

Development of GeO₂ and LaF₃ based glass ceramics

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor in technology

In

Ceramic Engineering

BY

Amit Kumar Biswal

Under the guidance of

Prof. Sumit Kumar Pal



Department of Ceramic Engineering

National Institute of Technology, Rourkela

2011



**NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA**

2011

CERTIFICATE

This is to certify that the thesis entitled, “Development of GeO₂ and LaF₃ based glass ceramic” submitted by **Mr. Amit Kumar Biswal (Roll No. 107CR010)** in partial fulfillment of requirements of the award of Bachelor in Technology in Ceramic Engineering in National Institute of Technology, Rourkela is a bonafide work carried out by him under my supervision and guidance.

To the best of my knowledge the work reported does not form part of any other thesis or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

DATE- 11/05/2011

Prof. Sumit Kumar Pal
Dept. Of Ceramic Engineering
National Institute of Technology
ROURKELA 769008

ACKNOWLEDGEMENT

With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude to Prof. Sumit Kumar Pal, Department of Ceramic Engineering, N. I. T. Rourkela, for introducing this research topic and for his guidance, constructive criticism and valuable suggestions throughout this research work. It would have not been possible for me to complete this project report without his help and constant encouragement. I wish that, he will keep in touch with me in future and will continue to give his valuable advices.

I extend my whole hearted thanks to Prof. J. BERA, Head of Department, for his cooperation. I am also thankful to Prof. Santanu Bhattacharyya, Prof. S. K. Pratihari, Prof.R.Mazumdar, Prof.B.B.Nayak, Prof.R .Sarkar, Prof.D.Sarkar & Prof.A.Choudry for their valuable suggestions and encouragements at various stages of the work.

I also want to have a grateful regards towards Mr.P.K.Mohanty for his assistance and efforts towards my project in helping me for my project lab.

My deep sense of gratitude to M.Tech and PhD scholars, Ganesh bhai, Geeta didi, Abhisek bhai, Bhabani bhai and others who had extended their helping hand for completion of my project.

I want to thank all my branch mates for their constant supports and motivations.

Finally thank and appreciation to every one else, involved in this project at National Institute of Technology, Rourkela.

12th May, 2011

Amit Kumar Biswal

Contents

	Page no.
Abstract	6
Chapter 1 INTRODUCTION	7
Chapter 2 LITERATURE REVIEW	8
2.1 Rare earth doped optical glass	8
2.2 Key factors of upconversion	10
2.3 Conclusion	14
Chapter 3 OBJECTIVE OF THE PROJECT	17
Chapter 4 EXPERIMENTAL WORK	18
4.1 Batch preparation	18
4.2 Glass melting	20
4.3 Heat treatment	21
4.4 Characterization	21
4.4.1 Thermal characterization	21
4.4.2 X-ray Diffraction	22
Chapter 5 RESULTS AND DISCUSSIONS	23
5.1 Thermal analysis	23
5.1.1 Differential scanning calorimetric (DSC)	23
5.1.2 Thermo gravimetric analysis (TGA)	25
5.2 Phase analysis: Characterization by XRD	26
Chapter 6 CONCLUSION	42

List of figures	Page no.
Figure 2.1 <i>Simplified energy-level diagram of Er³⁺ ions and The possible upconversion mechanisms</i>	14
Figure 2.2 <i>Possible energy transfer mechanism of Er³⁺/Yb³⁺</i>	15
Figure 5.1(a) <i>DSC curve for glass sample with no ErF₃ addition</i>	25
Figure 5.1(b) <i>DSC curve for glass sample with 0.5% ErF₃ addition</i>	25
Figure 5.1(c) <i>TG curve for 0% EF</i>	26
Figure 5.1(d) <i>TG curve with 0.5% EF</i>	27
Figure 5.2 (a) <i>XRD of 44.5GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-0.5ErF₃</i>	28
Figure 5.2(b) <i>XRD of 44GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-1ErF₃</i>	29
Figure 5.2(c) <i>XRD of 44GeO₂-20Na₂O-10ZnF₂-25LaF₃-1ErF₃</i>	30
Figure 5.2(d) <i>XRD of 44.5GeO₂-20Na₂O-10ZnO-25LaF₃-0.5ErF₃</i>	32
Figure 5.2(e) <i>XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 600⁰C</i>	35
Figure 5.2(f) <i>XRD of 64.5GeO₂-15Na₂O-5ZnO-15ErF₃-0.5ErF₃ heated upto 700°C</i>	36
Figure 5.2(g) <i>XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 550°C, holding period-1hr</i>	37
Figure 5.2(h) <i>XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated at 550°C, holding period- 4hr</i>	39
Figure 5.2(i) <i>XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 650°C, holding period-4hr</i>	40

List of tables

Table 5.2(a) ----- Peak list of XRD of 44.5GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-0.5ErF₃

Table 5.2(b) ----- Peak list of XRD of 44GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-1ErF₃

Table 5.2(c) ----- Peak list of XRD of 44GeO₂-20Na₂O-10ZnF₂-25LaF₃-1ErF₃

Table 5.2(d) ----- Peak list of XRD of 44.5GeO₂-20Na₂O-10ZnO-25LaF₃-0.5ErF₃

Table 5.2(e) ----- Peak list of XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃
heated upto 600^oC

Table 5.2(f) ----- Peak list of XRD of 64.5GeO₂-15Na₂O-5ZnO-15ErF₃-0.5ErF₃
heated upto 700^oC

Table 5.2(g) ----- Peak list of XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃
heated upto 550^oC, holding period-1hr

Table 5.2(h) ----- Peak list of XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃
heated at 550^oC, holding period- 4hr

Table 5.2(i) ----- Peak list of XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃
heated upto 650^oC, holding period-4hr

Abstract

In this project, glass of composition 45GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃ was prepared. Optimization of fraction and size of LaF₃ crystal was done by heat-treating the glassy matrix with fixed minimum amount of Er in the glassy matrix to maintain transparency of glass. The effect of heat treatment on solubility of rare earth ions in fluoride nano crystals will be examined. Based on this Er concentration will be optimized. To observe the effect of rare earth on crystallization, glass samples were examined under DSC to find the crystallization temperature. Phase identification was done by XRD analysis.

Chapter 1

Introduction

Rare earth doped oxy-fluoride transparent nano- glass ceramics find applications in numerous photonic devices including up conversion lasers, color display, sensors and optical data storage. These glass ceramics are more appropriate for such kind of applications due to their low phonon energies in comparison to oxide glasses also excellent mechanical strength, thermal stability and chemical durability in comparison to fluoride glasses. Long highly efficient up-conversion luminescence of rare earth ions had already been obtained in PbF₂ and CdF₂ nano-crystals. However, since Pb and Cd are toxic substances, the demand for alternative materials are increasing. LaF₃ can be taken as alternative material for PbF₂ and CdF₂. Therefore, the effect of rare earth doping into LaF₃ nano-crystals in oxide glass matrix are of scientific and technical interest.

In this proposed work, GeO₂ glass matrix is taken as host matrix for development of LaF₃ nano-crystals.

Chapter 2

Literature review

2.1 Rare earth Doped Optical Glasses

Glasses doped with rare earth ions are getting interest for their application in several photonic applications, such as fiber amplifiers, upconversion lasers and three-dimensional optical devices. For these practical importances, the glassy host should possess a minimal absorption coefficient within the wavelength region of interest, and it should have capability of incorporating rare earth ions, low vibration energy, transparency and high refractive index.

Advantages of the conventional glass and glass ceramic processing:

1. Glasses can be synthesized in various shape and size without any limitation by melt quenching methods. Costly instruments are not required for the fabrication of glassy materials.
2. For practical purposes, oxide glasses have an advantage over fluoride glasses due to their mechanical strength, thermal stability and chemical durability.
3. It is well known that glass crystallization is one of the effective methods for fabrication of nanostructures.

Disadvantages of oxide glasses:

1. Due to rare earth clustering tendency, maximum doping level is limited.
2. Large phonon energy of oxide glass increases the non-radiative decay, which reduces the luminescence efficiency.

On the other hand, fluoride glasses are having following advantages

1. Fluoride materials offer a low phonon environment, which is favorable to enhance radiative rate and quantum efficiency.
2. Fluoride single crystals are able to produce narrow fluorescence line widths and enhanced emission cross section relative to glasses.
3. Fluoride nano crystals are preferred over oxide one to avoid non radiative transitions.[1]
4. The solubility of rare earth ions is larger in fluoride medium than in oxides.[2]

However, stability and fiberizability of fluoride glasses remain problematic. Hence, they are unsuitable for practical use. In addition, fluoride crystals have maximum size limitations.

The invention of rare earth doped oxyfluoride glass ceramics with fluoride nano crystals have got greater attention due to their excellent optical properties like fluoride crystals and good mechanical, thermal and chemical properties like oxide glasses. The advantages of these materials are that the rare earth ions remain incorporated selectively inside the fluoride crystals after heat treatment and the glass ceramics remain transparent due to smaller size of precipitated crystals than wavelength of visible light.

2.2 Key factors towards the enhancement of upconversion

The incorporation of rare-earth ions into fluoride crystalline environment with large energy band gap and low phonon energy is essential for the enhancement of up-conversion fluorescence properties of oxyfluoride glass ceramics. Not only the rare earth ions concentration, but also the thermal treatment conditions, and the microstructure of glass ceramics affect the up-conversion fluorescence of the material.

Judd-Ofelt theory explains that, the enhancement of up conversion is related to the decrease in intensity parameter Ω_2 [3,4] Ω_2 is sensitive to the environment present around the rare-earth ions, and the value of Ω_2 decreases with change of the environment from a covalent oxide bond to a predominantly ionic bond with the fluorides [5]. The volume fraction of crystals and crystallinity of rare earth ions in glass ceramic increases with increase in temperature. Hence more amount of rare earth ions are located at a more symmetrical site, which decreases the value of Ω_2 . With the increase in heating temperature and the holding period, there is significant increase in the intensities of near infrared and up-conversion emissions. Since more fraction of rare-earth ions are incorporated into the precipitated fluoride nano-crystals having lower phonon energy. The upconversion luminescence of rare earth ions is usually regulated by the multiphonon relaxation. The energy gap between two successive levels and the phonon energy of the host control the multiphonon relaxation. [6]. The lesser is the phonon energy of the host; the lower is the multiphonon relaxation probability.

. The environment of host and its modification, as well as the concentration and distribution of the rare-earth ions in the crystalline and noncrystalline part of the host matrix affect the emission parameters like intensity, efficiency, cross section, line width, and lifetime. These parameters play an important role for selection of the rare earth doped luminescent materials.

Among the oxide glasses germanium glasses possess an unique combination of low glass transition temperature (T_g) as well as a lower phonon energy (850 cm⁻¹)[7]The above property coupled with high mechanical strength, high chemical durability, and temperature stability with good transmission in the infrared region. This glass system is a promising material for technological applications such as new lasing materials, up-converting phosphorus, and optical waveguides. Due to low phonon energy this germanium is expected to be less affected from phonon quenching which is very useful for efficient upconversion [8] Apart from this, germanium also have high refractive index (~1.7) which could result in a larger radiative transition rates of rare-earth ions.

Among the fluorides, LaF₃ and BaF₂ are ideal hosts for rare earth ions since they have extensive solid solution capability with all rare earth ions. LaF₃ has lower phonon energy 350 cm⁻¹ [9] and the maximum phonon energy in BaF₂ is 346 cm⁻¹[10].

The effect of Er doping in BaF₂ and LaF₃ containing oxyfluoride glass ceramic are well established. Qiao *et. al.*[10] reported the upconversion luminescence intensity of Er³⁺ in the BaF₂ containing silicate glass ceramics increased significantly with increasing annealing time. They observed emission bands around 520 nm, 540 nm and 651 nm which can be assigned to $^2H_{11/2} \rightarrow 4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions respectively. Hu *et. al* [11] observed similar emission in Er³⁺ doped BaF₂ containing oxyfluoride glass ceramics. In these systems the possible upconversion luminescence mechanisms of the Er³⁺ ions can be described by: (a) excited state absorption (sequential two-photon absorption) (ESA), and (b) energy transfer (ET) upconversion processes. Tanabe *et. al*[12] reported that with the increasing annealing temperature and time, the fluorescence intensity at 540 nm and around 1000 nm in Er doped LaF₃ containing oxyfluoride glass ceramics increase and the lifetime of the $^4S_{3/2}$ level became longer. Due to the similar ionic

radius and the same valence as La³⁺, Er³⁺ ion is one of the most useful rare earth dopants. It can be utilized for the upconversion lasers of visible green emission. Therefore, the spectroscopic properties of Er doped oxyfluoride transparent glass ceramic have drawn a great attention.

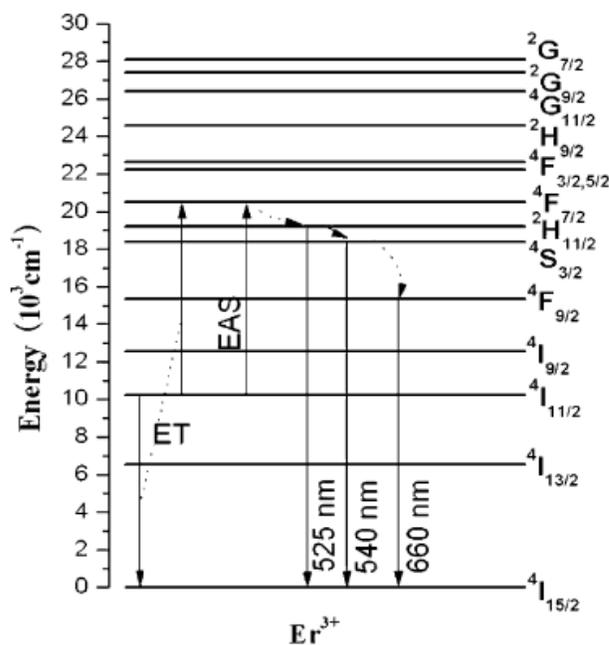


Fig2.1. Simplified energy-level diagram of Er³⁺ ions and the possible upconversion mechanisms.

Another method to obtain efficient upconversion from Er containing glass ceramics emission is by co-doping with Yb³⁺ ions [13]. Sun *et al* [14], reported up-conversion fluorescence property under 975 nm excitation in Er³⁺/Yb³⁺ codoped oxyfluoride bismuth–germanium glass. They observed that the intense green and weak red emissions centered at 525, 546, and 657 nm, corresponds to the transitions ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, respectively, at room temperature. A. Biswas *et al* [15] reported efficient upconversion emissions at 379, 407, 450, 490, 520, 540 and 660 nm 973 nm excitation in the transparent 0.1ErF₃–0.1YbF₃–5LaF₃–94.8SiO₂ (mole%) glass-ceramics. The results indicate that this sample is a very good infrared-

to-ultraviolet upconverter. Qiao *et al* [16] reported intense upconversion luminescence and the corresponding stark-split peaks in BaF₂ containing silicate based glass ceramic, where Er³⁺ and Yb³⁺ had been incorporated with BaF₂ nanocrystals. The NIR luminescence decay curves indicate that the Er³⁺ and Yb³⁺ co-doped glass ceramic have higher luminescence efficiency than the precursor glass. Chen *et al* [18] also reported comparable upconversion emission for oxyfluoride glass ceramic containing CaF₂ nano-crystals codoped with Er³⁺/Yb³⁺. The possible energy transfer mechanism of Er³⁺/Yb³⁺ is shown in Fig.2.2

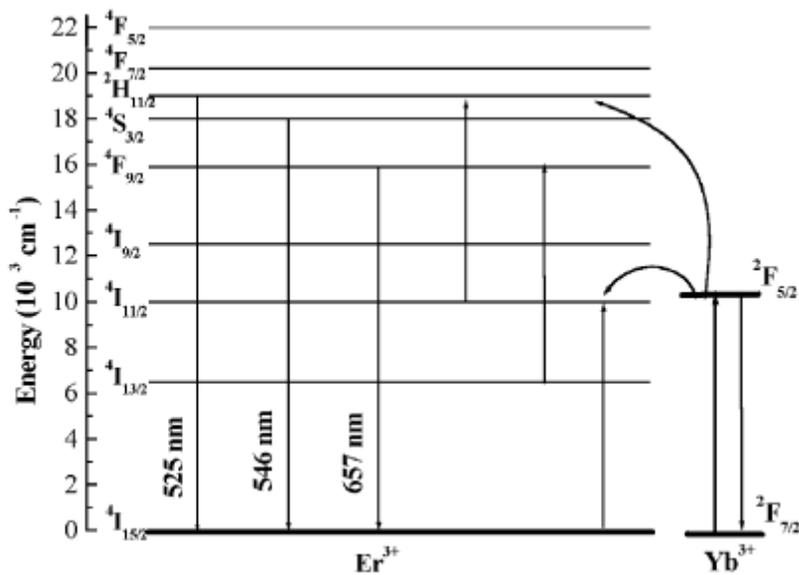


Fig 2.2 Possible energy transfer mechanism for Er³⁺/Yb³⁺

2.3 It can be concluded that

1. Germanium glass could be a good host materials for rare earths due to its low phonon energy compared to silicate glass and good mechanical strength
2. There is no significant report on germanate glass ceramic containing BaF₂ and LaF₃ nanocrystals. These crystals have very low phonon energy. Enhanced upconversion luminescent properties for Er and Er/Yb rare earths are already reported for these crystals
3. Er and Er/Yb show different emissions which make them suitable for different optoelectronic application which depend on heat treatment.
4. Luminescent property can be enhanced by thermal treatment and composition control, which requires no special equipment.

So the development of BaF₂ and LaF₃ containing transparent nano glass ceramic based on germanium and doping with Er and Er/Yb are of immense scientific and technological interest.

2.4 Reference

1. Daqin Chen, Yuansheng Wang, Yunlong Yu, *Journal of Solid State Chemistry* 179 (2006) 1445.
2. M. Mortier, F. Auzel, *J. Non-Cryst. Solids* 256–257 (1999) 361
3. B.R. Judd, *Phys. Rev.* 127 (1962) 750
4. G.S. Ofelt, *J. Chem. Phys.* 37 (1962) 511
5. M. Bettinelli, A. Speghini, M. Ferrari, M. Montagna, *J. Non-Cryst Solids* 201 (1996) 211
6. R. Reisfeld, L. Boehm, Y. Eckstein, N. Lieblich, *J. Lumin.* 10 (1975) 193
7. Z. Pan, S.H. Morgan, *Journal of Luminescence* 75 (1997) 301
8. Giorgio Turri, Vikas Sudesh, Martin Richardson, Michael Bass, Alessandra Toncelli, and Mauro Tonelli *J. Appl. Phys.* 103, (2008) 093104
9. Matthew J. Dejneka, *Journal of Non-Crystalline Solids* 239 (1998) 149
10. Xvsheng Qiao, Xianping Fan and Minquan Wang, *Scripta Materialia* 55 (2006) 211
11. Zhongjian Hu, Yuansheng Wang, En Ma, Daqin Chen, Feng Bao, *Materials Chemistry and Physics* 101 (2007) 234
12. Setsuhisa Tanabe, Hideaki Hayashi, Teiichi Hanada, Noriaki Onodera, *Optical Materials* 19 (2002) 343
13. C. Strohhofer, A. Polman, *J. Appl. Phys.* 90 (2001) 4314
14. Hongtao Sun, Chunlei Yu, Zhongchao Duan, Lei Wen, Junjie Zhang, Lili Hu, Shixun Dai, *Optical Materials* 28 (2006) 448
15. A. Biswas, G.S. Maciel, C.S. Friend, P.N. Prasad, *Journal of Non-Crystalline Solids* 316 (2003) 393
16. Xvsheng Qiao, Xianping Fan, Minquan Wang, Xianghua Zhang, *Journal of Non-Crystalline Solids* 354 (2008) 3273–3277

17. Daqin Chen, Yuansheng Wang, En Ma, Yunlong Yu, Feng Liu, *Optical Materials* 29 (2007) 1693
18. A.S. Gouveia-Neto, E.B. da Costa, L.A. Buenob, S.J.L. Ribeiro, *Journal of Alloys and Compounds* 375 (2004) 224
19. M. Mortier, P. Goldner, C. Chateau, M. Genotelle, *Journal of Alloys and Compounds* 323–324 (2001) 245
20. F.C. Guinhos, P.C. Nobrega, P.A. Santa-Cruz, *Journal of Alloys and Compounds* 323–324 (2001) 358
21. Chao Liu, Jong Heo, *Materials Letters* 61 (2007) 3751
22. A.S. Gouveia-Neto, E.B. da Costa, L.A. Bueno, S.J.L. Ribeiro, *J. Lumin.* 110 (2004) 79.
23. Jianrong Qiu, G. Lakshminarayana, Hucheng Yang, *Journal of Solid State Chemistry* 182 (2009) 669
24. Jianrong Qiu and G. Lakshminarayana *Physica B* (2009), doi:10.1016/j.physb.2008.11.083
25. Paolo Ghigna, Corrado Tomasi, Adolfo Speghini, Marco Bettinelli, and Marco Scavini *J. Appd. Phys* 105, (2009) 023519
26. Guanshi Qin, Weiping Qin, Changfeng Wu, Dan Zhao, Jisen Zhang, Shaozhe Lu, Shihua Huang, Wu Xu *Journal of Non-Crystalline Solids* 347 (2004) 52
27. Kaushal Kumar and S. B. Rai; *Solid State Communications*, 58 (2007) 142

Chapter 3

Objective of the project

- 1) Development of rare earth doped LaF₃ based glass and glass ceramic.
- 2) Optimization of fraction and size of LaF₃ nano crystals by heat treatment in GeO₂ glass matrix with fixed minimum amount of Er to maintain transparency in glass ceramic.
- 3) The effect of heat treatment on solubility of rare earth ions in fluoride nano crystals will be examined. Based on this Er concentration will be optimized.

Chapter 4

Experimental work

4.1 Batch preparation

For the development of GeO₂-LaF₃ based glass ceramic, we took the following glass composition as parent glass composition.



We doped various amount of ErF₃ to the parent glass composition to study the effect of its addition. ErF₃ doped various batch compositions are given in tables.

Table 4.1 (batch 10g)

Compound	Mole%	Weight (g)
GeO ₂	44.5	4.011
Na ₂ O	10	0.53
NaF	10	0.36
ZnF ₂	10	0.885
LaF ₃	25	4.19
ErF ₃	0.5	0.019

Table 4.2 (batch 10g)

Compound	Mole%	Weight(g)
GeO ₂	44	3.90
Na ₂ O	10	0.53
NaF	10	0.36
ZnF ₂	10	0.885
LaF ₃	25	4.19
ErF ₃	1	0.19

Table 4.3(batch 10g)

Compound	Mole%	Weight (g)
GeO ₂	44	3.84
Na ₂ O	20	1.0
ZnF ₂	10	0.885
LaF ₃	25	4.18
ErF ₃	1	0.19

Table 4.4 (batch 10g)

Compound	Mole%	Weight(g)
GeO ₂	44	3.96
Na ₂ O	20	1.05
ZnO	10	0.68
LaF ₃	25	4.16
ErF ₃	0.5	0.094

The batch was prepared by using high purity GeO₂ (99.99%), BaF₂ (99.99%), ErF₃ (99.99%), Na₂CO₃ (anhydrous), ZnF₂ (99.99%), high purity ZnO. All these raw materials were weighed to prepare 10 g of batch of each composition. Precautions were taken to avoid the contact of batch with moisture. The batch was finely ground before melting to avoid inhomogeneity.

4.2 Glass Melting

Glass samples were prepared by normal glass quenching method. After preparation of the batch, each batch was taken in clean platinum crucible. The platinum crucible was cleaned by washing it with concentrated HNO₃. Then, the sample system with platinum crucible was put inside the raising hearth furnace. The sample with the platinum crucible was covered with a platinum lid to avoid contact of moisture and loss of fluorine from the system during glass melting. Each batch was heated up to 1450° C and was soaked for 90 minutes. Then the molten glass was quenched by pouring it onto a brass plate. All the glasses were annealed at 400-600°C for 2hour to remove the thermal strain in the glass.

4.3 Heat Treatment

The DSC-TGA curve gave us the idea about the glass transition temperature (T_g) and crystallization temperature (T_c). However, since the glass sample was heated at greater heating rate and under the nitrogen atmosphere during DSC/TGA, the samples were heat treated at relatively lesser temperature & at slower heating rate (1°C/min) in tube furnace. The sample were heated at 550°C , 550°C , 600°C , 650°C , 700°C , 800°C for range of soaking hours from 1hr to 5 hr.

4.4 Characterization

4.4.1 Thermal Characterization

Differential Scanning Calorimeter (DSC) shows thermal transformation behavior of the sample. When the sample undergoes any transformation, it either absorbs energy (endothermic) or releases it (exothermic).

Similarly, Thermo Gravimetric Analysis (TGA) is the study of mass change of a sample as a function of temperature. This technique is useful for transformation involving absorption or release of gases from a sample containing condensed phase.

Hence, in our experiment thermal decomposition of the preferred glass samples were studied by using Differential Scanning Calorimetric and Thermo Gravimetric (DSC-TG). During DSC-TG analysis, the sample was heated upto 800°C at 10°C/min under nitrogen atmosphere to identify the crystallization temperature of the sample.

4.4.2 X-Ray Diffraction

Since we require development of nano sized crystals inside glass matrix, the phase identification of those crystals were done by X-ray diffraction analysis of glass samples. This was done by Philips' X-ray diffractometer with Nickel filtered Cu K α radiation (1.5406Å). The diffraction was done at angle 10-60° with scanning speed 0.025°/sec.

Chapter 5

Results and discussion

5.1 Thermal analysis: DSC/TGA curves

5.1.1 Differential Scanning Calorimetric (DSC)

DSC of original glass samples with 0% ErF₃ & 0.5% ErF₃ was done to obtain the crystallization temperature of the sample. While DSC was done at 10K/min upto 800⁰C, the heat treatment of the glass was done at 1-2⁰ K/min hence, due to high heating rate of DSC the crystallization temperature obtained was more than the actual temperature of crystallization as predicted by Kissinger equation, which is

$$\ln(T_c^2 / \phi) = E/R T_c + K$$

Where K is constant, T_c is crystallization temperature, φ is heating rate, E is enthalpy

Figure 5.1(a) DSC curve of 0% EF

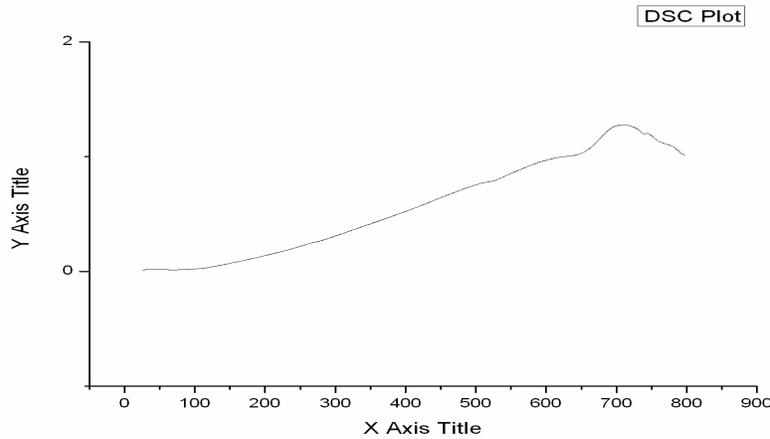


Fig 5.1(a) shows DSC curve for glass sample with no ErF₃ addition. The curve shows one exothermic around $650 \pm 20^{\circ}\text{C}$ which is crystallization temperature of this sample.

Figure 5.1(b) DSC curve of 0.5% EF

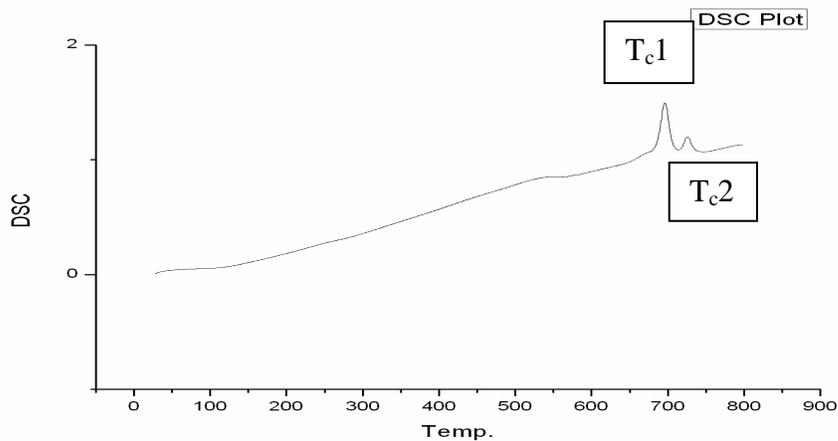
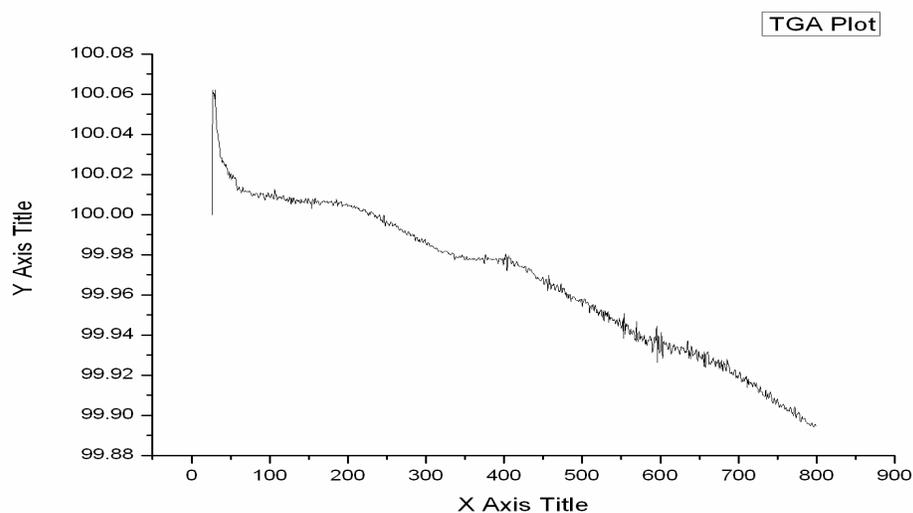


Fig 5.1(b) shows DSC curve for glass sample with 0.5% ErF₃ addition. The curve shows one exothermic around $690 \pm 10^{\circ}\text{C}$ which is crystallization temperature of this sample

DSC curves showed one exothermic peak in both samples. Crystallization temperature thus obtained was around $650 \pm 20^{\circ}\text{C}$ for 0% ErF₃ & $690 \pm 10^{\circ}\text{C}$ for 0.5% ErF₃. Hence, with the help of this DSC data, heat treatment of the glass sample was scheduled at 550-800⁰C temperature for different soaking periods. However, fig 5.2(b) shows two exothermic peaks T_{c1} and T_{c2}. The first peak explains crystallization of LaF₃ and another peak may explain the crystallization of glass matrix. Moreover, the figures showed that crystallization temperature increased with dopant concentration.

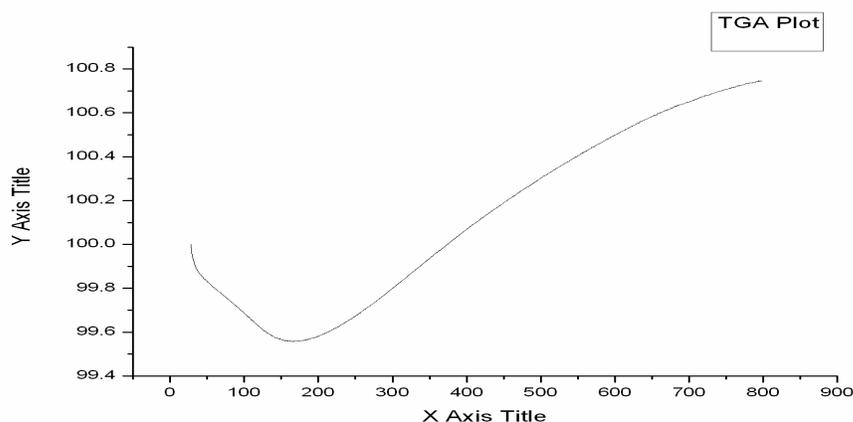
5.1.2 Thermo-Gravimetric Analysis (TGA)

Figure 5.1(c) TG curve for 0% EF



TG curve obtained at 800⁰C and 10⁰C/min shows the decrease in mass of the sample. This decrease in mass explains that, the sample undergoes thermal decomposition with increase in temperature.

Figure 5.1(d) TG curve with 0.5% EF



This TG curve showed positive mass change i.e. mass of the sample increased with temperature.

No relevant reasoning or explanation was found for this behavior.

5.2 Phase analysis: Characterization by XRD

5.2.1 Glass composition

45GeO₂-10 Na₂CO₃ - 10NaF-10ZnF₂ - 25LaF₃ (mole %)

To this composition 0.5mole% and 1mole% of ErF₃ was added the obtained glass was heated for different temperatures at 1-2°C/ min and heat treated samples were subjected to XRD analysis for phase identification.

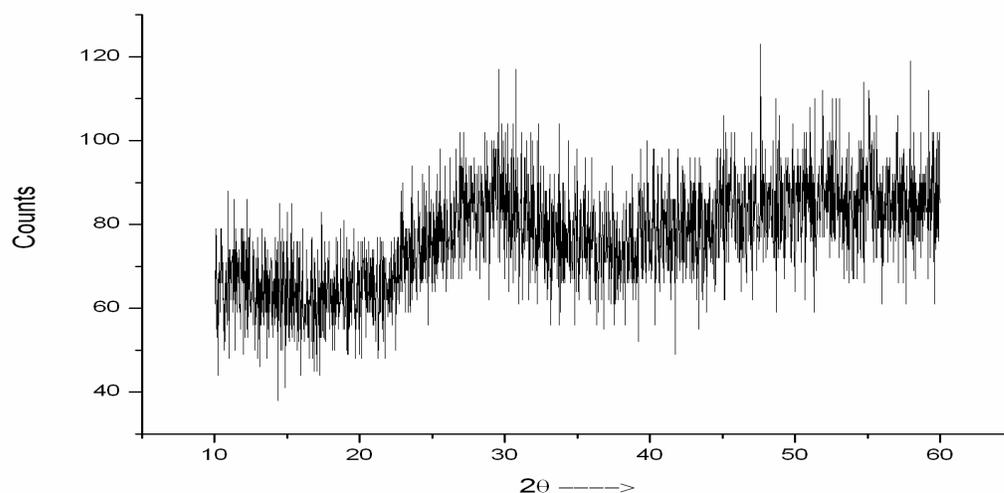


Fig 5.2(a) XRD of glass-ceramic sample of composition 44.5GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-0.5ErF₃

Heat treatment at - 600°C and 2°C/min

Scanning rate – 0.025°/sec

Soaking period-1hour

Table 5.2(a)

Peak no.	2θ	d-spacing	Phase	Reff-code
1	36.5864	2.45615	Unidentified peaks	NA
2	47.6154	1.90825	Unidentified peaks	NA
3	55.1330	1.66451	Unidentified peaks	NA

In this case, although we got a transparent glass ceramic sample but we did not get LaF₃ crystalline phase and the peaks were not identified. Hence, it could be concluded that fluorine being the volatile element may be evaporated from glass matrix.

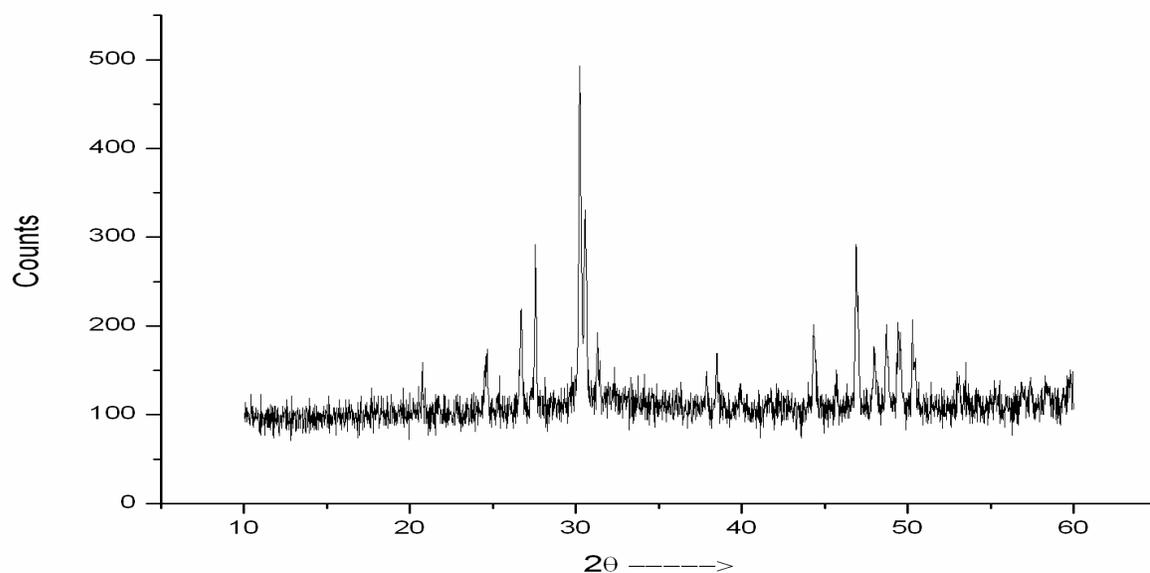


Fig 5.2(b) XRD of glass-ceramic sample of composition 44GeO₂-10Na₂O-10NaF-10ZnF₂-25LaF₃-1ErF₃

Table 5.2(b)

Peak no.	2θ	d-spacing	Relative intensity	Phase	Reff-code
1	24.6177	3.61	16.33	ZnF ₂	72-2104
2	26.6835	3.34	31.01	LaOF	17-0280
3	27.5640	3.23	52.86	LaF ₃	82-0684
4	30.2315	2.95	100	ZnF ₂	72-2104
5	37.8830	2.37	10.88	LaF ₃	82-0684
6	38.4761	2.33	16.11	ZnF ₂	72-2104
7	44.3438	2.04	26.78	LaOF	17-0280
8	50.2844	1.81	28.88	LaF ₃	82-0684

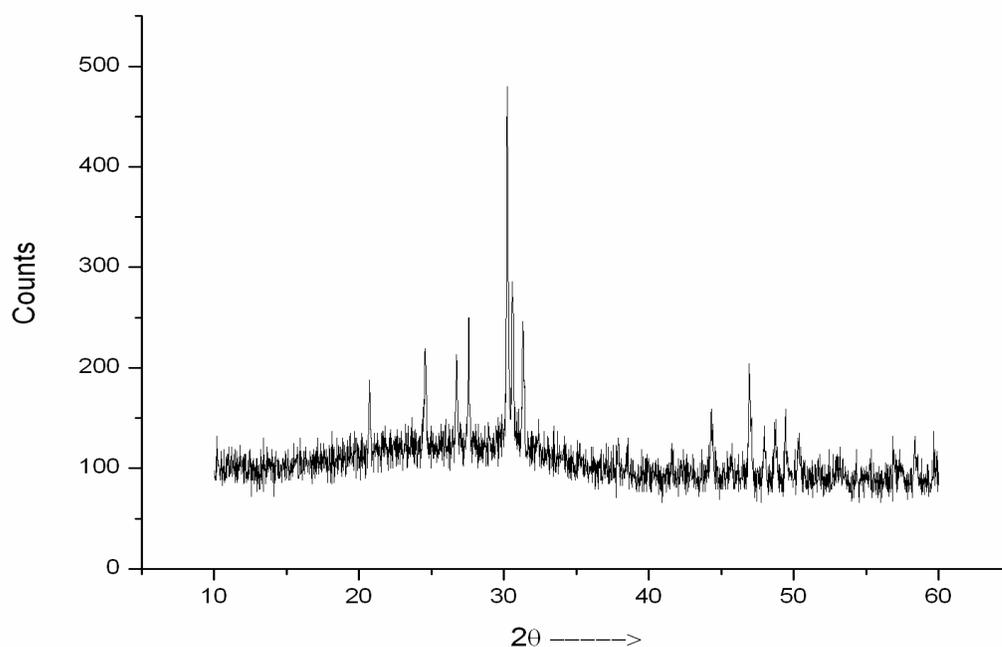


Fig 5.2(c) XRD of sample of composition 44GeO₂-20Na₂O-10ZnF₂-25LaF₃-1ErF₃

Table 5.2(c)

Peak no.	2θ	d-spacing	Relative intensity	Phase	Reff-code
1	24.58	3.62	23.70	ZnF ₂	72-2104
2	26.74	3.33	24.22	GeO ₂	83-0547
3	27.56	3.23	36.45	LaF ₃	82-0684
4	30.23	2.95	100.00	ZnF ₂	72-2104
5	37.89	2.37	5.97	LaF ₃	82-0684
6	46.92	1.93	26.95	GeO ₂	83-0547
7	49.41	1.84	15.51	LaF ₃	82-0684
8	50.36	1.81	10.24	ZnF ₂	72-2104

In case of Fig 5.2(b), we increased the amount of ErF₃ from 0.5mol% to 1mol% and in case of fig 5.2(c) we used NH₄F instead of NaF as the source of fluorine. Ammonia being volatile will escape and it will not change the composition. In both the cases, we got ZnF₂ as the major phase and trace amount of LaF₃ crystals but the glass sample lacked transparency without being heat-treated. Hence, it was concluded that, glass lost its transparency due to the presence of greater amount of fluorine in the glass sample which act as a good crystalizing agent hence crystallization was favored.

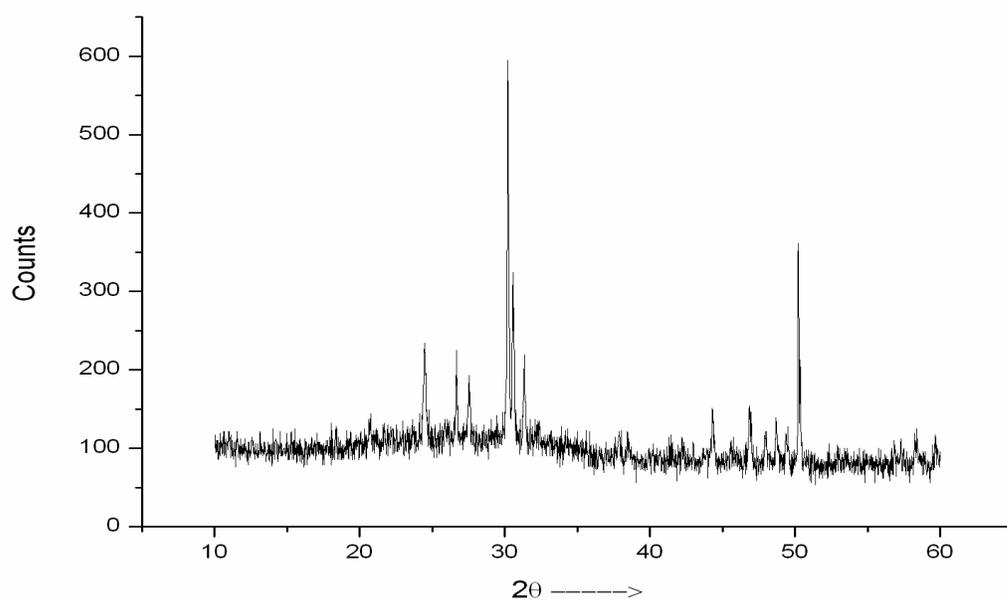


Fig 5.2(d) XRD of sample 44.5GeO₂-20Na₂O-10ZnO-25LaF₃-0.5LaF₃

Table 5.2(d)

Peak no.	2θ	d-spacing	Relative intensity	Phase	Reff-code
1	24.4889	3.635	25.40	ZnF ₂	72-2104
2	26.6642	3.343	22.98	GeO ₂	83-0546
3	27.5414	3.238	14.36	LaF ₃	82-0684
4	30.2087	2.958	100.00	ZnF ₂	72-2104
5	38.4811	2.339	5.08	ZnF ₂	72-2104
6	50.2294	1.8148	58.36	LaF ₃	82-0684
7	58.3358	1.580	5.58	GeO ₂	83-0546

Since presence of fluorine caused the loss of transparency in the previous glass samples, therefore in case of fig 5.2(d) we replaced ZnF₂ with ZnO, because oxygen provides better refractive index than fluorine. However, in this case also we did not get transparent glass.

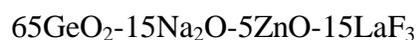
Therefore, the possible reasons for the loss of transparency of glass samples are

1. GeO₂ has lower melting temperature than LaF₃.
2. Amount of GeO₂ in the glass sample was less where as amount of LaF₃ in the glass sample was more.in the previous batches the ratio GeO₂:LaF₃ was 1.8.

5.2.2 Glass composition

Since the previous glass samples lacked transparency due to above reasons, we increased the ratio of GeO₂:LaF₃ from 1.8 to around ~4.4.

Hence our new glass sample was



We doped 0.5mol% of ErF₃ to the parent glass composition and subjected the batch for molten quenching method. In this case, we got transparent glass sample. Then we subjected the glass sample for heat treatment at different temperature for different soaking period. Then we subjected the glass-ceramic samples for XRD analysis.

Bulk density of glass sample:

Dry weight: 6.2736g

Suspended weight: 4.8556g

Soaked weight: 6.2752g

$$\text{Bulk density} = \frac{\text{Dry weight}}{\text{Soaked wt.} - \text{Suspended wt.}}$$

Bulk density = 4.419

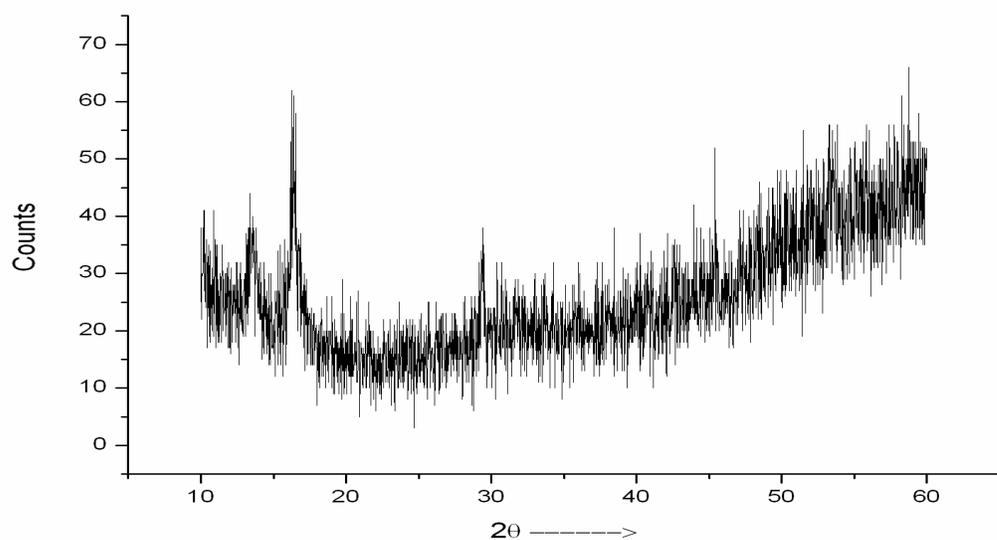


Fig.5.2 (e) XRD of sample 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃

Heat treatment at-600°C and 1°C/min

Holding period-1hour

Scanning rate- 0.025°/sec

Table 5.2 (e)

Peak no.	2θ	d-spacing	Relative intensity	phase	Reff-code
1	10.4417	8.472	17.28	NA	NA
2	13.5423	6.538	36.86	NA	NA
3	16.3809	5.411	100.00	Na ₂ GeO ₃	00-018-1217
4	29.3845	3.039	40.82	Er ₂ O ₃	00-043-1007
5	53.4384	1.713	25.07	Er ₂ O ₃	00-043-1007

In this case, of fig 5.2(e), we did not get LaF₃ phase and we got some unidentified peaks. Therefore, we changed the heating temperature and holding period of glass sample.

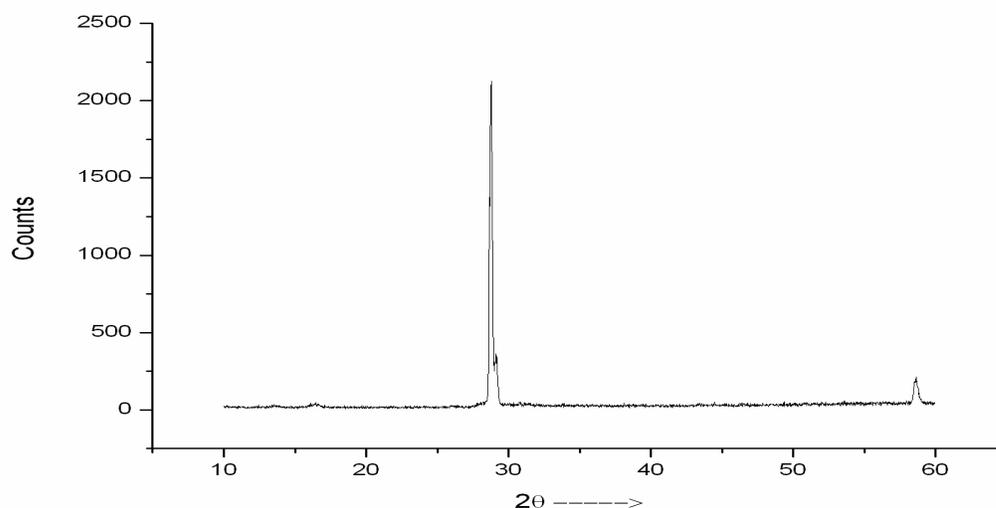


Fig 5.2(f) XRD of the sample 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 700°C

Holding period: 1 hour

scanning rate: 0.025°C/min

Fig 5.2(f)

Peak no.	2θ	d- spacing	Relative intensity	phase	Reff-code
1	16.4247	5.397	0.86	Un identified	NA
2	28.6518	3.113	62.47	GeO ₂	01-072-1149
3	28.7708	3.103	100.00	GeO ₂	01-072-1149
4	29.1713	3.061	11.94	Er ₂ O ₃	01-077-0462
5	58.5307	1.575	6.86	Un identified	NA

In this case, of Fig 5.2(f) we got GeO₂ as the major phase. This happened possibly due to the crystallization of glass matrix. Some un identified peaks were also found.

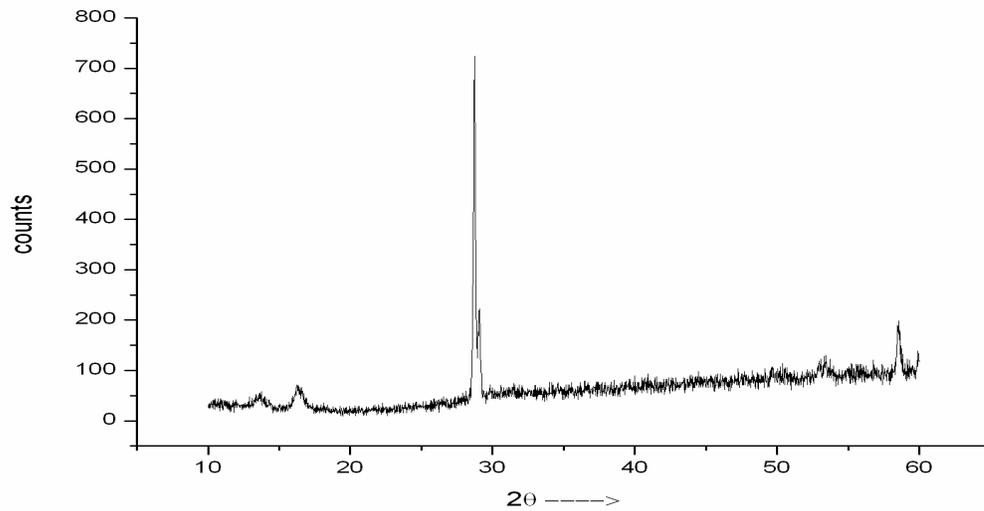


Fig 5.2(g) XRD of the sample 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 550°C

Holding period: 1 hour

scanning rate: 0.025°/sec

Table 5.2(g)

Peak no.	2 θ	d-spacing	Relative intensity	phase	Reff-code
1	28.7294	3.107	100.00	GeO ₂	01-071-0651
2	29.0578	3.073	25.25	Er ₂ O ₃	01-077-0461
3	49.6464	1.836	2.93	LaF ₃	01-078-1864
4	58.1803	1.722	2.29	Er ₂ O ₃	01-077-0461
5	57.8273	1.594	1.97	Er ₂ O ₃	01-077-0461
6	58.4988	1.576	12.91	LaF ₃	01-078-0461

In this case, of Fig 5.2(g) we got Er₂O₃ as major phase along with this, we got trace amount of LaF₃ crystalline phase. Therefore, we further subjected the glass sample to different heating temperature and different holding period to optimize the amount of LaF₃ crystalline phase.

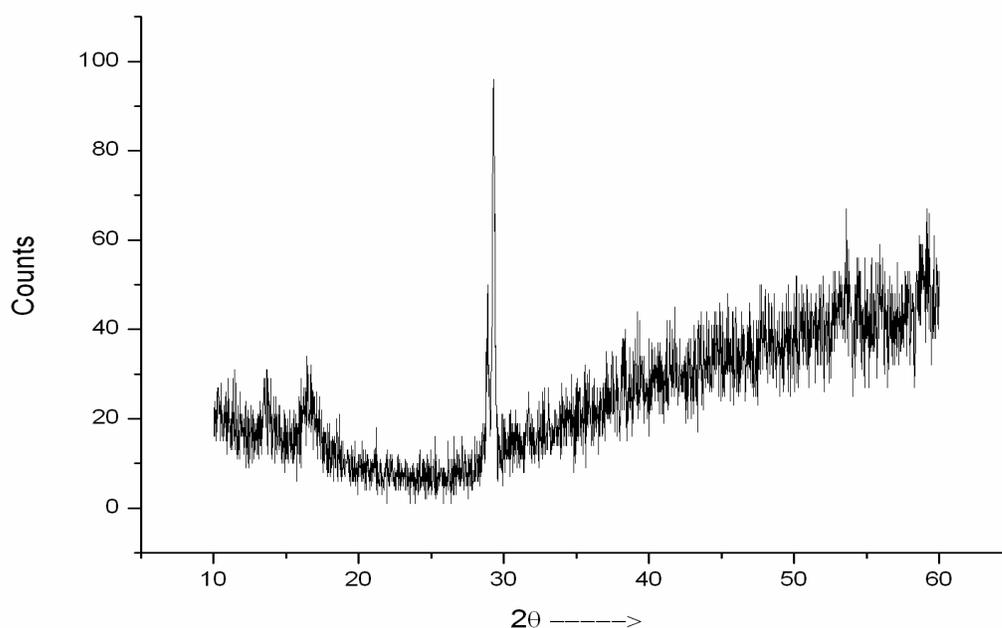


Fig 5.2(h) XRD of 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated at 550°C at 1°C/min

Holding period- 4hour

Scanning rate-1°/sec

Table 5.2(h)

Peak no.	2θ	d-spacing	Relative intensity	phase	Reff-code
1	16.3657	5.4164	12.43	Er ₂ O ₃	77-0460
2	22.2573	3.9942	3.40	NA	NA
3	29.2907	3.0491	100.00	Er ₂ O ₃	77-0460
4	47.8295	1.9017	6.41	NA	NA
5	53.2820	1.7178	7.81	Er ₂ O ₃	77-0460

In this case, of Fig 5.2(h), we got Er₂O₃ as the major phase and some unidentified peaks. We again lost the crystallinity of LaF₃ phase.

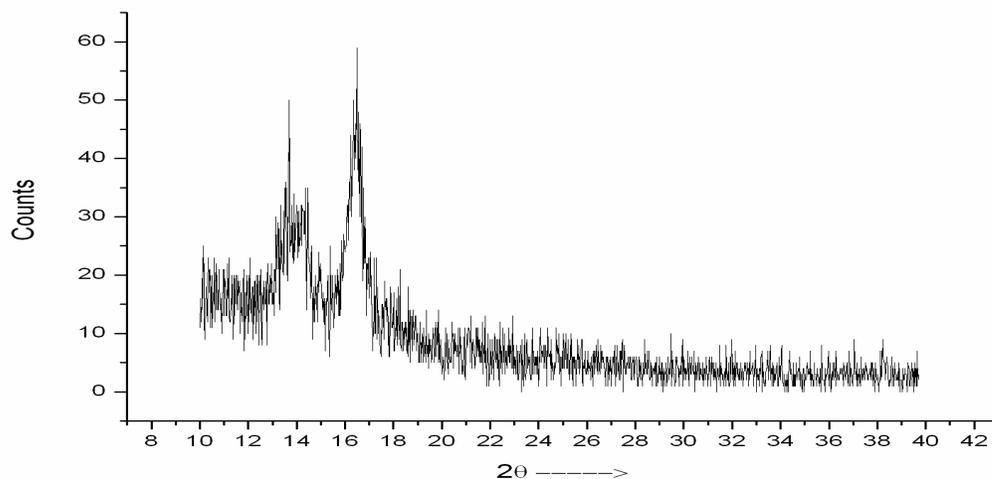


Fig 5.2(i) XRD of the sample 64.5GeO₂-15Na₂O-5ZnO-15LaF₃-0.5ErF₃ heated upto 650°C

Holding period: 4 hour

Scanning rate: 0.025°/sec

Table 5.2(i)

Peak no.	2θ	d-spacing	Relative intensity	Phase	Reff-code
1	13.5357	6.54185	38.72	NA	NA
2	14.3470	6.17369	37.57	Na ₂ GeO ₅	34-1290
3	16.5405	5.37120	100	Na ₂ GeO ₃	18-1217

In this case, of Fig 5.2(i) we found Na₂GeO₃ as major phase. Another phase obtained was Na₂GeO₅.

All the XRD patterns show crystallization of mainly GeO₂ and Er₂O₃ as major phases. Only fig5.2 (f) showed trace amount of LaF₃ phase. Hence, it was concluded that crystallization of LaF₃ not only depends upon the batch composition but also depends upon thermal treatment.

Chapter 6

Conclusion

- 1) The composition for glass must contain GeO₂: LaF₃ >=4.38 so that glass melting takes place a lower temperature and a transparent glass can be obtained.
- 2) Fluorine loss can be avoided by covering the crucible with a lid.
- 3) Excess fluorine containing glasses is prone to self crystallization
- 4) Due to self crystallization glasses lost it transparency
- 5) The LaF₃ crystals are in nanometer range because due to formation of LaF₃ crystals the glass did not lost it transparent nature
- 6) The crystallite sizes of LaF₃ nano crystals are below 200 nm.