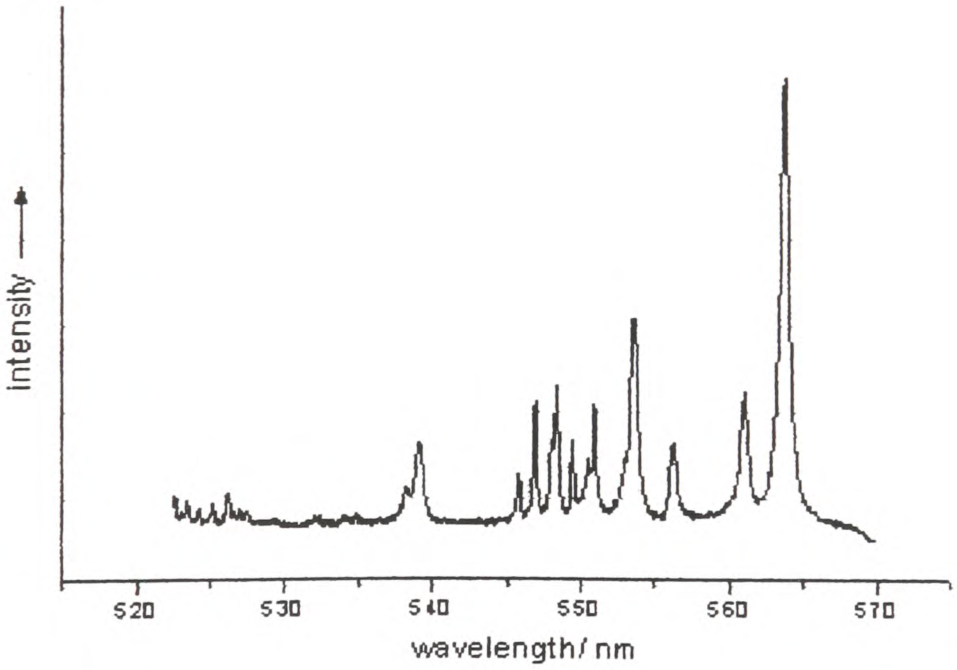


Figure 9.2 Anti-Stokes emission spectrum of Yttrium oxide doped with ytterbium and erbium.

9.3.2 Analysis of Glass Samples

Glass samples synthesised using the method described in section 8.2.2 were analysed under 660nm excitation. No luminescence was obtained in these samples. However a distinctive emission was detected from some of the samples containing titanium (the synthesis of these samples has been described in section 8.2.6). Similar samples synthesised with aluminium present also showed anti-Stokes luminescence.

9.3.3.Preparation and Analysis of Titanium Dioxide Anti-Stokes Emitters

For comparison purposes different forms of titanium oxide were doped with ytterbium and erbium oxides and their luminescence was analysed.

Samples were prepared from titanium (IV) ethoxide (Aldrich Technical Grade), ytterbium nitrate pentahydrate (99.9%), erbium nitrate pentahydrate (99.9%) (all from Aldrich) and ethanol (absolute, Merck BDH). A solution of titanium (IV) ethoxide (0.02M) in 25ml ethanol was prepared in a 250ml beaker and continually stirred. Ytterbium nitrate solutions (0.004M) and erbium nitrate solutions (0.0004M) were made up in de-ionised water to a volume of 25ml. This solution was slowly added to the titanium ethoxide solution whilst stirring. Once the solution formed a gel the stirring was stopped. This gel was then dried in an oven at 100°C. The resulting dried product was fired in a furnace at 750°C for 2 hours in order to produce the anatase structure and 1150°C for 2 hours to produce the rutile form.

9.3.4 Analysis of Europium Doped Glasses

Europium doped glass samples synthesised in the manner described in section 8.2.2 were also studied. These were excited using ultra violet light and were compared to europium doped samples synthesised in section 5.3.1 which do not contain fluoride ions.

9.4 Results and Discussion

The europium doped samples showed similar results to the erbium doped samples. It was found that the samples containing fluoride ions showed very little luminescence compared to the samples without fluoride present. This suggests that the europium ions are being separated with the fluoride ions forming crystallites within the glass matrix. The lack of luminescence from the fluoride-containing glasses implies that concentration quenching is occurring as europium ions generally luminesce in nearly all host matrices apart from in europium compounds themselves and hence in these samples the europium ions are the sole metal cations in these glassy samples.

No Anti-Stokes emission was observed in the silica glass matrices in the absence of Ti^{4+} ions, even though in many of the clear glasses small precipitated crystallites were observed. The crystallites appeared to be YbF_3 and ErF_3 type materials - the erbium fluoride crystallites are most likely to be self-quenching.

Glass ceramics were prepared containing Ti^{4+} ions which show some anti-Stokes luminescence. Figure 9.3 shows a TEM micrograph showing the crystallites present in a titanium-containing sample. This sample consists of 0.14mol% Er^{3+}, 0.85mol% Yb^{3+} and

7 mol% Ti^{4+}. A fluoride content of 4 mol% was added at the mixing stage of the synthesis of this sample (see section 8.2.1). This sample was fired to a temperature of 700°C at a rate of 2°C min^{-1} – this sample was cooled back to room temperature at a rate of 10°C min^{-1}. This sample has not been annealed. The crystallite size of the particles shown in figure 9.3 is of the order of 5-6nm in length along the longest edge. These particles were not expected to contain fluoride ions based on the fact that the main anti-Stokes peak was not in the same region as that expected for a fluoride lattice doped with erbium. Figure 9.4 shows the anti-Stokes emission from the glass ceramic sample in figure 9.3 and can be compared with figure 9.1 showing the anti-Stokes emission from a YF_3 matrix containing Er^{3+} and Yb^{3+}. It can be seen quite clearly that these two emission spectra are not alike. The main emission peak for the glass-ceramic is closer to the region expected for that of an oxide lattice. Figure 9.2 shows the anti-Stokes emission spectrum for Y_2O_3 containing Yb^{3+} and Er^{3+}.

The Raman spectrum of the sample in figure 9.3 shows bands at 144, 392, 512 and 636cm^{-1} (see figure 9.5). These indicate the presence of the anatase form of titania in this sample which has arisen from the presence of the Ti^{4+} ions in the original sol-gel mixture. A recent literature report also refers to the formation of this anatase phase being formed during sol-gel processes[8].

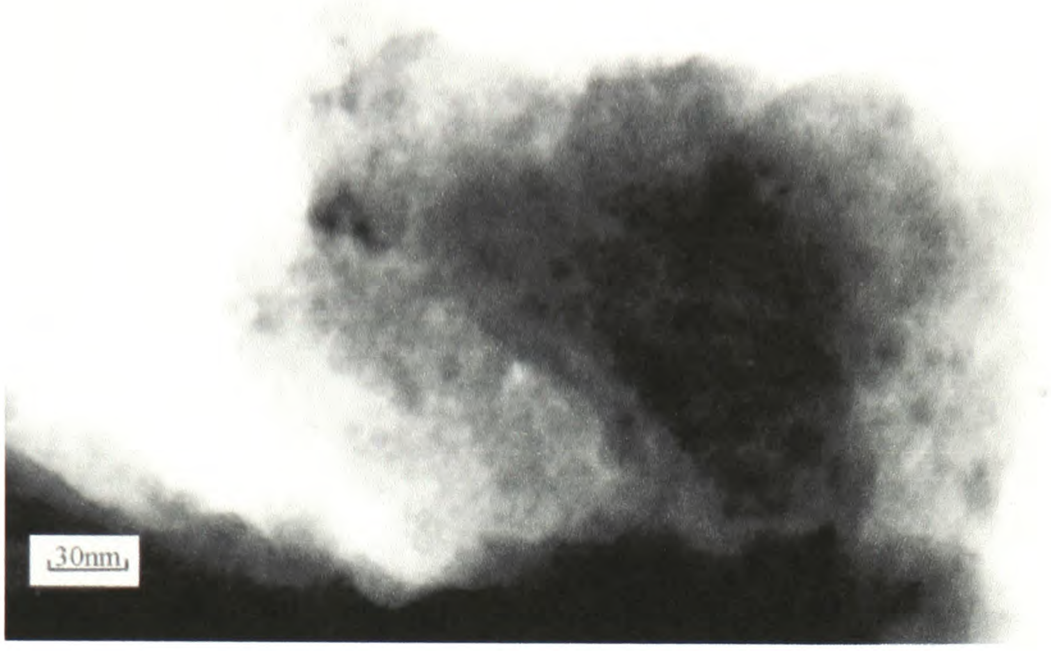


Figure 9.3 TEM picture of crystallites in glass ceramic

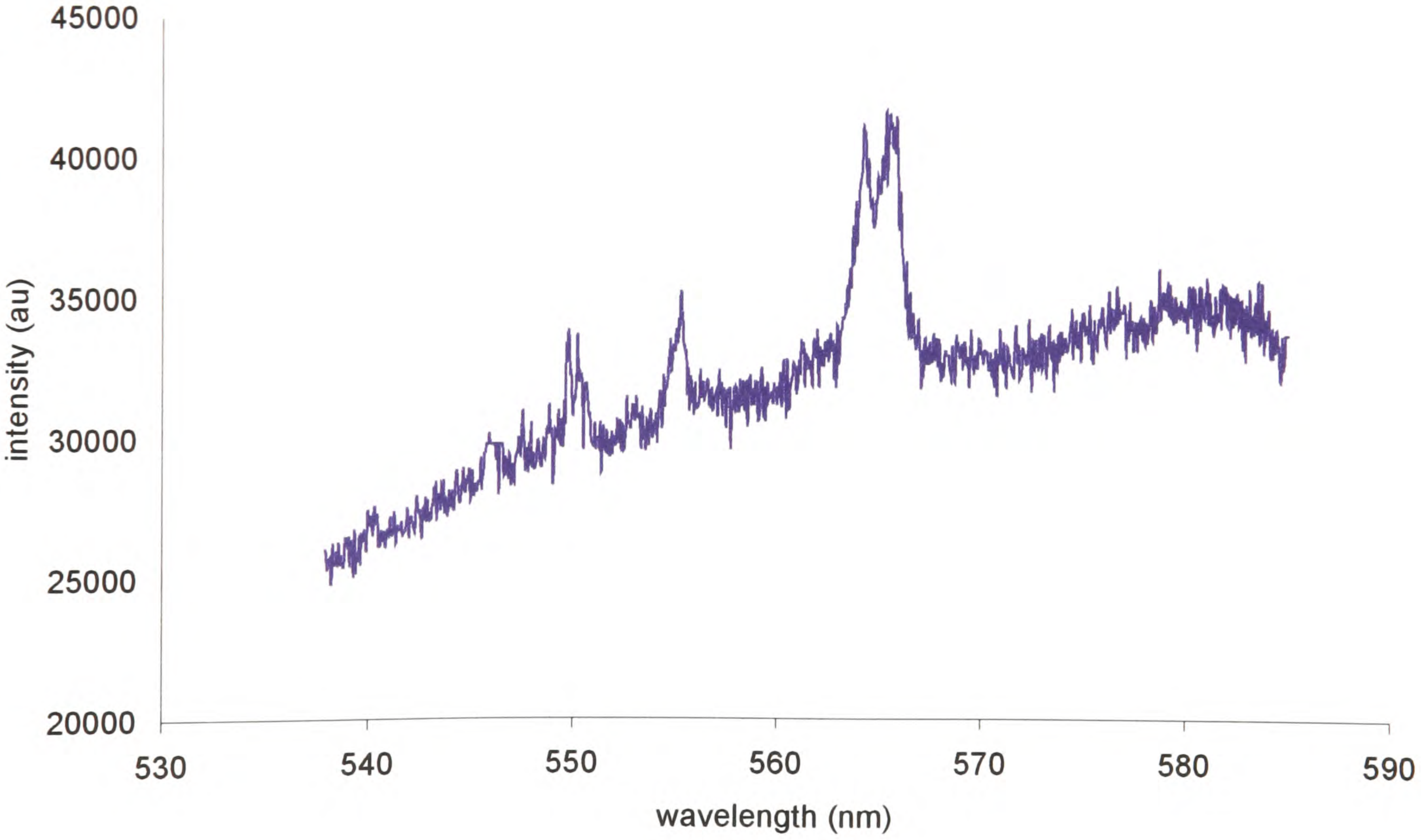


Figure 9.4 Anti-Stokes emission from glass ceramic

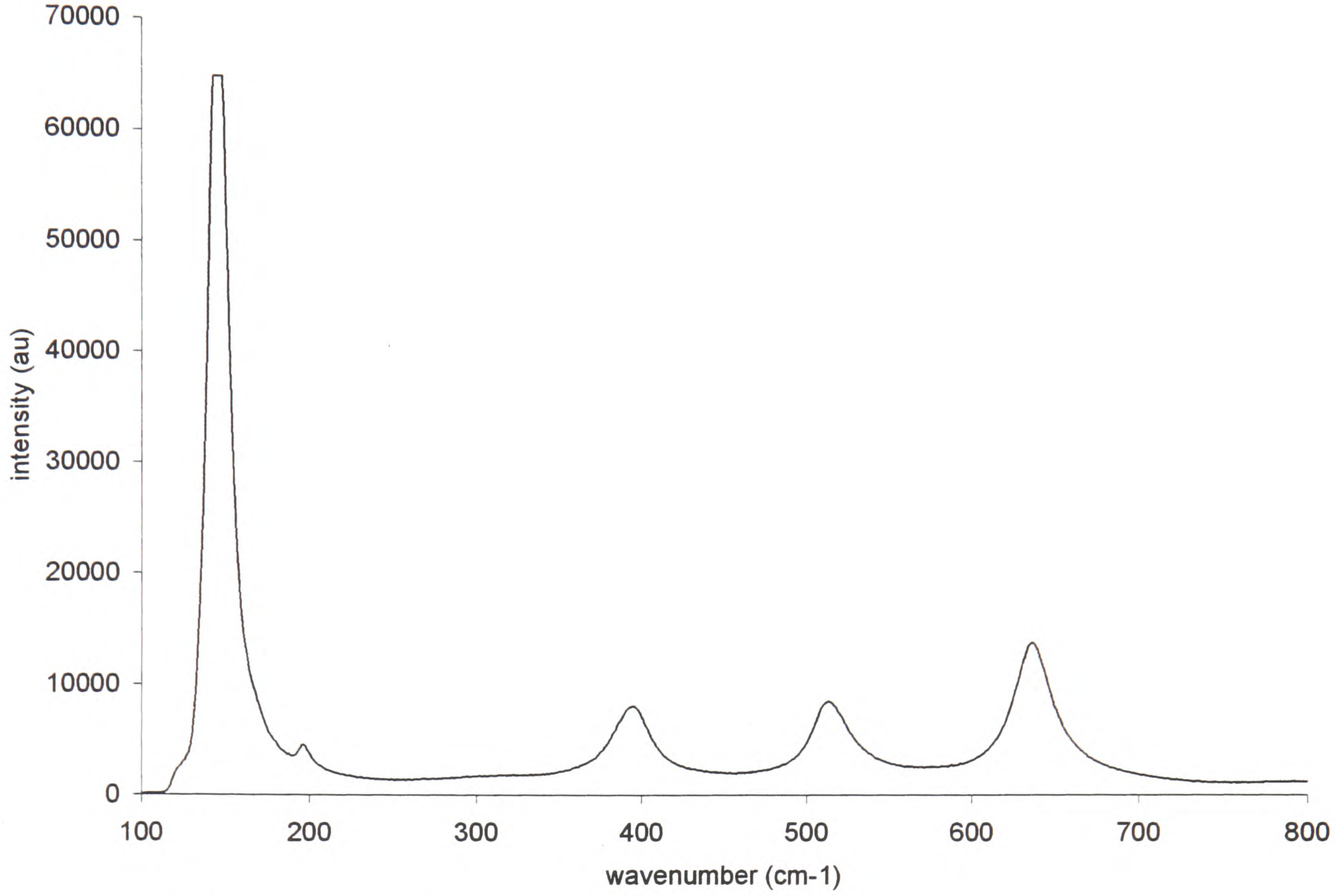


Figure 9.5 Raman spectrum of glass ceramic

In comparison, the sample of ytterbium and erbium doped anatase as synthesised in section 9.3.3 gave a similar Raman spectrum to the glass-ceramic in figure 9.3 (see figure 9.6). The anti-Stokes emission of the anatase is given in figure 9.7 and here it can be seen to be very similar to that of the glass ceramic confirming that the anatase phase present in the glass ceramic is responisble for its anti-Stokes' emission. This emission has a yellow colour overall and is about one seventh as intense as that from YF_3 doped with ytterbium and erbium ions.

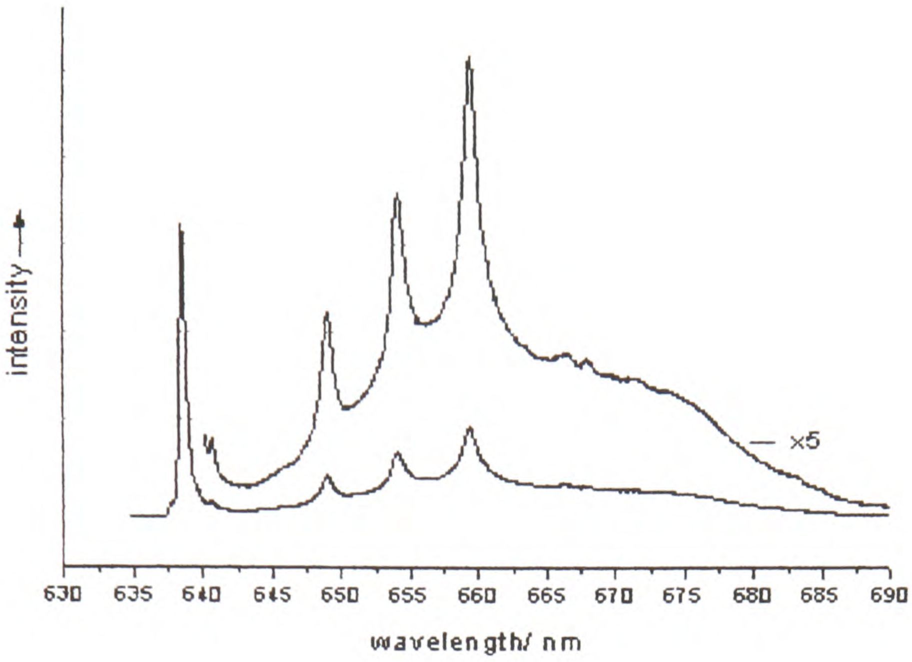


Figure 9.6 Raman spectrum of anatase doped with ytterbium and erbium

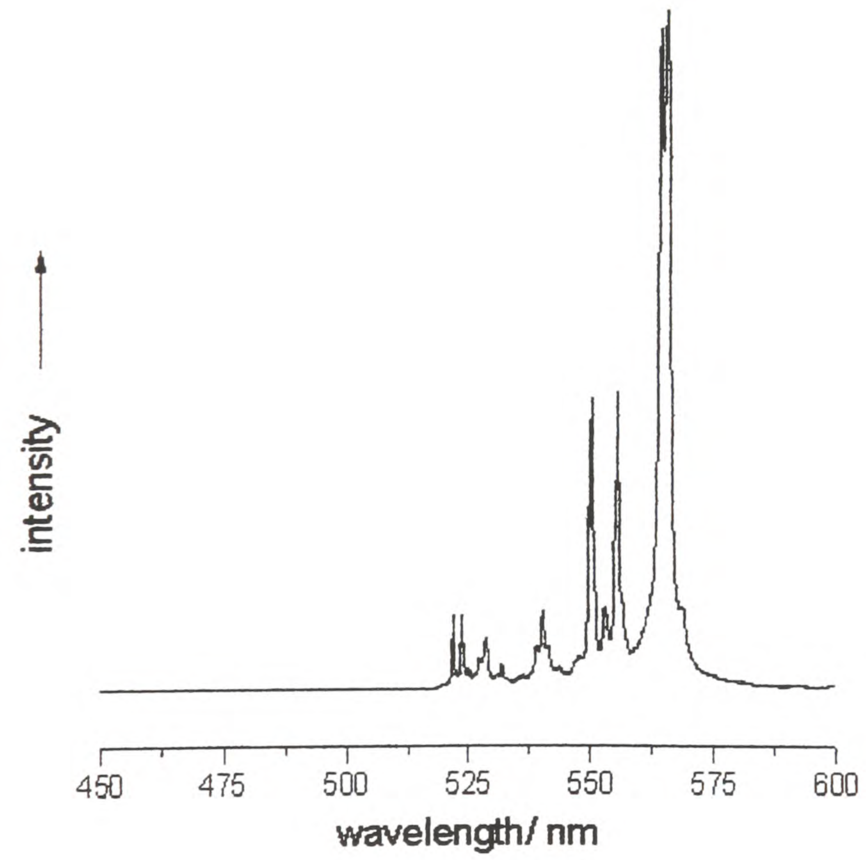


Figure 9.7 Anti-Stokes emission of anatase doped with ytterbium and erbium

When the anatase form of titanium dioxide is heated to 950°C the rutile phase is produced, as identified by bands at 447 and 610cm^{-1} in the Raman spectrum (see figure 9.8). This phase also produced anti-Stokes emission with a different spectrum to that of the anatase and about two orders of magnitude weaker in intensity (see figure 9.9).

The anatase phase produced Stokes emission (see figure 9.8) in the same wavelength region as the Stokes emissions of YF_3:Yb, Er and Y_2O_3:Yb, Er phosphors (see figures 9.1 and 9.2). The rutile phase also gave Stokes emission which was about ten times brighter than that observed from the anatase phase.

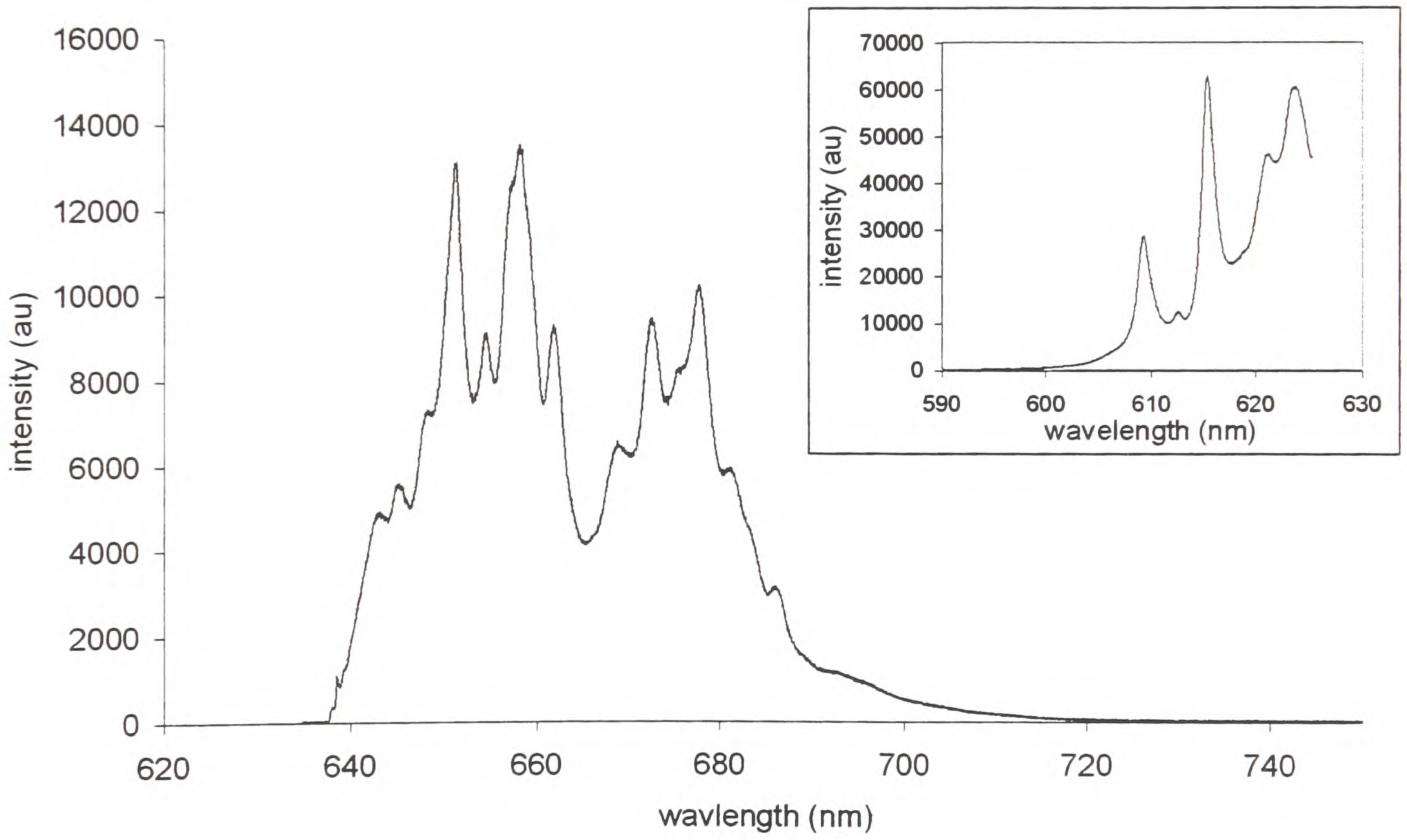


Figure 9.8 Stokes and Raman emission of rutile doped with ytterbium and erbium. The Raman spectrum in the anti-Stokes region is shown in the inset.

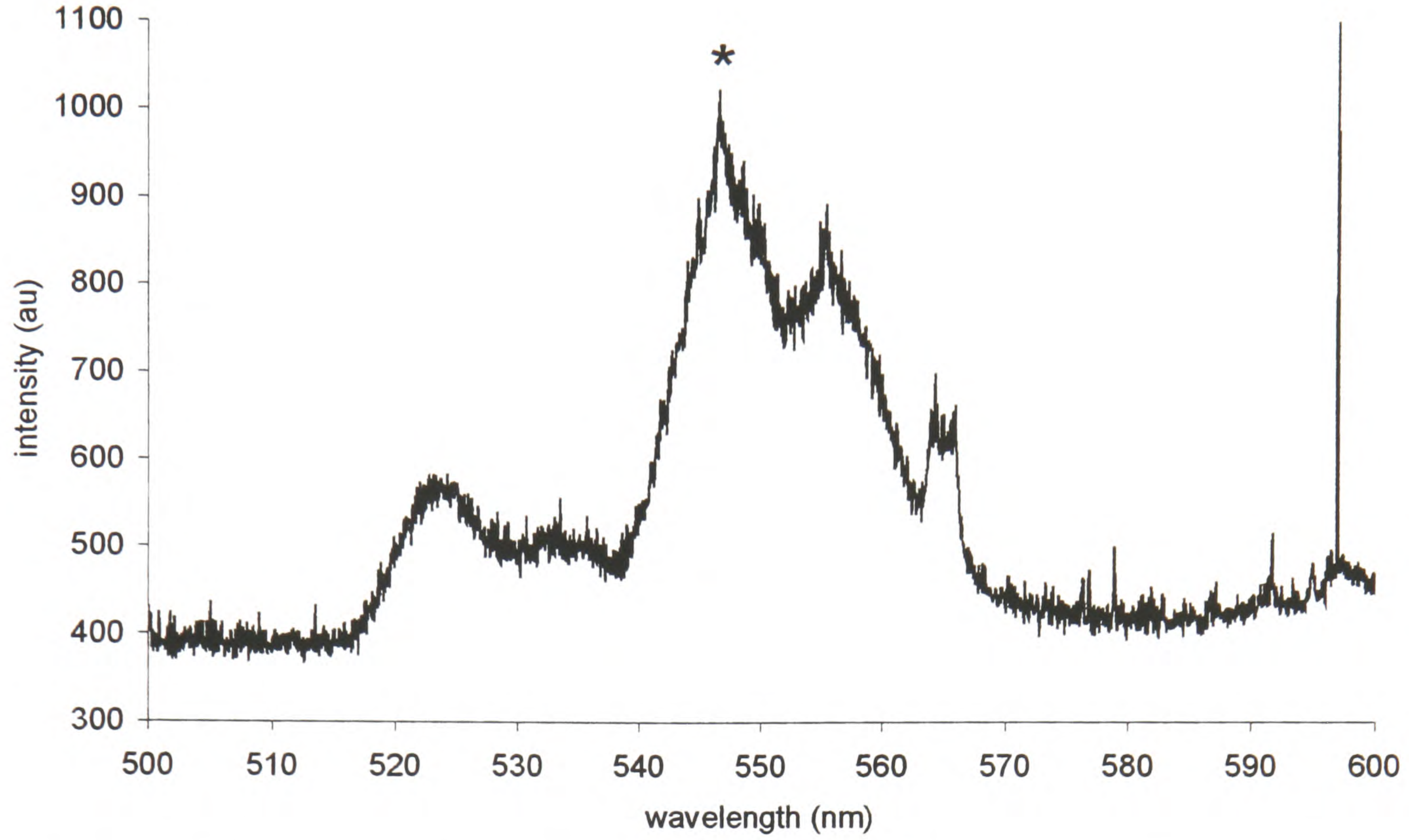


Figure 9.10 Upconversion emission from TiO_2:Yb,Er rutile/anatase. This sample was originally that which showed the upconversion emission in figure 9.4. For this spectrum the sample was annealed at 800°C for 6 hours. The asterisk indicates the leakage of a mercury line from the room lights.

Having established that the anti-Stokes emission is originating from TiO_2 based phases, analysis was performed on samples of the glass-ceramics that had been annealed. In figure 9.10 the anti-Stokes emission from the same glass-ceramic in figure 9.3 after it had been annealed at 800°C for 6 hours. By annealing at this temperature crystal growth occurs (see figure 9.11 for the TEM micrograph of this sample ahowing crystallites of the order of 7-12nm) and the rutile phase was expected to become dominant. There is some residual emission from the anatase phase which is more enhanced than prior to annealing but the rutile is predominantly the origin of the anti-stokes emission. This emission from the rutile is of a similar intensity to that of the rutile material synthesised in section 9.3.3 but lacks some of the fine structure.

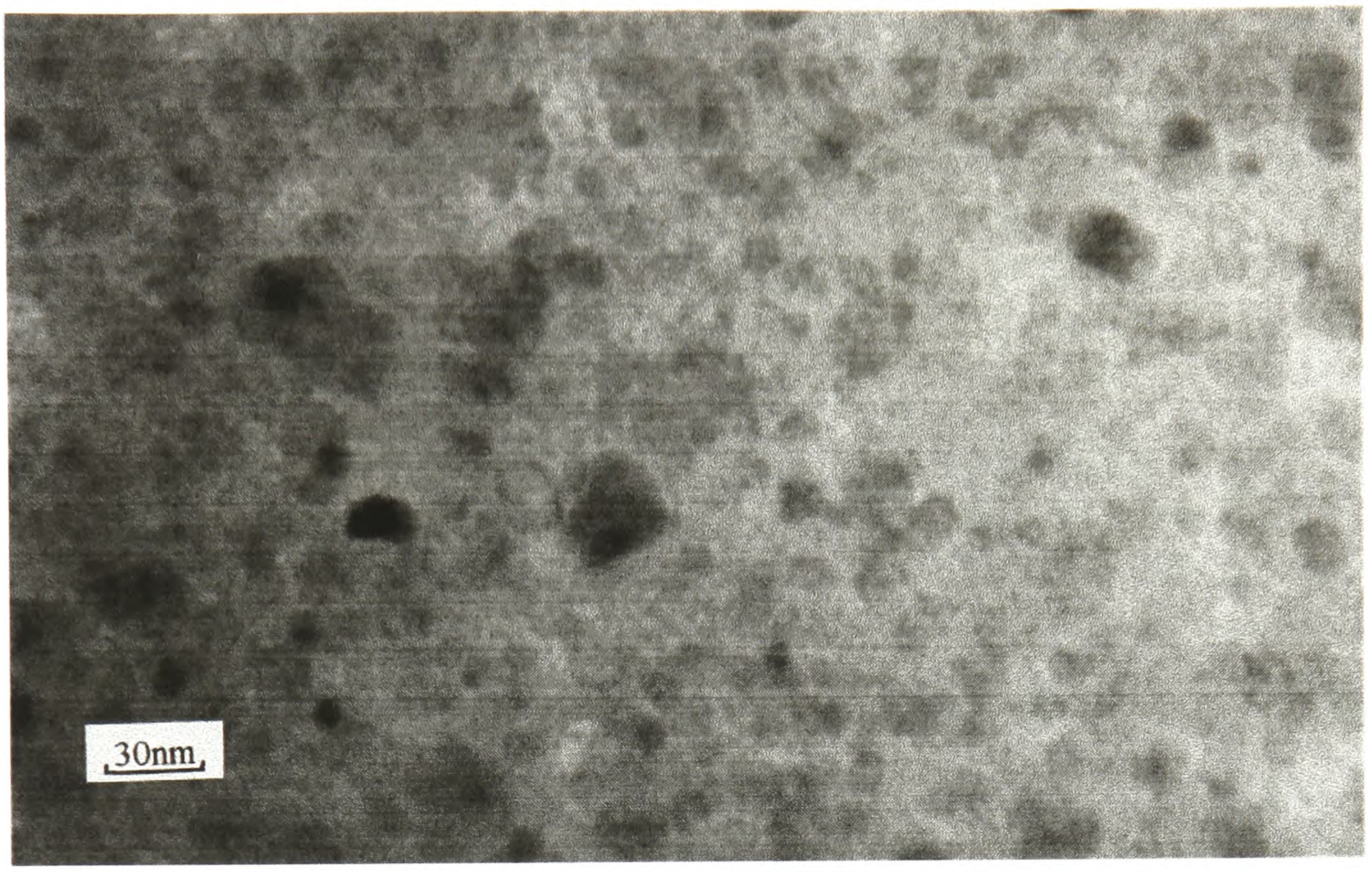


Figure 9.11 TEM (magnification 330000x) of glass ceramic (mainly rutile doped with ytterbium and erbium) as shown originally in figure 9.3 but annealed at 800°C for 6 hours. Crystallites are 7-12 nm in diameter.

Figure 9.12 shows the anti-Stokes emission of a glass-ceramic from the same batch as that in figure 9.3 after it has been fired up to 1100°C followed by annealing at 400°C for 10 hours. Clearly there is some rutile present caused by the initial firing at 1100°C but the emission from the anatase phase is stronger and the Raman bands show primarily the presence of anatase. The crystallites in this samples are shown in figure 9.13 and are of the order of 8-11 nm.

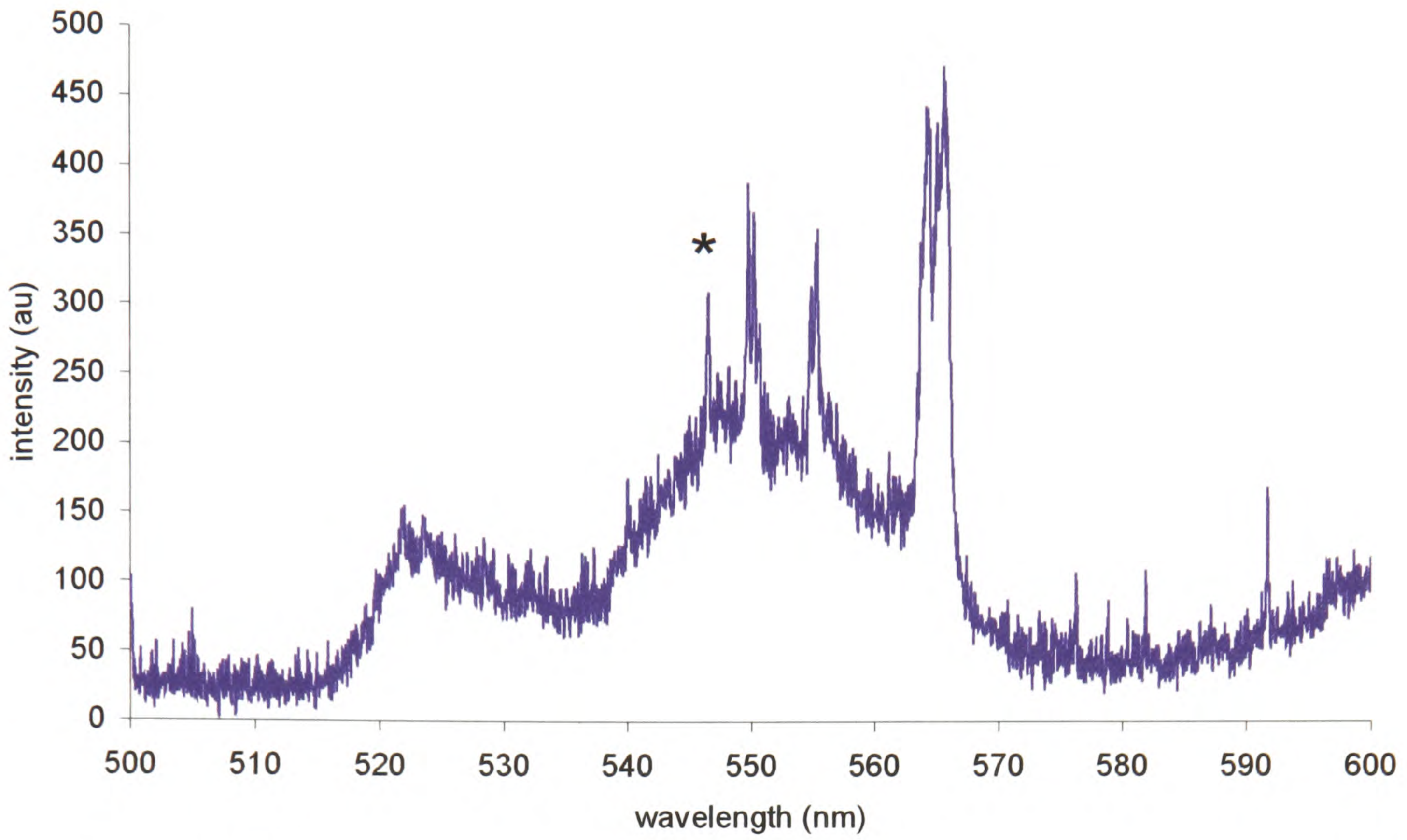


Figure 9.12 Upconversion emission from TiO_2:Yb,Er rutile/anatase. This sample is from the same batch as the sample in figures 9.3 and 9.10, but initially fired at 1100°C rather than 990°C and then annealed at 400°C for 12 hours. The asterisk indicates the leakage of a mercury line from the room lights.

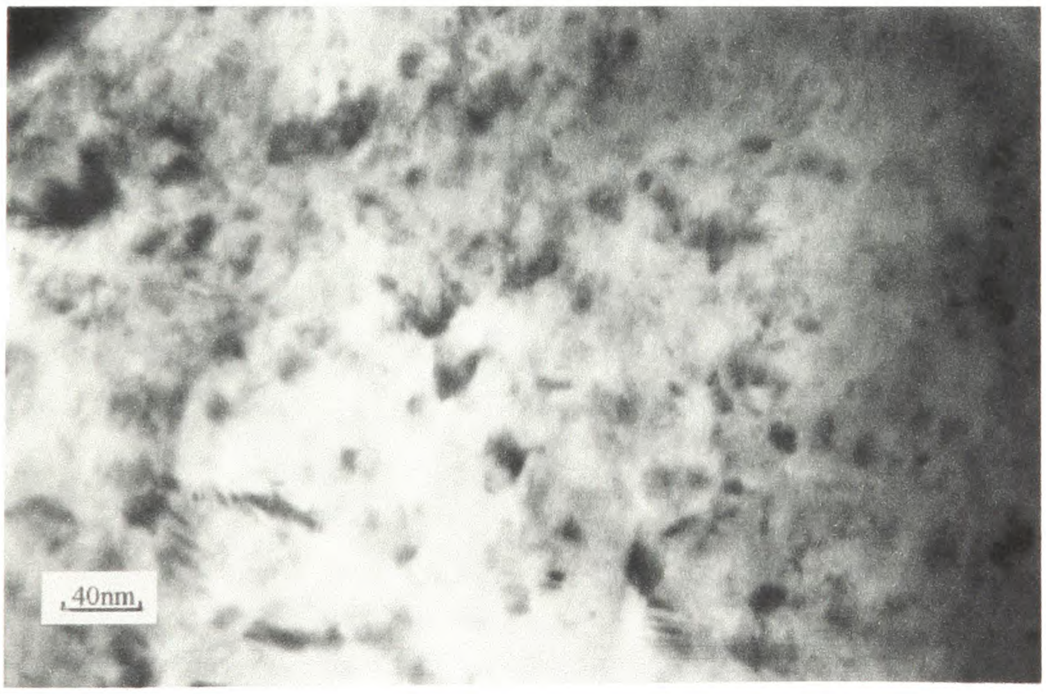


Figure 9.13 TEM (magnification 270000x) of glass ceramic of figure 9.12.

For confirmation, a second glass-ceramic sample was treated in this manner. Its composition contained 0.25mol% Er^{3+}, 1.1mol% Yb^{3+}, 4 mol% F^-, 10mol% Ti^{4+} and 84.65mol% SiO_2. Figure 9.14 shows the anti-Stokes emission from this sample after heating to 990°C and then rapidly cooled (not annealed) and figure 9.15 shows this sample's emission after firing to 1100°C followed by annealing at 400°C for 10 hours. The second spectrum is clearly more developed than the first. TEM analysis of this sample after each firing treatment (figures 9.16 and 9.17) shows that without annealing the crystallites are of the order of 3-4 nm whereas after annealing the size is 9-12 nm. Raman spectra for this sample before and after annealing shows the presence of anatase phase only.

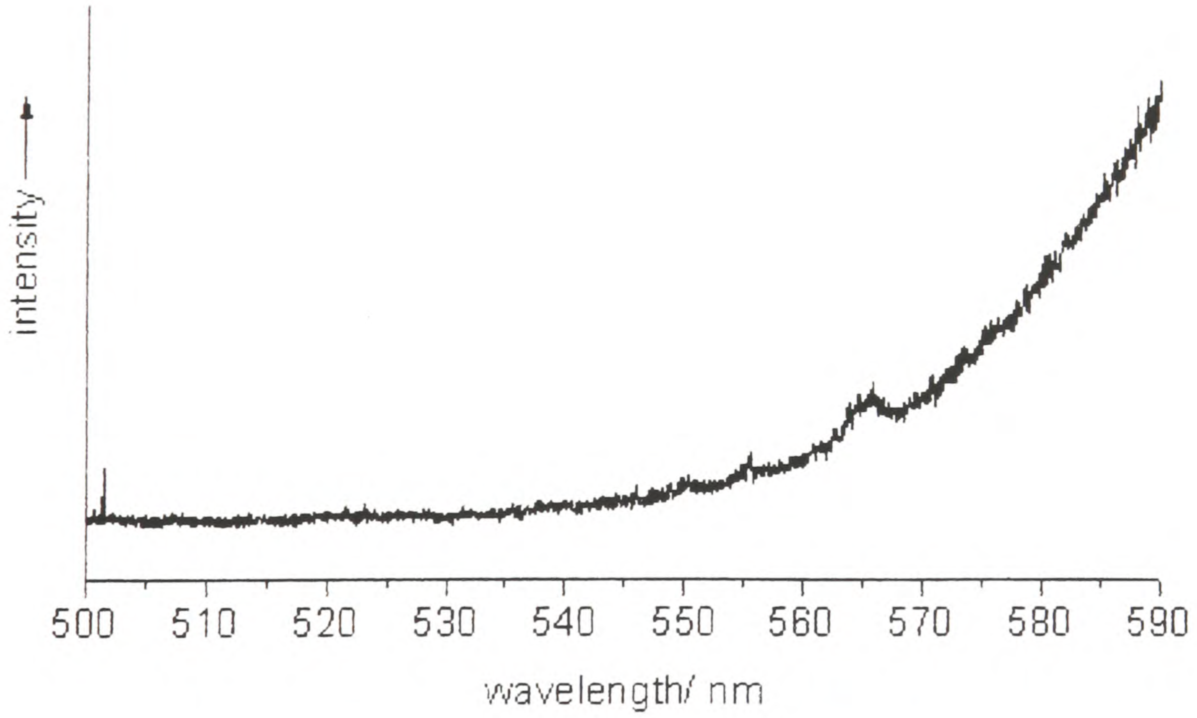


Figure 9.14 Anti-Stokes emission of second glass ceramic containing anatase phase doped with ytterbium and erbium fired at 990°C

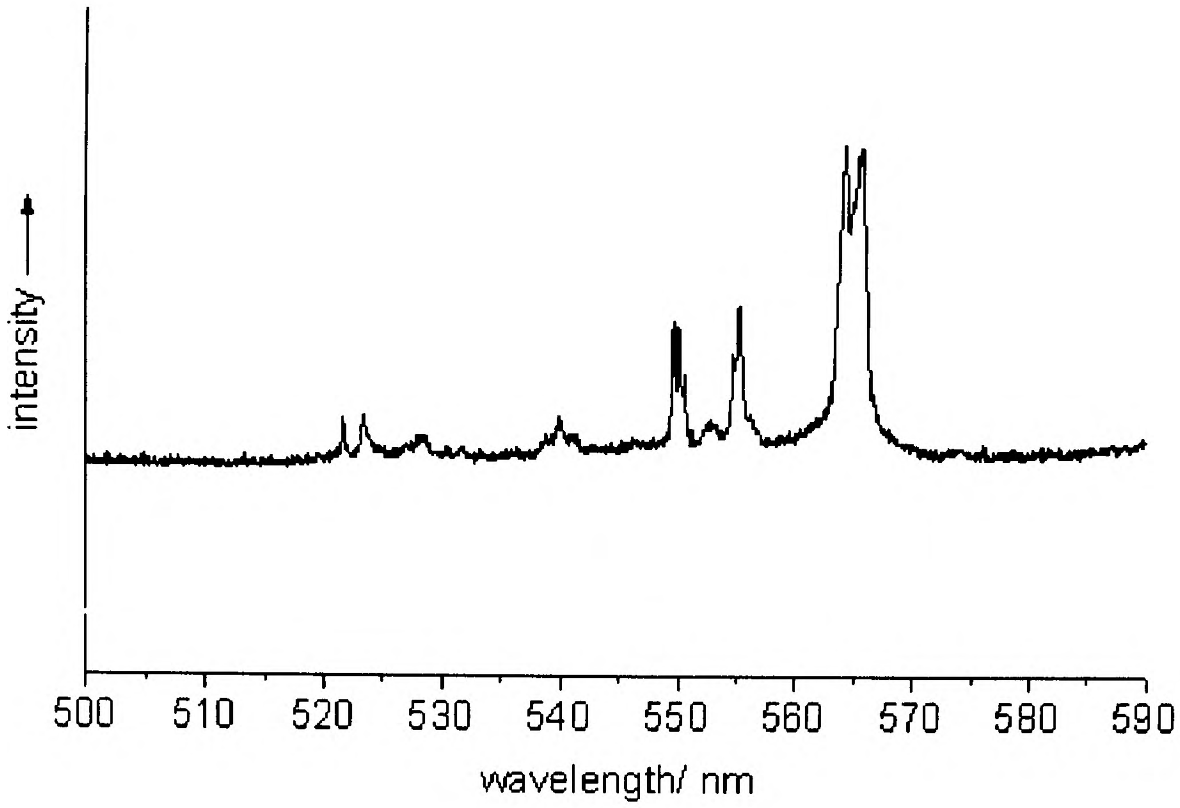


Figure 9.15 Anti-Stokes emission of second glass ceramic containing anatase phase doped with ytterbium and erbium fired at 990°C then annealed at 400°C for 12 hours.

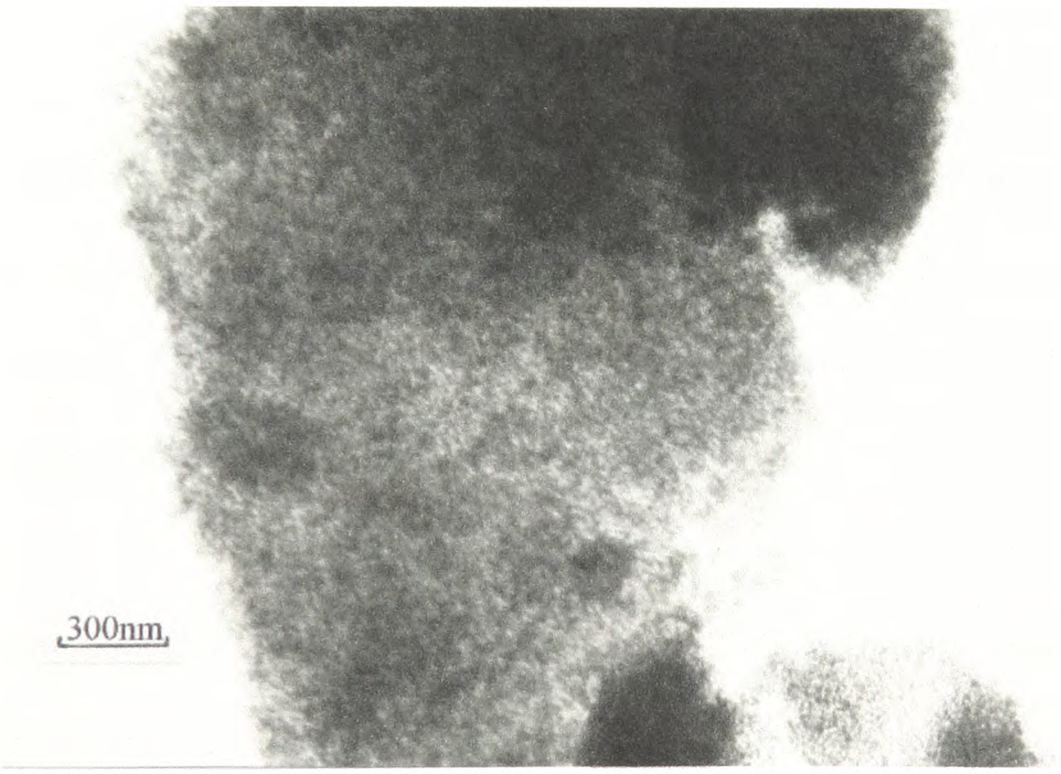


Figure 9.16 TEM (magnification 50000x) of anatase doped with ytterbium and erbium heated to 990°C and not annealed.

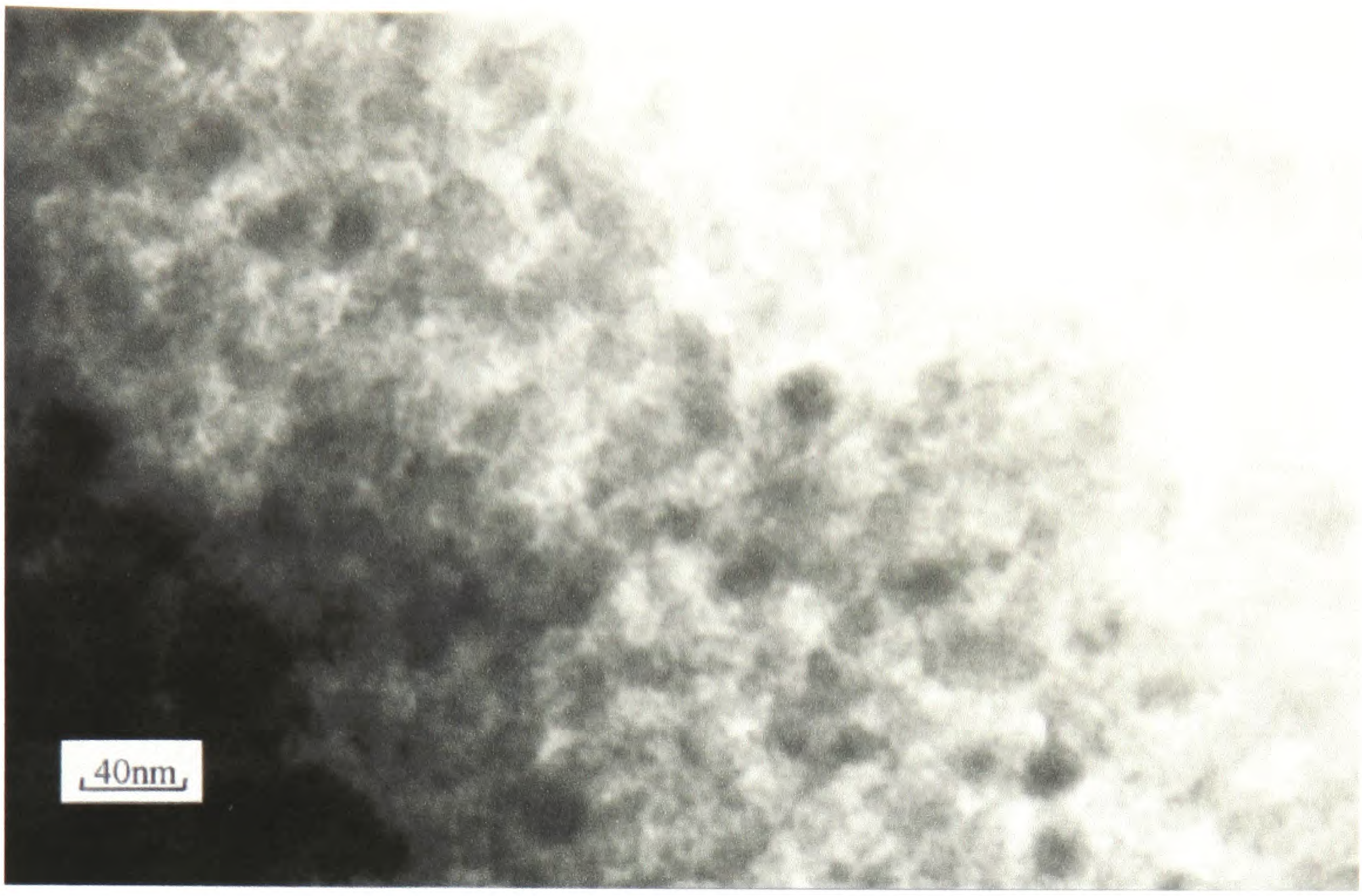


Figure 9.17 TEM (magnification 270000x) of sample in figure 9.16 but annealed at 400°C for 12 hours after firing at 990°C.

X-Ray diffraction analysis of these samples showed that all samples were highly amorphous. Some peaks were observed and are shown in table 9.2. The majority of peaks can be identified with the anatase and rutile phases of titanium dioxide, although there are certain phases in some samples that have not been identified.

A sample containing 0.25% Er, 1.10% Yb, 2%F and 10%Al showed weak green anti-Stokes luminescence centred at 550nm. This emission seems to be quite unstructured compared to that of the titanium containing samples. A second similar sample with 0.5%Er and 4%F was tested and gave a similar emission. This was much weaker than that of the first sample suggesting that there is some concentration quenching occuring. See figure 9.18. These samples were fired at a rate of 2°Cmin^{-1} to 1100°C then annealed at 400°C for 10 hours.

Table 9.2 Principle peaks observed in XRD analysis of glass ceramics containing TiO_2 phases.

Anatase		Rutile	
d	I/I_0	d	I/I_0
3.52	100	3.25	100
2.378	20	2.487	50
1.892	35	1.6874	60
1.6999	20		
1.665	20		

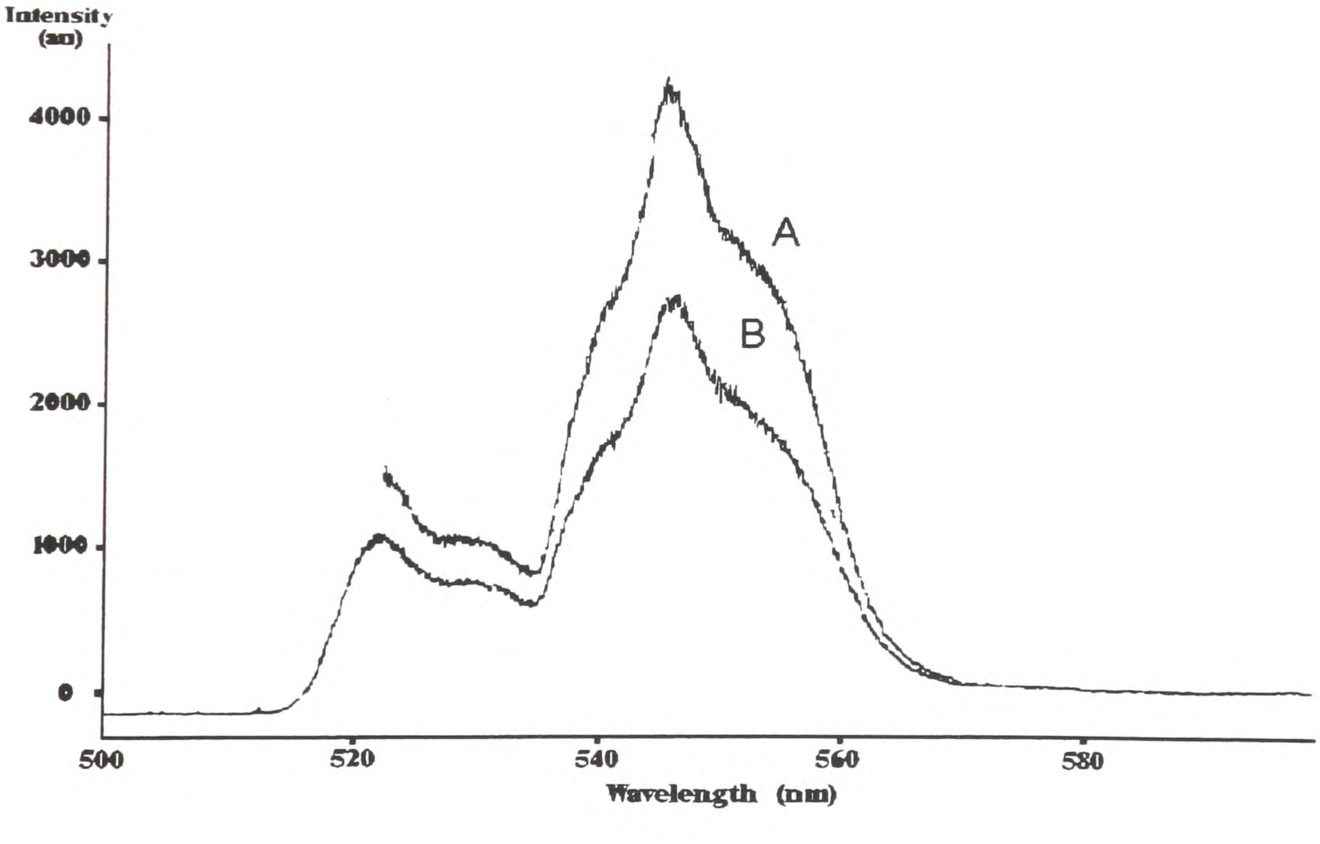


Figure 9.18 Anti-Stokes emission from glass ceramics containing 10mol% aluminium.

Figure 9.18 Anti-Stokes emission from glass ceramic containing 10mol% aluminium.

9.5 Conclusions

Several points can be made from this section of work:

- As we get luminescence from rare earth doped samples which do not have fluoride ions present, this suggests that in the presence of fluoride rare earth ions are entering a crystalline phase within the glass samples and are the sole metal cations present in these phases hence quenching any potential luminescence.
- As we do get luminescence from samples doped containing fluoride and titanium and that the phases containing titanium have been successfully identified as titanium oxide forms, the crystalline phases in these glasses must be TiO_2:Yb, Er.
- The fluorine has either bonded to the rare earth element ions, that are not in the TiO_2 phase, or to the silicon or has been evaporated during the firing process.
- Yb^{3+} and Er^{3+} doped glass-ceramics have been produced which contain anatase which have an anti-Stokes emission in the yellow region of the spectrum. This TiO_2 phase can be converted to another phase, rutile, which has significantly reduced anti-Stokes emission.
- Glass-ceramics can be prepared containing either of the two titania phases, rutile and anatase, or a mixture of both depending on the annealing conditions used.
- As sol-gel techniques are employed to synthesise these glass-ceramics the firing temperatures can be chosen over a wide range, production of these materials and selection of a required titania phase is rendered facile.

References:

1. R. A. Hewes and J. F. Sarver, Phys. Rev. 182 (1969) 427
2. J. L. Somerdijk, J. Lum. 4 (1971) 441
3. S. Bergh and G. Dean, "LED's" 1976, Chapter 4, "Upconverters (Infrared to Visible)", Clarendon Press, Oxford.
4. M. Dejneka, J. Non Cryst. Solids, 239 (1998) 149
5. M. Dejneka, MRS Bull., 23(11) (1998) 57
6. P. A. Tick, N. F. Borelli, L. K. Cornelius and M. A. Newhouse, J. Appl. Phys. 78(11) (1995) 6367
7. Y. Kawamoto, R. Kanno and J. Qui, J. Mat. Sci., 33 (1998) 63
8. S. M. Bayliss, S. Heutz, G. Rumbles and T. S. Jones, Physical Chemistry and Chemical Physics, 1(15) (1999), 3673

Chapter 10 - Conclusions and Further Work

The following conclusions cam be drawn from this piece of work:

- Glasses were synthesised based on a silica matrix containing aluminium, titanium, zirconium and dopant levels of rare earth elements.
- The factors that promote the synthesis of transparent and crystallite-free samples of these glasses have been investigated.
- The fluoridation of these glasses has also been investigated.
- The effect of fluorine on the sol-gel chemistry of silica and the rare earth element ions has also been studied.
- The luminescence of these samples has been analysed.
- In rare earth element doped silica samples, the presence of fluoride causes the rare earth cations to form crystallite phases within the glass matrix - i.e.: glass ceramics.
- These glass ceramics also form in the presence of titanium and produce distinct anti-Stokes emissions depending on the form of titanium dioxide present, which can be influenced depending on the heat treatment of the sample.
- Anti-Stokes emissions have also been detected from aluminium containing glass ceramics.

Following the findings from this work the following recommendations for further work are made:

- The incorporation of other metal cations into these glass ceramics, for example: gallium, indium, niobium and tantalum.
- The incorporation of other rare earth cations that can exhibit anti-Stokes luminescence, for example: thulium, holmium, samarium and praseodymium.
- Methods of forming these crystallite phases within the glass matrix without the use of hydrogen fluoride.