FABRICATION OF LANTHANIDE-DOPED GLASSES AND THEIR POSSIBLE APPLICATION AS UV DETECTORS

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DEDICATION

This thesis is dedicated to Treasa, Colm and Barry for their support and understanding.

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CONTENTS

Abstract

This work describes the preparation of lanthanide-doped glasses and examines the performance potential of these glasses as UV detectors. All presently available UV detection systems are extremely expensive and most are unstable to some degree.

A number of the lanthanides fluoresce within the spectral response region of commercial photomultiplier tubes and glass is a suitable material for use in vacuum systems. Rare earth ions are readily incorporated into a glass matrix and the manufacturing costs of such detectors could be comparatively low.

The lanthanides were prepared in two types of glass matrices i.e. borate and silicate systems.The borate is of interest as the composition used has not been reported in the available literature.The silicate matrix used is a well established commercial composition.

The prepared glasses were characterised using a range of techniques including X-ray diffraction,infrared spectroscopy,absorbance and luminescence measurements.

Measurements on the glasses in the UV region 200-300nm were made using a normal incidence monochromator and a deuterium lamp source. Studies were undertaken of the comparative responses from the doped glasses and other detector systems.In particular, comparison was made with sodium salicylate-a phosphor commonly used in XUV/VUV detection systems- as well as with plastic scintillators.

Glass absorbs strongly in the UV and the possibility of energy transfer from the host glasses to the dopant ions is discussed. The 4f electron behaviour of the lanthanides is cited with the view to explaining the effects observed. Further possible developments of the project are discussed.

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THE GLASSY STATE AND DETECTION SYSTEMS

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THE GLASSY STATE AND DETECTION SYSTEMS

1.1.GLASS AS A MATERIAL

The use of glass as a basic material has been of fundamental importance in the technological development of modern society.The versatile nature of its properties (e.g.transparency,malleability) together with its relatively low production costs allow an extremely wide range of applications.It is a familiar material present in almost every building,transport vechicle and a wide range of domestic appliances such as the electric light bulb.Glass with its ability to form a vacuum-tight envelope has played an important role in technological developments such as the cathode-ray tube and the valve.When ground and polished to form a lens it is the key component of the telescope,microscope and camera,although plastic lenses are now available.

In recent years glass has been applied,mainly in the form of optical fibre in the crucially important and developing area of optoelectronics.This technology combines the information carrying capacity of light with the transmission capability of optical fibre.The

applications are enormous in the area of optical telecommunications,medical diagnostics,optical interconnects in electronic integrated circuits and semiconductor lasers.

1.1.1.Historical Perspective

Although a key material in modern society, glass was first invented or discovered in the Bronze Age during the period 5000-4000 B.C.The first glass objects to be made were opaque beads of various colours.[1.1]. These ancient glasses were produced, as is most common glass today,using sand and an alkaline fluxing agent such as potash or soda ash.Sand(silica) has a high melting point(> 1700°C) but the addition of a fluxing material reduces the liquidus temperature to a level obtainable in a wood burning arrangement.In ancient times the soda was obtained from natural deposits[1.2] (natron lakes in the western desert of Egypt)and potash was produced from the ashes of burnt wood.The molten glass was formed by firing these materials to a high temperature in a furnace.The oldest pot furnace dates from the 14th century B.C.[1.2].The first known recipes for making glass date from the 7th century B.C.and these are preserved on hieroglyphic tablets[1.2].The Romans used a multi-chamber furnace in which the glass was also

cooled.

Just before the Christian period[1.1] a turning point came with the invention of the glassmakers' blowpipe.This revolutionised glass production in that hollow ware could be manufactured.In combination with moulding techniques the blowpipe allowed the production of vessels of almost every conceivable shape and size.By the 3rd century A.D.domestic glass objects such as plates,bowls,beakers and bottles were produced in the Roman world in a profusion not to be equalled until the 15th century[1.2].Many of these pieces survive in museums today.

Exquisite glass pieces were produced in Venice during the 15th and 16th centuries.In England lead crystal was introduced by Ravenscroft about 1676 and this composition is the basis of lead crystal production today.Considerable automation was introduced into container glass production in this century. However,traditional techniques such as the use of the blowpipe,moulding and 'marvering'are still used in Ireland today in the production of the world renowned Waterford lead crystal.

Whilst glass as a material has been known for at least 6000 years its structure is not fully understood and the very definition as to what constitutes a glass is a matter of controversy.

1.2. DEFINITION OF GLASS

The precise definition as to what constitutes a glass has long been a contentious issue among glass technologists.The much quoted definition of glass as a supercooled liquid is unsatisfactory.However, this description does recognise that the arrangement of atoms or molecules in a glass matrix possess a permanence similar to that in a crystalline solid and a randomness similar to that characteristic of liquids. The American Society for Testing Materials[A.S.T.M.] in 1945 proposed the following definition:
"Glass is an inorganic product of fusion which has cooled to a rigid condition without crystallising"
This definition is satisfactory for the more familiar glasses,however,it does not cover non-crystalline solids prepared by deposition from the vapour phase,or by sputtering in a low pressure system.These have the chemical composition and apparently identical properties to glasses produced in the conventional manner i.e. from a melt.The definition does not include glasses produced from organic materials e.g.glycerol.

To overcome these difficulties the U.S.National Research Council proposed the more general definition:
"Glass is an x-ray amorphous material which exhibits the

glass transformation this being defined as that phenomenon in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties,such as heat capacity and expansion coefficient,from crystal-like to liquid-like values.

Pye[1.3] et al suggests as a working definition the following: "Glass is a transparent or opaque solid composed of a single or multiple non-crystalline phase(s)"

The volume-temperature diagram [after Rawson(1.4)] is useful in elucidating the formation of a glass(Fig.1.1)

If the melt crystallizes on cooling,this is usually accompanied by a marked increase in density at the melting point T_f .No such change occurs if the melt supercools.The volume decreases along the line b—e.At temperatures near T_f structural changes occur very rapidly with increase in viscosity of the melt.Beyond this point as the viscosity increases with falling temperature,structural changes occur increasingly slowly until eventually the viscosity becomes so high that no further such changes become possible.A decrease in slope is then found in the volume-temperature curve (point e).This is known as the transformation temperature or the glass transition temperature Tg.Only

below Tg is it correct to describe the material as a glass.

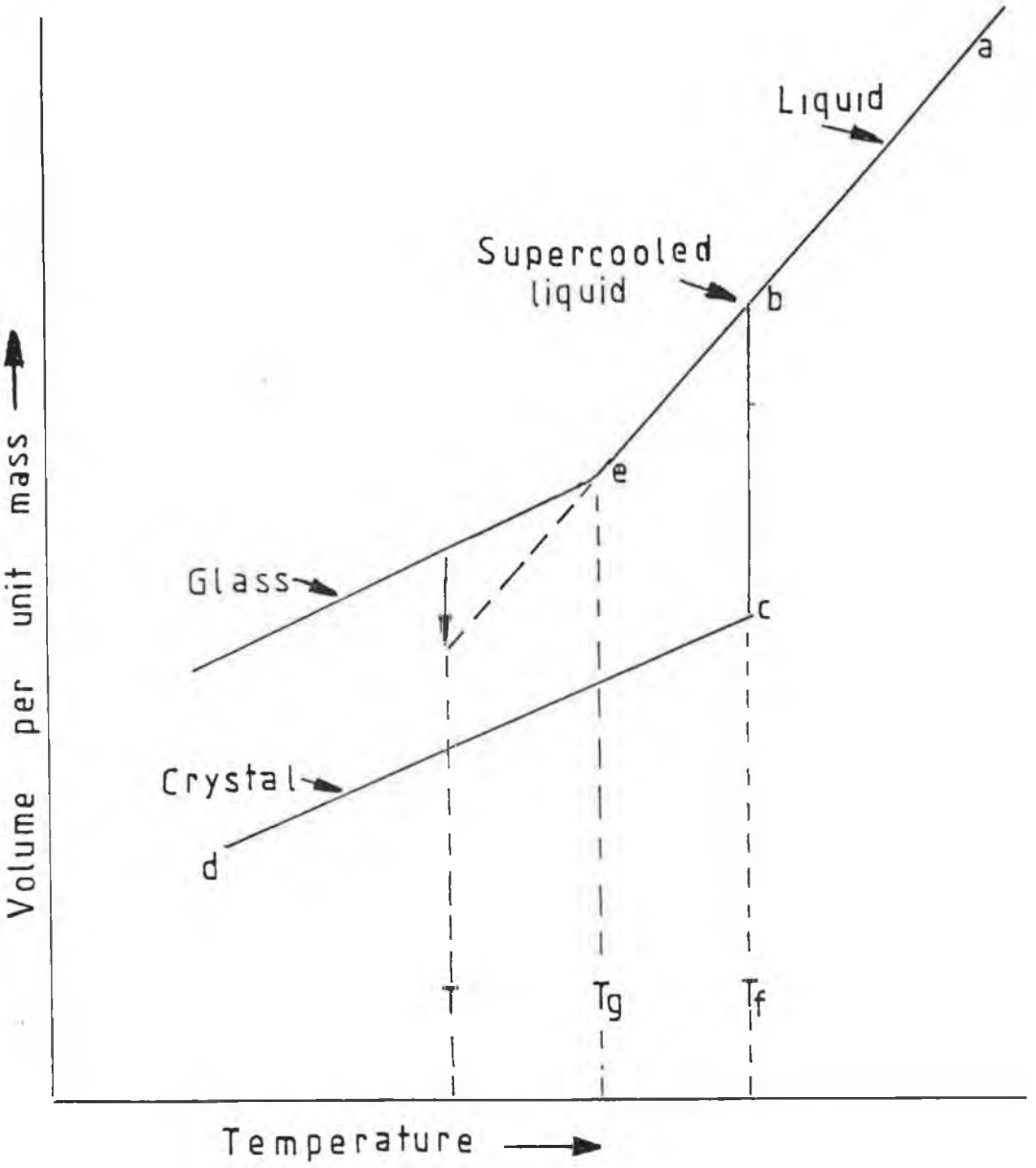


FIG.1.1 Relationship between the glassy, liquid and solid states.(Rawson, 1980)

1.3. Glass structure - General theory

Glass technologists tend to divide glass making materials into three classes based on the function of the component in the glass structure.These are:-

(a) Network Formers (NWF)

(b) Network Modifiers (NWM)

(c) Intermediates (I)

Examples of NWF - SiO_2, B_2O_3, P_2O_5, GeO_2.

Examples of NWM - Na_2O, Li_2O, CaO.

Examples of I - Al_2O_3, TiO_2, PbO.

Kuan-Han Sun and Huggins[1.5] calculated for the first time, the heat of dissociation of various oxides or oxide components in crystals and glasses.These were determined by the authors from lattice energy data. The bond strengths for the various M-O single bonds were calculated by using the co-ordination numbers,known or assumed for the elements in oxide or oxide

components.Sun[1.5]calculated the M-O single-bond linkages in all common glasses.The bond strengths of all the glass formers were found to be greater than 80 kilocalories per Avogadro bond,that of intermediates between 60-80 kilocalories and modifiers were found to have values below 60 kilocalories.The values obtained by Sun are listed in Table 1.1 for the oxides of interest.

Table 1.1 - Bond Strengths

Element	Valence	Dissociation Energy (kilocals.)	Co-ordination No.	Single Bond Strength (kilocals.)
Si(nwf)	4	424	4	106
B(nwf)	3	356	3	119
Al(i)	3	317-402	6	53-67
Na(nwm)	1	120	6	20
Li(nwm)	1	144	4	36
Ca(nwm)	2	257	8	32

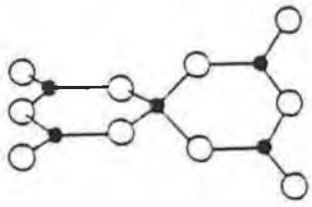
The position of Al_2O_3 as an intermediate is somewhat anomalous.It is known that Al^{3+} ions can replace Si^{4+} in the structure of crystalline silicates[1.4],thus forming AlO_4 tetrahedra.This however,can only occur if other positively charged ions are introduced at the same time e.g. Na^+ to balance the charges.It is expected that the compound $Na_2O.Al_2O_3.6SiO_2$ which forms a glass would have a structure similar to that of silica glass itself;all of the aluminium ions being incorporated in the tetrahedral position and an equal number of sodium ions being present in the voids -probably in the neighbourhood of the AlO_4 tetrahedra.The presence of non-bridging oxygens is not essential with this particular structure.However,it is also known that in crystalline silicates the aluminium ion may be surrounded octahedrally by oxygen ions in which case it is not replacing silicon ions in the network.This is likely to occur if insufficient numbers of sodium ions are introduced into the structure to obtain a balance of charges.

1.3.1 STRUCTURAL THEORY OF BORATE GLASSES

The theory of borate glass structure due to Jan Krogh-Moe is by now widely,if not universally accepted.Krogh-Moe has postulated that borate glasses are not merely a random network of BO_3 triangles and

(a)

The boroxol group

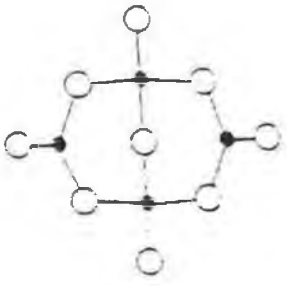


(b)

The penraborate group

(c)

The triborate group



(d)

The diborate group

FIG.1.2 Structural borate groups(Pye et al., 1978)

BO_4 tetrahedra joined at the corners but instead they actually contain well-defined and stable borate groups as segments of the disordered framework.[1.6] Those borate groups which are included in the glass structure should be identical with groupings which occur in crystalline borates of compositions similar to those of the glasses.However,due to possible thermodynamic or kinetic considerations not all polyborate anions existing in the crystalline materials need be found in the glasses.Perhaps the most general statement of Krogh-Moe's theory is that borate glass will contain significant numbers of at least some of the polyborate groupings which occur in related crystalline materials.

In the case of alkali borate glass which is of particular interest in this work,Krogh-Moe has postulated that only four different kinds of structural groupings exist in the composition interval up to 34 mol% alkali oxide.These are boroxal,pentaborate, triborate,and diborate groups and are illustrated in Fig.1.2. Krogh-Moe used thermodynamic(1.7) and infra-red(1.8) studies to support his theory.

The more specific theory of Krogh-Moe asserts that pentaborate and triborate groups always occur in pairs,such pentaborate-triborate pairs are collectively referred to as 'tetra-borate groups' even though they

might not always be connected. The relative numbers of these groups as a function of glass composition is not quantitatively predicted by Krogh-Moe's theory. Indeed the probable existence of a few 'loose' BO_3 and BO_4 configurations in the alkali borate glasses can be anticipated on the basis of an X-ray determination of their presence in the compound $K_2O_3.8B_2O_3$ [1.9].

1.3.2 Metaborate and tetraborate groups

Krogh-Moe has emphasized in a number of papers [1.10, 1.11, 1.12] that the co-ordination requirements of modifier cations such as Li^+ are fairly strict. These are outlined as follows:-

(1) These ions must always be located in the neighbourhood of those borate groups with an excess negative charge.

(2) The ions will tend to attract and share other such negatively charged groups in order to screen themselves more effectively. [1.13].

Krogh-Moe has also stated [1.14] that the cation co-ordination sphere is to a considerable extent governed by the requirements of the borate polymer

network and not only by the cation itself. Thus the foreign modifier cations may demand and achieve a certain co-ordination sphere subject only to the constraints of what negatively charged polyborate structural groupings are available in the melt.Below 20mol% alkali oxide,the tetraborate group is the most prevalent polyborate anion[1.14]. Krogh-Moe has also cited several pieces of evidence for a partial dissociation of tetraborate groups into diborate groups together with boroxol groups.[1.15].

1.3.3 THE STRUCTURE OF SILICATE GLASSES

The structure of silicate glasses is an area of enormous complexity and still the subject of debate among glass technologists.Prior to the early 1930's glass structure was considered in terms of the physical chemistry of aqueous solutions.Grebenshchikov and Favorskaya[1.16]in 1931 had produced evidence to support the hypothesis that silicate glasses represent a rigid silica sponge saturated with silicates.This hypothesis first touched on the problem of the chemical inhomogeneous structure of complex glasses and upon the possibility of distinguishing between separate chemical compounds contained within them.

In 1932 Zachariasen[1.17] published his classical paper in which he suggested the hypothesis of glass structure as being a random space ionic network.This approach has ever since influenced thinking about the structure of silicate glasses.However,it should be pointed out that Zachariasen's paper was essentially speculative in nature and was as much concerned with proposing a set of structural rules for glass formation in inorganic systems as with discussing glass structure.

Zachariasen put forward the following rules for spatial arrangement of the $(SiO_4)^{2-}$- tetrahedra:-

(1) An oxygen atom must not be linked to more than two metal atoms.

(2) The number of oxygen atoms surrounding the cation must be small (four in the case of SiO_4).

(3) The tetrahedra (or polyhedra) must share corners only and not edges or faces.

Silica glass represents the simplest case as only the SiO_4 tetrahedra form its network.(Figs.1.3 & 1.4)

In a series of papers published in the 1930's and 1940's, Warren and his colleagues confirmed Zachariasen's model by X-ray Diffraction studies of a number of oxide glasses of simple composition. More recently Warren and Mozzi(1.18) in 1969 examined the structure of silicate glasses using improved

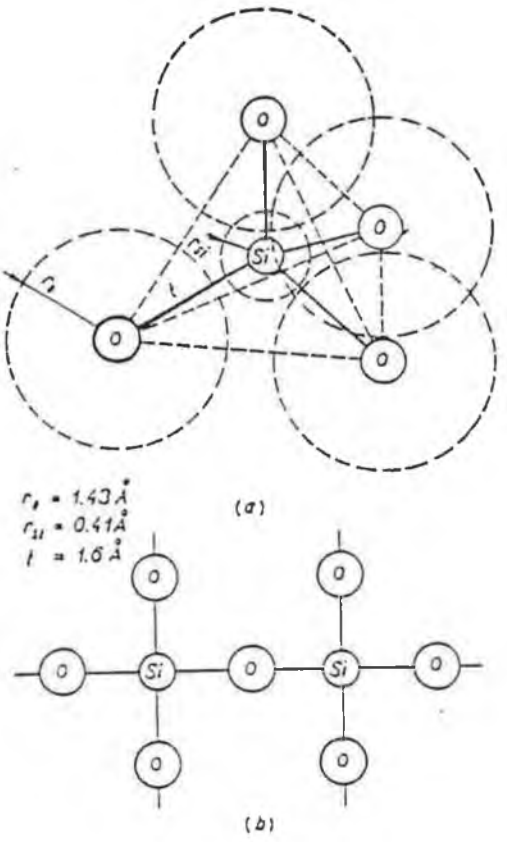


Fig.1.3 The $(SiO_4)^{2-}$ tetrahedron and its two dimensional representation.(Rawson, 1980)

techniques. The more recent work led to slightly different conclusions but the differences with the earlier work were not significant.

A feature of the glass state considered by Zachariasen is that since the polyhedra are joined only at their corners,the structures are relatively open containing large voids. Warren's X-ray studies indicated where the sodium ions in a Na_2O-SiO_2 glass are situated and this is illustrated in Fig.1.4.The Na^+ions are situated in the voids which are several Angstroms in diameter within the network formed by the SiO_4 tetrahedra. The oxygen ions introduced together with the sodium ions in the form of Na_2O are incorporated by the rupture of some of the Si-O-Si linkages present in the silicate glass.Each two Na^+ ions added to the glass result in a break in one bond between two tetrahedra.The bridging oxygen is replaced by two non-bridging oxygens bonded to the sodium ion.The extra negative charge is compensated for by the positive charges of the alkali ion.These arrangements are illustrated in Fig.1.5.The effect of the bond breakage is to loosen the structure resulting in a lower density and weakening of the bond strength leading to a lowering of the fusion temperature.

If the molecular ratio of Na_2O and SiO_2 is

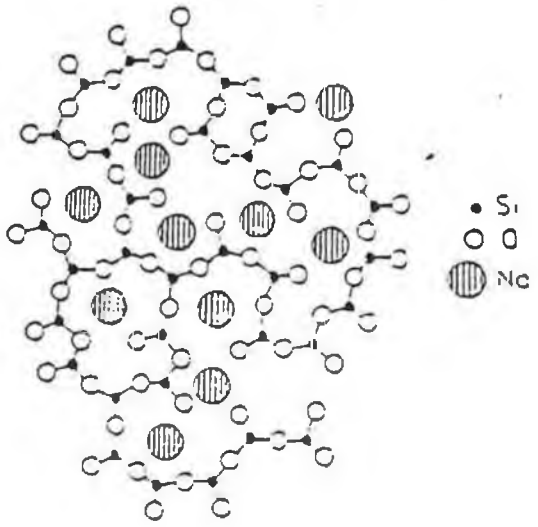


Fig.1.4. Structure of Na_2O-SiO_2 glass

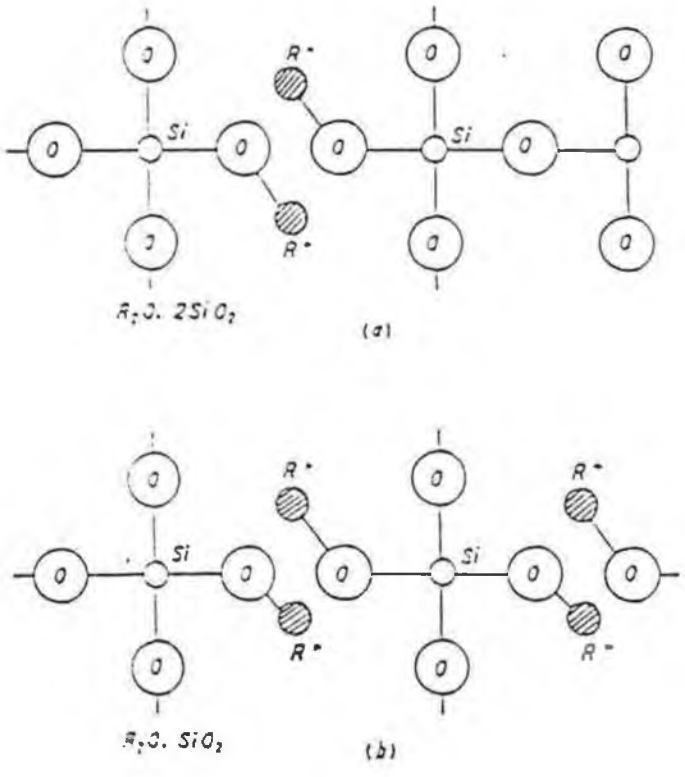


Fig.1.5. Two-dimensional representation of silicate glasses, showing the non-bridging oxygen ions connected to alkali ions R^+.

1:2(disilicate composition) the average number of bridging oxygens in each tetrahedron is three.These tetrahedra are still capable of forming a three dimensional network and many glasses exist with the disilicate composition.If further quantities of Na_2O are added eventually the metasilicate composition $Na_2O.SiO_2$ is achieved as illustrated in Fig.1.5. In this case there are only two bridging oxygens in each tetrahedron.This leads to the formation of infinite chains or ring structures. The Na-O bonds are largely ionic in character and much weaker than the Si-O bonds which have a strongly covalent character and hence are more directional.It is believed that most of the oxides of Group 1&2 elements enter the glass structure in a manner similar to Na_2O.

1.3.4 Lanthanides in glass

The incorporation of lanthanides into a glass structure would require the simultaneous creation of three extra negative charges in most cases. Three non-bridging oxygens would be expected to neutralise every two Ln ions. In order to reduce the electrostatic energy to a minimum,it would be expected that the non-bridging oxygens should be located as near as possible to the Ln ion.

1.4 Present systems and lanthanide-doped glasses as a UV/VUV detection system

1.4.1 Ultraviolet radiation

Ultraviolet radiation is grouped according to wavelength into two major divisions- the ultraviolet(UV) and vacuum ultraviolet(VUV).Whilst there is no absolute boundary between the regions these are generally divided[1.19] as follows:-

Ultraviolet(UV)	---	400-200nm
Vacuum ultraviolet(VUV)	---	200-0.2nm

The ultraviolet is further subdivided into the near UV (400-300nm) and the middle UV (300-200nm).
The vacuum ultraviolet region covers a very large energy range - 6 eV to 6keV; however,it can be conveniently subdivided depending upon the optical instrument employed[1.19].V.Schumann built the first vacuum spectrograph and made the first investigation of VUV radiation.The region from 200 to 125nm is now known as the Schumann region.
The shorter wavelength section of the VUV overlaps the soft X-ray region(<30nm) of the electromagnetic spectrum.The difference between the two regions is that UV or optical radiation corresponds to energy changes of the outer electrons of an atom or ion,whereas

X-radiation corresponds to energy changes of the inner electrons.

The UV subdivisions are charted in Fig.1.6 but the limits shown should not be regarded as definite boundaries.

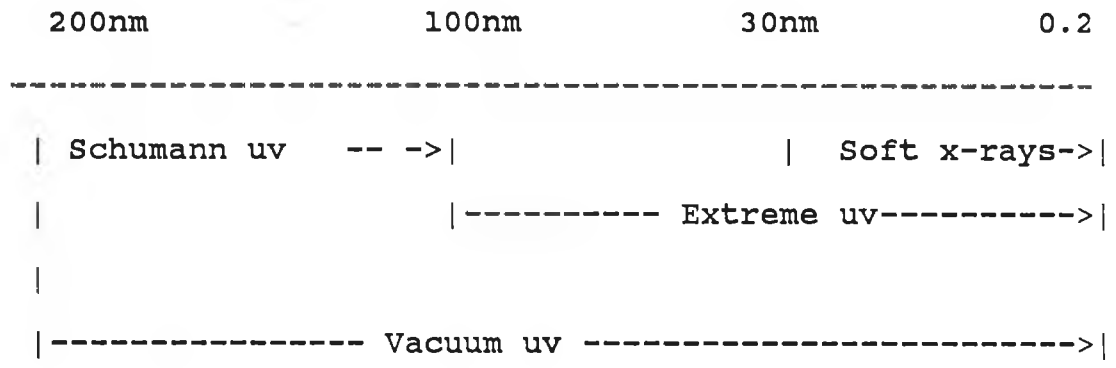


Fig.1.6 Wavelength range/nomenclature of vacuum ultraviolet

1.4.2 Detection Systems

The underlying principle of all detectors is the interaction between radiation and matter. In the case of detection of UV/XUV radiation,various techniques are available which involve the use of sensitized photographic plates,photoionization of gases, fluorescence methods, photoelectric effect,chemical

changes,photoconductivity, and thermal effects.All of these methods have advantages and disadvantages.One of the most commonly employed methods is to use fluorescent effects which converts the radiation to the longer-wavelength response region of a photomultiplier tube.At present,most spectral investigations in the XUV and VUV regions are performed photographically. In the 4-20nm region the photographic plates used for fast recording (Kodak 101-01) are extremely expensive.Most research groups use the less expensive (and slower) Kodak SWR plates but these suffer the disadvantage that they have reduced contrast and consequently are poor for recording weak features.

In recent years investigations in the XUV/VUV region have been made using photomultiplier tubes or linear diode arrays(LDA).In both cases an intermediate luminescent material must be used because XUV radiation will not penetrate through to the photocathode of a photomultiplier tube or will cause rapid degradation of the quantum efficiency of the silicon diodes in an LDA,so that response can vary quite dramatically between successive exposures and eventually (after less than six months) the device becomes useless.

The fluorescence method involves applying a phosphor coating to the front window of a photomultiplier tube or alternatively using a glass slide with a

phosphoresent coating placed in such a position that the radiation falls on the luminescent material before entering the tube.The phosphor absorbs the radiation and then luminesces within the spectral response region of the tube and is detected in terms of the current/voltage output from the photomultiplier system.

The most commonly used coating material is sodium salicylate [HOC_2H_4COONa].This is a white lustrous solid soluble in water,alcohol or glycerol. In the wavelength region 60-300nm sodium salicylate has the property that its fluorescent quantum yield is almost independent of wavelength. [1.20,1.21]. It has a high quantum efficiency and its fluorescence occurs in a wavelength region centred at 443nm which matches the wavelengths of maximum sensitivity of a large number of photomultiplier tubes.

The main disadvantages in using sodium salicylate are that it requires preparation each time it is used and its response depends on the thickness of the coating applied. It is also easily rubbed off(or may fall off) a glass slide or the photomultiplier envelope and more seriously tends to deteriorate in performance particularly when subjected to UV radiation for any length of time.

Thin plastic scintillators are commercially available

and are used in detecting UV/XUV radiation but these do not have the wide wavelength detection range of sodium salicylate and are easily damaged.If a luminescent glass could be produced which gave the performance of sodium salicylate then this would be a much more satisfactory arrangement than the present system and would be of commercial interest. Glass scintillators are presently being manufactured by Nuclear Enterprises Ltd.[1.22] in Scotland but these are used only in the detection ofneutrons, beta particles and in the area of neutron radiography. It is well established that many of the lanthanide ions fluoresce when subjected to a wide range of radiation. Lanthanide atoms exhibit an intense 4d -4f resonance,typically 1-2 nm in width in their photoabsorption spectrum the peak of which occurs at about 10 nm in Lanthanum and then shifts to shorter wavelengths with increasing atomic number. The peak cross-section at resonance is typically 30 Mbn [1.23]. Due to its large width this feature must decay very rapidly ($\Delta t \sim 10^{-16}$s) by autoionisation into the continuum while the core 4d hole decays by Auger emission leading to the formation of doubly or triply ionised lanthanide atoms [1.24].The filling of these vacancies in 5s, 5p shells should lead to considerable cascading and

ultimately to visible luminescence.Due to the enormous cross-section,photons with energies sufficient for 4d-4f excitation should be absorbed within about 20 nm of the surface by a lanthanide ion. This should lead to the emission of one or more less energetic electrons which will interact with the host material and lose their energy rapidly since range is almost proportional to energy.This should ideally trigger some radiative processes in the glass matrix itself,though there will also be competition from non-radiative processes. Glass itself is well known as a UV absorbent material and an energy transfer mechanism might exist whereby the UV radiation could be transferred to the lanthanide ion - the glass acting as 'sensitizer' and the lanthanide as 'activator'.Some rare-earth ions such as Cerium and Terbium are known to luminesce within the response region of commercial photomultiplier tubes.Such a system would be more robust and chemically resistant than those presently in use.More reliable UV-detecting photomultipliers are required to operate in hostile environments e.g.in the presence of organic reagents and in space projects.The high softening point of glass together with its physical characteristics and chemical resistance would permit its use under extreme environmental conditions where other scintillating materials could not be used.

Thorn EMI produce a photomultiplier tube [1.25] with a quartz window capable of detecting UV radiation in the range 175-350nm. Magnesium fluoride windows are also used in special UV and solar blind photomultipliers to detect VUV radiation extending to 110nm.All of these systems are extremely expensive. However,glass detectors would have comparatively low fabrication costs and are also capable of being cast into almost any shape or size.

Borosilicate glass is already being used to form the envelope for commercial photomultiplier tubes used in detecting radiation at wavelengths greater than 350nm.If a lanthanide could be incorporated into this glass which extended the detection range of the normal photomultiplier tube this would significantly reduce the cost of manufacturing special UV detector tubes with expensive window materials such as Magnesium or Lithium fluoride.These materials also tend to be hygroscopic and deteriorate in hostile environments.Alternatively,the glasses could be produced as an end window to suit any size of photomultiplier tube and it is envisaged that these could be placed over the front window of the tube in much the same manner as a filter is fitted to a camera lens. Another possibility would be to use the lanthanide-doped glass as a coating over a LDA array.

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Chapter 2

FABRICATION OF GLASSES

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FABRICATION OF GLASSES

2.1 Introduction

An expertise in glass fabrication was established in the School of Physical Sciences at Dublin City University(formerly NIHE,Dublin) in the early 1980's.This work was carried out under the direction of Dr.A.R.Spowart and the main focus of interest was in developing neutron scintillating glasses doped with Cerium(Ce) and Terbium(Tb).These materials also contained enriched Lithium $^{6}_{3}Li$ used as a neutron detector through the $^{6}Li(n,\alpha)$ reaction.The optimum form of Cerium-doped lithium aluminosilicate glass as a scintillator was also studied.The work described here developed from this earlier experimental work.

2.2.Equipment

The glass making equipment available was an electrically heated Stanton Redcroft vertical tube furnace (max.temp 1600°C)together with alumina crucibles.Other ancillary equipment included a refractory tripod and alumina collars for use with the furnace.An annealing muffle furnace (max.temp.1000°C) was also available.A feature of this furnace was a

controlled fan system to enable the chamber to be cooled at a pre-determined rate.A "Pyreco" furnace (max.temp.1550°C) was also available.This furnace was electrically heated with elements of silicon carbide located in the roof of the furnace chamber.

2.3 Experimental Procedure

2.3.1 Preparation of glasses

The first attempt to fabricate a glass was made using the vertical tube furnace.The composition of the batch was as shown in Table 2.1 and the furnace temperature was set to 1450°C.The batch was mixed manually using a spatula.

Table 2.1 Initial glass composition

	Percentage (by mass)
Silica (SiO_2)	55.0
Magnesia (MgO)	25.0
Alumina (Al_2O_3)	12.0
Lithia (Li_2O)	5.5
Neodymium(Nd_2O_3)	2.5

All of the batch materials were of analytical grade and the silica was in the form of fumed silica.The low bulk density of this type of silica made mixing of the batch extremely difficult.

A portion of the batch was placed in a flat-bottomed alumina crucible which was then raised on a refractory tripod into the centre of the furnace.The large bulk of batch materials necessitated repeated filling of the crucible,followed by a heating cycle,until all of the batch was loaded.The most serious problem experienced was the fracture of the alumina crucible and subsequent loss of material.This may in part be due to thermal shock which occurred due to the heating and cooling of the crucible during batch loading.This method of preparation was abandoned due to the many operational difficulties experienced.

2.3.2.Melting and casting operation

The batch composition was changed by introducing the glass former "Spectroflux" into the batch.This material consists of a eutectic mixture of 80% lithium metaborate and 20% dilithium tetraborate which have the important properties of low melting point(840°C) and low viscosity and is manufactured by Johnson Matthey Ltd.

The first melt attempted had the composition given in Table 2.2

Table 2.2 Trial Composition	Percentage (by mass)
Silica(SiO_2)	36.6
Alumina(Al_2O_3)	12.2
Spectroflux	50.1
Praseodymium(Pr_2O_3)	1.0

The silica and alumina were of analytical grade and ground to pass a 100 micron screen.Mixing of the batch ingredients was carried out using a Glen Creston shaker which was found to give an intimate mix of the batch materials superior to hand mixing.

2.3.2.1 Initial Trials

The batch was placed in a platinum crucible and heated to 1200°C for a period of 60 minutes.However when removed it was extremely difficult to pour due to the high viscosity of the melt.Further quantities of Spectroflux were added and the temperature raised to 1300°C.Using this composition it was possible to pour

the molten mix without difficulty.However the glass cracked on cooling and it was returned to the furnace in the platinum crucible.This was found to introduce gas inclusions("seed") into the glass.Eventually,after heating for a further 30 minutes a glass disc was formed by pouring into a platinum/gold casting dish.The glass had the expected green colour due to the presence of Praseodymium and appeared to be of reasonable optical purity.Pre-heating of the platinum/gold mould was found to prevent the rapid cooling of the glass on pouring.This allowed the glass to flow and to fill the mould before reaching its glass transition temperature.

Using the new composition together with these improved techniques proved to be a much more manageable method of fabricating the lanthanide-doped glass samples.

2.3.2.2 Furnace

The furnace used was the chamber"box" furnace manufactured by Pyreco Ltd.The elements were of silicon carbide and these were located in the roof of the furnace chamber.The position of the elements may have tended to produce a temperature gradient within the chamber.However,this possibly assisted in creating convection currents within the glass and assisted in

achieving homogeneity of the batch during the melting operation.Many commercial glass melting furnaces use oil or gas in a similar top firing arrangement.
The box furnace was extremely convenient in the placing and removal of crucibles.However,the heat blast on opening the door of the furnace made it uncomfortable to work in the vicinity and the door was opened only for the shortest possible time.It was necessary to use protective goggles,visor and asbestos-type gloves when working within the furnace blast.A platinum-tipped tongs was also necessary to transport the crucibles in and out of the furnace and also to prevent contamination of the melt from the iron tongs.

2.3.2.3 Platinum Crucible

Platinium due to its high melting point(1769°C) and extremely good resistance to chemical attack is ideal in crucible form as a glass containing material.Other important properties of platinium include a high thermionic work function and a coefficient of thermal expansion (9.1×10^{-6} per °C)[2.1] matching that of silicate glass.Molten glass is a very aggressive material and the earlier problems using alumina crucibles was possibly due to attack on the crucibles in addition to thermal shock.The main disadvantages in using platinum crucibles are that they are extremely

expensive and easily damaged during handling.

2.3.3 Standardisation of glass preparation

After a number of trials and compositional changes the preparation procedure was standardised.The final composition of the borate glasses was as outlined in Table 2.2.It was possible to produce doped glass samples using Spectroflux and the lanthanides only.However,these tended to be extremely hygroscopic as would be expected with such a high alkali borate level.The addition of both silica and alumina was found to improve the resistance to ambient humidity when the glasses when exposed to normal atmospheric conditions.The final standardised composition may not be the optimum composition in terms of long term stability of the glasses.

Table 2.3 Standardised Glass Composition

Batch composition	Percentage (by mass)
Spectroflux	73-83 approx.
Silica(SiO_2)	8.3
Alumina(Al_2O_3)	8.3
Lanthanide	0.1-10

The standardised composition expressed as oxides for 0.1% lanthanide is as follows:-

Lithia(Li_2O)	22.9
Boric Oxide(B_2O_3)	60.4
Silica(SiO_2)	8.3
Alumina(Al_2O_3)	8.3
Lanthanide	0.1

A typical batch had a mass of 9.5g

2.3.3.1. Batch mixing

The batch materials were placed in a plastic vial and three silica glass beads added .The vial was then sealed with a plastic cap and tape.The mixing operation was carried out by placing the vial in a Glen Creston shaker for 10 minutes.After mixing was complete the glass beads were removed from the powder using a spatula.The glass beads were found to help in the homogenisation of the batch.

2.3.3.2. Melting

The homogenised powder was then transferred to a platinum crucible which was then placed in a furnace

previously heated to 1200°C. If the batch is heated from room temperature gas inclusions or 'seed' were found to be present in the finished glass.
After 10 minutes in the furnace the crucible was removed and swirled to assist in homogenisation of the molten glass.

2.3.3.3. Casting

A platinum/gold casting dish containing a 42 mm diameter mould was pre-heated in the furnace,then removed and placed on a flat refractory surface.Using a platinum-tipped tongs the crucible containing the batch was removed from the furnace and poured into the mould as quickly as possible. When the mould and glass bead had cooled to below red heat the mould was placed over a jet of air produced by a small air pump.This sudden cooling assisted in the release of the glass from the casting dish.The mould was then inverted over an asbestos-type glove and the underside tapped with the platinum-tipped tongs.Normally the glass disc was released and then allowed to cool on the glove or returned tc the casting dish.A more satisfactory arrangement would be to use two platinum dishes,if available,and to pass the glass piece from the mould to a second platinum dish to cool.

2.3.3.4 Annealing

The glass samples were annealed to release stress in the glass, by placing the pieces in a furnace at 700°C on a platinum dish and allowing them to cool to room temperature over a 24-hour period.

2.3.3.5 Preparation of lanthanides in a borate matrix

Using the standard procedure outlined in this section lanthanide-doped borate glasses were prepared and details of these are given in Table 2.4.

Table 2.4 Lanthanide-doped glasses --borate matrix

Lanthanide	Percentage	Oxidation State	Comment
Cerium(Ce)	1.0	4	As CeO_2
	5.0	4	As CeO_2
	10.0	4	As CeO_2
Cerium(Ce)	1.0	4	Addition of 1%$SnCl_2.2H_2O$*
	1.0	4	Addition of 2%$SnCl_2.2H_2O$*
	5.0	4	Addition of10%$SnCl_2.2H_2O$*
Cerium(Ce)	5.0	3	As $CeCl_3.7H_2O$

Table 2.4(cont.)

Praseodymium(Pr)	0.7	3	As Pr_2O_3
	1.0	3	As Pr_2O_3
	2.5	3	Co-doped with 2.5%Nd_2O_3
	10.0	3	As Pr_2O_3
Neodymium(Nd)	2.5	3	Co-doped with 2.5%Pr_2O_3
	5.0	3	As Nd_2O_3
Samarium(Sm)	0.5	3	As Sm_2O_3
	5.0	3	As Sm_2O_3
Europium(Eu)	0.5	3	As Eu_2O_3
	5.0	3	As Eu_2O_3
Gadolinium(Gd)	0.5	3	As Gd_2O_3
	5.0	3	As Gd_2O_3
Terbium(Tb)	0.5	3/4	As Tb_2O_3/Tb_2O_4
	5.0	3/4	As Tb_2O_3/Tb_2O_4
Dyprosium(Dy)	0.5	3	As Dy_2O_3
	5.0	3	As Dy_2O_3
Holium(Ho)	0.5	3	As Ho_2O_3
	5.0	3	As Ho_2O_3

Table 2.4(cont.)

Erbium(Er)	0.5	3	As Er_2O_3
	5.0	3	As Er_2O_3
Thulium(Tm)	0.5	3	As Tm_2O_3
	5.0	3	As Tm_2O_3
Ytterbium(Yb)	0.5	3	As Yb_2O_3
	5.0	3	As Yb_2O_3

*Stannous Chloride($SnCl_2.2H_2O$) was added to the Cerium batch in an attempt to convert Ce^{4+} ions to the Ce^{3+}state without the use of a reducing atmosphere in the furnace which is the standard reduction technique.

2.3.4 Preparation of silicate glasses

Having overcome the problems of crucibles and furnace involved in the preparation of the simpler borate glasses it was decided to attempt again to prepare lanthanide-doped silicate glasses.The composition of the first sample is shown in Table 2.5.

Table 2.5 - Initial silicate glass composition

	Percentage (by mass)
Silica(SiO_2)	50.0
Sodium oxide (Na_2O)	30.0
Calcium oxide (CaO)	18.0
Samarium (Sm_2O_3)	2.0

The silica used was of 99.99% purity from the Aldrich Chemical Ltd. and the sodium and calcium were in carbonate form and of analytical grade.The Samarium was in oxide form (Sm_2O_3) and produced by Koch-Light Ltd.The 12g batch was mixed as with the borates and then heated at 1380°C for 16 hours in a platinum crucible.This composition was found to be extremely difficult to pour in the molten state and the heat blast from the furnace made working extremely uncomfortable.The "glass" formed was found to be a white opaque material.

2.3.4.1. Compositional Change

In view of the difficulties experienced it was decided

to change the silicate glass composition to a well established commercial container glass composition.Details are given in Table 2.6.

Table 2.6 Final Silicate glass composition

	Percentage (by mass)
Silica(SiO_2)	74.0
Sodium Oxide(Na_2O)	13.0
Calcium Oxide(CaO)	11.0
Lanthanide	2.0

All of the batch materials were of analytical grade and in powder form (100 microns).

2.3.4.2 Melting Procedure

The batches were placed in a vial and mixed in the same manner as the borate glasses.The homogenised powders were then transferred in a platinum crucible to a furnace previously heated to 1380-1400°C.After 3-4 hours the molten batch was swirled to assist the refining process.The batch was then left for a further 22 hours.

2.3.4.3 Casting

It was necessary due to the high viscosity of the glass to pour the molten glass into the mould as quickly as possible.It was found that the casting process was best carried out in the furnace itself.This was much more difficult than casting the borate glasses and extremely uncomfortable due to the higher temperatures and the necessity to cast within the furnace itself.Protective heat shielding ,a remote control unit or a different furnace arrangement would be required to cast silicate glass without discomfort.

2.3.4.4 Mould Release

Due to the lower thermal expansion/contraction of the silicate glass it was more difficult to release the glass from the mould.However,using cooling air and tapping the underside of the mould generally freed the glass.Sticking of the silicate glass to the platinum/gold mould was also a problem but this was largely overcome by having the casting dish in a highly polished state using "Hyprez" diamond paste as a polishing medium

2.3.4.5 Annealing

Annealing was carried out as with the borate glasses by placing the pieces in a furnace heated to 700°C and

cooling to room temperature over a 24 hour period.

2.3.4.6 Preparation Difficulties

Due to the problems experienced in the preparation of the these glasses only three samples of lanthanide-doped silicate glasses were prepared.These contained Terbium(Tb), Samarium(Sm) and Europium(Eu) each at a level of 2% of oxide by mass.

2.3.4.7 Other glasses

Silicate and borate glasses containing Chromium ions were also prepared for spectroscopic study by the Optoelectrcnics Group at Dublin City University.A paper based on this work was published in the Proceedings of the Conference on 'Disordered Systems and New Materials' at Varna,Bulgaria in 1988.[2.2]

2.3.5 Characterisation of prepared glasses

In addition to the doped glasses produced, two blank glasses containing all of the constituents of both the borate and silicate glasses(except the lanthanide constituent) were prepared.These blank glasses were characterised using three techniques:-

1. X-Ray Diffraction Analysis

2. Fourier Transform infra-red spectroscopy

3. Refractive Index determination

2.3.5.1 X-Ray Diffraction Analysis

The two samples were ground to pass a 75 micron screen and then mounted in an aluminium sample holder before being placed in a Jeol JXA Diffractometer.The X-rays were generated ($Cu_{K\alpha}$) using a Cu tube with a manganese filter,the pulse height analyser was set at $1*10^3$ c.p.s.with a time constant of 1.These are sensitive settings for the instrument and any crystalline phase present at a level of about 5% by mass should be detected by the diffractometer.
Both analyses gave the broad pattern associated with amorphous materials.However,in the case of the borate glass a small diffraction peak did appear at 26.65°2θ(3.343Å) with a peak to background ratio of about 1:1. This is the main diffraction line for quartz(SiO_2) and may indicate that although the silica dissolved in the glass it retained some degree of crystallinity.The short batch melting time (20mins.) may account for this partial retention of its original structure.

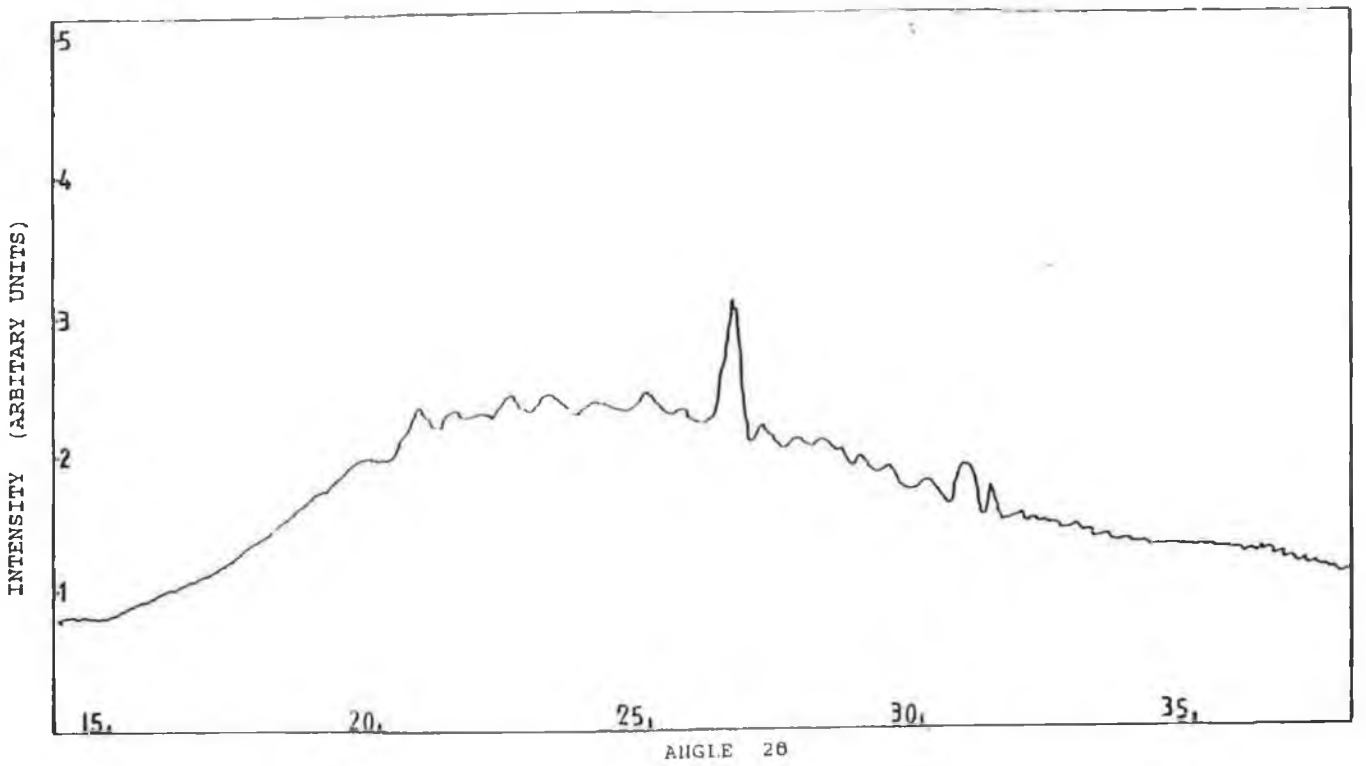

FIG.2.1. XRD PATTERN OF BORATE BLANK GLASS

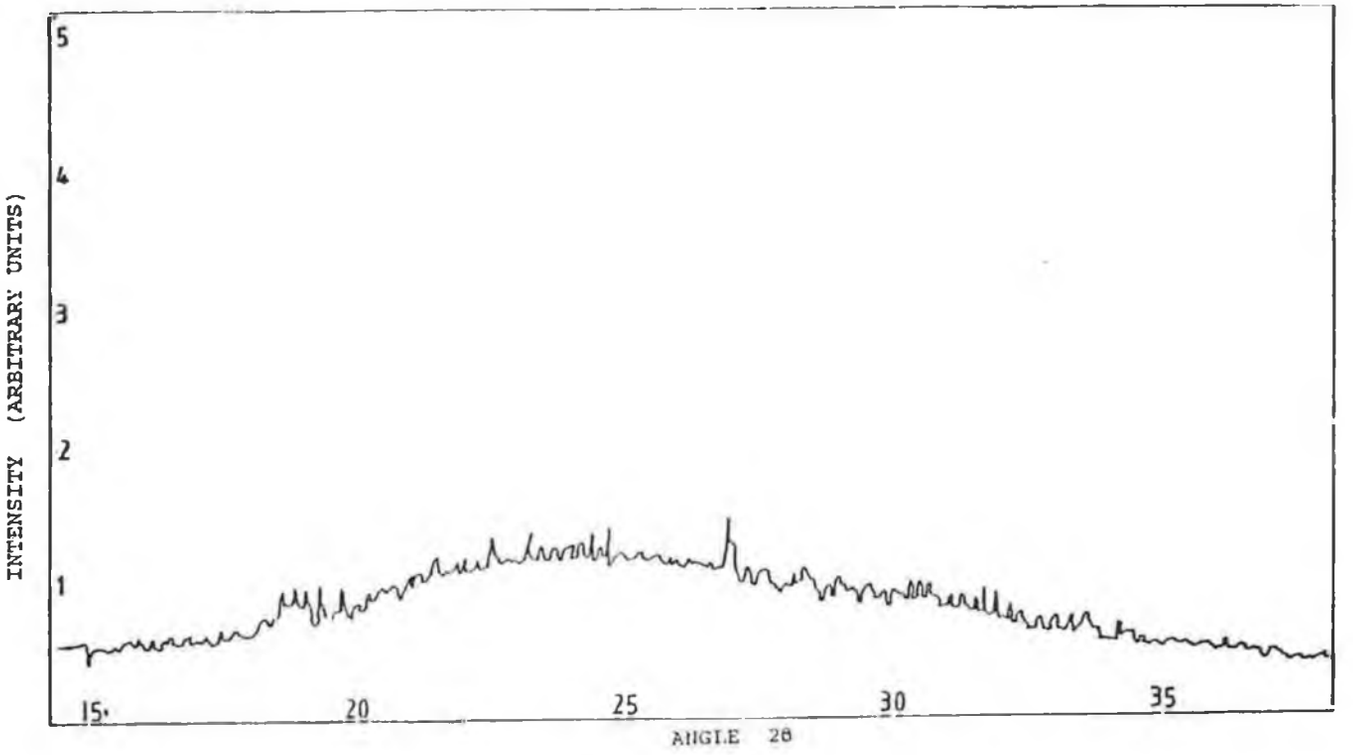

FIG.2.2. XRD PATTERN OF SILICATE BLANK GLASS

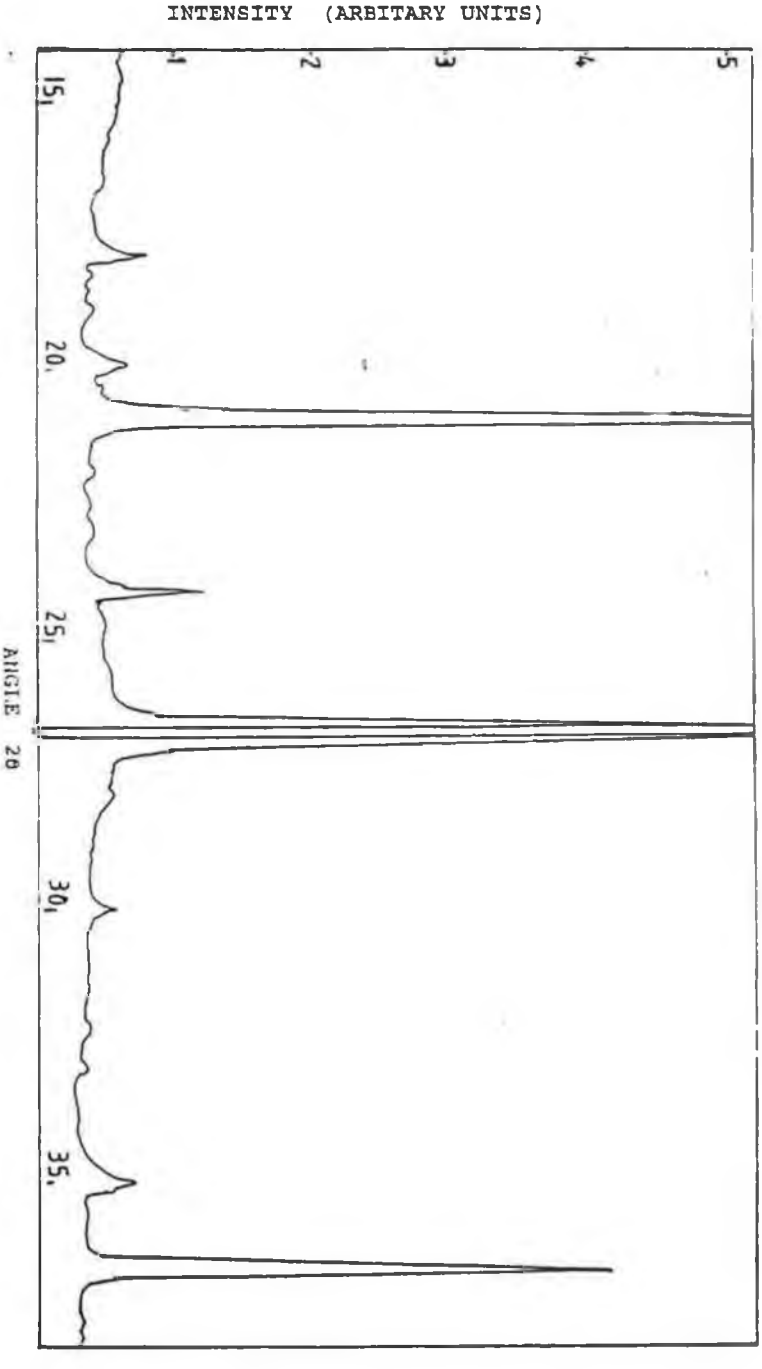

FIG. 2.3. XRD PATTERN OF CRYSTALLINE SILICA

In the case of the silicate glass no diffraction lines were found to be present in the diffractogram indicating the absence of any detectable crystalline phase.

The diffractograms are shown in Figs.2.1. & 2.2.The diffraction pattern for crystalline silica with a peak to background ratio of about 60:1 relating to the main line (26.65 2θ)is shown for comparison purposes. (Fig.2.3.)

2.3.5.2 Infrared Spectroscopy

Samples from the two glass blanks were ground to pass a 100 micron screen and mixed with potassium bromide(KBr) at a 5% level of sample to KBr.

The mixtures were then formed into a 1 cm diameter disc using a laboratory press.These discs were then examined using a Nicolet 5DXB Fourier Transform Infra-red spectrometer at room temperature.The frequency maxima of the absorption peaks detected in the scans are shown in Table 2.6 .The infrared scan spectra are shown in Figs.2.4 & 2.5. A similar scan carried out on crystalline silica is shown for comparison purposes is shown in Fig.2.6.

Table 2.7 Infrared Analysis

Sample: Borate blank

Maximum Frequency(cm^{-1})	Comment
3427	Strong band -possibly OH stretch from moisture in the KBr
1417	Very strong band - B-O stretch
1023	Very strong band - Si-O stretch
457	Strong band -possibly O-Si-O deformation

Minor bands at 3418,2968,2935,2853,2369and 719 cm^{-1} were also present in the absorption spectra.

Sample: Silicate blank

Maximum Frequency(cm^{-1})	Comment
1040	Very strong band- Si-O stretch
466	Very strong band- possibly O-Si-O deformation

Minor bands at 2369 and 777 cm^{-1} were also detected.

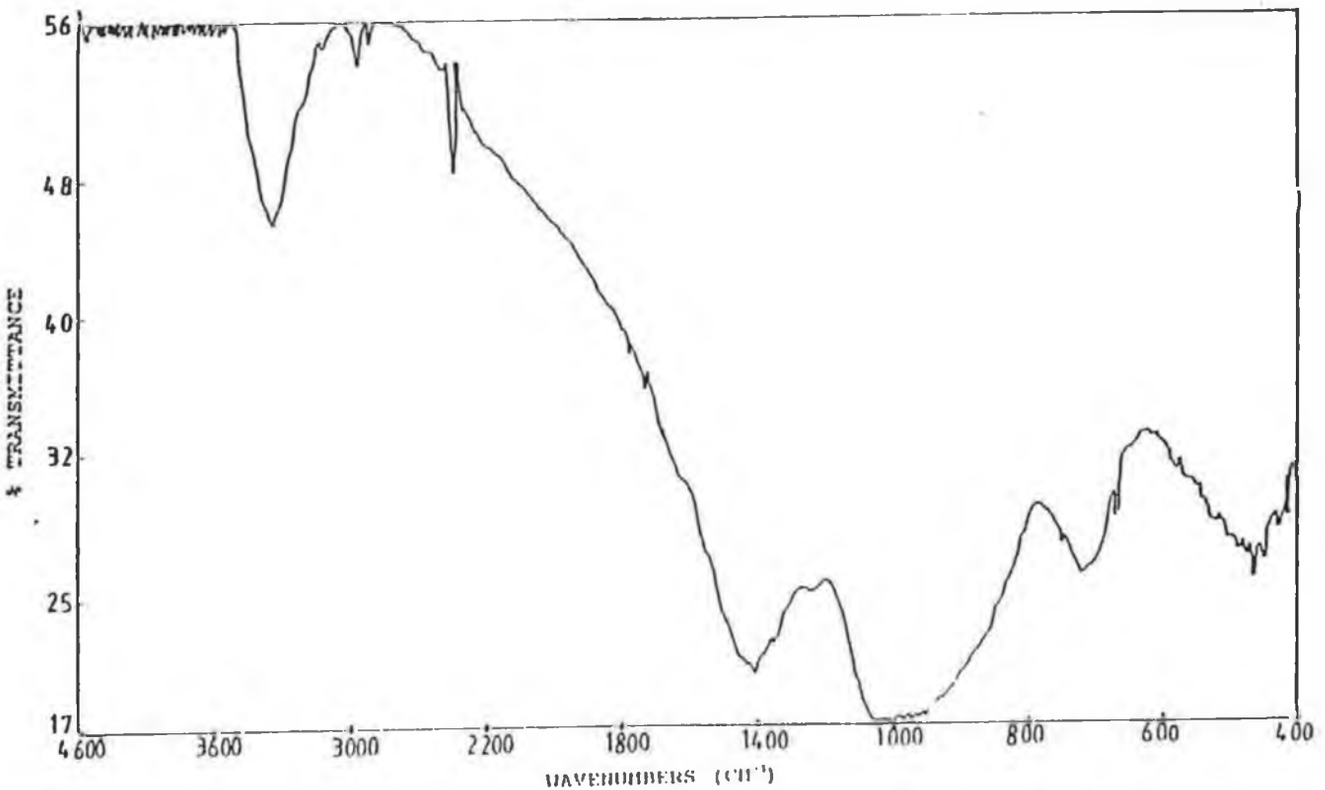

FIG.2.4. INFRARED SPECTRUM OF BORATE BLANK GLASS

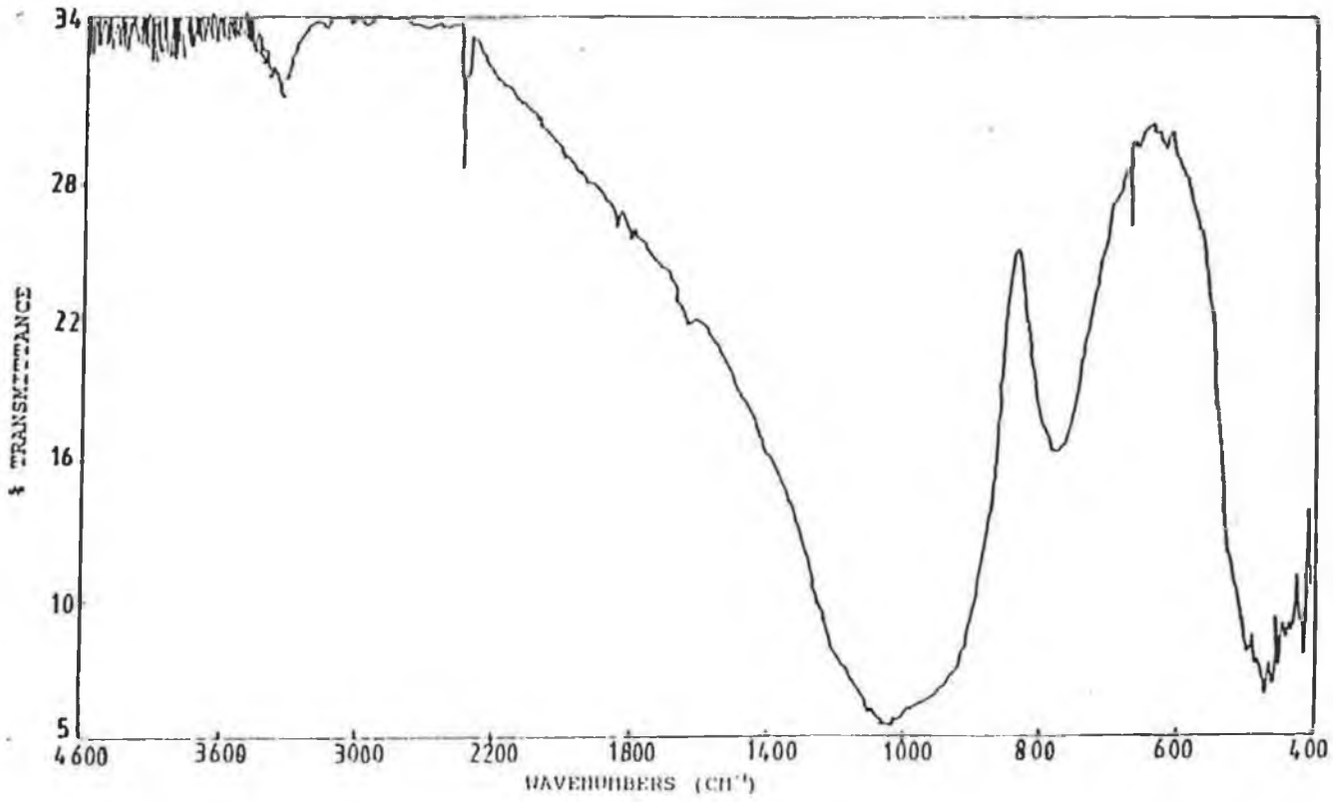

FIG.2.5. INFRARED SPECTRUM OF SILICATE BLANK GLASS

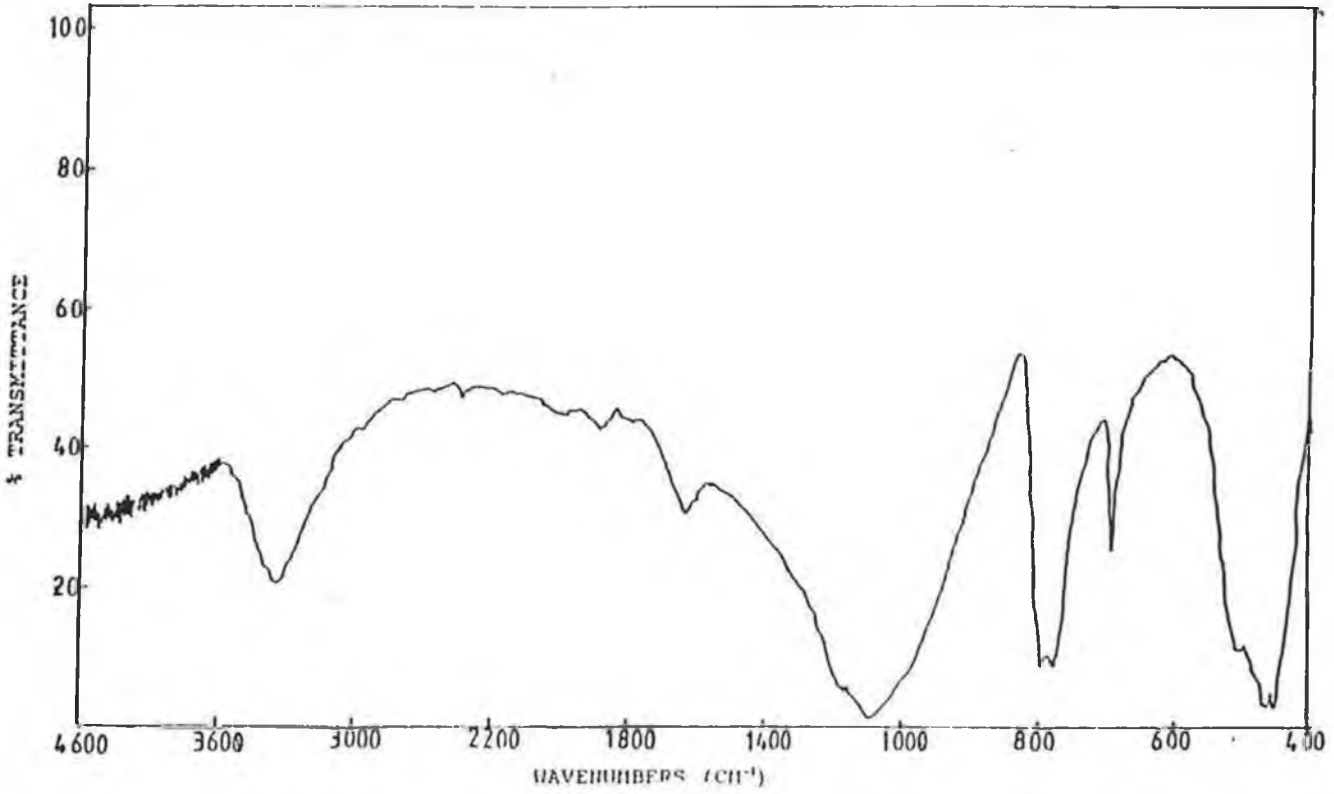

FIG.2.6. INFRARED SPECTRUM OF CRYSTALLINE SILICA

The infrared spectra for the blank glasses agree closely with the results obtained by Wong[2.3] who used B_2O_3-SiO_2 glasses prepared by chemical vapour deposition(CVD).Wong suggests that a band at 930cm^{-1} strongly indicates that it is a bond-stretching vibration of the Si-O-B linkages in the borosilicate lattice.The broad absorption band at 450cm^{-1} may also be due to overlapping contributions of the Si-O-Si and B-O-B bending modes.

The shape of the band at 920-1030 cm^{-1} detected in the borate blanks is such that it may contain the 930cm^{-1} vibration.The common bands at 2369 cm^{-1} may be due to an instrumental feature or contaminant from the laboratory press.

The infrared transmission spectra of the borate and silicate glasses are in general agreement with the work of Wong indicating that they are true glasses showing characteristic vibration spectra.

2.3.5.3 Refractive Index

The refractive indices of the two blank glasses were determined at a temperature of 10°C, using an Abbe Refractometer and sodium light(589nm).The samples were placed in a film of bromonaphthalene(μ-1.6620) and the latter was also used as a reference for the determination.The results are shown in Table 2.8.

Table 2.8 Refractive Index Determination

Sample	μ
Borate blank	1.565
Silicate blank	1.518

The error involved in this determination is at a level of ±1%.

The refractive index of glass depends mainly on the composition of the particular glass in question. The μ values for crown glass varies from 1.517 to 1.520 and flint glass lies within the range 1.575-1.890.The value quoted in the reference literature for quartz glass is 1.458, all measurements being made at 589nm(Na)[2.4]. Borosilicate glass manufactured by Corning has a refractive index value of 1.478 (Sodium D line)[2.5]. Normal borosilicate glass contains a much higher silica content(>80%) than the glasses prepared in this work so that some difference in value would be expected.It would appear that the higher the silica content the lower the refractive index value.

2.3.6 Summary

The X-Ray diffraction analyses carried out on the two prepared blank glass samples showed these to be mainly amorphous in character.The infrared scans illustrated the differences in structural composition between the two glasses,the borate showing the characteristic B-O bond stretch which was absent from the silicate glass infrared spectrum.The Si-O stretching from the silica(SiO_2) present in both samples was detected in each case. The refractive index values were within the range expected for glass.Generally, the properties of the samples were found to be characteristic of the type of glasses prepared.

References Chapter 2

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PLATE 1. GLASS-MAKING FURNACE

PLATE 2. GLASS SAMPLE RELEASED FROM PLATINUM MOULD

CHAPTER 3

OPTICAL CHARACTERISATION OF PREPARED GLASSES

3.1 Introduction

A microscopic inspection of the prepared lanthanide-doped glasses described in the previous chapter,showed them to be of good optical quality. Generally,they did not contain a large amount of"seed"or other visible defects which frequently occur in poor quality glass.The lanthanides were well dispersed throughout the glasses where colour could be used as a dispersion indicator.The thickness of the samples was somewhat variable but this was difficult to control during casting even though the same mass of batch was used in each preparation.

The batch materials used in the production of good optical glass are required to be spectroscopically pure and the finished glass should be free from defects such as refractory solids('stones'),gas inclusions('seed')and chemical inhomogenieties('striae').The prepared glasses showed none of these types of defects.

3.2 Optical properties of the Lanthanides

The lanthanide series of elements are those of atomic number 58 to 71 [Cerium(Ce) to Leutetium(Lu)] in Group 3A of the Periodic Classification.Lanthanum (Z = 57) although giving its name to the series,is normally excluded from the group due to the absence of 4f electrons in its ground configuration.

After Lanthanum the energy of the 4f orbital falls below that of the 5d,and subsequent electrons are added to the inner shielded 4f orbitals.The seven orbitals each with a capacity of two electrons give a total of 14 elements of this inner or f-type transition series before the 5d orbitals begin to fill again.

The series is remarkable for the similarity in behaviour of the elements in both their elemental state and in compounds.The occurrence of a particular thermodynamically stable oxidation state (+3),many instances of isomerism and the classical difficulties in separating one lanthanide from another,all demonstrate the remarkable similarity of many of the properties of these elements.

The mechanism by which lanthanide-doped glasses could act as UV detectors is expected to be absorption by the glass matrix of UV radiation and transfer of this energy to the lanthanide ion.The ion would then emit visible photons as a result of a cascade process by which the UV photon loses energy to the matrix resulting in the emission of a visible photon.This type of radiation is easily detectable using conventional detectors e.g. photomultiplier tubes.

As a first step in characterising these materials it was decided to look at the absorption and emission in the UV/visible of selected ions embedded in the borate and

silicate glasses.These results were then compared with published work relating to the same ions.

3.2.1 Electronic Configuration

The electronic configurations of these elements explain the phenomenon of similarity of the lanthanides, and is useful in the interpretation of emission/ absorption spectra of the elements.The ground state of the neutral lanthanum atom consists of a neutral xenon core with 3 electrons in the higher energy 5d and 6s orbitals:-

$$La = [Xe]5d^1\ 6s^2$$

It has been shown that both the energy and the spatial extension of the 4f orbitals decrease very abruptly as the nuclear charge increases beyond 57(La)[3.1].For example the nuclear binding energy of a single 4f electron drops from -0.95ev for the La atom to -5ev for the Nd atom.The ground-state configuration of these elements are shown in Table 3.1.

Table 3.1 Ground-state "Outer" electronic configuration

Element	Atomic number (Z)	Configuration	
		Idealised	Observed
Ce	58	$4f^1\ 5d^1\ 6s^2$	$4f^1\ 5d^1\ 6s^2$
Pr	59	$4f^2\ 5d^1\ 6s^2$	$4f^3\ 6s^2$
Nd	60	$4f^3\ 5d^1\ 6s^2$	$4f^4\ 6s^2$
Pm	61	$4f^4\ 5d^1\ 6s^2$	$4f^5\ 6s^2$
Sm	62	$4f^5\ 5d^1\ 6s^2$	$4f^6\ 6s^2$
Eu	63	$4f^6\ 5d^1\ 6s^2$	$4f^7\ 6s^2$
Gd	64	$4f^7\ 5d^1\ 6s^2$	$4f^7\ 5d^1\ 6s^2$
Tb	65	$4f^8\ 5d^1\ 6s^2$	$4f^9\ 6s^2$ (or $4f^8\ 5d^1\ 6s^2$)
Dy	66	$4f^9\ 5d^1\ 6s^2$	$4f^{10}\ 6s^2$
Ho	67	$4f^{10}\ 5d^1\ 6s^2$	$4f^{11}\ 6s^2$
Er	68	$4f^{11}\ 5d^1\ 6s^2$	$4f^{12}\ 6s^2$
Tm	69	$4f^{12}\ 5d^1\ 6s^2$	$4f^{13}\ 6s^2$
Yb	70	$4f^{13}\ 5d^1\ 6s^2$	$4f^{14}\ 6s^2$
Lu	71	$4f^{14}\ 5d^1\ 6s^2$	$4f^{14}\ 5d^1\ 6s^2$

According to Moeller[3.2] the configurations listed in Table 3.1 are those most consistent with spectral and atomic beam resonance data.

3.2.2 Oxidation States

Even during pioneering studies it was observed that in their commonest compounds the lanthanides are uniformly tripositive.The early investigators recognised tetrapositive Cerium(Ce) and higher-valent Praseodymium(Pr) and Terbium(Tb) as the dark-coloured oxides Pr_6O_{11} and Tb_4O_7 .However,it was not until the present century that dipositive Europium(Eu), Ytterbium(Yb) and Samarium(Sm) were characterized. Although all of the lanthanides have been obtained in the +2 state by trapping in solid alkaline earth halide matrices[3.3],dissolution in aqueous systems result in rapid oxidation to the +3 state of all the species except Europium(EuII).Even this species has only a comparatively short half-life with respect to oxidation in aqueous solution.[3.4] Solid compounds capable of preparation in a state of purity are limited to derivatives of the ions:-Eu^{2+} ,Yb^{2+} ,Sm^{2+} and Tm^{2+} [3.5].

3.3 Luminescent glasses

Weyl[3.6] classified luminescent glasses into three groups according to the role of the glass phase in producing the fluorescence:-

(a) Glasses containing crystalline fluorescence centres

(b) Glasses containing energy isolated atoms or

molecules.

(c) Glasses containing fluorescent ions.

The luminescent glasses systems of classes(a) and (b) appear to be inherently unstable.In the case of luminescent glasses of type (c) the luminescence originates from the fluorescent ions dissolved in the glass.These glasses contain no crystalline phase and are true glass phosphors unlike (a) and (b) types which are largely unstable and of limited practical application.

3.3.1 Luminescence of lanthanides in glass

The luminescence of lanthanides in a glass matrix was reported [3.7] over a century ago.In the early 1940s,numerous luminescent glasses were developed for use in photoluminescent devices e.g.the envelopes of gas discharge lamps filled with mercury vapour.Various glass compositions were reported for this purpose,such as Tl-activated silicates[3.8],Manganese-Cerium co-activated phosphate or lead-activated alkali and alkaline earth metaborates and metaphosphates[3.9] However,no practical applications of these glasses in fluorescent lamps were reported,probably because the fluorescent intensity and efficiency of these glass phosphors was impractically lower than than those of crystalline phosphors.

In the year following the discovery by Maiman of the ruby laser,Snitzer (1961),[3.10] reported the laser action of a potassium barium silicate glass containing 2% by mass of neodymium oxide(Nd_2O_3).This discovery of a lasing phenomenon in a doped glass gave a strong impetus tc the development of improved lanthanide-activated luminescent glasses.

Systematic investigations were carried out on the fluorescence of rare earths in glasses,particularly that of neodymium but also a number of lanthanides ions such as Er^{3+} ,Yb^{3+} ,and Ho^{3+} in a wide range of glass compositions.Reisfield[3.11] investigated the absorption, fluorescence and energy transfer of rare-earths ions in various inorganic glasses,such as silicates, germanates, borates and phosphates.A remarkable similarity was found to the behaviour of the same ions in a crystalline matrix.The principal difference between the fluorescence of lanthanides in glasses and that in crystals is the inhomogeneous broadening due to the presence of multiple activator sites in the glasses having slightly different symmetries.

Dieke [3.12] in 1961 examined the emission spectra of doubly and triply ionised rare earths (except Pm).The spectra were photographed under controlled excitation produced by a dc arc and mild and hot spark

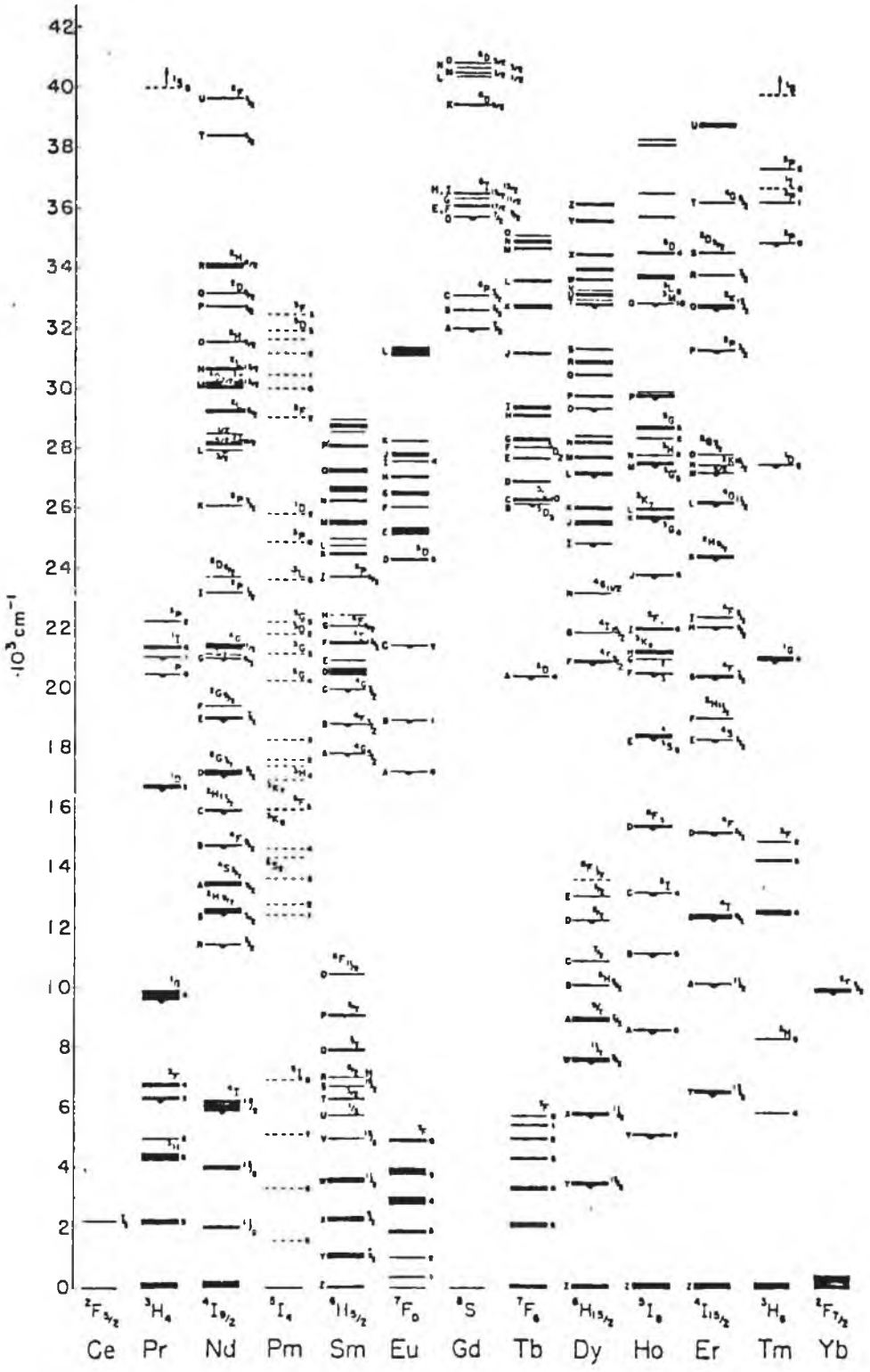


Fig.3.1. ENERGY LEVELS OF THE TRIVALENT LANTHANIDE IONS IN $LaCl_3$

discharges.The data was obtained using three spectrographs.

Dieke found that the emission lines occurred in clusters and that they changed systematically from one rare earth to the next.This suggested that analogous groups have a similar origin in each element.

Dieke et al produced a detailed chart showing the lower energy levels of the 4fn configuration for the triply ionized rare earths obtained from crystal absorption and fluorescence spectra.(Fig.3.1).In most cases the trivalent lanthanide was contained in a crystalline salt (anhydrous chlorides).As expected,no data was available for Pm^{3+} and there was some doubt as to the identification of some of the levels in the case of Ho^{3+}.

In 1963 Karapetyan[3.13]also carried out an extensive study of lanthanide activated silicate,borate and phosphate glasses of simple composition.Selecting a base glass of the composition $Na_2O.CaO.5SiO_2$ the luminescence of a number of the rare earths was determined using filtered mercury discharge-tube radiation.The spectra obtained are reproduced in Fig.3.2.

The Samarium glasses examined by Karapetyan were found to be of pale yellow in colour and to exhibit an intense orange luminesence under UV stimulation the bands peaking at 560,596,640,705,787,895 and 936 nm.Karapetyan found that in the case of Sm the luminescence intensity

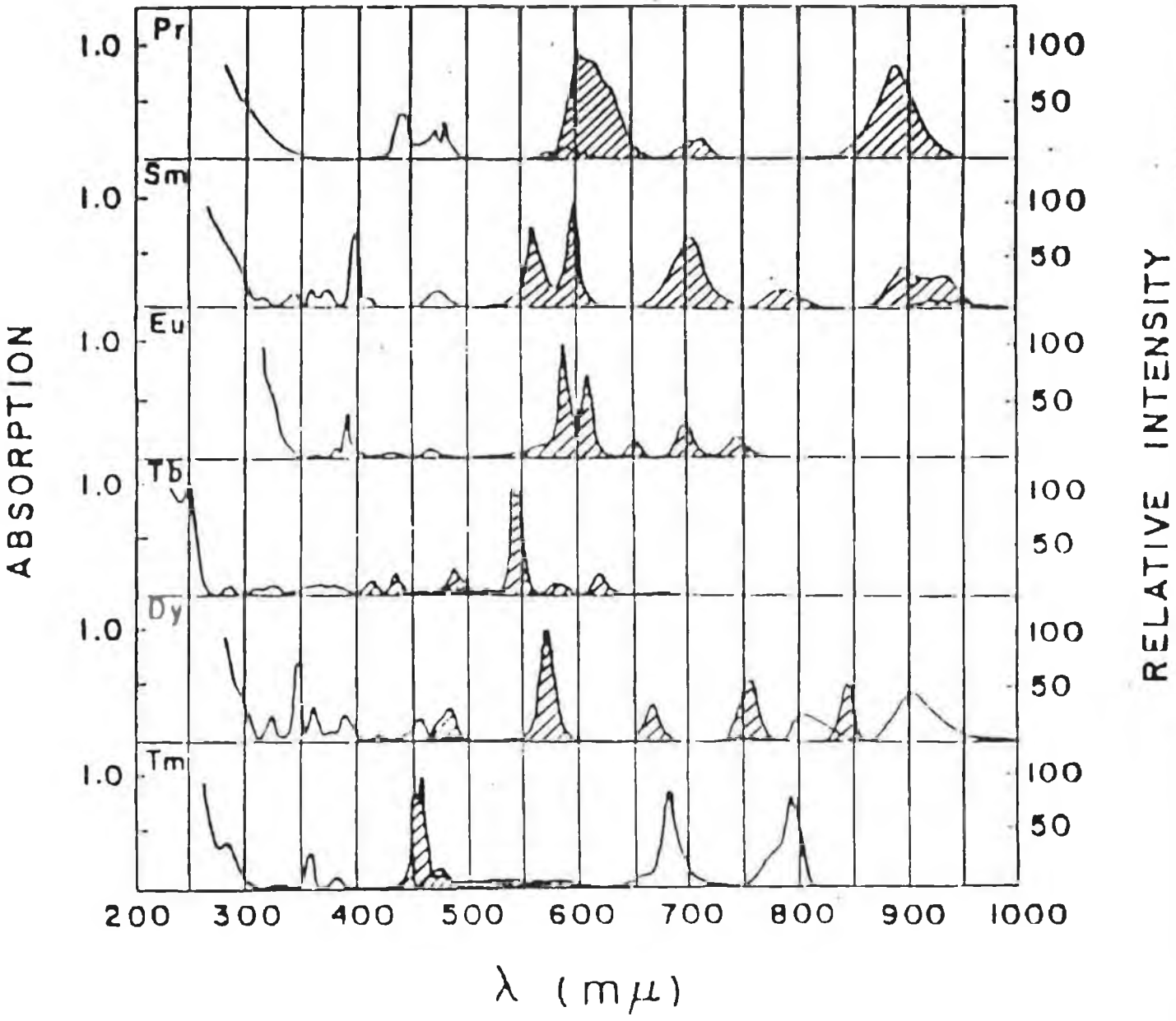


Fig.3.2. ABSORPTION AND LUMINESCENCE(hatched) SPECTRA OF GLASSES WITH LANTHANIDE ACTIVATORS. Activator concentrations:- Pr ,1%; Sm ,2.5%; Eu ,2.5%; Tb ,5%; Dy ,5%,Tm ,5%. (Karapetyan 1963)

increased monotonically up to a level of 10% Sm with no significant quenching.Variation in the oxidising and reducing conditions during melting of the glasses was found to have no significant effect on the luminescence. Trivalent Europium glasses were found to be colourless and to exhibit a red luminesence under UV radiation.The spectrum consisted of a large number of luminescence bands peaking at 587,609,653,698 and 746nm. At low concentrations of divalent Europium(0.1%) the luminescence was found to be in the blue area of the spectrum the band peaking at 460nm.At concentrations greater than 1% Eu^{3+} the glasses were yellow in colour and the luminescence band was found to peak at 525nm. Lowering of the temperature to 77 K changed the luminescence of Eu^{3+} activated glass from red to the yellow region of the spectrum.This alteration was found to be due tc the appearance of a broad band in the yellow-green region peaking at 540nm while the 587 and 609nm bands remained unchanged.

Terbium glasses were found by Karapetyan to be colourless and to luminesce in the green region of the spectrum.At a concentration of 0.5% Tb a large number of narrow bands were detected peaking at 401,413,417,435 441,457,487,494,520,541,546,582,590,620,654 and 679nm.Increasing the terbium concentration was found to cause the bands below 470nm to disappear with no change

in intensity of the longer wavelength bands.Alteration of the oxidation-reduction conditions during the glass preparation stage and lowering of the temperature to 77 K were found to cause only minor changes in luminescence.

Wargin and Karapetyan[3.14] in 1959 studied Cerium-actiated glasses and observed a luminescence peak at 330nm the band extending to 410nm in both silicate and phosphate glasses.A concentration quenching was found to occur at 1.5% cerium in silicate glass.In a sodium diborate glass 0.05% cerium showed a luminescence peak at 400nm when the cerium was strongly reduced to the Ce^{3+} form.

Rindone and Sproull[3.15](1964) studied the luminescence in the visible region of rare-earth ions in lanthanum calcium borate glasses.The base glass composition used was 50%B_2O_3 ,40%La_2O_3 and 10% CaO.Europium was found to yield a red-orange luminescence whose peaks shifted from 600 to 610nm with increasing concentrations of the lanthanide.Samarium in the same base glass was found to have an orange luminescence with the band peaking at 600nm.Concentrations as low as 0.025% Sm_2O_3 were found to exhibit luminescence at at a level above 0.8% showed concentraticn quenching.Dysprosium glass showed a yellow-white luminescence with two sharp bands peaking at 485 and 580nm.Terbium glass in the same matrix

exhibited a light-green luminescence with two peaks,the principal one being centered around 550nm and the weaker one(about half intensity) appearing at 485nm.

Thulium glass was found to give an intense blue luminesence with a sharp band peaking at 460nm.

Rindone and Sproull further reported that cerium glass(0.05% CeO_2) gave an intense blue luminesence with the emission band extending to 550nm.Above this concentration it was found that the luminescence intensity gradually decreased until it reached a constant value in the range 0.4 to 0.8%(asCeO_2).

Holmium was found to exhibit a weak luminescence band below 575nm and concentration quenching occurred at levels of Ho_2O_3 above 0.5%.No luminescence bands in the 400-700nm region were observed in lanthanum calcium borate glasses with 0.1% Er_2O_3,Gd_2O_3,Ln_2O_3,Pr_2O_3,Nd_2O_3or Yb_2O_3.

The luminescence and absorption spectra of Eu^{3+} in silicate,borate and germanate glasses were studied by Kurkjian and co-workers in 1963[3.16].Using broad-band short wave radiation in the region 290-500nm,these authors determined the effects of the host glass composition on the luminescence spectra.

The luminescence of Tb^{3+} and of co-doped Tb^{3+} and Eu^{n+} in fused silica was studied by Nelson and colleagues[3.17] in 1964.Under 254.7nm radiation Tb^{3+} was shown to emit

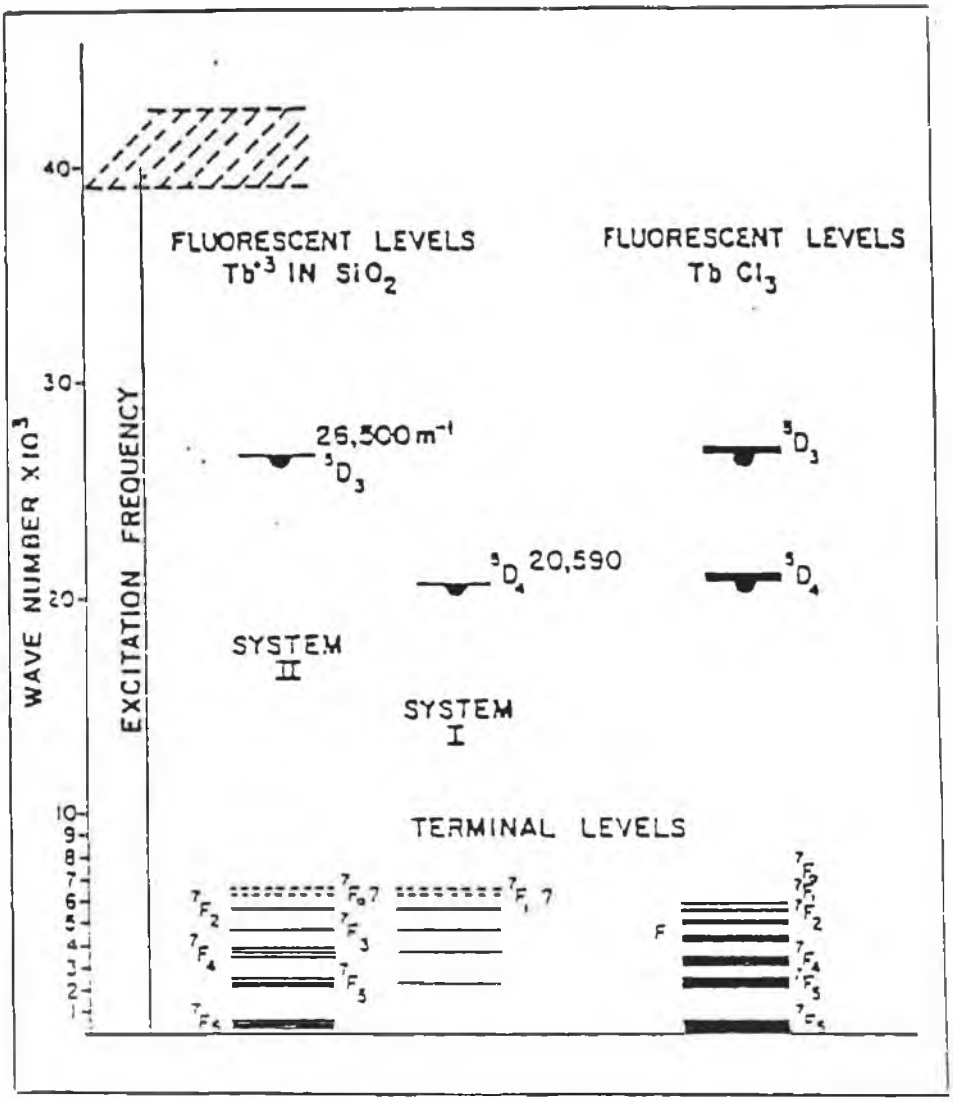


Fig.3.3. ENERGY-LEVEL DIAGRAM FOR TERBIUM IN FUSED SILICA. (Data on Terbium in silica from Nelson et al.,1964; data on Terbium chloride from Dieke et al.,1961)

at wavelengths ranging from 377nm to 653nm.Assignments of energy levels were made by comparison with those determined by Dieke et al (1961) for anhydrous terbium chloride.Two luminescent levels $^5D_3$ and $^5D_4$ were assigned to the Terbium ion.The energy level diagram for Terbium, based on the work of both Nelson and Dieke is shown in Fig.3.3.

Spowart[3.18] (1977) developed glasses doped with Ce or Tb as neutron scintillating materials.These glasses also contained enriched lithium ^6Li used as a neutron detector through the $^6_3Li(n,\alpha)$ reaction.The behavior of Cerium in the 3+ coordination state differs from that of other lanthanides in that it has only one 4f electron.Ce^{4+} was excluded as far as possible from these glasses due to its strong absorption band which overlaps the Ce^{3+} emission.The present interest in UV detectors largely developed as a result of neutron detection development work.

3.4 EXPERIMENTAL

3.4.1 Equipment

Absorption spectra of the samples were obtained at room temperature using a Shimadzu spectrophotometer Model UV-240 fitted with a special sample holder for use with solid samples.

Steady-state luminescence measurements were also carried out in the Optoelectronics Laboratories at Dublin City University.The experimental arrangement for the determination of these luminescence spectra is shown in Fig.3.4.

The samples were mounted at room temperature or placed in a variable temperature liquid nitrogen cryostat. Optical excitation was produced using either a 250W (Photophysics)Xenon arc lamp or a coherent Argon ion laser(Model 52) which pumped a coherent Cr-599 Dye laser(Rhodamine 6G dye).The excitation wavelengths passed through a ¼ metre Spex minimate monochromator before impinging on the sample.

The emission from the sample was dispersed through a Jobin Yvon 1 metre focal length monochromator with a 1200groove/mm diffraction grating.Output light emerging from the exit slit was detected using a Hamamatsu(R928) photomultiplier tube with a Hamamatsu(E717) base.The output from the photomultiplier tube was passed to a current measuring device which converted it to a voltage output.The resultant signal was plotted on paper using an x-y recorder or fed via a converter to a microcomputer and stored on disc.

3.4.2.Absorption and luminescence measurements

The absorption and luminescence measurements were

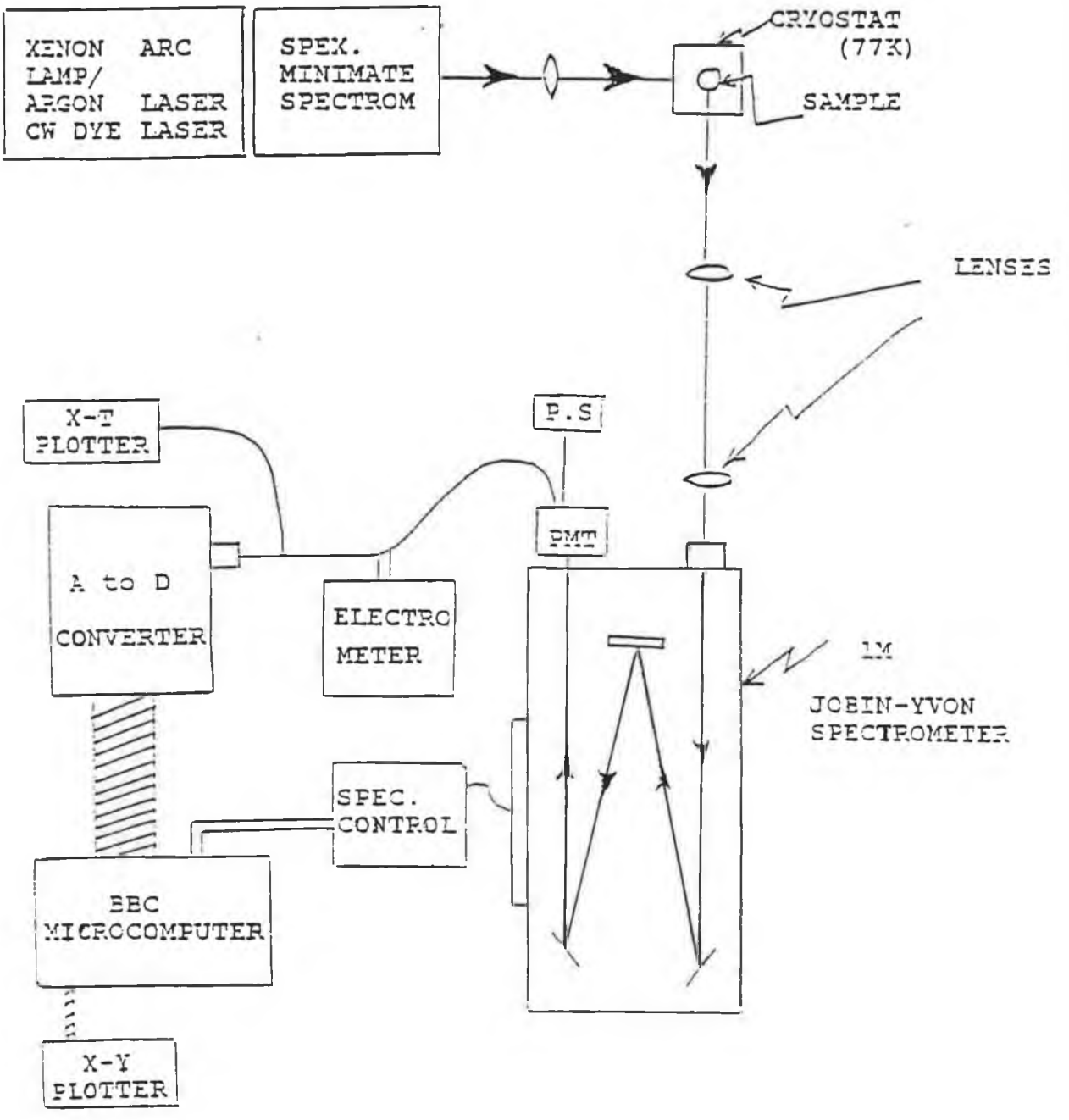


FIG.3.4. STEADY-STATE LUMINESCENCE MEASUREMENTS

carried out,in most cases at room temperature,on a selected number of the prepared doped glasses.The absorption measurements were made using blank borate or silicate glass as the reference.The doped ions selected were those which were likely candidates as UV detectors.

The samples for which absorption and luminescence spectra were obtained are as follows:-

- Terbium (1.0% borate)
- Europium(0.5% borate)
- Samarium (0.5% borate)

The spectral plots obtained are shown in Figs.3.5 to 3.10.

3.4.3 Absorption Spectra

3.4.3.1 Terbium- doped glass

The 1.0% Terbium-doped borate glass showed a strong absorption band centering at 225nm with minor bands at 316,360,426 and 594nm.The bands below 400nm are in broad agreement with those found by Karapetyan (Fig.3.2)The spectrum also contained possible minor emission bands at 310,325 and 356nm.The spectrum is shown in Fig.3.5.

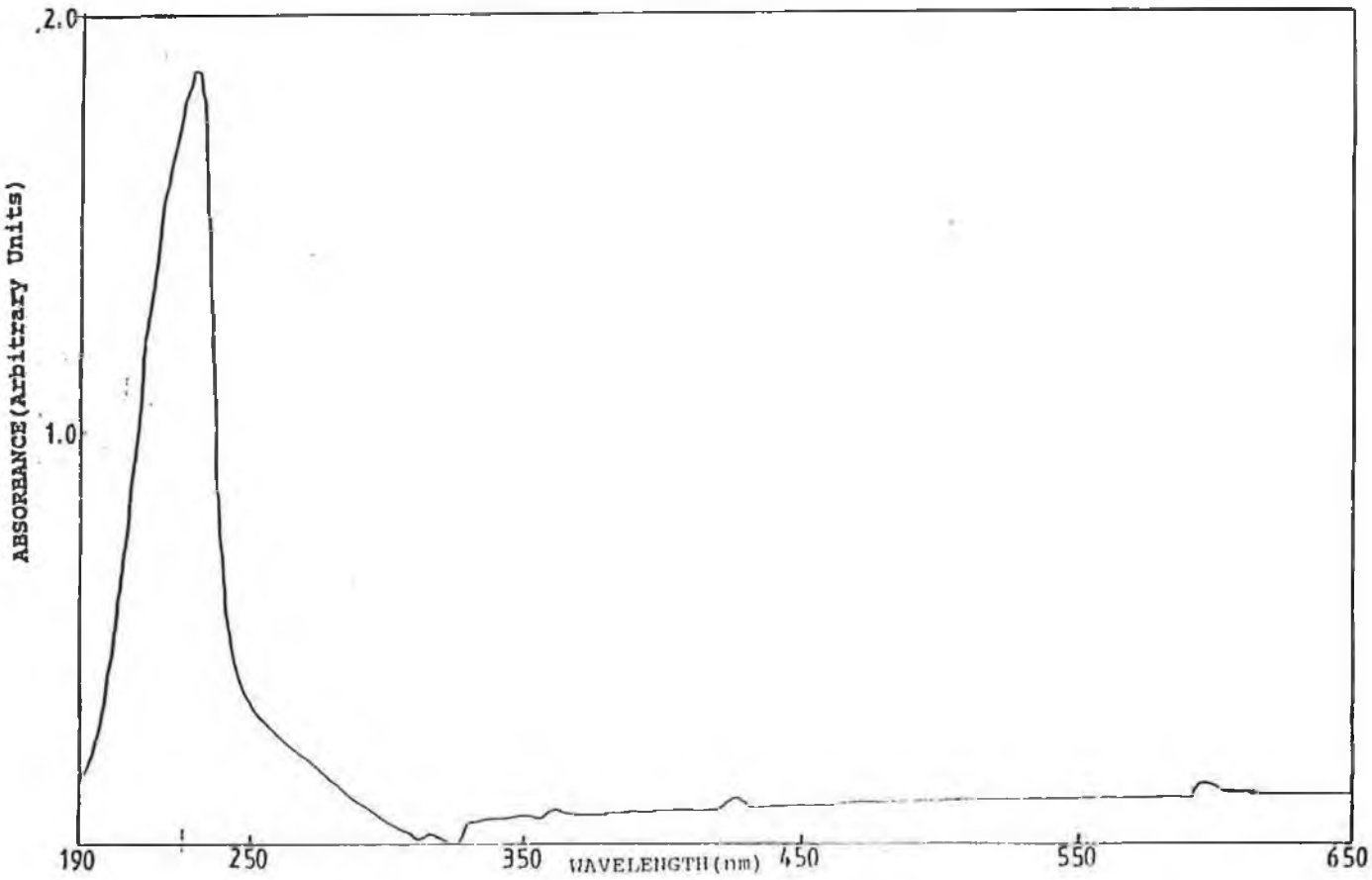


Fig.3.4. ABSORPTION SPECTRUM OF TERBIUM (I)

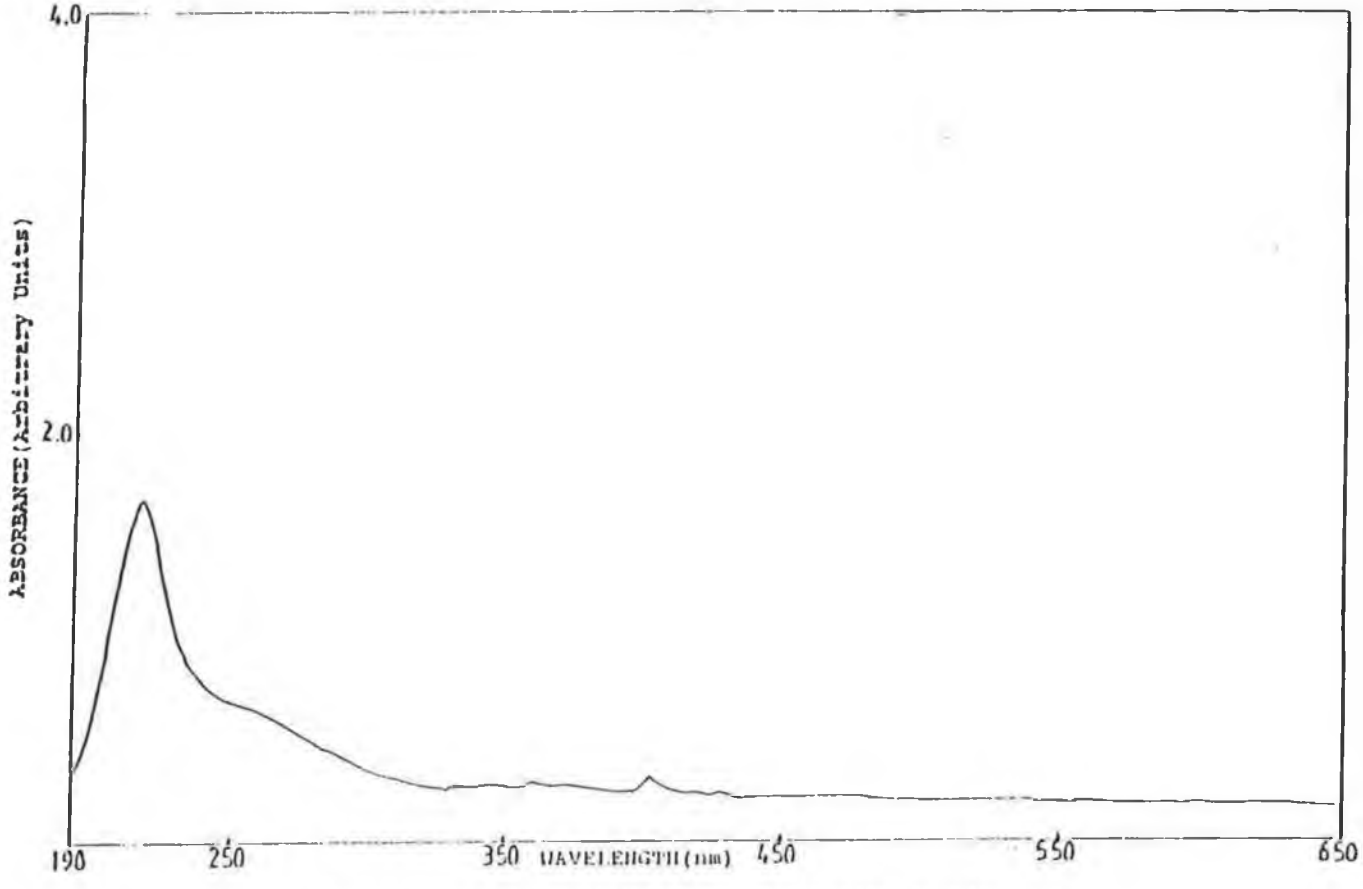


FIG.1.6. ABSORPTION SPECTRUM OF SAHARIUM (0.5%)

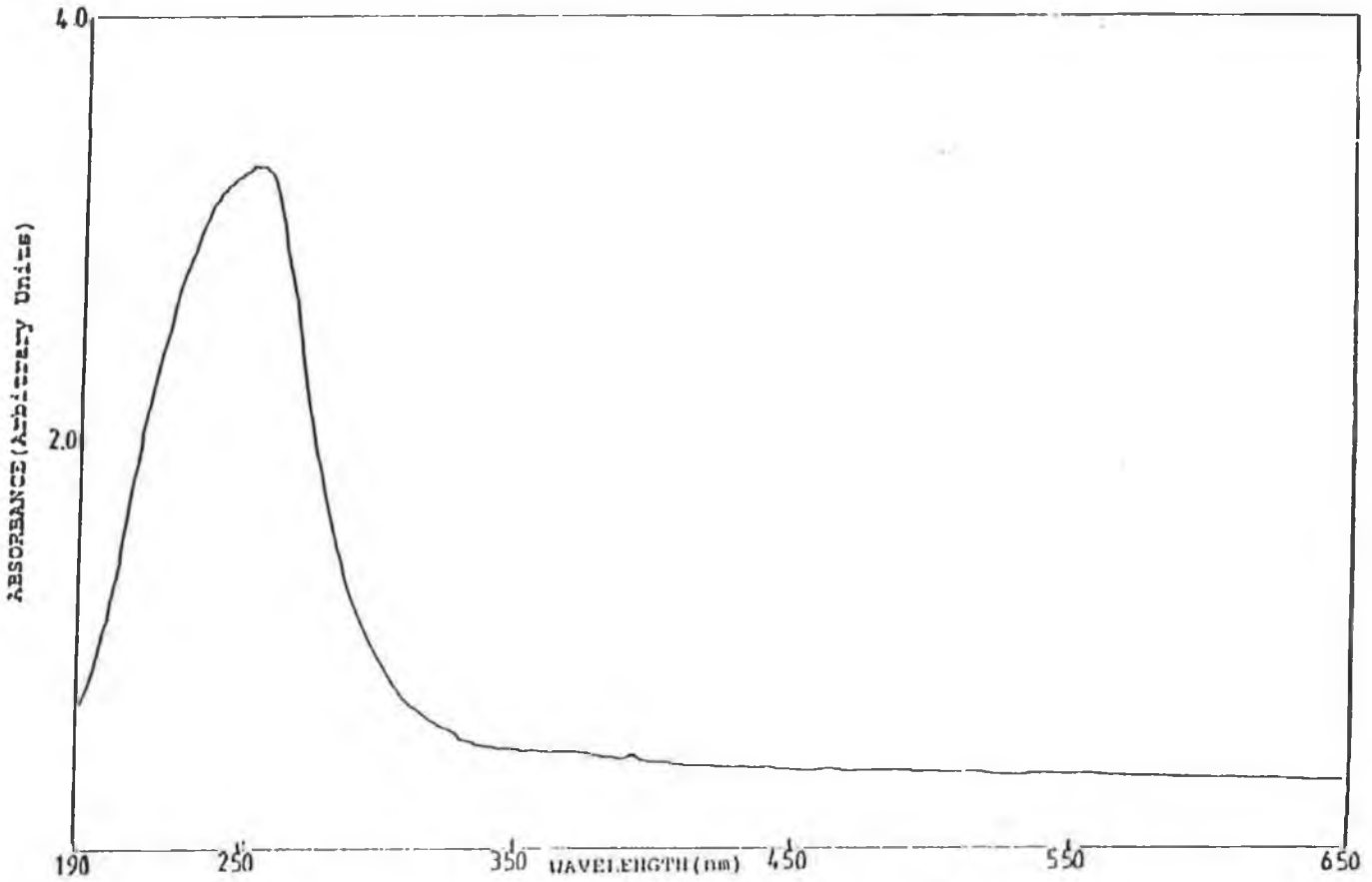


FIG.3.7 ABSORPTION SPECTRUM OF EUROPIUM(0.5%)

3.4.3.2 Samarium-doped glass

Samarium(0.5% borate) showed a primary absorption band at 214nm together with a possible absorption peak near 250nm.A further minor absorption band was present at 403nm.Karapetyan (Fig3.2) found absorption bands at these wavelengths but the band at 400nm was much stronger. There was little evidence of emission bands except possibly near 340nm.The absorption spectrum is shown in Figs.3.6.

3.4.3.3 Europium-doped glass

The Europium(0.5% borate) sample contained a broad absorption band centering about 250nm and a possible minor absorption peak at 394nm.These bands agreed quite closely with those found by Karapetyan (Fig.3.2)There was little evidence of emission bands.The spectrum is shown in Fig.3.7.

3.4.4 Luminescence measurements

The results from the luminesence measurements made on three lanthanide-doped glasses (Terbium,Samarium and Europium) are summarised in Table 3.2.These are compared with the published data on the same ions in glassy matrices.The spectra are shown in Figs.3.8,3.9 and 3.10.

Table 3.2 Luminescence Measurements

Sample Details		Published Data		
		Ref.3.13	Ref.3.15	Ref.3.16
Wavelength	Luminescence Lines nm	Luminescence Lines nm	nm	nm
TERBIUM (1%borate) --------- Excitation Wavelength 382nm Temp.300K	487 542 547 584 623	487 494 520 541 546 582 590 620 654 679	485 550	
SAMARIUM (0.5%borate) ---------- Excitation Wavelength 416nm Temp.300K	563 569 599 605 646 656 711	560 596 640 705 895 936	 peaking 600 787	
EUROPIUM (0.5%borate) ---------- Excitation Wavelength 398nm Temp.80K	579 588 592 596 611 615 619 653 689 703	 587 609 653 698 746	 600-610	580 585 595 610

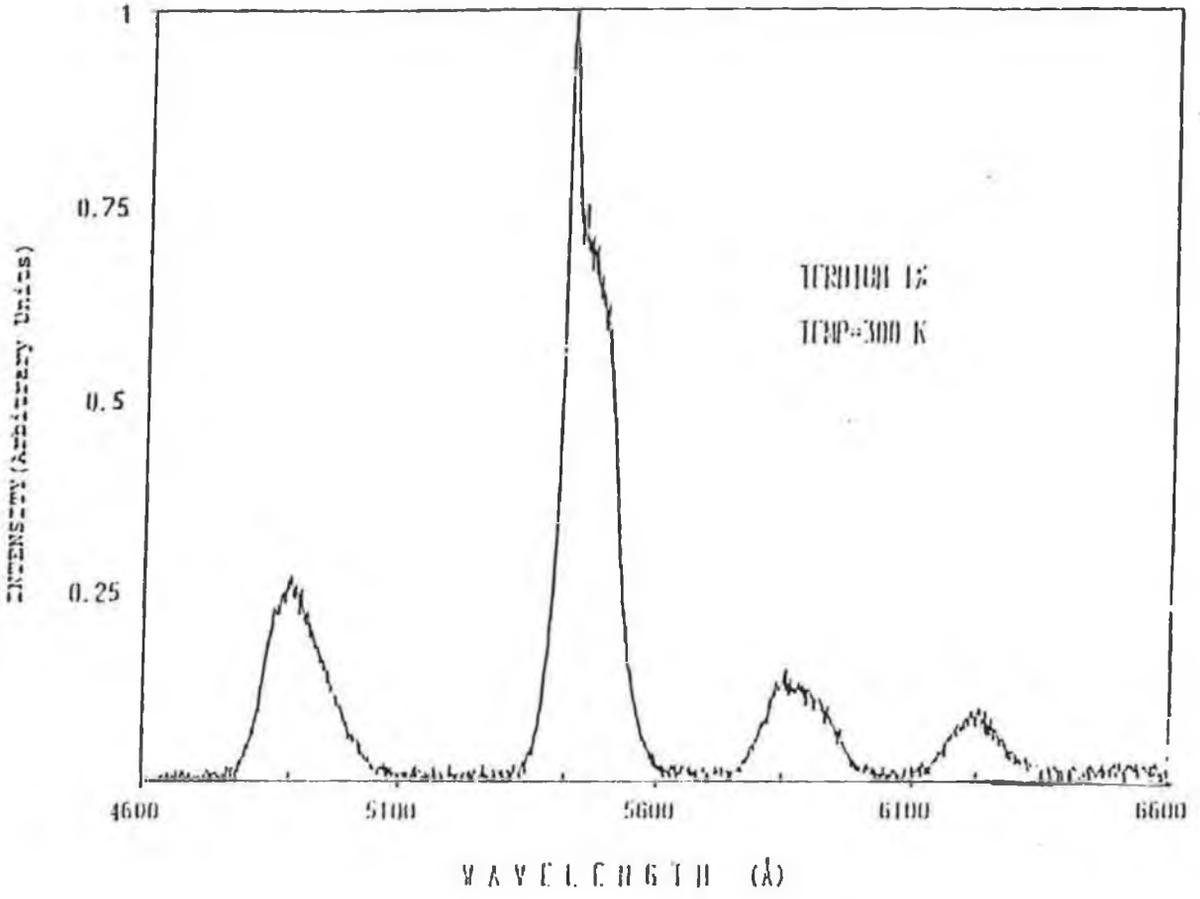
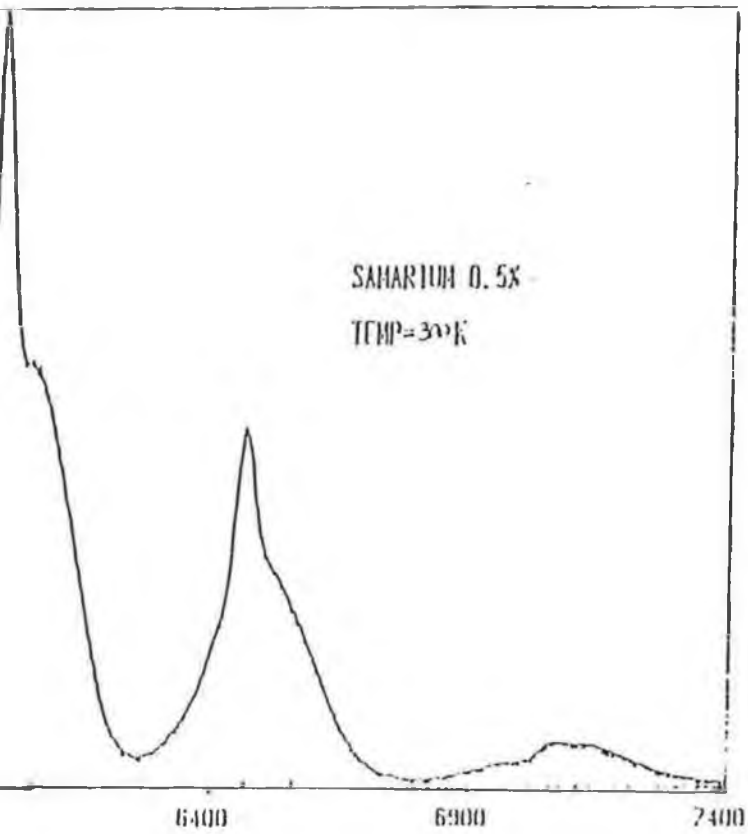


FIG.3.8 LUMINESCENCE SPECTRUM OF TERBIUM(III)

FIG.3.9



LUMINESCENCE SPECTRUM OF SAMARIUM(0.5%)

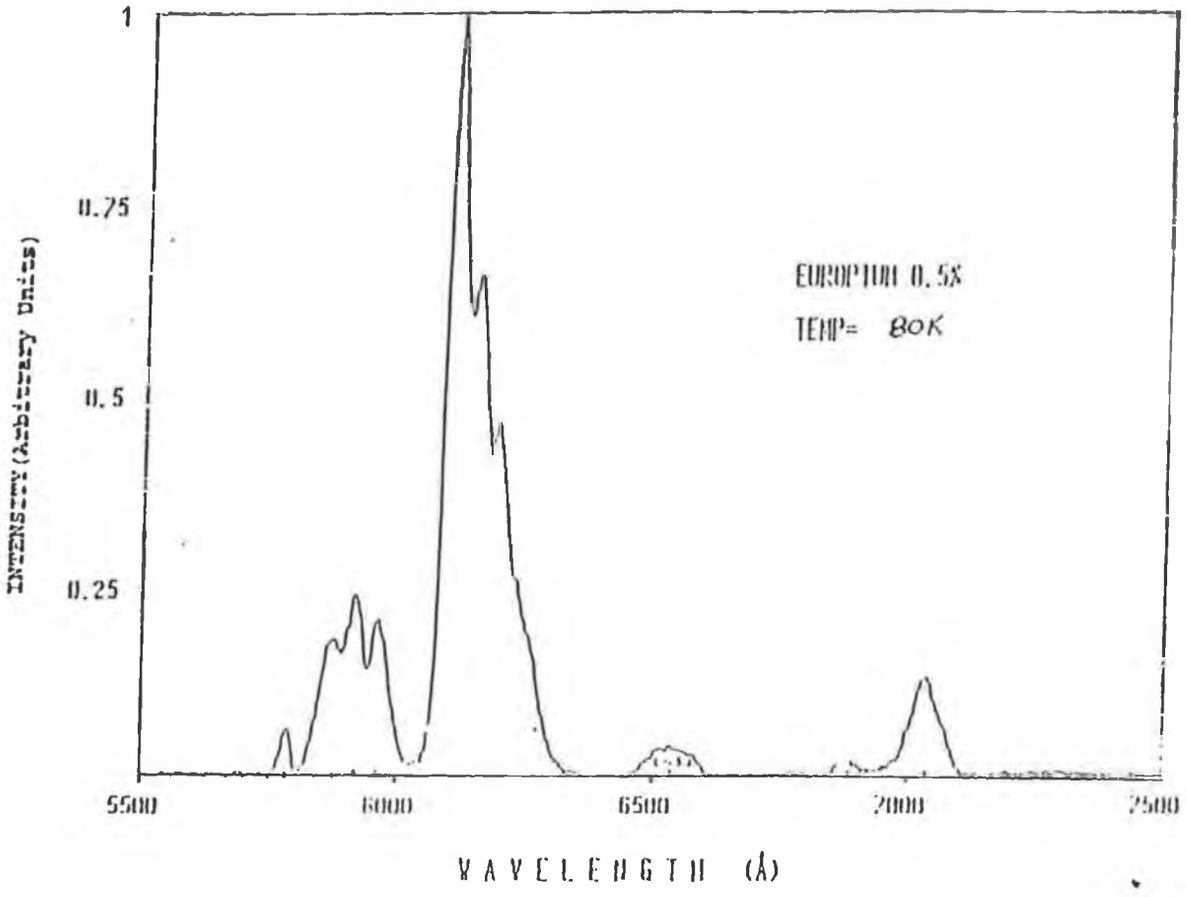


FIG.3.10 LUMINESCENCE SPECTRUM OF EUROPIUM(0.5%)

3.5.Summary of experimental results

Results from the luminescence and absorbance measurements agreed well with the published data for the same dopant ions in glass.There were some slight differences at particular wavelengths but this is to be expected due to differing experimental arrangements, glass compositions and possible oxidation states of the ions. There are variations,in any case,in the luminescence wavelengths of the lanthanides in the published data. Substantial improvements have also taken place in instrumentation since the comparative studies were carried out in the 1960's.The detection of absorption and luminesence at the expected wavelengths in the prepared glasses, demonstrates that the lanthanides were well dispersed throughout the samples and that the glasses were of sufficiently high quality for use in an optical system.

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CHAPTER 4

UV/XUV INVESTIGATION

4.1. Introduction

In order to assess the performance potential of the prepared glasses as UV detectors, comparative response studies were undertaken using established detector systems.The principal comparative material used was the extensively reported UV phosphor sodium salicylate.

4.2.Sodium Salicylate

Sodium salicylate is probably the most widely used phosphor in the detection of UV radiation. Its combination of high fluorescence quantum yield and response to an extremely wide wavelength range makes it a highly suitable detector material. It also has the property that its fluorescent quantum yield is almost independent of wavelength[4.1]. The luminescence of sodium salicylate peaks in the region of 443nm matching the maximum sensitivity region of most commercial photomultiplier tubes. Reported values for the absolute quantum yield of sodium salicylate have been quite variable.These range from a value of 25%(Inokuchi)[4.2] to 99%(Allison et al) [4.3] when measured at a wavelength of 254nm. Samson[4.4] suggests that from a practical point of view a value of 65% for the absolute quantum efficiency of sodium salicylate is a suitable compromise value within the wavelength range 40 - 340nm.

4.3 Equipment

Comparative response measurements in the middle UV region(200-300nm) were carried out using a 1-metre normal incidence monochromator and a single XUV measurement(13 nm) made using a grazing incidence spectrograph. The normal incidence monochromator was manufactured by P.Mc Pherson,Precision Instruments, Acton,Mass.U.S.A. and the grazing incidence spectrograph was supplied by Rank Precision Industries Ltd.(UK).

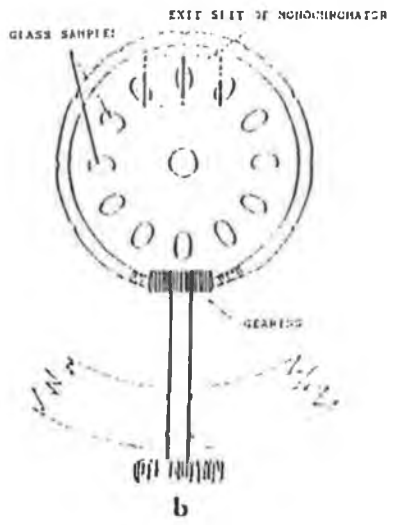
4.4 Experimental

The experimental arrangement used in the middle UV region is shown in Fig.4.1.The monochromator contained a tripartite grating and was equipped with a specially constructed multiple sample holder capable of holding 12 samples.By the use of an external geared arrangement it was possible to present samples in succession to the incident radiation.Fig 4.1(b)

The photomultiplier tube employed was a Thorn EMI tube No.9813B with a response range 300-600nm.The tube contained a bialkali photocathode,borosilicate envelope and beryllium/copper dynodes.

4.4.1. Calibration of monochromator

The diffraction grating was centrally aligned using a 5mW ruby laser at the inlet slit and adjustment of the



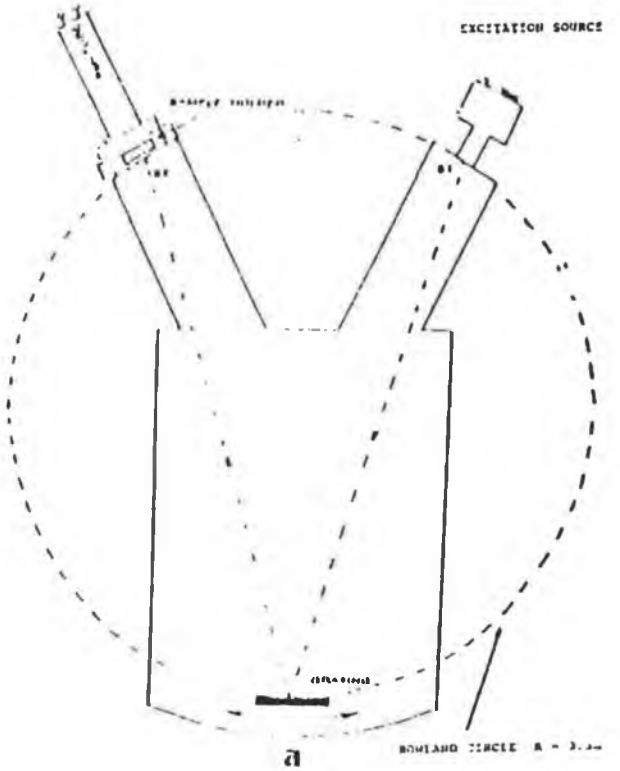


FIG.4.1. (a) NORMAL INCIDENCE MONOCHROMATOR

(b) SAMPLE HOLDER

FIG.4.1. NORMAL INCIDENCE MONOCHROMATOR

grating housing screws.The calibration was carried out using the 546nm line produced from a high pressure mercury lamp.The exit housing of the monochromator was removed and the green 546nm line focussed on to a screen placed in the position normally occupied by the exit slit.The instrument reading was adjusted to this line,the exit housing replaced,and checks on three other mercury lines made by running the instrument back and forward across the wavelength range of these lines.The instrument reading giving maximum response was noted using a chart recorder and these were compared with known mercury wavelengths[4.5].The readings are tabulated in Table 4.1.

Table 4.1 Calibration of monochromator

Mercury Lines(nm)	Instrument Readings(nm)			
	1st	2nd	3rd	4th
546.0	546.0	546.1	546.1	547.8
435.8	435.8	435.8	434.7	436.9
405.6	405.5	404.5	402.7	405.6
366.3	364.4	364.7	363.3	365.3

The mercury lines appeared at the position of the exit slit at a slight angle to the vertical.This may have

been due to the entrance slit not being quite parallel to the grating grooves. It was not possible to correct this difficulty completely by rotation of the grating due to the presence of a metal lug at the top of the grating housing.

Higher order mercury lines appeared on the inside wall of the monochromator casing and may have resulted in some scattered light entering the photomultiplier tube.

4.4.2 Experimental procedure (200-300nm region)

The glass samples under examination were cut and ground to fit the sample holder and the pieces fixed to the holder using double sided tape between the specimen spaces. Coatings of sodium salicylate of various thicknesses were prepared by dissolving the phosphor in methanol and spraying onto glass slides.A section of the plastic scintillator (NE 102)was also used for comparative purposes. The photomultiplier response represents any radiation entering the tube within its detection range.The radiation detected should consist of luminescence only or possibly small amounts of scattered light reflected from the internal walls of the monochromator. Radiation from the excitation source should not be detected as this was in all cases(except

possibly at 300nm) below the response range of the tube. It was also decided to determine as far as possible the effect of sample thickness on the luminescence response by preparing specimens of various thicknesses from one sample (Terbium 5% borate). The initial results obtained are shown in Table 4.2.

Table 4.2 Comparative Responses - Initial Results

Sample No.	Doped ion	Glass Type	Conc %	PM (mv)
1	Terbium	Borate	1	34
2	Praseodymium	Borate	0.7	35
3	Samarium	Borate	1	39
4	Neody/Praes.	Borate	0.5/0.5	30
5	Chromium	Borate	0.5	33
6	Ytterbium	Borate	0.5	5
7	Sod.Salic.			39
8	Erbium	Borate	0.5	27
9	Chromium	Silicate	0.1	39
10	Samarium	Silicate	2	48
11	Sc.Plastic			38
12	Terbium	Silicate	2	31

4.4.2.1 Deuterium Lamp

The initial results indicated that the 254nm line of the mercury lamp employed was probably very weak - this is not uncommon in the case of high pressure mercury lamps. It was decided to replace it with a high brightness Deuterium lamp with an output in the range 160nm-400nm peaking at 190nm.

Table 4.3 Relative response(mV) of sodium salicylate with variation in coating thickness

Coating Thickness mg/cm	Wavelength(nm) 200	210	220	230	240	250	260	270	280	290	300
	mV										
0.7	87	214	284	300	302	292	263	218	188	138	109
2.2	103	253	311	333	330	309	274	233	188	152	119
5.4	90	216	265	280	282	266	238	204	167	136	107
11.3	80	189	210	214	206	183	151	122	99	78	57

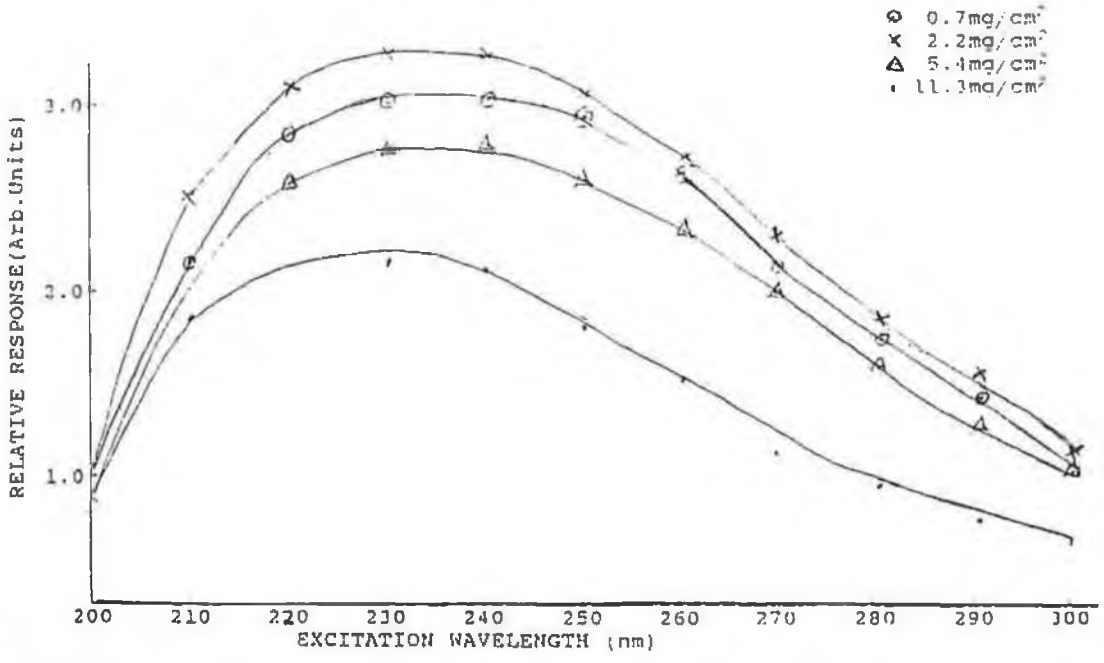


Fig.4.2 RELATIVE RESPONSE OF VARIOUS THICKNESSES OF SODIUM SALICYLATE

4.4.2.2 Response of sodium salicylate

A series of coated glass samples of sodium salicylate were prepared - the thickness of coating ranging from 0.7 - 11.4 mg/cm^2. The response details obtained for these using the normal incidence monochromator are given in Table 4.3 and Fig.4.2.

4.4.2.3 Sample arrangement and measurements

The prepared series of coated samples of sodium salicylate of various concentrations (0.7-11mg/cm^2) were mounted into the sample holder and these were used as reference samples in all measurements.Each of these samples together with the doped glasses were presented four times to the incident radiation. Results were obtained by presenting the samples successively in four revolutions of the sample holder to the incident radiation and measuring the response. The final result was taken, in all cases, as the mean of the four readings.

4.4.3 Experimental Results

It was decided to ratio the response of the samples to that of sodium salicylate using the term Relative Luminescence Response (RLR) and calculating the ratio according to the formula:-

$$RLR = \frac{\theta_1 - \theta_2}{\theta_3 - \theta_2}$$

where θ_1 = P.M tube sample reading

θ_2 = P.M.tube background reading(no sample)

θ_3 = P.M.tube reading - Sodium Salicylate

The sample of sodium salicylate which gave the maximum response (2.2 mg/cm^2)was taken as representing an RLR value of unity for comparative purposes.

Sample details are listed in Table 4.4 and the calculated Relative Luminescence Response values for all of the samples examined are given in Tables 4.5.

The results for the samples which gave the highest RLR values -Terbium and Erbium- are illustrated graphically in Figs.4.3 and 4.4.

Table 4.4. Sample Details

Sample No.	Doped ion	Matrix	Conc.(%)	Sample Thickness(mm)
1	Cerium (Ce^{4+})(no $SnCl_2$)	Borate	1.0	2.736
2	Cerium (Ce^{4+})(+ 2%$SnCl_2$)	Borate	1.0	3.377
3	Cerium (Ce^{4+})	Borate	5.0	3.205
4	Cerium (Ce^{4+})	Borate	10.0	2.554
5	Praseodymium (Pr^{3+})	Borate	1.0	3.204
6	Praseodymium (Pr^{3+})/	Borate	2.5	2.781
	Neodymium (Nd^{3+})	Borate	2.5	2.537
7	Samarium (Sm^{3+})	Borate	1.0	2.833
8	Samarium (Sm^{3+})	Borate	5.0	2.574
9	Samarium (Sm^{3+})	Silicate	2.0	1.140
10	Europium (Eu^{3+})	Borate	0.5	3.710
11	Europium (Eu^{3+})	Borate	5.0	2.705
12	Europium (Eu^{3+})	Silicate	2.0	1.436
13	Gadolinium (Gd^{3+})	Borate	0.5	3.500
14	Gadolinium (Gd^{3+})	Borate	5.0	2.635
15	Terbium (Tb^{3+}/Tb^{4+})	Borate	1.0	2.935
16	Terbium (Tb^{3+}/Tb^{4+})	Borate	5.0	2.630
17	Terbium (Tb^{3+}/Tb^{4+})	Borate	5.0	1.885
18	Terbium (Tb^{3+}/Tb^{4+})	Borate	5.0	1.357
19	Terbium (Tb^{3+}/Tb^{4+})	Borate	5.0	0.636

20	Terbium (Tb^{3+}/Tb^{4+})	Borate	1.0	0.973
21	Terbium (Tb^{3+}/Tb^{4+})	Silicate	2.0	1.946
22	Dysprosium (Dy^{3+})	Borate	0.5	2.345
23	Dysprosium (Dy^{3+})	Borate	5.0	2.768
24	Holmium (Ho^{3+})	Borate	0.5	2.691
25	Holium (Ho^{3+})	Borate	5.0	2.742
26	Erbium (Er^{3+})	Borate	0.5	2.981
27	Erbium (Er^{3+})	Borate	5.0	2.812
28	Thulium (Tm^{3+})	Borate	0.5	2.770
29	Thulium (Tm^{3+})	Borate	5.0	2.731
30	Ytterbium (Yb^{3+})	Borate	0.5	2.970
31	Ytterbium (Yb^{3+})	Borate	5.0	2.710
32	Blank	Borate	0.0	2.521
33	Blank	Silicate		2.773
34	Plastic Scintillator NE 102	-	0.0	

Table 4.5 Relative Luminescence Response

Sample No.	Wavelength (nm)										
	200	210	220	230	240	250	260	270	280	290	300
2	0.0	0.0	0.03	0.12	0.19	0.24	0.27	0.28	0.30	0.33	0.36
3	0.0	0.0	0.0	0.0	0.0	0.03	0.01	0.0	0.0	0.01	0.0
4	0.0	0.0	0.0	0.0	0.0	0.05	0.02	0.01	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.02	0.02
15	0.18	0.20	0.19	0.11	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16	0.35	0.39	0.42	0.33	0.27	0.13	0.07	0.07	0.02	0.0	0.0
17	0.29	0.37	0.37	0.35	0.29	0.13	0.08	0.07	0.01	0.0	0.0
18	0.31	0.34	0.33	0.29	0.24	0.13	0.07	0.06	0.01	0.0	0.0
19	0.51	0.59	0.61	0.51	0.46	0.34	0.37	0.43	0.35	0.35	0.41
20	0.28	0.32	0.32	0.25	0.10	0.06	0.05	0.05	0.01	0.02	0.0
21	0.10	0.20	0.27	0.31	0.26	0.13	0.05	0.03	0.02	0.01	0.0
23	0.0	0.0	0.0	0.0	0.0	0.02	0.01	0.01	0.01	0.01	0.0
27	0.03	0.14	0.14	0.17	0.24	0.32	0.35	0.38	0.37	0.38	0.41
31	0.0	0.0	0.0	0.0	0.05	0.08	0.04	0.01	0.01	0.02	0.0
32	0.0	0.01	0.01	0.03	0.13	0.13	0.11	0.10	0.10	0.11	0.10

No measurable response was detected from sample nos.1,5,6,7,8,9,10, 11,13,14,22,24,25,26,28,29,30,32,33,34.

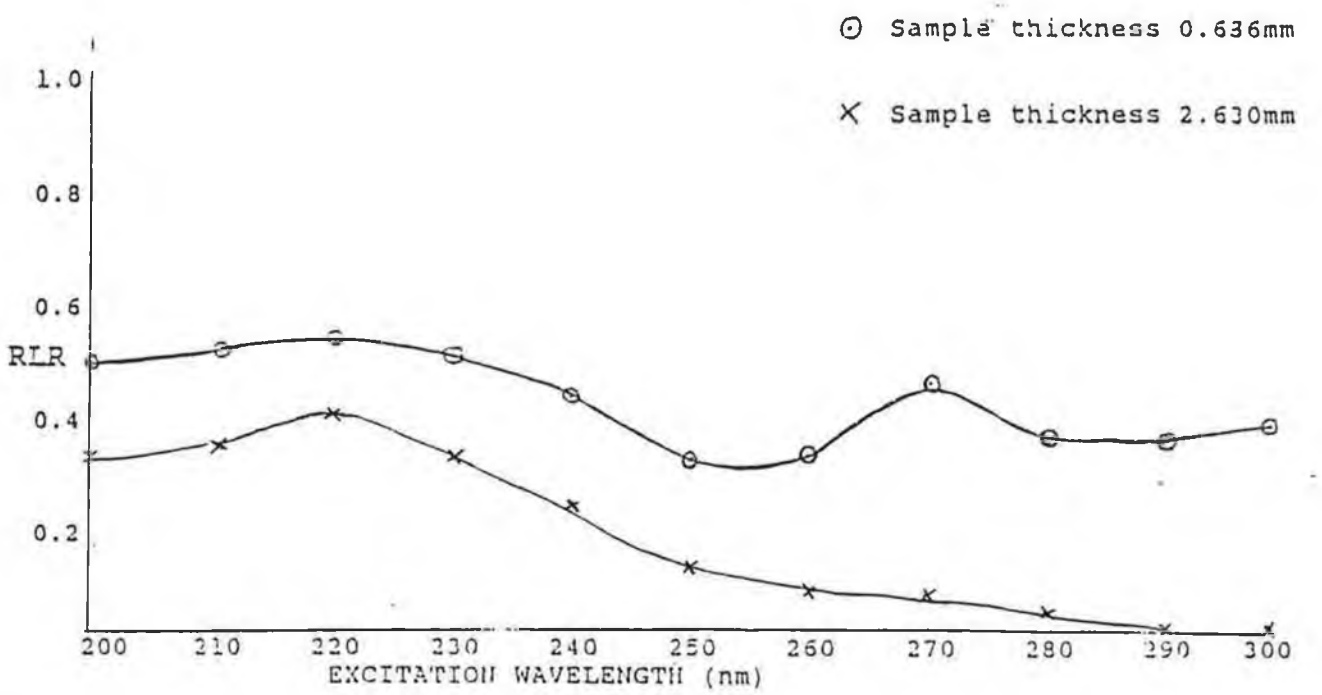


Fig.4.3 RELATIVE LUMINESCENCE OF TERBIUM(5%)

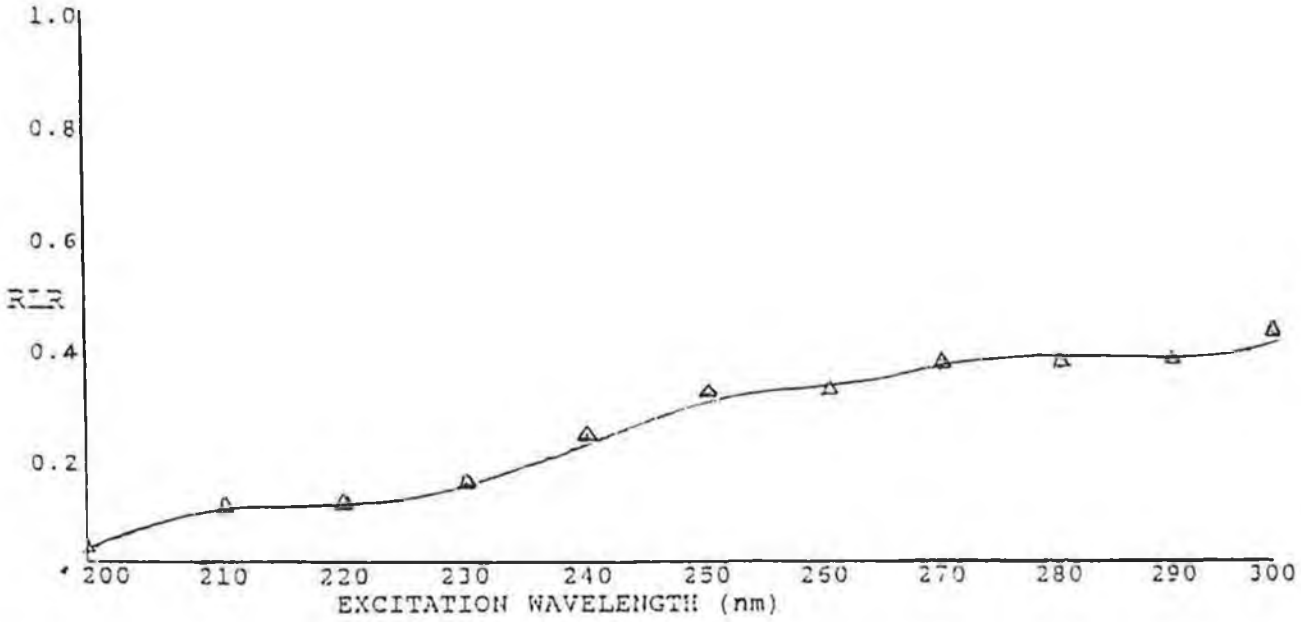


Fig.4.4 RELATIVE LUMINESCENCE OF ERBIUM(5%)

4.4.3.1 Variation of response with thickness

As the doped glass samples varied significantly in thickness a series of specimens from the same sample were prepared to determine the degree of self-absorption of luminescence with increasing sample thickness. Sample preparation was extremely difficult and it was possible only by manual grinding and polishing of the specimens.Retention of the specimen on a lapping wheel using a standard holder was found to be too difficult due to the high speed of the wheels so that a manual operation was the only practical method of sample preparation available.

Silicon carbide paper (600-1200 grit) was used in a wet grinding process and 'Hyprez' diamond paste (6-1um) employed in the polishing phase.

The doped sample Terbium (5% borate) was chosen due to its high luminescence response during the comparative tests.The variation is shown in Table 4.6 and Figs.4.3 and 4.5.

Table 4.7 RLR of various thicknesses of Terbium(5%-borate)

Sample Thickness (mm)	Wavelength (nm)/ RLR									
	200	210	220	230	240	250	260	270	280	290	300
2.630	0.35	0.39	0.42	0.33	0.27	0.13	0.07	0.07	0.02	0.0	0.0
1.885	0.29	0.37	0.37	0.35	0.29	0.13	0.08	0.07	0.01	0.0	0.0
1.357	0.31	0.34	0.33	0.29	0.24	0.13	0.07	0.06	0.01	0.0	0.0
0.636	0.51	0.59	0.61	0.51	0.46	0.34	0.37	0.43	0.35	0.35	0.41

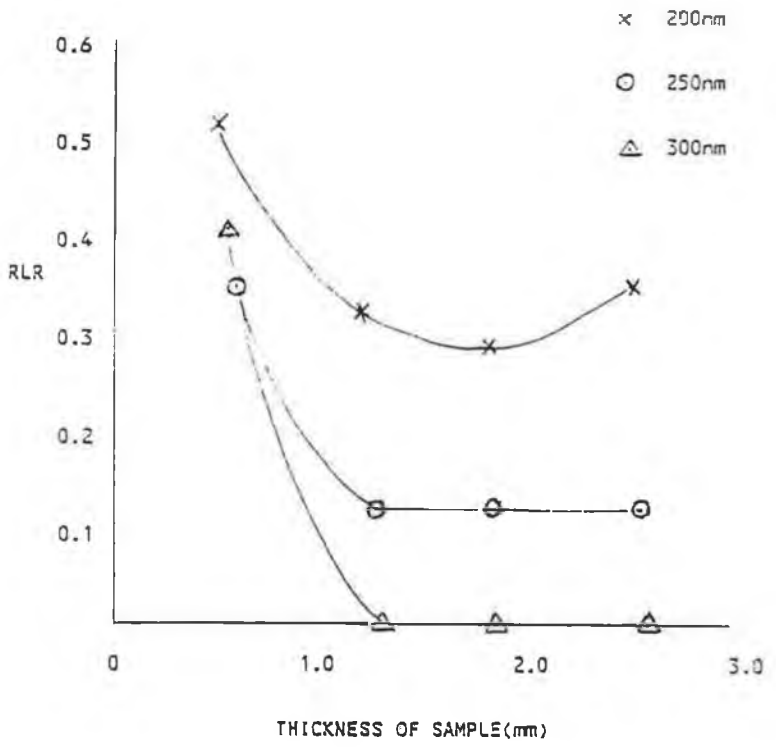


Fig.4.5 VARIATION OF RLR OF TERBIUM(5%) WITH THICKNESS OF SAMPLE

4.4.4 XUV Investigation

The XUV investigation was carried out using a 2m grazing incidence spectrograph Model E580.Ltd. The grating has a radius of curvature of 2m and is used in a Rowland circle mounting. The instrument is designed to cover the wavelength range 0.5nm to 95nm in the first order with a 576 line per mm grating with a blaze angle of 1.6^{0}.The chamber is evacuated using an Edwards Type ES roughing/backing pump together with an oil diffusion pump. The instrument is designed to operate as either a photographic spectrograph or as a photoelectric monochromator.

The excitation source was a plasma produced by focusing the output of a JK ruby laser(1.5J) onto a tungsten target. The wavelength chosen was 13nm with a 1nm bypass.The experimental set-up was as shown in Fig.4.6. The laser excitation triggered the oscilloscope and the response was recorded. The photomultiplier tube was a Hamamatsu type (R1450) with a 350-650nm response range. Comparative responses were measured between a borate glass sample (5% Terbium-0.636mm),TPB(Plastic scintillator),sodium salicylate and NE102.

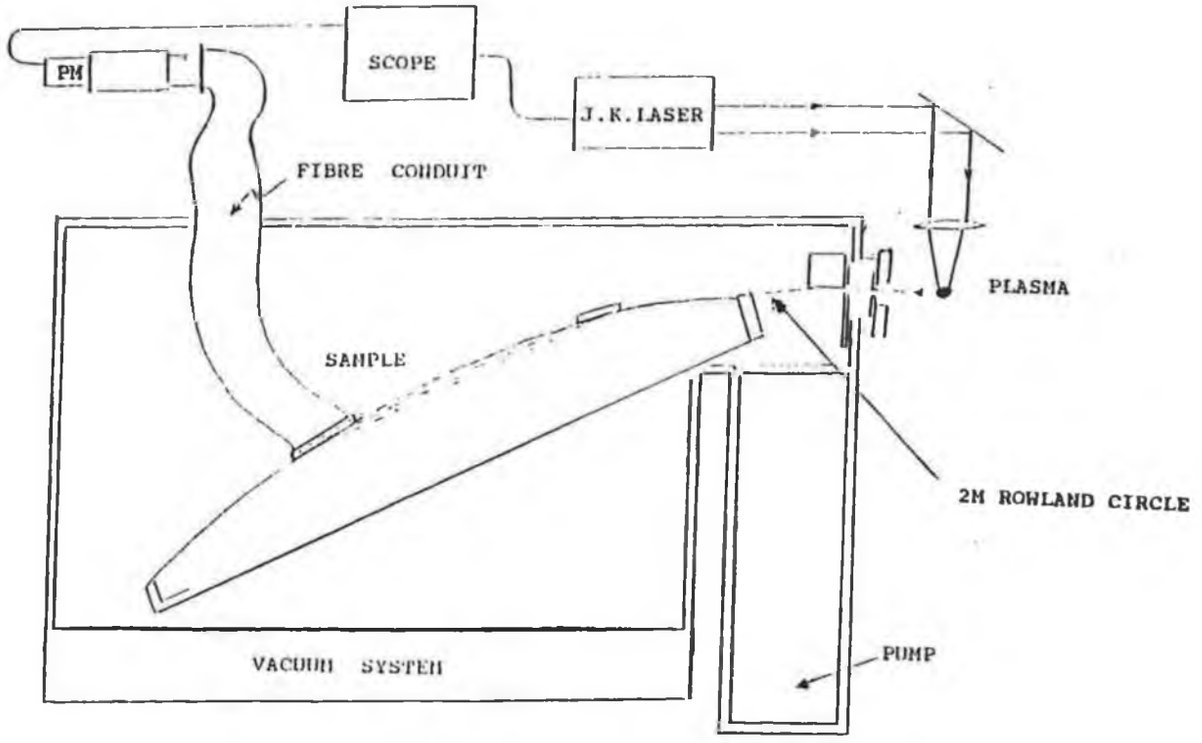


FIG. 4 6 GRAZING INCIDENCE SPECTROGRAPH

4.4.4.1 XUV Results

The noise level due to scattered light from the laser gave a 40mV output from the photomultiplier tube. The response from the TPB, sodium salicylate and NE102 samples were at a level of 600mV. The borate glass sample did not yield a detectable signal above that of the background noise level from the laser.

4.5. Spectroscopic considerations

From the results obtained the three most likely lanthanides which may have potential as UV detectors are Cerium, Terbium and Erbium.The response of the first two elements was predictable to some extent but the results from the Erbium glass was unexpected.It is possible to explain the luminescence behaviour exhibited by these elements from spectroscopic considerations.

CERIUM Cerium differs from all other lanthanides in having only one 4f electron.This single electron can give rise to two energy levels: $^2F_{\frac{7}{2}}$ and $^2F_{\frac{5}{2}}$ .The excitation process is therefore $4f^{n}$ --- $4f^{n-1}5d^{1}$ and emission is from the 5d state. The 5d orbital lies close to the surface of the ion and as such is strongly influenced by variations in the energy environment provided by the disordered crystal field of the glass host.Consequently,the 5d state

is split into many components depending on the site symmetry of the cerium activator.This results in a broad emission band (340-480nm) centred about 350nm. Spowart(1976)[4.1]estimated that the separation of the 4f-5d band was about 25 $\times$ 10^3 cm^{-1}.Thus the 4f electron requires its energy in units of about 3eV for transfer to the excited 5d state. The RLR results for Ce^{3+} show it responding strongly at 300nm.

TERBIUM Tb^{3+} was found by Dieke (1961) to have two luminescence levels, $^5D_3$ and $^5D_4$ when embedded in Terbium chloride.The bands observed for transitions from $^5D_4$ level to the $^7F_6$ multiplet were called Band System I and those from $^5D_3$ to $^7F_6$ Band System II.When irradiated at 253.7nm Dieke and his colleagues found it possible to excite both band systems.The emitted light ranged from 377-653nm - most of the radiation being within the spectral response of photomultiplier tubes.
All of the Terbium-doped samples examined luminesced to some extent when irradiated in the wavelength range 200-300nm.Peak response was obtained with the excitation wavelength at 220nm.The most sensitive response was obtained from the Terbium(5%) sample ground and polished to 0.636nm.(Fig.4.1).This result illustrates the absorption of the luminescence by the glass matrix and

gave an indication of the depth of penetration of the UV radiation in its interaction with the glass.Further work would be required to determine the optimum thickness giving maximum UV response.Samples containing higher Terbium ion concentrations would also be required to determine at what level concentration quenching occurs. There is some evidence in the results for the Terbium ion that the the response is binodal with peaks at 220 and 270nm. The excitation process of the Tb^{3+} ion is almost certainly $4f^8$ -- $4f^7$ $5d^1$ to leave the half-filled 4f orbital as stable $4f^7$.

ERBIUM

Erbium in a glass matrix (as Er^{3+}) is known to lase at liquid nitrogen temperatures, when singly doped, and at room temperature when sensitised with Yb^{3+}. In the first case[4.4] the pulsed threshold is 1100 J in a Li-Mg-Al-silicate glass,and the main absorption bands were found to be at 375nm(30nm wide) and at 520nm(40nm wide). The Yb assisted Er laser[4.5] was found to have a lower threshold - 700J. The transfer of excitation energy takes place from the metastable $^2F_{\frac{5}{2}}$ (Yb^{3+}) level to $^4I_{11/2}$ (Er^{3+}) level.Large quantities of Yb were required(up to 15% Yb_2O_3) in association with 0.25% Er_2O_3. Pumping was achieved through the 900-1000nm absorption band of Yb Under these conditions,the Erbium emission was found to

be five times stronger than that of Yb.

In the present work, the RLR of Erbium(5%) was comparable to that of Terbium(5%). The response was better than Terbium particularly when excited at wavelengths above 240nm for a sample of similar thickness. The response of a co-doped sample of both these ions would be interesting to determine.

Research at the University of Strathclyde has indicated that Erbium has potential as an activator in a tunable laser system. The advantages of using Er^{3+} is that it is efficient, tunable(1.5 μm) produces high gain and has a long fluorescent lifetime. The luminescence of Erbium examined was that which takes place in a three level system cascading from $^4S_{\frac{3}{2}}$ to $^4F_{\frac{9}{2}}$ to $^4I_{\frac{9}{2}}$. Work at the same University is presently examining the use of co-dopants Nd^{3+} and Er^{3+}in a polarised fibre laser system and the potential of an Erbium fibre amplifier for optical fibre telecommunication purposes.

4.6. Conclusions

The RLR method may be regarded as a rapid technique to 'screen' the potential of the Lanthanide ions as possible UV detectors, rather than an absolute method of measuring their luminescence output.The results from Table 4.5 pointed towards Cerium(Ce^{3+}) Terbium(Tb^{3+}) and Erbium(Er^{3+}) as possibly having UV detection potential and worthy of

further study.The emergence of Ce^{3+} and Tb^{3+} as possible dopants for UV detection is not surprising as these two ions luminesce strongly within the spectral response region of the photomultiplier tube employed in the experimental arrangement.However, the response of Er^{3+} was surprising as this ion is reported to luminesce only weakly within the spectral region examined. The Samarium and Europium ions luminesce strongly in the visible region but these samples did not yield a detectable RLR possibly due to the absence of absorption bands in the 200-300nm region.

The XUV investigation showed no detectable response in the case of 5% Terbium (borate matrix) at a wavelength of about 13nm indicating possible self-absorption of any Auger emission due to the depth of sample used(0.636mm).

References Chapter 4

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CHAPTER 5

OVERVIEW OF PROJECT

5.1 Discussion of experimental results

After the initial difficulties with furnace and crucibles were overcome a series of 31 Lanthanide-doped glasses were prepared.A lithium borate matrix of new composition was used in the fabrication process.Three silicate glasses containing lanthanide ions were also prepared using a well established commercial composition.

The prepared samples have been shown to exhibit the expected characteristics of glass and using absorption and luminescence spectra to be of good optical quality.It would be desirable to have further processed the glasses to achieve samples of equal thickness but highly specialised grinding and polishing equipment would be required to produce such specimens.

The comparative response study (200-300nm)using a normal incidence monochromator gave some indication as to the performance potential of the doped glasses as UV detectors. Luminescence responses to excitation in the UV of up to 60% of those obtained using sodium salicylate were obtained with particular ions. The work using the grazing incidence spectrograph explored the possibility of using the glasses as VUV/XUV detectors. However,no response was obtained to XUV

excitation, although only one doped sample was examined at one wavelength.These results point towards the necessity of using thin glass films or CVD coatings in order to possibly obtain results comparable to tetraphenyl-butadiene(TPB) or sodium salicylate.

5.2 Theoretical Considerations

5.2.1 General

The absorption of UV radiation by a material is electronic in nature and is concerned with the occurrence of processes with energies in excess of 3eV.Two types of electronic transition are possible; (a) promotion from a localised orbital on one ion to a higher energy level - 'exciton' (b) promotion to the conduction band. If the excitation transfers the electrons to an orbital lying wholly or partly on another atomic species then the observed absorption is referred to as a 'charge transfer' process.
In the case of excitation into a conduction band,the absorption coefficient rises with decreasing photon wavelength to a plateau value while transitions to a localised level result in a normal optical band with a well defined maximum value.In either case the transitions are of an allowed nature and absorption coefficients are therefore extremely high.

For most glasses such as the ones described in this thesis the conduction band lies at very high energies and the UV absorption is due primarily to exciton transitions.For oxide glasses these are considered to consist mainly of transitions on the same oxygen ion(particularly non-bridging types).In glasses containing heavier element cations e.g.germanate glasses the conduction band lies at lower energies and may overlap the exciton levels with the result that such glasses have absorption edges near the visible and are photoconducting.In the case of chalcogenide glasses the conduction band falls at such low energy levels that absorption occurs in the visible and even infrared regions and always involve promotion to conduction bands. Due to the high values of absorption coefficients in UV processes sample thicknesses in the submicron range are necessary if complete absorption bands are to be determined by transmission techniques.Such samples are usually unattainable without the use of highly specialised equipment and the majority of UV studies on glassy systems have therefore been limited to the measurement of an absorption edge.This is not a well defined quantity and has been arbitrarily taken as the wavelength where transmittance in a given sample thickness could just be measured,usually at a level of about 0.5%.

5.2.2 Energy Transfer

As far as it can be determined the first documented instance[5.2] of lanthanide to lanthanide energy transfer in a solid was the case of Gd - Sm in a matrix of SrS reported by Tomaschek in 1924.Additional evidence of 4f ion -ion interactions was put forward in 1949 by Pringsheim[5.3] and Botden and Kroger[5.3].However,major studies were not carried out until Van Uitert initiated his work in 1960 [5.4]. Interest has always has remained high since then because of the numerous applications of energy transfer to various technologies.

According to Imbusch(1978)[5.5] the host material itself may absorb radiation(usually in the UV) and the energy transferred non-radiatively to dopant ions. The example quoted is $YVO_4:Eu^{3+}$ the vanadate group of the host material absorbing UV light,then transferring its energy to the Eu^{3+} ions,which subsequently emit characteristic Eu^{3+} luminescence.It was envisaged that this type of mechanism might also operate in the case of lanthanide doped glasses.

The UV absorption edges of blank borate and silicate glasses described in this work were found to be 250nm and 290nm respectively.Most rare earth oxides have UV cut-offs > 5eV(248nm) although Europium and Terbium are exceptional in having cut-offs at 295nm and 275nm respectively. There

is no clear evidence from the results obtained that energy transfer was involved in the luminescence of the lanthanides in the glass matrix employed. It would have been more satisfactory to have examined more samples in the XUV region but this is a further research project.

5.3 Development of the project

It would be desirable to extend the study in the XUV/VUV region to cover all of the prepared samples using both an evacuated normal incidence and grazing incidence spectrograph. It would also be useful to carry out a study of the Lanthanide ions in the divalent state - possibly using the stannous chloride reduction technique.

In order to explore the possibility of energy transfer further it would be interesting to prepare chalcogenide glasses containing the ions used in this work. This would produce glasses with absorption edges at much longer wavelengths than those described in this work.

Work could also continue on glass thin films using the lanthanides Terbium, Cerium and Erbium. The ideal method of preparation is probably chemical vapour deposition(CVD) as described by Wong(1978) [2.3]. Vitreous thin films formed by vapour deposition are well established and have played an important role in the planar technology of fabricating microelectronic devices and circuits.These are also used in xerographic,memory and threshold switching

devices. The technology to produce these vitreous films is available and it would be interesting to explore the property correlations between thin film silicates and silicate glass as a bulk material.A better understanding of the structure of the glassy state might result.,
The response of the ions Terbium and Erbium in the near UV may also be of interest as possible ions to be considered in the development of inorganic luminescent solar collectors (LSCs).[5.6]
In general,the study of the lanthanides has been confined to crystalline matrices with some work on particular ions in glassy hosts. The environment of these ions in a vitreous matrix is still uncertain.There has also been little work on the behaviour of these ions in the VUV or XUV regions and this could be a rewarding area of research.
The spectroscopy of the lanthanides in glass is of immense importance. These can be employed as spectroscopic probes in elucidating glass structure but more importantly because a number of the lanthanide ions lend themselves to lasing action. Glass lasers are of major current interest as prospective fusion-promoting energy sources.

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APPENDIX A

APPENDIX A

Reduction of Cerium(4+) with stannous chloride

Introduction Cerium oxide is usually only available commercially in the Ce^{4+} form. However,due to the overlap of the absorbance and luminescence bands in Cerium(4+), more efficient luminescence has been found to occur when the ion Ce(3+) is used.(A.1). Normally the technique is to reduce the higher oxide state at elevated temperatures in a tube furnace using a gas such as carbon monoxide. This is a difficult operation requiring a tightly sealed furnace chamber and an exhaust outlet. If the Ce^{3+} form could be produced in a glass matrix by the incorporation of a reducing agent in the batch materials this would provide a much more convenient method of producing the desired oxidation state.

Stannous chloride was chosen because of its strong reducing properties and as far as is known it has no deleterious effects on the luminescence of Ce^{3+} .

Sample Preparation A series of borate glass samples were prepared using various quantities of stannous chloride and a fixed amount(1%) of Ce^{4+} in oxide form. The glasses were prepared in the manner described in Chapter 2.

Absorption Spectra The absorption spectra of the glasses were obtained using a Perkin Elmer UV spectrophotometer Model 8452A.The absorption spectra (Figs.A.1.-A.2) of the two glasses did reveal differences indicating that part or all of the Ce^{4+} ions may have been reduced. The peaks shown in Table A.1 are in broad agreement with those found by Spowart[A.1] for Ce(3+) in the absorption spectrum of $LiYF_4$ crystal doped with 1% Ce^{3+}. Spowart [A.2] also refers to an absorption peak at 326nm for Ce^{3+} in lithium aluminosilicate glasses.

Table A.1 Absorption Bands of Cerium-doped glasses

Cerium with $SnCl_2 2H_2O$ nm	Cerium without $SnCl_2 2H_2O$ nm	Spowart ref.[3.36] CeriumIII nm
190	195	190-200
215	band absent	205-210
240-250	band absent	240-250
295- 310	band absent	295

The absorption spectra are interesting in that the addition of stannous chloride appears to have had at

least some reducing effect on the oxidation state of the Cerium +4 ion. The absorbance peaks for the reduced species are in good agreement with those found by Spowart[A.1] Further work would be required to determine if all of the Ce^{4+} ions were converted to the lower state and to assess the optimum level of stannous chloride required.

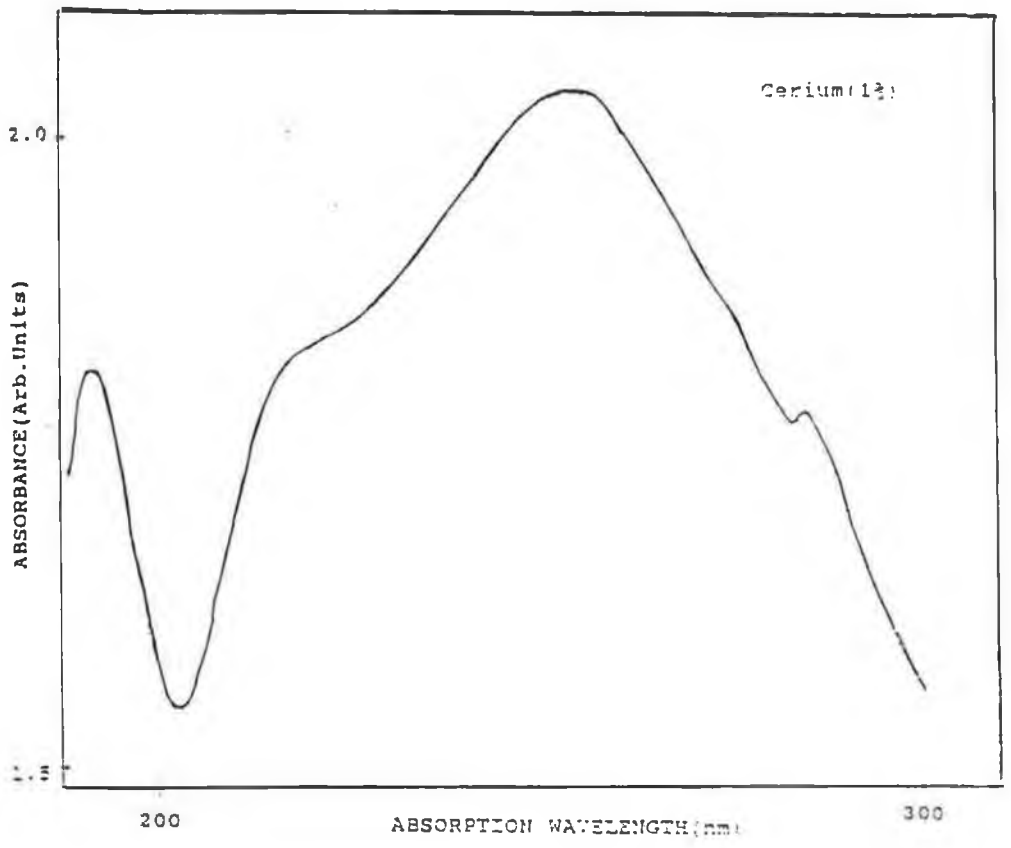

FIG.A1. ABSORPTION SPECTRUM OF Ce^{4+} alone

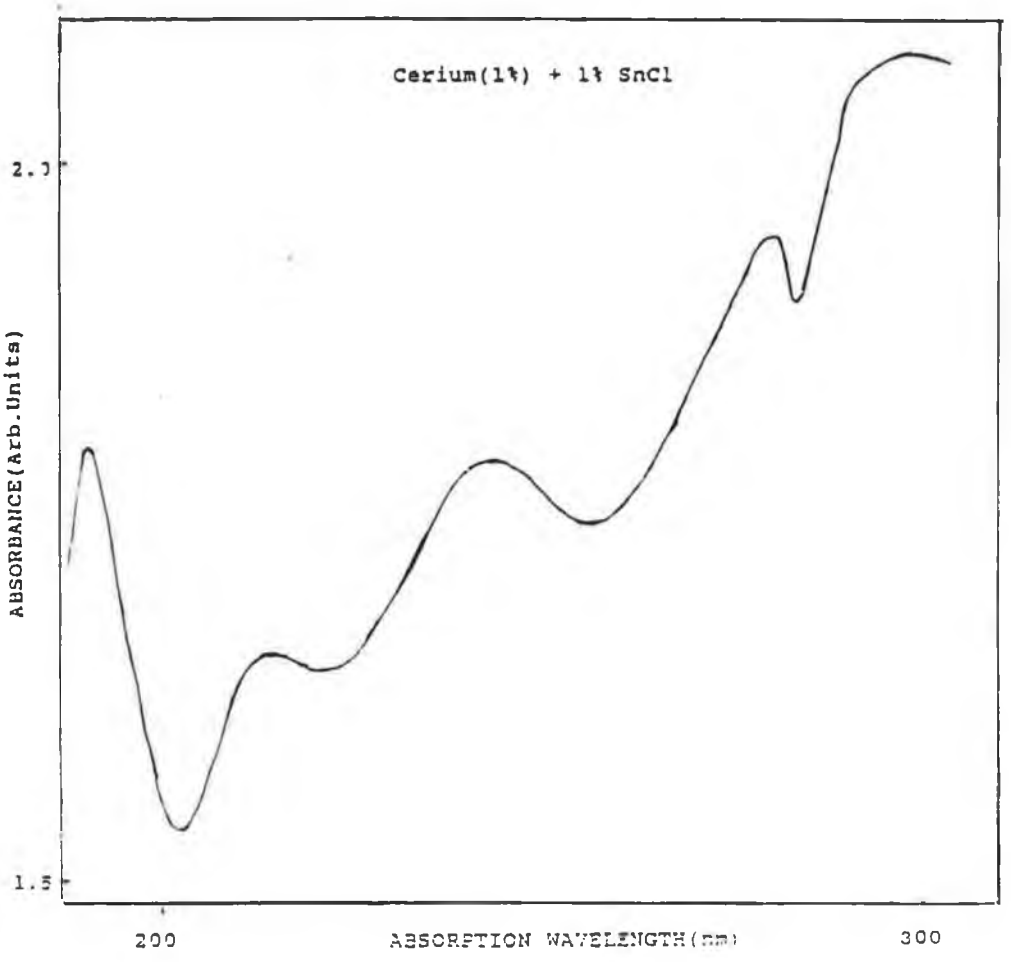

Fig.A2 ABSORPTION SPECTRUM OF Ce^{4+} with $SnCl_2.2H_2O$

References Appendix A

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