



An Investigation into the Effects of Composition and BaF₂ Content on the Structure and Crystallization Behavior of SiO₂-Al₂O₃-K₂O-BaF₂ Oxyfluoride Glasses

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ABSTRACT

Nowadays, oxyfluoride glasses have received much attention from photonic researchers as they benefit from the advantages of both oxide and fluoride glasses (low phonon energy in parallel with high mechanical and chemical durability). The purpose of this paper was to study the different glass compositions in SiO₂-Al₂O₃-K₂O-BaF₂ system and investigate the BaF₂ effects on their crystallization behavior and structure. Therefore, various chemical compositions with different amounts of BaF₂ (20, 30, and 40mol%) were chosen and melted in alumina crucibles at 1450°C. The sample could not melt with the lowest percentage of BaF₂. On the other hand, the glass composition containing the highest amount of BaF₂ was not able to show high transparency due to the phase separation that occurred in it. Finally, the sample with a 30mole ratio of BaF₂ was chosen as the optimized sample due to the favorable transparency. XRD patterns showed that the samples were amorphous and it somehow proved the low transparency in the presence of higher amounts of BaF₂ arose from phase separation than the unwanted crystallization. According to the DTA results, the crystallization peak of the fluoride phase decreased from 693°C to 678°C by increasing the content of BaF₂. FT-IR spectra approved the oxyfluoride structure of the glasses. Higher BaF₂ content increased the absorption of peaks in FT-IR spectra since it results in a more discontinuous structure. Fluorine loss was higher for the glass containing the highest amount of BaF₂ due to the lower amount of Al₂O₃ in its composition.

1. INTRODUCTION

Importance of rare-earth (RE) ions doped materials is due to their potential applications such as optical fibers, amplifiers, optical storages, solar cells, etc. [1, 2]. The most essential parameter in the preparation of a luminescence material is actually choosing an optimal host. Candidate host material should have high optical transparency, low phonon energy, and favorable solubility of rare-earth ions [2]. Oxide glasses are used as hosts of RE ions since they have high transparency, mechanical strength, chemical stability, and easy fabrication procedure. However, they suffer from high phonon energies (more than 1000cm⁻¹), which lead to non-radiative relaxation of excited-RE ions [3]. On the other hand, fluoride materials do not have the limitation of high phonon energy, but the lack of mechanical and

chemical durability makes their preparation and application under ambient atmosphere too difficult [4]. Therefore, oxyfluoride glass-ceramics, which were invented in 1993 by Ohwaki and Wang [5], achieved a very high interest of researchers. In these new materials, RE ions enter the fluoride nanocrystals that have low phonon energy, and consequently, exhibit more intensive luminescence emissions than other glassy materials. Moreover, embedding these fluoride nanocrystals in an oxide glass matrix based on Al₂O₃-SiO₂ overcomes the above-mentioned problems for pure fluoride materials [6]. Among the different oxyfluoride glass-ceramics introduced until now, systems containing MF₂ (M=Ba, Ca, Sr) nanocrystals have been studied more. It is due to their low cost and non-toxic raw materials. Further, MF₂ nanocrystals have high

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solubility of RE ions and give a better matching of refractive index with aluminosilicate glass [7].

The majority of studies are devoted to the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$ system and there are only a few types of research about systems containing BaF_2 nanocrystals. Whereas, BaF_2 has less phonon energy than CaF_2 , offers a more extended IR transmittance window, and achieves transmission up to $9\mu\text{m}$ [8]. Hence, it is tried to study $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ glass and glass ceramic system in the present paper. For this purpose, different chemical compositions with various amounts of BaF_2 were chosen and the effects of these changes on transparency, structure, and crystallization behavior of prepared glasses were investigated.

2. EXPERIMENTAL PROCEDURE

Three chemical compositions containing different amounts of BaF_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ system were selected (Table 1). According to these compositions, high purity materials were weighted, mixed, and completely homogenized. That is worth to say that, K_2O is a flux agent. Sb_2O_3 and As_2O_3 were added to batches as refining agents to prepare bubble-free samples. 50g of batches were melted in covered alumina crucibles at 1450°C for 1 hour. Melted glasses were poured on preheated stainless steel molds to give them disc-like shapes. To diminish the internal stress of samples, annealing at 550°C for 1 hour was carried out.

TABLE 1. Different chemical compositions of glasses in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ system (mole ratio)

Composition Sample code	$\text{SiO}_2/\text{Al}_2\text{O}_3$	SiO_2	Al_2O_3	BaF_2	K_2O
GBF40	3	45	15	40	5
GBF30	2.5	50	20	30	5
GBF20	2.2	55	25	20	5

XRD analysis was used to study the amorphous nature of glasses and identifying the precipitated crystalline phases in heat-treated samples (taken by Philip Xpert-MMD system). Differential thermal analysis (DTA) curves were plotted with the rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ to measure crystallization peak temperatures of samples using DTG-60AH Shimadzu equipment. the ASTM C169-16 standard method was used. The glasses were mixed with sodium hydroxide granules through the grinding method to obtain the fluorine loss amount in glasses. The obtained mixtures were melted in covered

alumina crucibles at 900°C . the achieved melts poured to 500ml polyethylene beaker containing 90°C -distilled water. A total ionic strength adjustment buffer (TISAB) solution was used to adjust ionic strength and minimize the undesirable fluoride coordinating ability of impurities. The TISAB solution was prepared with 57ml of glacial acetic acid, 58.0g of sodium chloride, and 12.0g of sodium citrate in 500ml of distilled water under constant agitation. The pH of the solution was adjusted to 6.0–6.5 with $\text{NaOH } 6\text{mol}\cdot\text{l}^{-1}$ and the addition of water continued till completing the volume to 1l. The solution was kept in polyethylene flasks. Standard NaF solution prepared by dissolution of fluorides in distilled water for obtaining calibration curves. The potentiometric determination was performed with a fluoride ion-selective and a reference electrode (saturated calomel electrode) using the Orion dual star model of Thermo fisher company's equipment. Each millivolt (mV) measurement was made after stirring the solution for 2min and then leaving it for 4min. Then the fluorine amount ($\text{g}\cdot\text{ml}^{-1}$) was obtained according to the calibration curves. Finally, the lost amount of fluorine was calculated by differences of fluorine content in the chemical composition of samples and their measured fluorine content [9].

UV-Vis-NIR spectra of samples, recorded by UV-Vis Shimadzu 1700 spectrophotometer, were used to investigate the effect of chemical composition and BaF_2 content on the transparency of glasses. FT-IR analysis was performed to obtain some structural information about samples (using FT-IR Tensor 27 Brucker device).

3. RESULTS AND DISCUSSION

3.1. Results of Melting

After melt/shaping process at 1450°C for 1 hour, sample GBF20 did not melt and it remained as an unmelted powder in the crucible. It is attributed to the high amounts of SiO_2 and Al_2O_3 , and consequently, lower percentage of BaF_2 in its composition, which elevates its refractoriness degree. Other samples were melted successfully, whereas, sample GBF40 containing the highest content of BaF_2 , demonstrated phase separation during the melt/quenching process. Therefore, sample GBF40 was less transparent than GBF30 (Figure 1). The resulted phase separation is ascribed to the high content of fluoride ions in sample GBF40. It is reported that anions like F^- and Cl^- can increase the phase separation in glasses [10]. Therefore, partially substitution of oxygen by fluorine breaks down the glass network and its viscosity decreases, and consequently phase separation speeds up in glass [11].



Figure 1. The image of disc-like shaped and polished GBF40 and GBF30 samples

3.2. DTA Results

Figure 2 presents the DTA curves of samples. For both GBF40 and GBF30 samples, two exothermic peaks are observable. The presence of two exothermic peaks is DTA curves, which are reported by other researchers too [12-14]. The first peak (at 693°C and 678°C for GBF30 and GBF40 samples, respectively) is attributed to the crystallization of the BaF₂ phase, which is in agreement with other reports with small differences [12-16]. The diversity of the peak temperature of the BaF₂ crystallization in various references is sparked off the different chemical composition, additives, and dopants used for preparing samples. Furthermore, the second exothermic peak is appeared due to the crystallization of the glassy matrix [12], which is not discussed in many types of research [14-17].

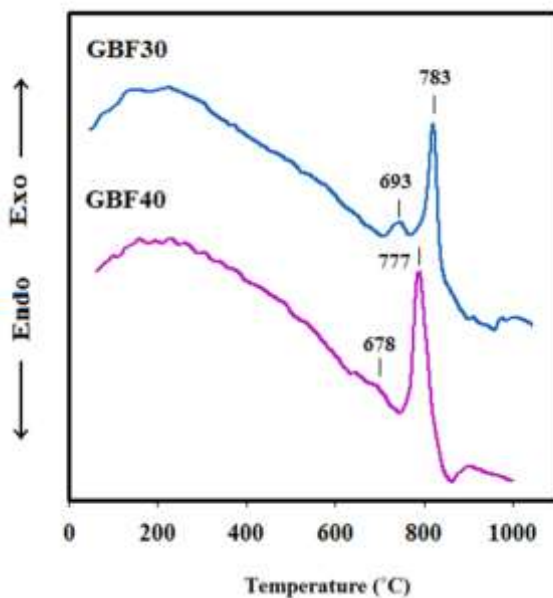


Figure 2. DTA cures of GBF40 and GBF30 samples

The lower peak temperature of the crystallization of BaF₂ in GBF40 (678°C) in comparison with GBF30

(693°C) could be attributed to the phase separation in this sample, which has a high amount of BaF₂. It is clarified that the addition of fluorine ions to the glass structure introduces nonbridging oxygens. Hereby, the viscosity of the glass decreases, which facilitates the mobility of ions, which provokes the phase separation and crystallization, consequently [11]. On the other hand, the crystallization mechanism of oxyfluoride glasses is a diffusion-controlled process; hence, adding higher amounts of glass network modifier agents (here the fluorides) results in readily movement and diffusion of ions, and consequently, lower crystallization temperatures [18,19].

The peak temperature of the glassy matrix is higher for the GBF30 sample (783°C) and XRD results prove that the precipitated crystalline phase at second peak temperatures is BaAl₂Si₂O₈ (Figure 3(c)).

3.3. XRD Patterns of Glassy and Crystallized Samples

As shown in Figure 3(a), there is no observable peak in XRD patterns of glass samples. The absence of peaks in the XRD pattern of GBF40 sample, somewhat approves that the smoky non-transparent regions in this glass is due to the phase separation and not related to unwanted crystallization. No crystalline peak was observed in GBF30. Moreover, two amorphous humps are distinguishable in the XRD results of both samples. This implies that two separate crystalline phases can precipitate each of the glasses and it is in agreement with the existence of two exothermic peaks in DTA curves.

In Figure 3(b) patterns of heat-treated glasses at first and second exothermic peaks of DTA curves, are presented. If both samples experience the heat treatment at their first peak temperature of their DTA results, BaF₂ nanocrystals would be the only precipitated crystalline phase, while heat-treating at second peak temperatures results in crystallization of two different crystalline phases, i. e., BaF₂, and BaAl₂Si₂O₈ (Figure 3(c)). Based on XRD results and using Scherrer equation (Equation 1), the mean crystal size of BaF₂ nanocrystals was calculated and it was 10nm for GBF30 and 16nm for GBF40.

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

According to Bocker et. al. [20], when BaF₂ crystals appear in the glassy matrix, SiO₂-Al₂O₃ rich layers surround these crystals. Therefore, to grow the size of crystals, ions diffuse the SiO₂-Al₂O₃ rich layers. When the fluoride ion, which is considered as barrier layers. The amount should be high enough to keep viscosity low to allow ions as a consequence, in sample GBF40 higher BaF₂ percentage results in larger BaF₂ crystals than GBF30.

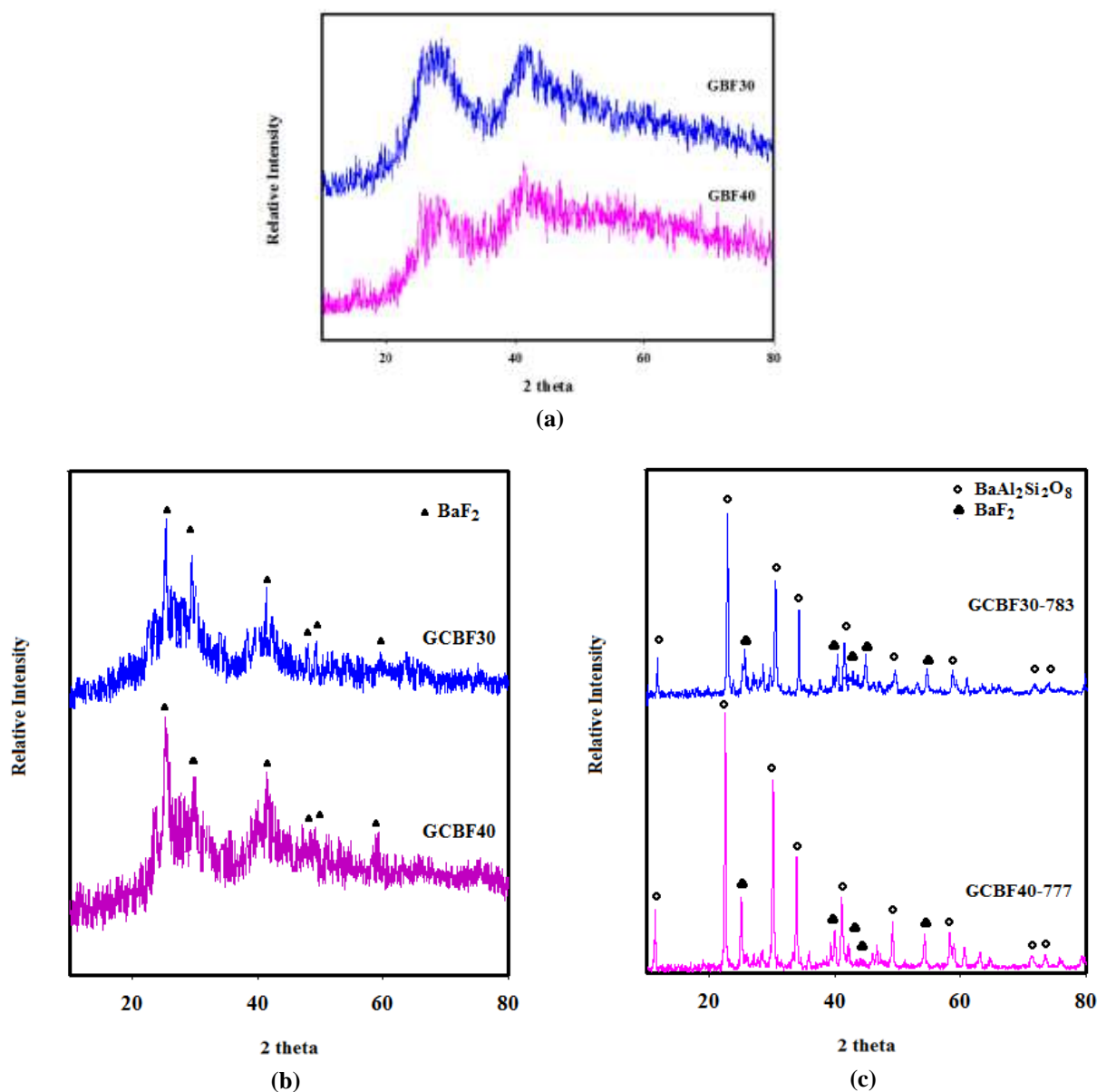


Figure 3. XRD patterns of (a) glassy samples and glass-ceramic samples heat-treated at (b) first and (c) second exothermic peak temperatures according to DTA curves

3.4. UV-Vis-NIR Spectra and Structural Study

UV-Vis-NIR transmission spectra of glasses are shown in Figure 4. There is a sharp increase in absorption at wavelengths close to the band-gap that manifests itself as an absorption edge. This outcome demonstrates the amorphous nature of these compounds. Generally, the absorption edge of glasses is affected by the strength of oxygen binding and the number of non-bridging oxygens in the glass network. The addition of glass

modifiers and network breaking agents, like fluoride ions, causes breaking oxygen bonds. In this way, the number of non-bridging oxygens (NBO) grows and the absorption characteristics change. As BaF_2 content increases, the NBOs increases and then, the bond edge should move to lower energies, which is observable in Figure 4. However, the inordinate red shifting of absorption edge of GBF40 is due to the phase separation within its network and based on Rayleigh and Mie scattering effect [21].

That is worth to notice that, both samples have high transmissions without decrement (approximately higher than 90%) in the UV-Vis-NIR region up to 2500nm.

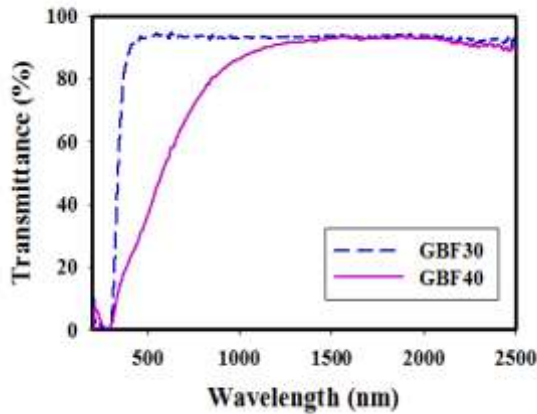


Figure 4. UV-Vis-NIR spectra of GBF40 and GBF30 samples

FT-IR spectra of samples are presented in Figure 5. Peaks placed at 445, 700, and 985 cm^{-1} are ascribed to bending, symmetric stretching, and asymmetric stretching vibrations of Si-O-Si bonds, respectively [22, 23], which imply the silicate-like structure of glasses. Besides, the absorption peak at 587 cm^{-1} is due to the presence of Ba-F bonds in samples [24]. Therefore, the oxyfluoride structure of the studied samples is somewhat proved.

In oxyfluoride glasses, fluorides behave in three ways: (1) as network modifier agents (2) stay as free fluoride ions (3) bond with cations such as Ca^{2+} or Al^{3+} . Each of these roles is taken based on the content of modifying oxides in glass [25]. It is also proved that if oxide content increase, fluorides would not exist as Si-F bonds and F⁻ ions would have a high tendency to bond Al^{3+} cations rather than Si^{4+} , which results in peaks at 1460, 1741, and 1640 cm^{-1} in FT-IR spectra and no evidence of Si-F bond (which usually places at 945 cm^{-1} [26]) is observable [27-29].

Si^{4+} cations are replaced by Al^{3+} and form peaks at 1160 cm^{-1} , which overlaps with the peak of asymmetric-stretching Si-O-Si bonds [30].

It is obvious in Figure 5 that the transmittance of overall FT-IR spectrum changes for varying amounts of BaF_2 in the glass composition. In fact, the glass network gets weaker in the case of higher BaF_2 content and thus, the absorption of the whole spectrum increases [31]. In spite of the absorption of silicate bonds, fluorine-based bonds, i.e., Ba-F, and Al-F, do not demonstrate a very significant sharpening for the GBF40 sample. As discussed above, fluoride ions bond to Al^{3+} and Ba^{2+} cations. Bonding to Al^{3+} reduces fluorine loss in

oxyfluoride glasses [9]. In sample GBF40, Al_2O_3 amount is higher than that of GBF30. Therefore, the lower Al^{3+} ions per fluoride anions causes higher fluorine loss, and consequently, the intensity of fluoride-based bonds does not change as it was expected. Fluorine loss analysis also confirms this claim. In other words, fluorine loss in GBF40 is 38% while it is only 25% for GBF30.

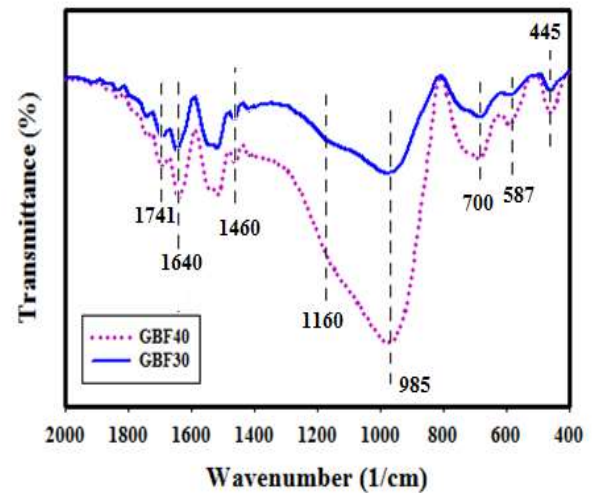


Figure 5. FT-IR spectra of GBF40 and GBF30 samples

4. CONCLUSIONS

- 1- According to DTA results, the crystallization temperature for GBF30 glass (693 $^{\circ}\text{C}$) was higher than the GBF40 (678 $^{\circ}\text{C}$) sample, which implies the more depolymerization of glass network in presence of higher fluoride content.
- 2- The only precipitated crystalline phase at the first peak temperature of both samples was BaF_2 .
- 3- Due to the Rayleigh and Mie scattering effect of phase-separated parts in the GBF40, band edge shifts to higher wavelengths.
- 4- Owing to the lower amount of Al_2O_3 in GBF40, higher fluorine loss occurred in comparison with GBF30 sample.

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