

Development of GeO₂-BaF₂ based glass ceramic

A PROJECT REPORT

Submitted by

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(Under the guidance of Prof. Sumit Pal)

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CERTIFICATE

This is to certify that this report titled “**Development of GeO₂-BaF₂ based glass ceramic**” is the bonafide work of Mr **Kamalnayan Srivastava (Roll no. 107CR030)** who carried out the work under your supervision and guidance. Certified further, that 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.

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Abstract

Degree and Branch : *B.Tech, Ceramic engineering*

Month and Year : *April 2011*

Title of the Project Work : *Development of GeO₂- BaF₂
Based Glass Ceramic*

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In the present work, the glass of composition **45GeO₂-10 Na₂CO₃ -10NaF-10ZnF₂-25BaF₂ (mol %)** was prepared to investigate the crystallization behavior of BaF₂ in the parent glass matrix. To accelerate the crystallization and to develop the up conversion fluorescence property ErF₃ was doped in 0.5%, 1 % and 1.5 % (mol %). NH₄F was added to compensate the fluorine loss. The glass composition was changed to 65GeO₂-15 Na₂CO₃ - 5ZnO - 15BaF₂ (mol %) due to excess of BaF₂ phase in the original composition leading to high temperature of glass melting & crystallization of GeO₂ before the crystallization of BaF₂. The casted glass was subjected to thermal treatment between 550 – 800⁰C at a heating rate of 1-2⁰ C/min for different soaking time ranging from 1 hr to 5hr. To observe the effect of rare earth on crystallization, glass samples were examined under DSC to find the crystallization temperature. Phase authentication was carried out using X-Ray diffraction analysis.

Chapter 1

Introduction

The rare-earth doped solid-state up-converter can find applications in numerous photonic devices including color displays, up-conversion lasers, sensors, infrared laser viewers, and optical data storage etc. For these applications rare earth doped oxy-fluoride transparent nano- glass ceramics, are more appropriate for practical applications due to their low phonon energies compared to oxide glasses as well as excellent chemical durability and mechanical strength compared to fluoride glasses. Since long highly efficient up-conversion luminescence of rare earth ions are obtained in PbF₂ and CdF₂ nano-crystals. Today, the demand for alternative materials of Pb and Cd is growing, since they have been designated as toxic substances. BaF₂ can be considered as alternative material for PbF₂ and CdF₂. Therefore, the effect of rare earth doping into BaF₂ nano-crystals in oxide glass matrix are of scientific and technical interest.

In this proposed work GeO₂ glass matrix has been chosen as host matrix for development of BaF₂ nano- crystals and the effect of Er³⁺ doping upon efficient up-conversion will be examined.

Chapter 2

Literature Review

2.1 Rare-earth doped optical glasses

Rare-earth doped low phonon optical glasses are important materials for infrared solid lasers, optical broadband amplifiers, up-conversion laser, and visible display devices etc. For this purpose the glassy host is required to possess a minimal absorption coefficient within the wavelength region of interest, plus the capability of incorporating large rare earth concentrations, low vibrational energies, transparency and a high refractive index.

Advantages of conventional glass and glass ceramic processing are as follows

1. Glasses can be synthesized in various shapes and without the same size limitation by melt quenching method. No costly instrument is required for fabrication of glassy materials
2. For practical applications, oxide glasses have an advantage superior to fluoride glasses due to their chemical durability, thermal stability, and mechanical strength.
3. It is well recognized that crystallization of glass is one of the effective methods for fabrication of nanostructures

But Limitation of oxide glasses are:

1. The maximum doping level is limited due to rare-earth (RE) clustering tendency.
2. Large phonon energy of these oxide glasses increases the non-radiating decay rate that reduces the luminescence efficiency.

On the other hand fluorides materials have the following advantages.

1. Fluoride material can offer a low phonon environment favorable to enhance the radiative rate and quantum efficiency.
2. Fluoride single crystals can produce narrow fluorescence line widths and enhanced emission cross sections relative to glasses
3. Fluoride nano- crystal is preferred over the oxide one mainly to avoid non-radiative transitions [1]
4. The solubility of the rare earth is also larger in the fluoride medium than in the oxide [2]

But poor chemical and mechanical properties and low laser damage threshold make fluorides unsuitable for practical use and also are costly to produce. Fluoride crystals also have maximum size limitation.

The invention of rare earth ions-doped transparent oxy-fluoride glass ceramics containing fluoride nano-crystals have attracted great interest due to their excellent optical properties like fluoride crystals and good mechanical, chemical properties like oxide glasses. The advantages of these materials are that the rare earth ions are incorporated selectively in the fluoride crystal phase with lower phonon energy after heat-treatment and the material remains transparent due to much smaller size

(which is essentially in nanometer range) of precipitated crystals than the wavelength of visible light.

2.2 Key factors towards enhancement of up-conversion fluorescence

The portioning of rare-earth ions into fluoride crystalline environment with large band gap and low phonon energy is necessary for the enhancement of up-conversion fluorescence properties of oxy-fluoride glass ceramics. It is well known that, besides the rare earth ions concentration, the thermal treatment condition, and the microstructure of glass ceramics, also affects the up-conversion fluorescence of the material.

According to Judd-Ofelt theory, the enhancement of up conversion is attributed to the decrease in parameter Ω_2 [3,4] Ω_2 is sensitive to the environmental configuration symmetry of rare-earth ions, and it decreases with the changing of the host from a covalent bond with the oxide ligand to a predominantly ionic bond with the fluorides [5]. With the increasing of thermal treatment temperature, the volume fraction of crystals as well as the crystallinity of fluoride nano-crystals containing rare earth ions increases, thereby causing more rare earth ions to be located at a more symmetrical site, which results in the decrease of Ω_2 . With an increase in the heating temperature, the emission lifetime, the quantum efficiency and the intensities of near-infrared and up-conversion emissions increases significantly, due to the fact that more fraction of rare earth ions incorporated into the precipitated fluoride nano-crystals of lower phonon energy. It is well known that the up-conversion luminescence of rare earth ions is usually baffled by the multi-phonon relaxation. The multi-phonon relaxation probability depends primarily upon the energy gap between two successive levels and the phonon energy of the host [6]. The smaller is the phonon energy of the host, the lower is the multi-phonon relaxation probability.

Thus it can be concluded that the luminescence properties of rare earth ions in transparent glass ceramic systems strongly depend on the chemical composition of the host and the thermal treatment conditions. Even a slight component modification of the host matrix or a change of annealing time and temperature influence glass de-vitrification and the degree of rare earth incorporation into the crystalline phase. The local environment and its modification, as well as the concentration and distribution of the optically active ions in the crystalline and non-crystalline 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 up-conversion [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, BaF₂ is an ideal host for rare earth ions since they have extensive solid solution capability with all rare earth ions. The maximum phonon energy in BaF₂ is 346cm⁻¹ [10].

The effect of Er doping in BaF₂ containing oxy-fluoride glass ceramic are well established. Qiao *et.al.*[10] reported the up-conversion luminescence intensity of

Er³⁺ in the BaF₂ containing silicate glass ceramics increased significantly with increasing annealing time. They have 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 oxy-fluoride glass ceramics. In these systems the possible up-conversion luminescence mechanisms of the Er³⁺ ions can be described by: (a) excited state absorption (sequential two-photon absorption) (ESA), and (b) energy transfer (ET) up-conversion processes. From the above literature, it is evident that the luminescence properties of rare earth ions in BaF₂ containing glass ceramic systems strongly depend on the chemical composition of the host as well as on the thermal treatment conditions. 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 oxy-fluoride glass ceramics increase and the lifetime of the $^4S_{3/2}$ level became longer. Owing to the similar ionic radius and the same valence as La³⁺, Er³⁺ ion is one of the most useful rare earth dopants because it can be utilized as fiber amplifiers of 1.5 μm telecommunication range and for the up-conversion lasers of visible green emission. Thus it is interesting to investigate the evolution of spectroscopic properties of LaF₃ containing oxy-fluoride glass ceramic doped with Er³⁺ ions in these materials. A schematic energy diagram of different energy level of Er³⁺ ion is presented in Fig.1.

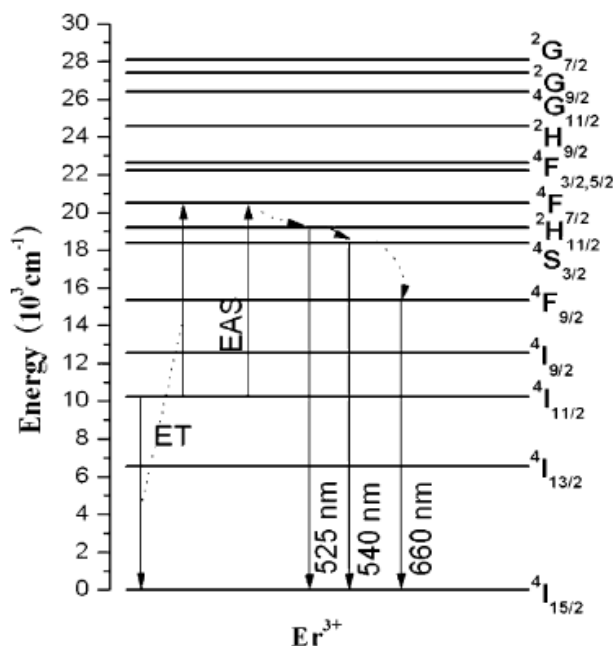
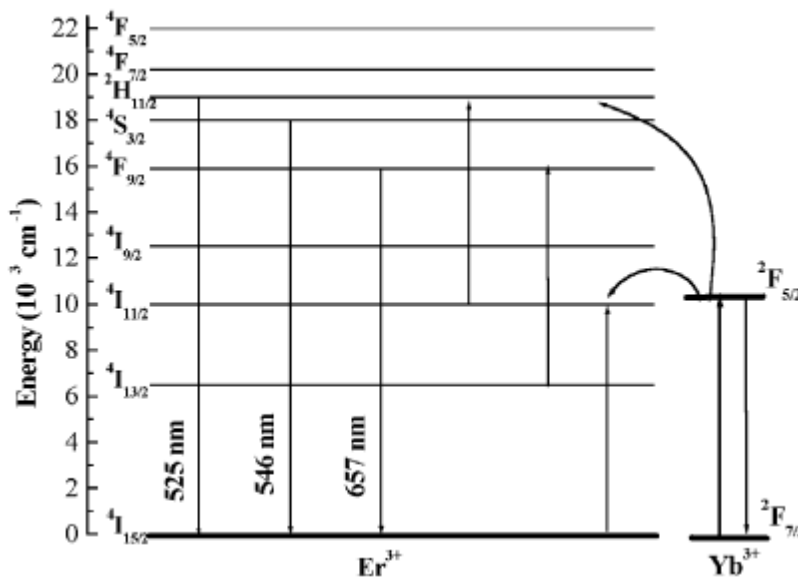


Fig 1. Simplified energy-level diagram of Er³⁺ ions and the possible up-conversion mechanisms

Another method to obtain efficient up-conversion 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⁺ co-doped oxy-fluoride bismuth–germanium glass. They observed that the intense green and weak red emissions centered at 525, 546, and 657 nm, corresponds to the transitions $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$, respectively, at room temperature. A. Biswas *et al* [15] reported efficient up-conversion emissions at 379, 407, 450, 490, 520, 540 and 660 nm 973 nm excitation in the transparent 0.1ErF₃–0.1YbF₃–5LaF₃–94.8SiO₂ (mol%) glass-ceramics. The results indicate that this sample is a very good infrared-to-ultraviolet up-converter. Qiao *et al* [16] reported intense up-conversion luminescence and the corresponding stark-split peaks in BaF₂ containing silicate based glass ceramic, where Er³⁺ and Yb³⁺ had been incorporated with BaF₂ nano-crystals. The NIR luminescence decay curves

indicate that the Er³⁺ and Yb³⁺ co-doped glass ceramic have higher luminescence efficiency than the precursor glass. Comparable up-conversion emission is also reported by Chen *et al* [18] for oxy-fluoride glass ceramic containing CaF₂ nano-crystals co-doped with Er³⁺/Yb³⁺. The possible energy transfer mechanism of Er³⁺/Yb³⁺ is shown in Fig.2.



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 nano-crystals. These crystals have very low phonon energy. Enhanced up-conversion 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 equipments.

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.

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Chapter 3

Scope of the project

Following is the glass composition to be prepared

45GeO₂-10 Na₂CO₃ - 10NaF-10ZnF₂- 25BaF₂ (host glass) (mol %)

Concentration of Er³⁺ will be varied from 0.1 mol% to 3 mol% and this variation will be done in exchange of BaF₂.

3.1 Objectives of the proposed project

- 1) Development of rare earth doped BaF₂ based glass and glass ceramic.
- 2) Optimization of fraction and size of BaF₂ 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.
- 4) The influence of thermal treatment and rare earth doping concentration on fluorescence property of glass ceramics will be examined.

Chapter 4

Experimental Work

4.1 Work plan

- All these glasses will be prepared by using high purity GeO₂, Na₂CO₃, NaF, ZnF₂, BaF₂, and ErF₃ as raw materials.
- To prepare glasses, each batch weighing about 20g will be mixed homogeneously and melted at 1250°C for 30 min in a covered corundum crucible in air. The melts will be poured onto a preheated copper brass plate and then pressed by another plate.
- All the glasses will be annealed below the glass transition temperature for 2 h to remove thermal strains.
- The densities of the glasses will be measured using the buoyancy method based on the Archimedes principle.
- It will be then thermally treated below the glass transition temperature for 2 to 8 hours to obtain nano crystals in glass matrix.
- T_g will be determined by DSC analysis (Netzsch). DSC measurements will be done, at a heating rate of 10°C per minute in N₂ atmosphere.
- The crystal phases will be identified by Phillips X-Ray Diffractometer with a Ni-filter and CuK α (1.542Å).

4.2 Batch Preparation

For development of GeO₂-BaF₂ based glass ceramics, parent glass composition was

45GeO₂-10Na₂O-10NaF-10ZnF₂-25BaF₂ (mol %)

To study the effect of ErF₃ addition, parent glass composition was doped with 0.5mol% ErF₃

ErF₃ doped batch composition is given below in the table

Table 4.1 (Batch = 10gm)

Compound	Mole%	Weight
GeO ₂	45	4.22
Na ₂ O	10	0.55
NaF	10	0.38
ZnF ₂	10	0.93
BaF ₂	25	3.92

Table 4.2 (Batch =10gm, 0.5ErF₃)

Compound	Mole%	Weight
GeO ₂	44.5	4.2
Na ₂ O	10	0.55
NaF	10	0.38
ZnF ₂	10	0.93
BaF ₂	25	3.92
ErF ₃	0.5	0.02

New Glass Composition:**65GeO₂- 15Na₂O - 5ZnO -15BaF₂ (mol %)****Table 4.3** (Batch =10gm, 0.5ErF₃)

Compound	Mole%	Weight
GeO ₂	64.5	6.25
Na ₂ O	15	0.854
ZnO	5	0.37
BaF ₂	15	2.41
ErF ₃	0.5	0.1

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 o 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.

4.3 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.

4.4 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 550⁰C, 550⁰C, 600⁰C, 650⁰C, 700⁰C, 800⁰C for range of soaking hours from 1hr to 5 hr.

4.5 Characterization

4.5.1 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.

4.5.2 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 & Discussion

5.1 Thermal analysis: DSC/TGA curves

5.1.1 Differential Scanning Calorimetry (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, and E is enthalpy

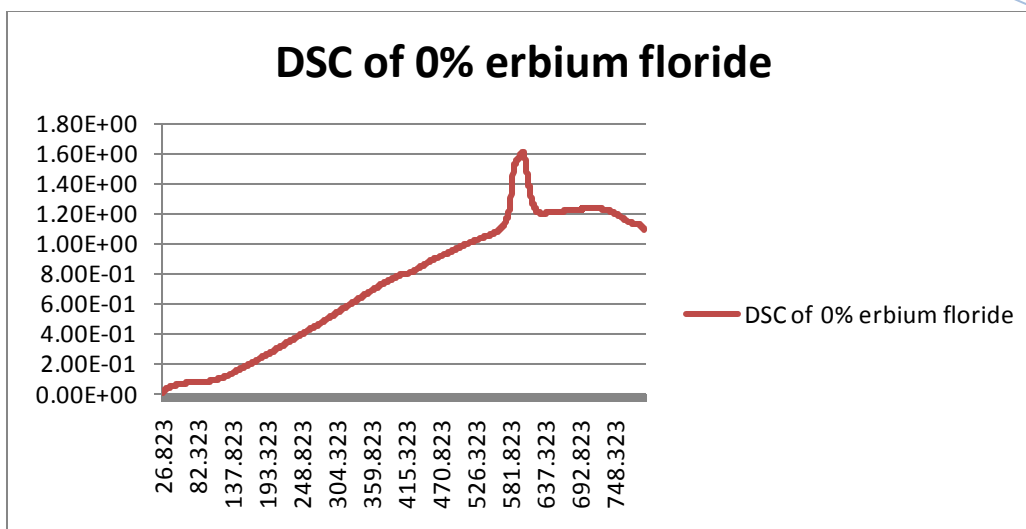


Fig 5.1(a) DSC curve for glass sample with no ErF₃

Fig 5.1(a) shows DSC curve for glass sample with no ErF₃ addition. The curve shows one exothermic around $580 \pm 20^{\circ}\text{C}$ which is crystallization temperature of this sample

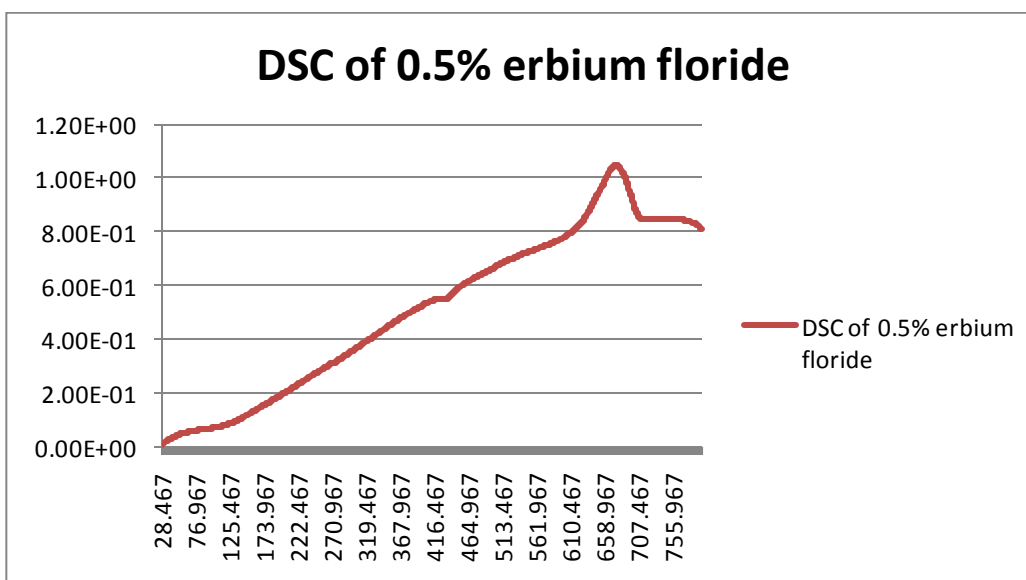


Fig 5.1(b) DSC curve for glass sample with 0.5% ErF₃

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 $580 \pm 20^{\circ}\text{C}$ 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 .Moreover, the figures showed that crystallization temperature increased with dopant concentration.

5.1.2 Thermo-Gravimetry Analysis (TGA)

TGA curves obtained at 10K/min upto 800⁰C showed positive mass change i.e mass of the sample increased with temperature. No relevant reasoning or explanation was found for this behavior

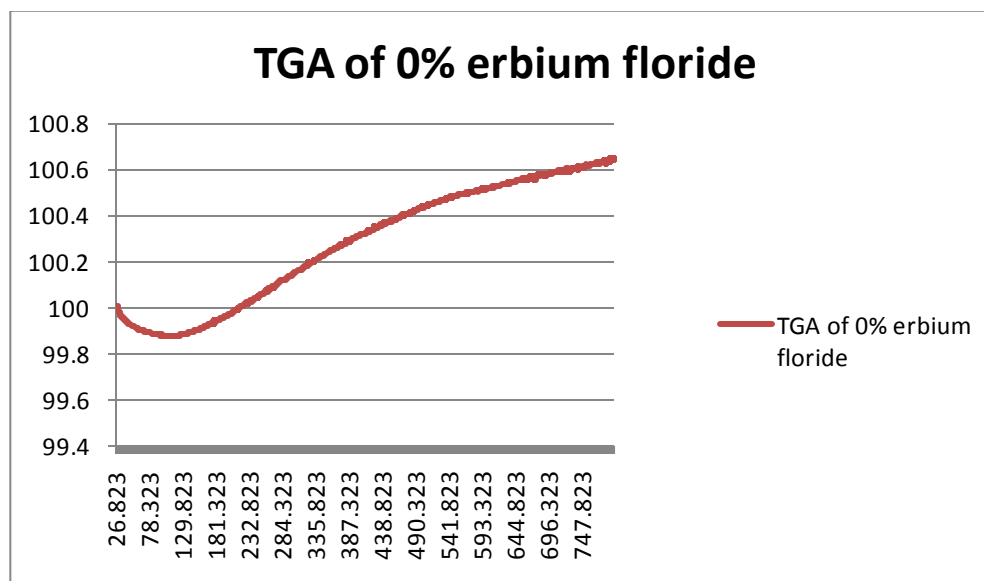


Fig 5.1(c) TGA curve for glass sample with no ErF₃

Fig 5.1(c) shows that glass without doping showed increment in mass on heating

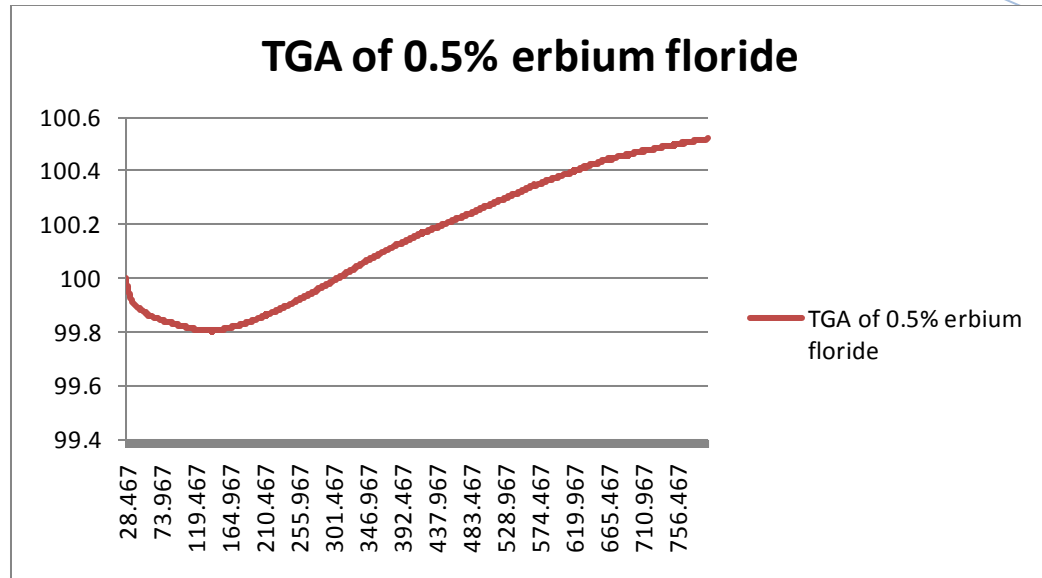


Fig 5.1(d) TGA curve for glass sample with 0.5% ErF₃

Fig 5.1(d) shows that glass with 0.5% ErF₃ also showed increment in mass on heating

5.2 Phase analysis: Characterization by XRD

5.2.1

Glass composition:

45GeO₂-10 Na₂CO₃ - 10NaF-10ZnF₂- 25BaF₂ (mol %)

To this composition , 0.5 mol% ErF₃ was added & the sample so obtained was heat treated at 550⁰C , 600⁰C , 650⁰C , 700⁰C , 800⁰C for 1 hr ,2hr , 3hr , 4 hr , 5 hr at a heating rate of 1-2⁰C/min .Heat treated samples were characterized by XRD & crystalline phases were identified

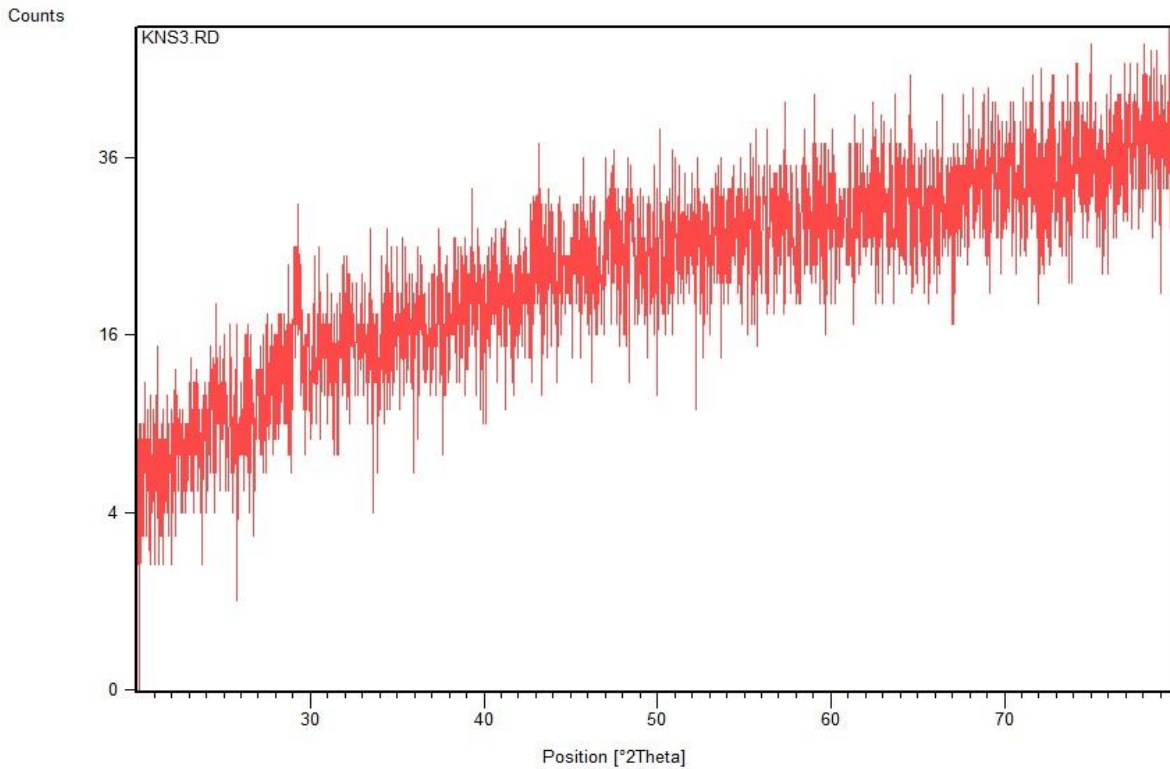


Fig 5.2(a) XRD of original glass sample without heat treatment

Fig 5.2(a) shows that original glass sample had no crystalline phase hence; the glass was completely amorphous and did not undergo any crystallization during glass melting

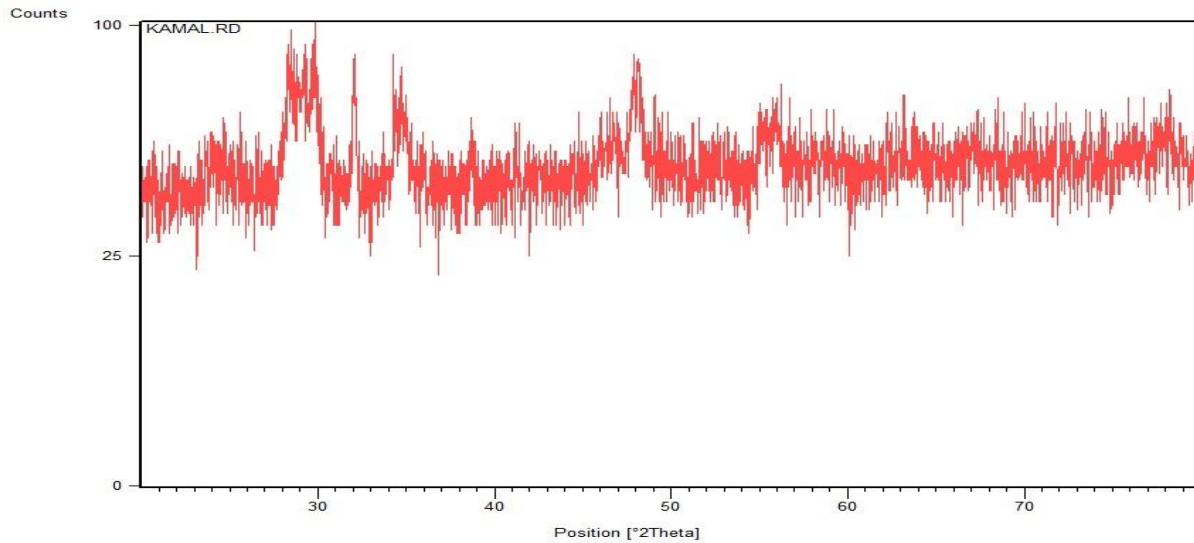


Fig 5.2(b) XRD of doped glass sample heat treated for 1hr at 600⁰C

Heat treatment: 600⁰C @ 2⁰C/min for 1hr

Scanning rate: 0.25⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
91.25	3.1446	21-0070	3.140	BaGeO ₃
100	2.998	01-0850	3.02	Na
99.96	2.792			Unidentified
53.10	2.591	18-0484	2.600	Er ₂ Ge ₃
65.04	1.8878	30-0142	1.893	BaO
38.58	1.6432			Unidentified
20.51	1.2217	30-0142	1.222	BaO

Fig 5.2(b) shows glass heated at 600⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Some phases remained unidentified while among the identified phases most of them were barium & germanium based compounds

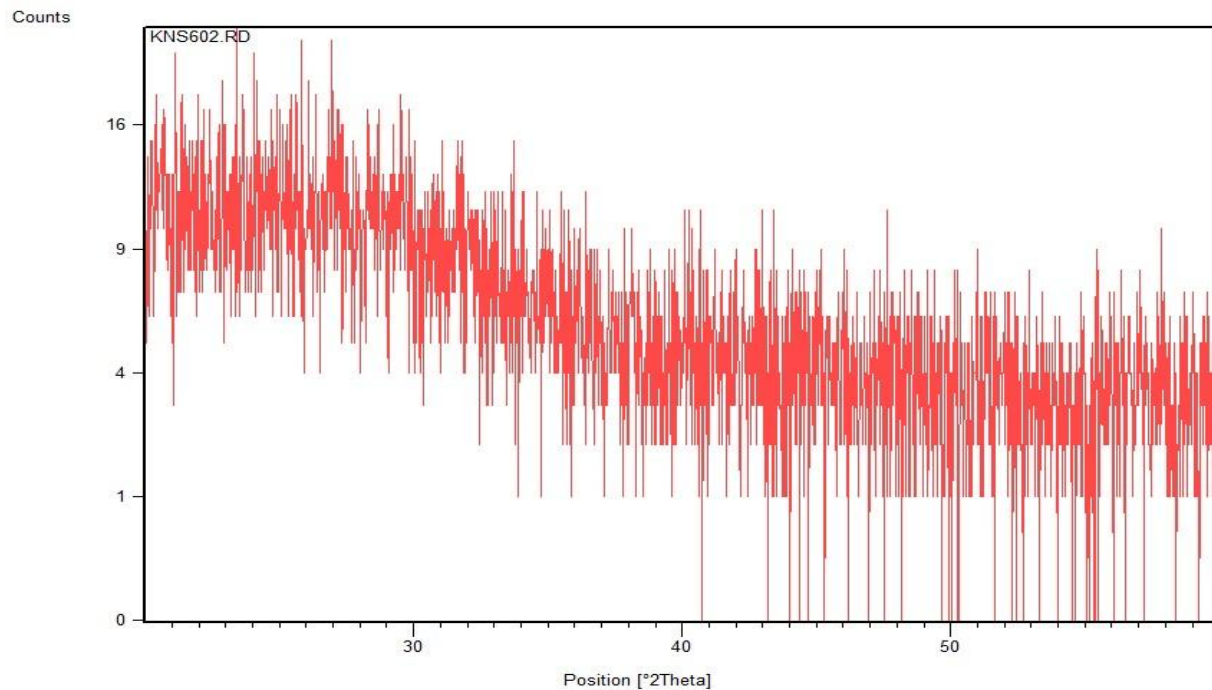


Fig 5.2(c) XRD of doped glass sample heat treated for 2hr at 600⁰C

Heat treatment: 600⁰C @ 2⁰C/min

Scanning rate: 0.04⁰/sec

Soaking time: 2hr

Fig 5.2(c) shows XRD pattern obtained by fast scanning at scanning rate of 0.04⁰/sec such that no peaks were observed while the sample heat treated at the same temperature of 600⁰C soaked for only one hour showed 4 major and 3 minor peaks. It was hence; concluded that scanning rate needs to be slow to observe clear peaks .Henceforth, scanning rate was maintained at 0.025⁰/sec.

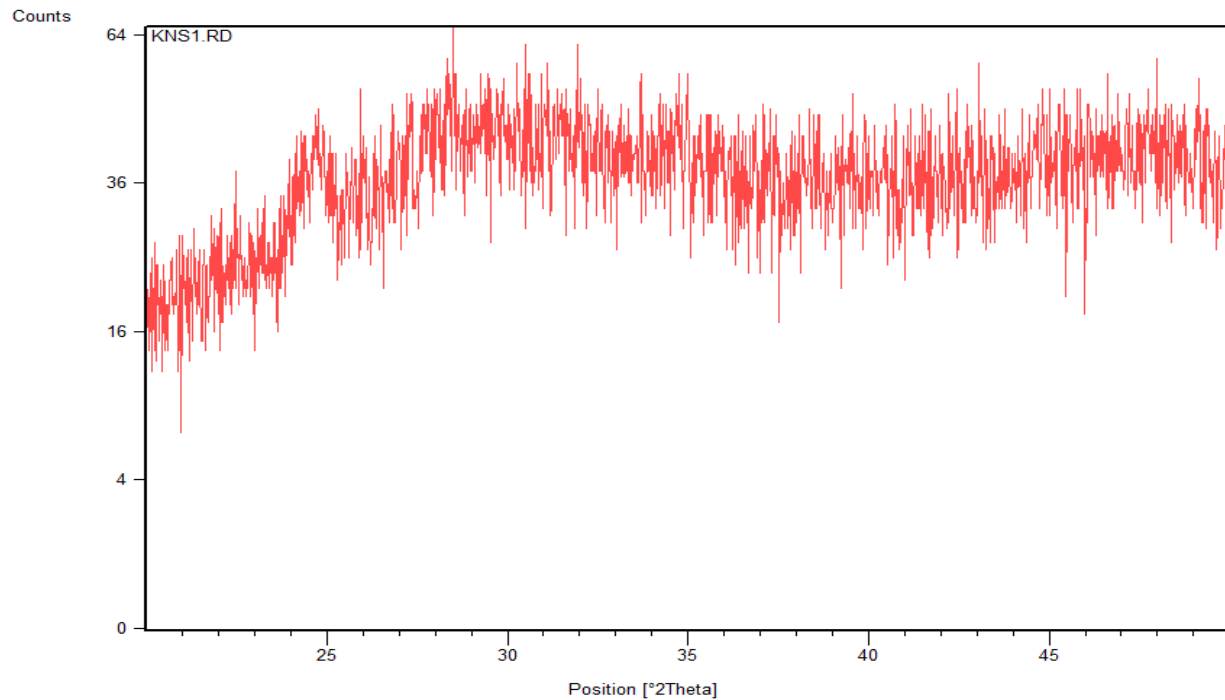


Fig 5.2(d) XRD of doped glass sample heat treated for 3hr at 600⁰C

Heat treatment: 600⁰C @ 2⁰C/min for 3hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	3.60497			Unidentified
81.41	3.139	21-0070	3.14	BaGeO ₃

Fig 5.2(d) shows glass heated at 600⁰C for 3hr although was found transparent but it did not show any BaF₂ phase. Only two peaks were observed. Some phases remained unidentified while the identified phase was BaGeO₃

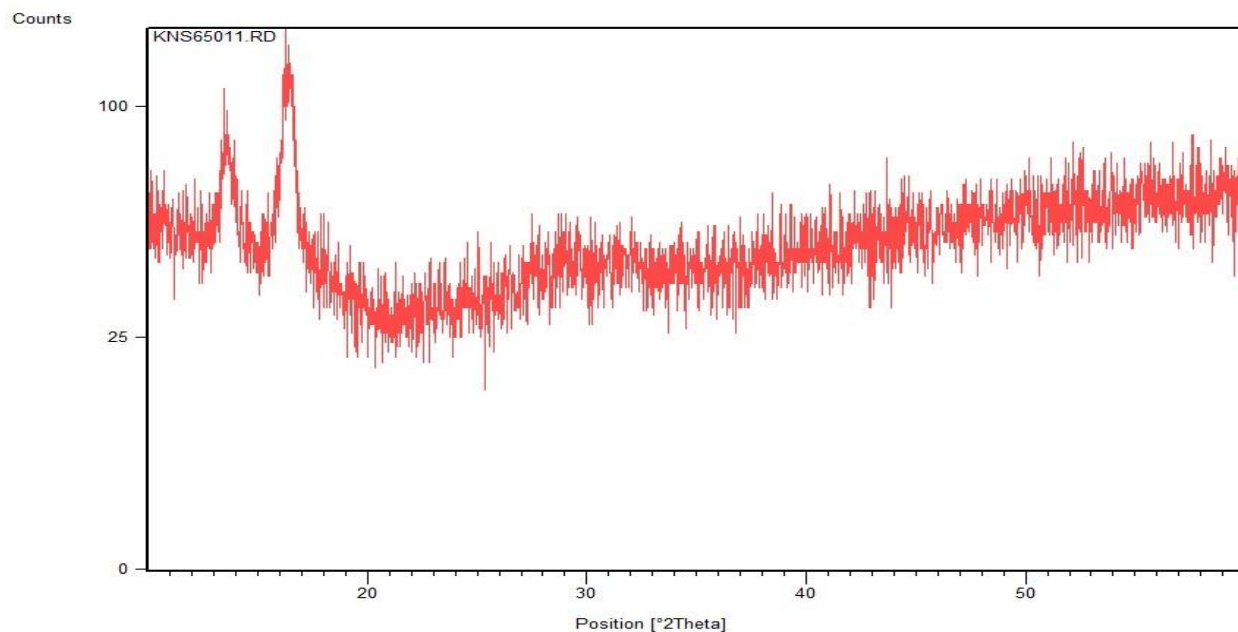


Fig 5.2(e) XRD of doped glass sample heat treated for 1hr at 650⁰C

Heat treatment: 650⁰C @ 1⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
54.8	6.544			Unidentified
100	5.4227	18-1217	5.440	Na ₂ GeO ₃

Fig 5.2(e) shows glass heated at 650⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Only two peaks were observed. Some phases remained unidentified while the identified phase was NaGeO₃

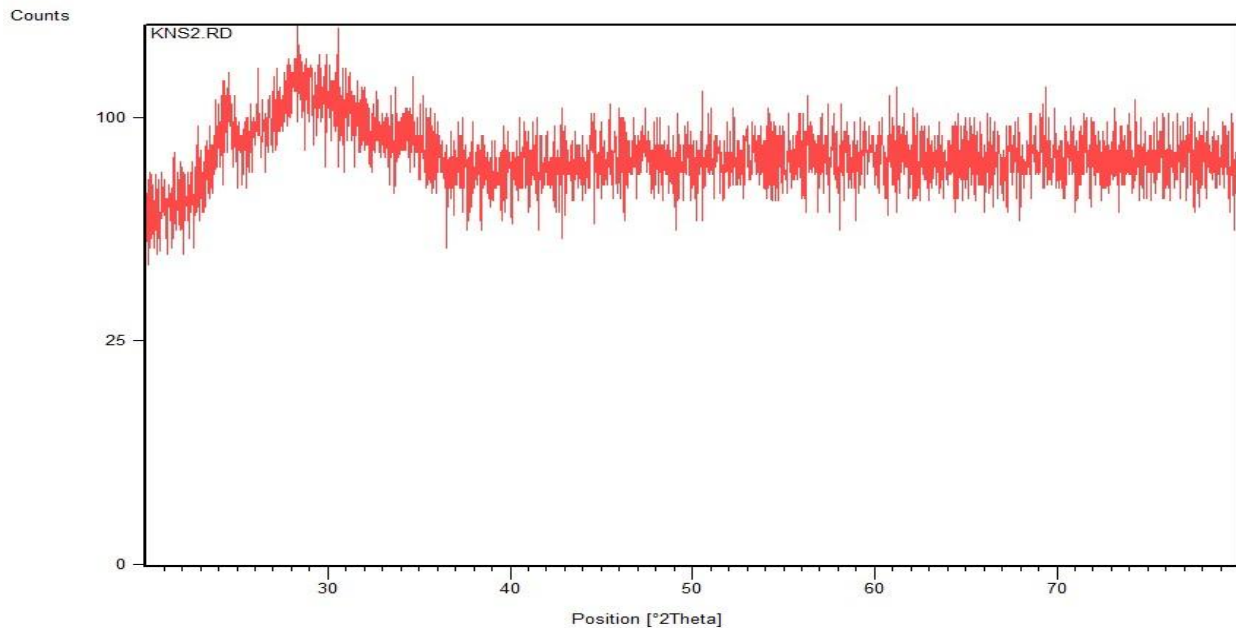


Fig 5.2(f) XRD of doped glass sample heat treated for 1hr at 700⁰C

Heat treatment: 700⁰C @ 2⁰C/min for 1hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	3.635	74-0924	3.645	BaGeF ₆
42.56	1.318			Unidentified
4.73	1.202			Unidentified

Fig 5.2(f) shows glass heated at 700⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed. Some phases remained unidentified while among the identified phase was BaGeF₆.

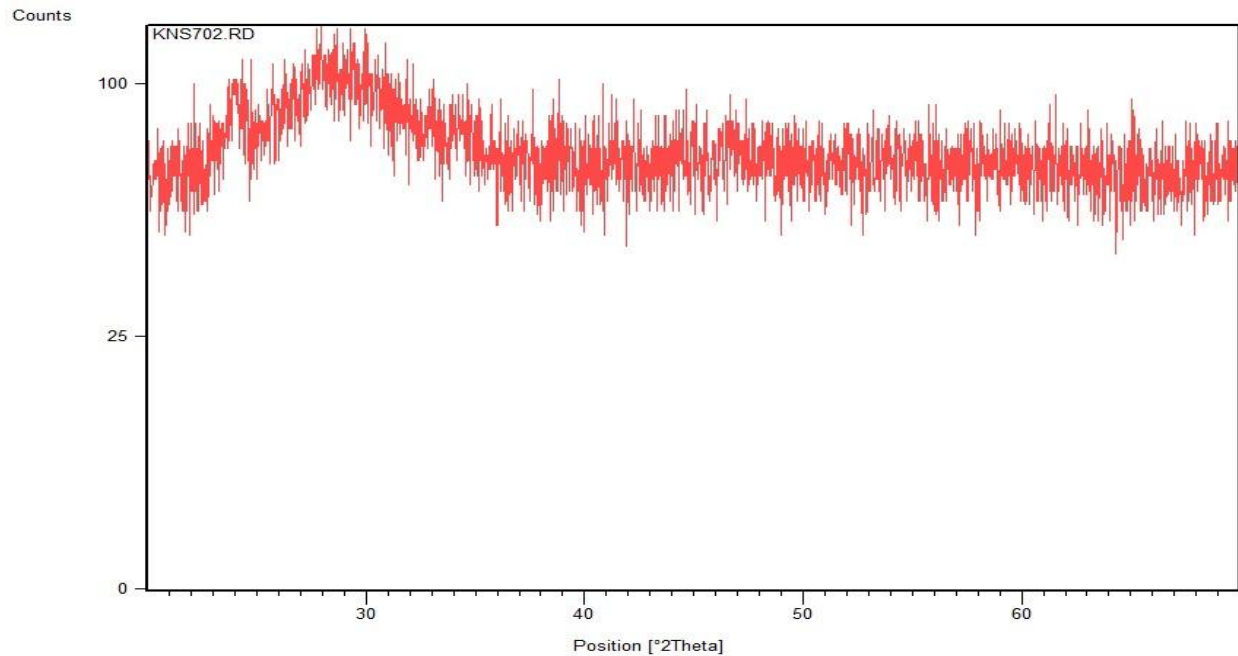


Fig 5.2(g) XRD of doped glass sample heat treated for 2hr at 700⁰C

Heat treatment: 700⁰C @ 2⁰C/min for 2hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	3.708			Unidentified
10.91	2.3018	36-1455	2.316	NaF
36.3	1.9391	45-1234	1.930	Ge ₄ Na

Fig 5.2(g) shows glass heated at 700⁰C for 2hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed. Some phases remained unidentified while the identified phases were Ge₄Na & NaF.

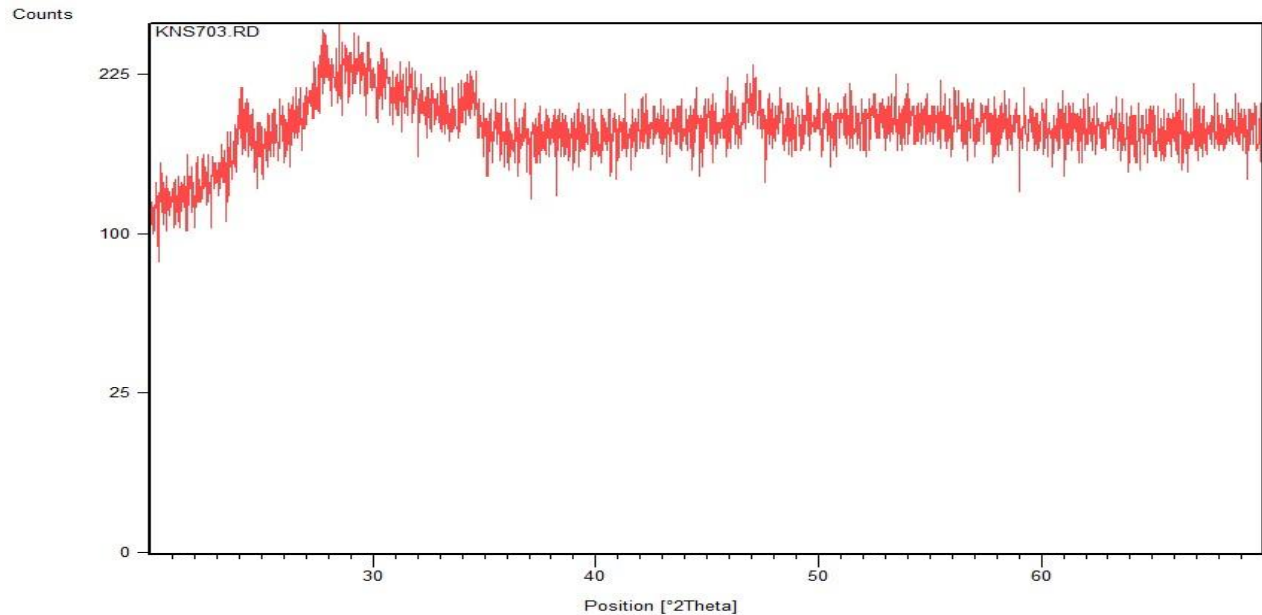


Fig 5.2(h) XRD of doped glass sample heat treated for 3hr at 700⁰C

Heat treatment: 700⁰C @ 2⁰C/min for 3hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	3.211	01-0764	3.200	BaO
69.57	1.931	45-1234	1.930	Ge ₄ Na
64.95	2.606	35-1054	2.605	ZnGeO ₃

Fig 5.2(h) shows glass heated at 700⁰C for 3hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed. Identified phases contained germanium based compounds like Ge₄Na, ZnGeO₃ & some BaO.

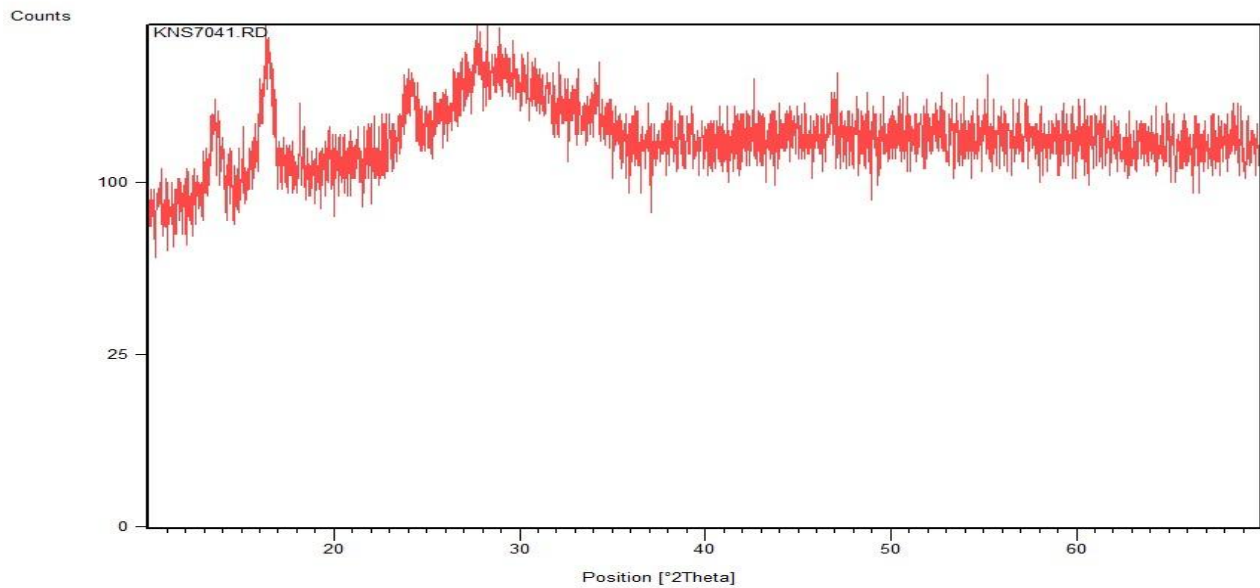


Fig 5.2(i) XRD of doped glass sample heat treated for 4hr at 700⁰C

Heat treatment: 700⁰C @ 1⁰C/min for 4hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
48.33	6.575			Unidentified
100	5.387	18-1217	5.44	Na ₂ GeO ₃
40.85	3.689			Unidentified
34.45	3.2157	77-0390	3.211	BaZnGeO ₄
23.18	2.6311	18-1217	2.640	Na ₂ GeO ₃

Fig 5.2(i) shows glass heated at 700⁰C for 4hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed. Some phases remained unidentified while the identified phases were mostly germanium based compounds like. Na₂GeO₃, BaZnGeO₄.

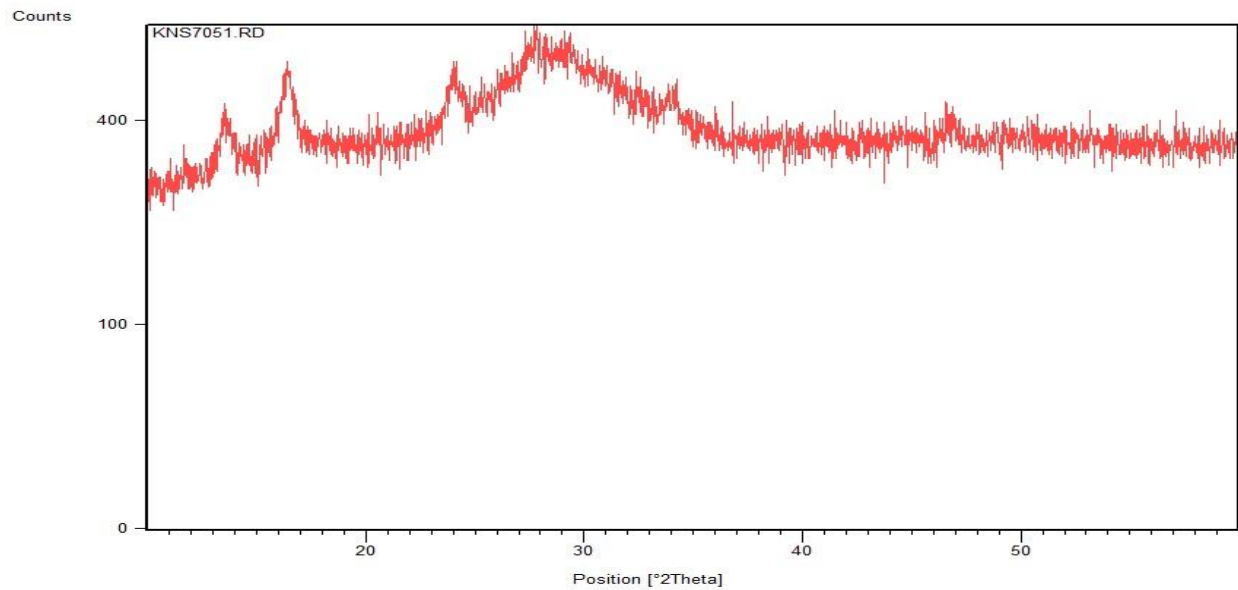


Fig 5.2(j) XRD of doped glass sample heat treated for 5hr at 700⁰C

Heat treatment: 700⁰C @ 1⁰C/min for 5hr

Scanning rate: 0.01⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
63.89	6.535			Unidentified
100	5.397	18-1217	5.44	Na ₂ GeO ₃
50.37	3.690			Unidentified
34.15	3.228	77-0390	3.211	BaZnGeO ₄
23.23	2.634	72-0822	2.627	F ₂
20.80	1.939	18-1217	1.94	Na ₂ GeO ₃

Fig 5.2(j) shows glass heated at 700⁰C for 5hr although was found transparent but it did not show any BaF₂ phase. Some phases remained unidentified while the identified phases were mostly germanium based compounds like. Na₂GeO₃, BaZnGeO₄. Traces of fluorine was also found.

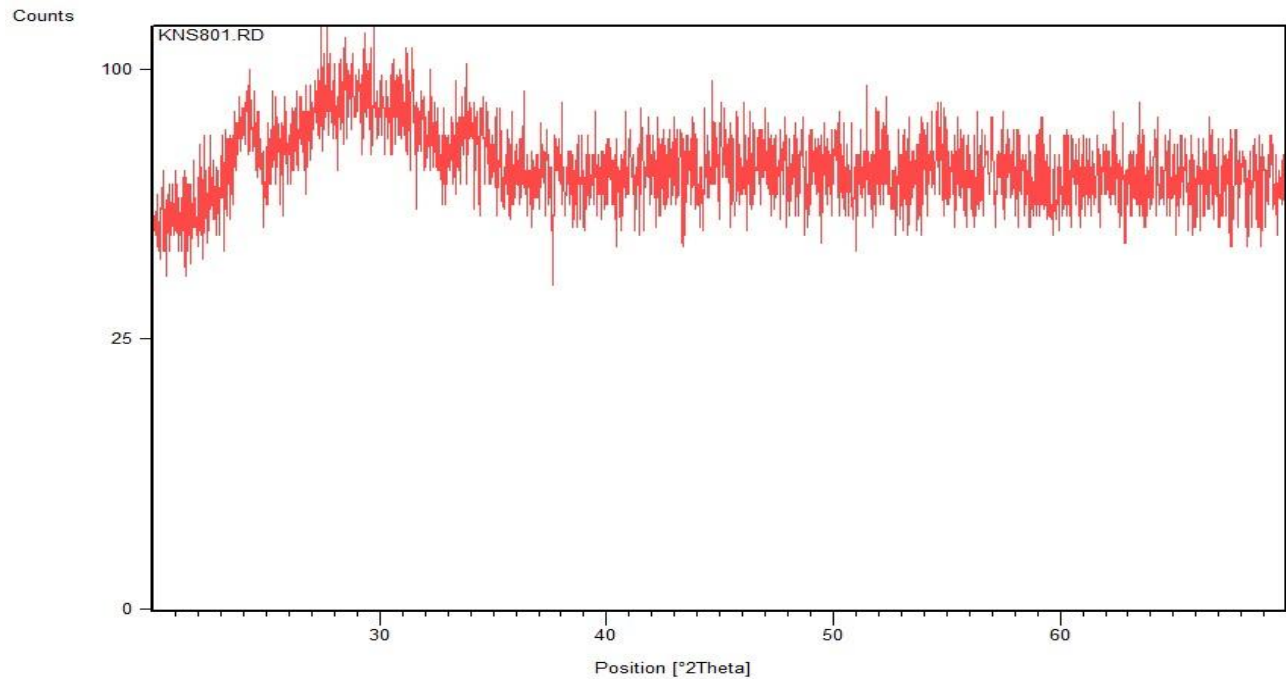


Fig 5.2(k) XRD of doped glass sample heat treated for 1hr at 800⁰C

Heat treatment: 800⁰C @ 2⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	3.662	74-0924	3.6458	BaGeF ₆
42.37	3.228			Unidentified
45.91	2.009	74-0924	2.104	BaGeF ₆

Fig 5.2(k) shows glass heated at 700⁰C for 5hr although was found transparent but it did not show any BaF₂ phase. Some phases remained unidentified while the identified phases were mostly barium- germanium based compounds like BaGeF₆.

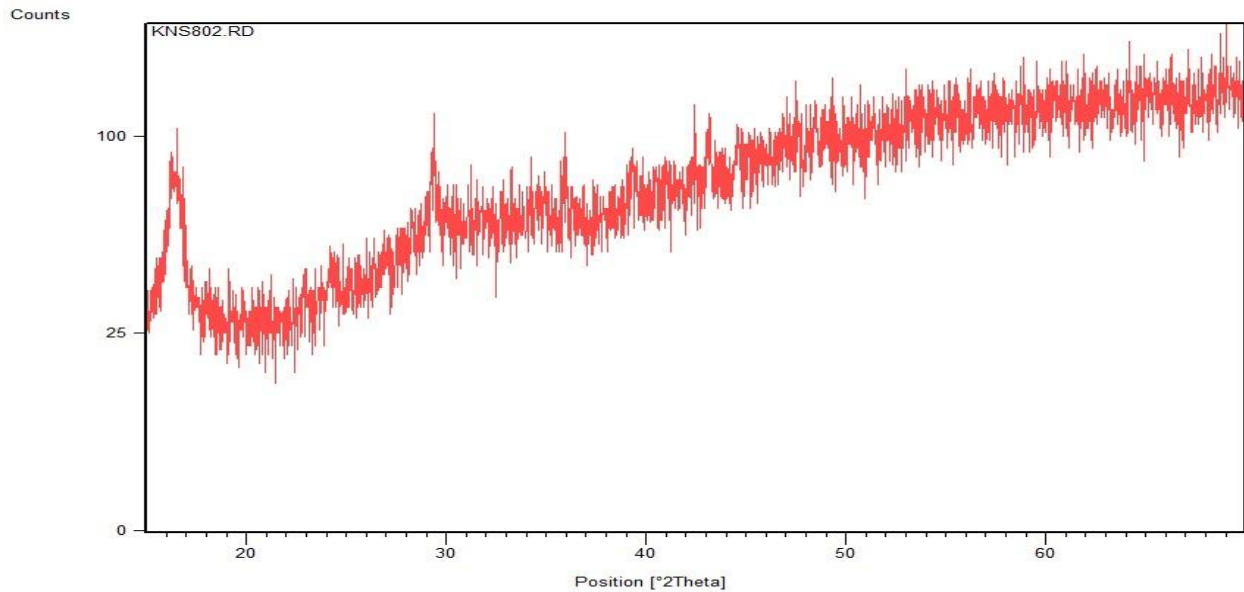


Fig 5.2(l) XRD of doped glass sample heat treated for 2hr at 800⁰C

Heat treatment: 800⁰C @ 2⁰C/min for 2hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
100	5.3606			Unidentified
88.61	3.039	22-0948	3.033	Na
17.61	2.579			Unidentified
50.43	2.498	18-0483	2.5	Er ₅ Ge ₃
44.65	2.0938			Unidentified

Fig 5.2(l) shows glass heated at 700⁰C for 5hr although was found transparent but it did not show any BaF₂ phase. Four peaks were observed .Some phases remained unidentified while the identified phases were mostly erbium- germanium based compounds like Er₅Ge₃.Traces of sodium was also found.

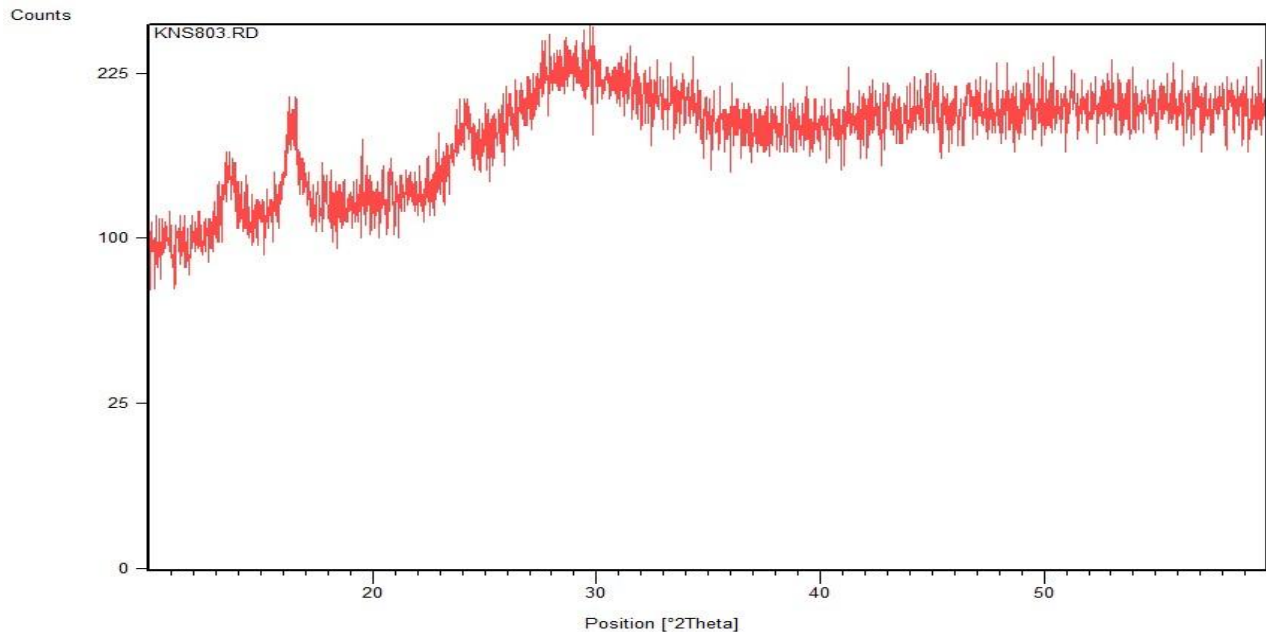


Fig 5.2(m) XRD of doped glass sample heat treated for 3hr at 800⁰C

Heat treatment: 800⁰C @ 2⁰C/min for 3hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
51.82	6.576			Unidentified
100	5.383	18-1217	5.44	Na ₂ GeO ₃
50.65	3.683	18-1217	3.63	Na ₂ GeO ₃
6.60	2.0254			Unidentified

Fig 5.2(m) shows glass heated at 700⁰C for 5hr although was found transparent but it did not show any BaF₂ phase. Four peaks were observed .Some phases remained unidentified while the identified phases were mostly sodium- germanium based compounds like Na₂GeO₃.

5.2.2

Glass composition:

45GeO₂-10 Na₂CO₃ - 10NaF-10ZnF₂- 25BaF₂ (mol %) + 20 % (W/W %) NH₄F

The analysis of previous XRD patterns did not show the required BaF₂ phase and hence, it was concluded that fluorine being volatile left the glass matrix & escaped into the atmosphere .It was hence, recommended to compensate the fluorine loss by adding 20wt. % of NH₄F .Ammonia being volatile will escape and will not change the composition. Thus, a sample of (10+2) gm was prepared. To this composition, 0.5 mol% ErF₃ was added.

The glass sample obtained lacked transparency without being heat treated .It was hence , inferred that during melting the glass had crystallized due to excessive fluorine which is believed to act as a good nucleating agent & hence , crystallization was favored .Fig 5.2(n) is the XRD pattern of opaque glass sample obtained .XRD showed required BaF₂ phase but with lack of transparency.

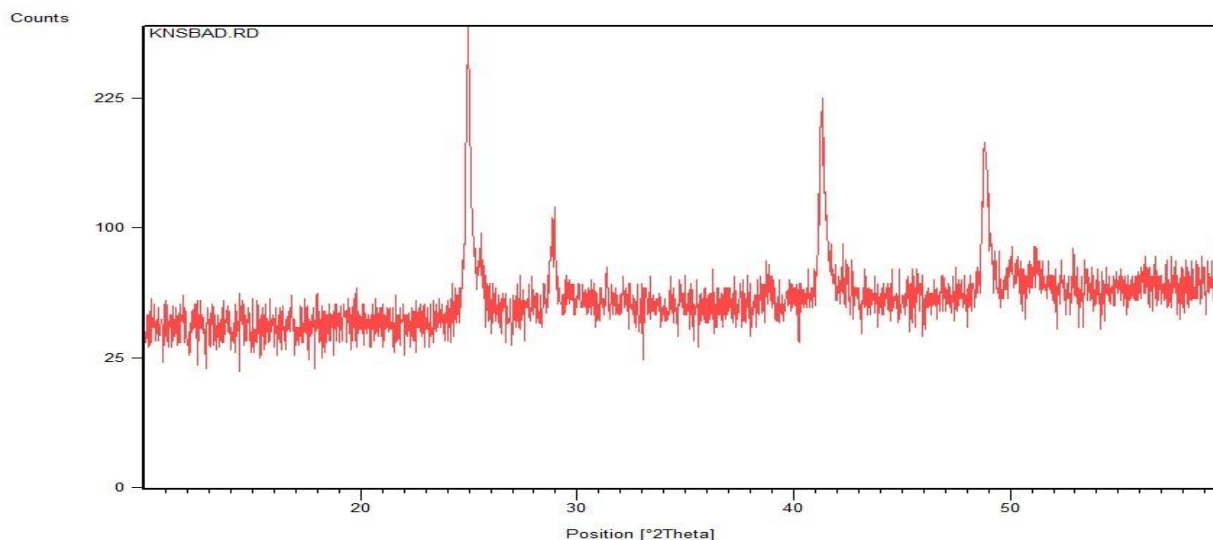


Fig 5.2(n) XRD of excess NH₄F glass sample without heat treatment

5.2.3

Glass composition:

65GeO₂–15 Na₂CO₃ – 5ZnO – 15BaF₂ (mol %)

With previous compositions either there was no BaF₂ phase or there was a lack of transparency in the sample. Moreover, the glass melting took place at higher temperature although the melting temperature of main phase GeO₂ was low. This might be due to higher %age of BaF₂ & low %age of GeO₂ in the composition. Hence, it was concluded that ratio between GeO₂ : BaF₂ needs to be changed. It was hence, increased from 1.8 to 4.34.

Moreover, XRD patterns showed most phases with GeO₂ which implies the tendency of GeO₂ to crystallize before BaF₂. To prevent loss of fluorine, the crucibles were covered with a lid during heat treatment.

To this composition, 0.5 mol% ErF₃ was added. & the so obtained samples were heat treated at 550⁰C, 600⁰C, 700⁰C for 1hr at heating rate of 1⁰C/min.

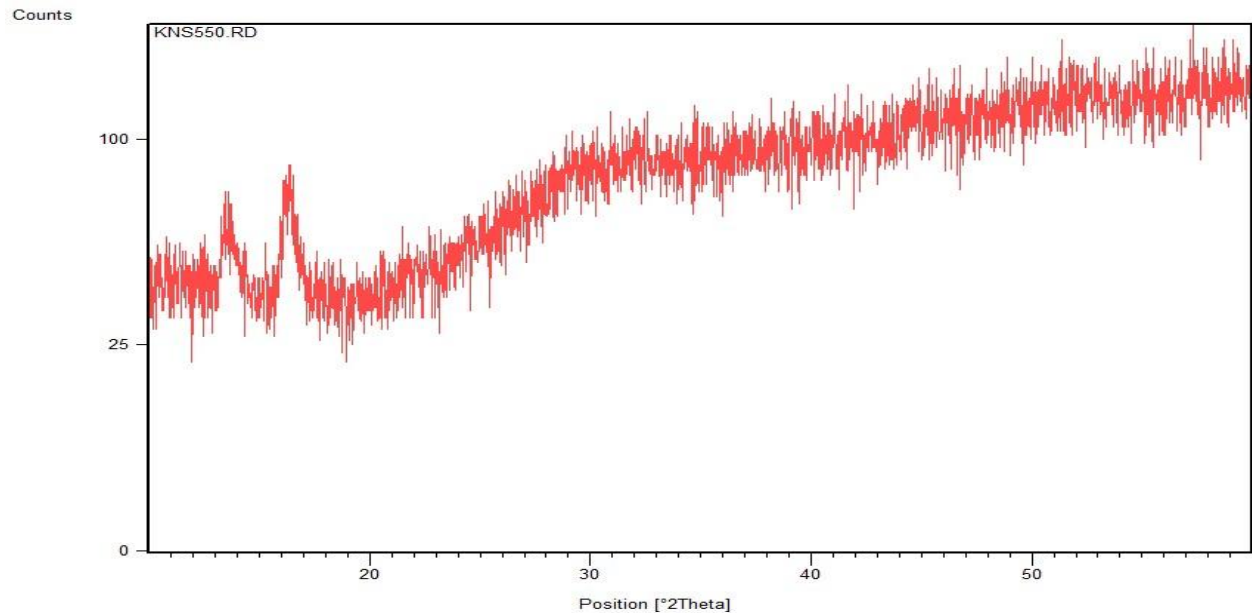


Fig 5.2(o) XRD of doped glass sample heat treated for 1hr at 550⁰C

Heat treatment: 550⁰C @ 1⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
56.97	6.52146			Unidentified
100	5.43623	00-018-1217	5.44	Na ₂ GeO ₃
37.29	4.75385			Unidentified

Fig 5.2(o) shows glass heated at 550⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed .Some phases remained unidentified while the identified phases were mostly sodium- germanium based compounds like Na₂GeO₃.

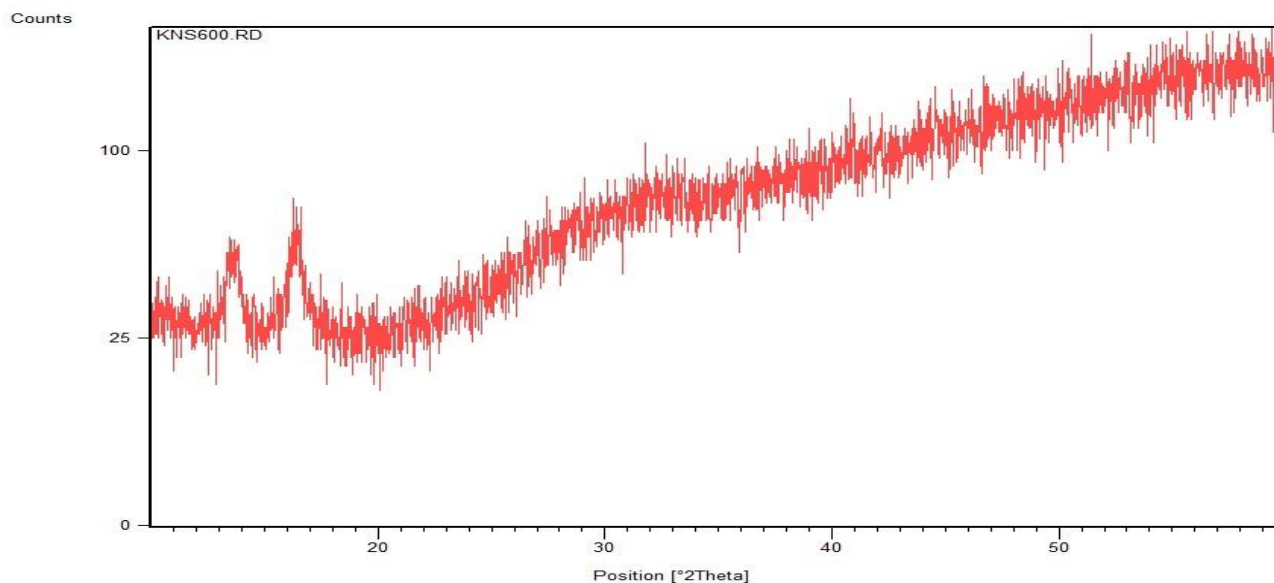


Fig 5.2(p) XRD of doped glass sample heat treated for 1 hr at 600⁰C

Heat treatment: 600⁰C @ 1⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
72.17	6.4473			Unidentified
100	5.3858	00-018-1217	5.446	Na ₂ GeO ₃
41.07	2.4918	00-018-1217		Na ₂ GeO ₃
24.34	2.2057	00-026-0178	2.18	BaO

Fig 5.2(p) shows glass heated at 600⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed .Some phases remained unidentified while the identified phases were mostly sodium- germanium based compounds like Na₂GeO₃. Traces of BaO were found.

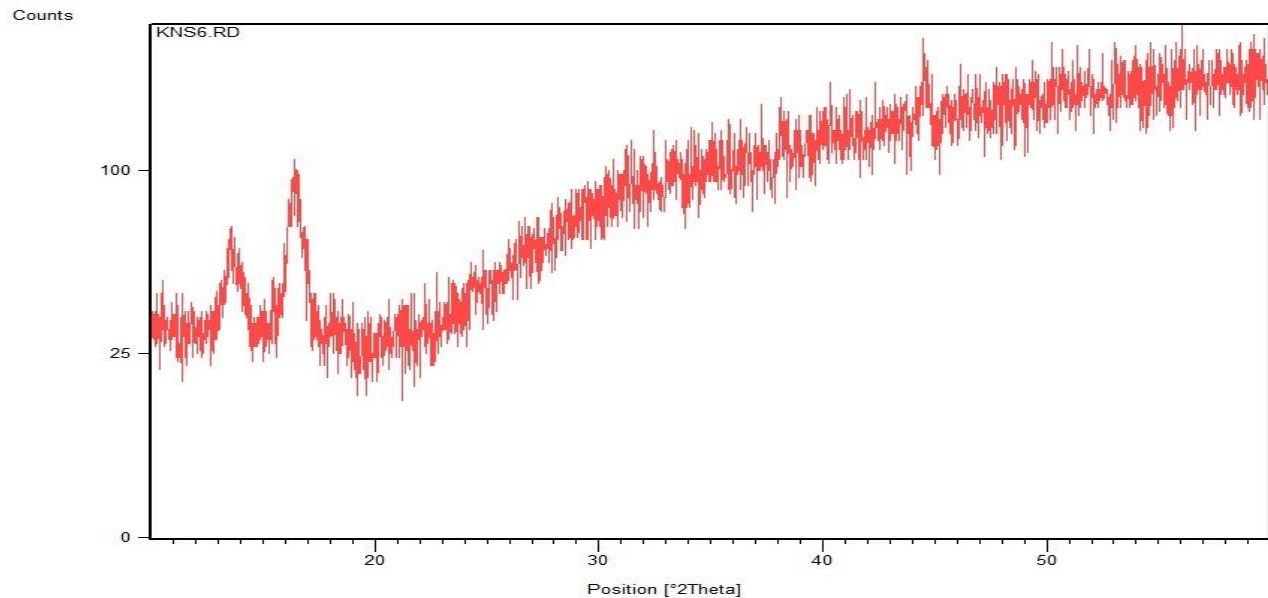


Fig 5.2(q) XRD of doped glass sample heat treated for 1hr at 700⁰C

Heat treatment: 700⁰C @ 1⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
52.19	6.5398			
100	5.3818	00-018-1217	5.44	Na ₂ GeO ₃
25.10	2.3562	00-018-1217		Na ₂ GeO ₃
61.31	2.0325	00-018-1217		Na ₂ GeO ₃

Fig 5.2(q) shows glass heated at 700⁰C for 1hr although was found transparent but it did not show any BaF₂ phase. Three peaks were observed .Some phases remained unidentified while the identified phases were mostly sodium- germanium based compounds like Na₂GeO₃.

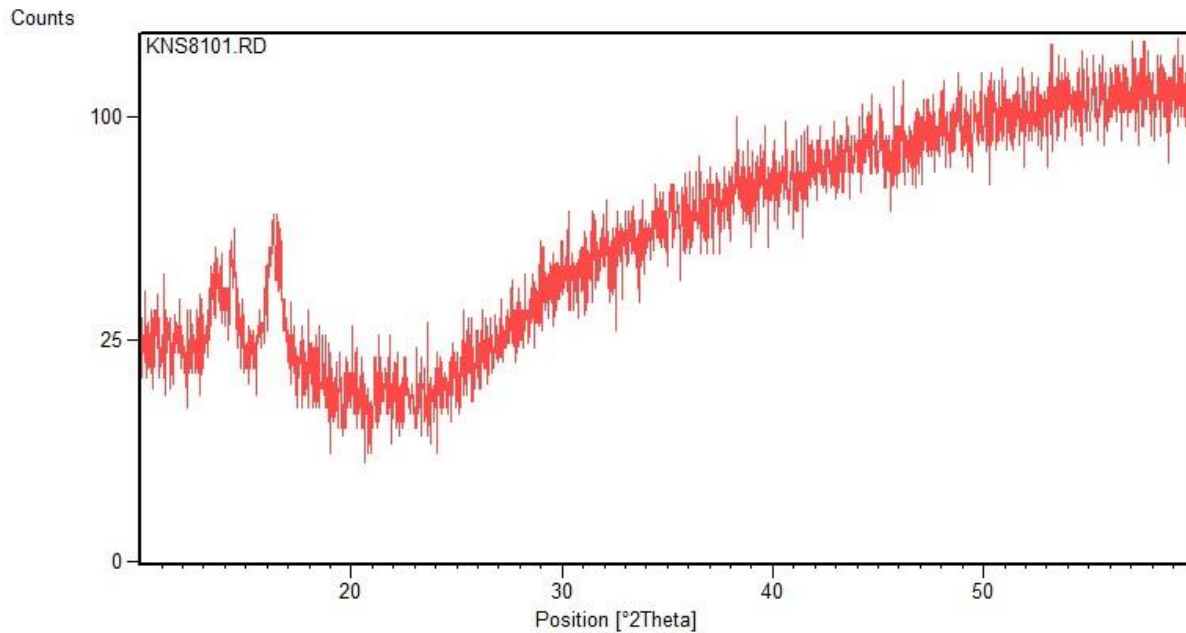


Fig 5.2(r) XRD of doped glass sample heat treated for 10hr at 800⁰C

Heat treatment: 700⁰C @ 1⁰C/min for 1 hr

Scanning rate: 0.025⁰/sec

Relative intensity	d-spacing	Reference code	d-spacing	Phase
43.57	6.552			Unidentified
65.73	6.157	34-1290	6,16	Na ₂ Ge ₂ O ₅
100	5.456	18-1217	5.44	Na ₂ GeO ₃
77.53	5.331			Unidentified
31.42	1.8622	02-1157	1.87	BaF ₂

Fig 5.2(r) shows glass heated at 800⁰C for 10hr was found transparent .The sample showed the presence of BaF₂ phase. Five peaks were observed .Some phases remained unidentified while the identified phases were mostly sodium- germanium based compounds like Na₂GeO₃. BaF₂ phase was found in traces at approx .49⁰

Chapter 6

Conclusion

- 1) The composition for glass must contain GeO₂: BaF₂ ≥ 4.38 so that glass-melting takes place at a lower temperature.
- 2) Fluorine loss can be avoided by covering the crucible with a lid
- 3) XRD analysis showed most phases with GeO₂ content which implies that GeO₂ crystallized before BaF₂.
- 4) With increase in soaking hours, crystalline fraction increased.
- 5) DSC analysis showed that with increase in doping content, crystallization temperature increased
- 6) Addition of more fluorine by adding NH₄F as fluorine source resulted in an opaque glass due to nucleating behavior of fluorine.