Research Article

Effect of Annealing on Optical Properties of ZnO·LiF·B\(_2\)O\(_3\) Glasses

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The melt-quench method is used to synthesize zinc fluoroborate glasses with compositions \(x\)ZnO·\((40-x)\)LiF·60B\(_2\)O\(_3\) (\(x = 0, 5, 10, 15, \) and 20). Optical characterization was carried out to examine the variation of optical bandgap energy (\(E_g\)) and Urbach energy (\(E_U\)) with respect to the concentration for the samples annealed at different temperatures (300\(^\circ\)C, 350\(^\circ\)C, and 400\(^\circ\)C). Annealing shows its effect on the samples with the variations in the values of \(E_g\) and \(E_U\). These variations are explained on the basis of formation of different molecular species like BO\(_3\)\(^-\) units, boroxol rings, and the change in the number of nonbridging oxygen atoms.

1. Introduction

Crystallization of a melt can be avoided by a sufficient fast cooling rate to form the amorphous phase. In borate glasses, boron-oxygen triangles bear sheet like structure with their ability to connect themselves to form a network. This characteristic has popularized B\(_2\)O\(_3\) as one of the best glass formers [1, 2]. The requirement of random arrangement of various atomic and molecular species is easily fulfilled in borate glasses. With the addition of alkali halides in borate glasses there appears modifications in some properties of these glasses due to variations that occurred in their structures [3–9]. These modifications are reported for the inclusion of LiF in the borate glasses [3]. Some oxygen atoms get replaced by fluorine ions in the network to form new units like BO\(_2\)F, BO\(_2\)F\(_2\), BOF\(_3\), and BO\(_3\)F [4–6]. There may be an increase in the number of nonbridging oxygen atoms due to the increase in polyhedral groups of boron and oxygen [7–9]. Modifications in microstructure of a substance are observed in terms of variations of various properties like optical, physical, electrical and structural, and so forth. Structure and therefore optical characteristics of a material are affected by nonhomogeneous cooling of the melt. The effect of annealing at different temperatures on optical and structural properties of B\(_2\)O\(_3\) glasses is reported so far [10–14]. In these glasses, there is always a possibility of formation of B\(_3\)O\(_6\) rings called boroxol rings, by the combination of BO\(_3\) groups. Raman spectroscopy reveals that for annealing temperature greater than the glass transition temperature, the concentration of boroxol rings increases with a decrease in temperature [13]. There appears a residual stress in such materials. During annealing of a glass, a thermodynamical and mechanical steady state is achieved after a specific time and temperature.

This paper reports the effect of annealing at different temperatures on optical properties of ZnO-LiF-B\(_2\)O\(_3\) glasses. With the addition of ZnO new molecular units are expected to be formed which affects the glass structure by changing the number of NBOs. Due to this reason optical bandgap energy and Urbach energy change with composition.

2. Experimental Details

2.1. Sample Preparation. Fluoroborate glasses containing ZnO with compositions xZnO·(40 – x)LiF·60B\(_2\)O\(_3\) (\(x = 0, 5, 10, 15, \) and 20) glasses were synthesized through melt-quench method using ZnO, LiF, and H\(_3\)BO\(_3\), reagent grade.
powders. Various powdered materials were taken in grams equal to their molecular masses and were mixed uniformly according to their percentage presence in various samples. The uniform mixture was heated at 1273 K for 30 minutes. The bubble-free melt formed was pressed between two carbon plates at room temperature. The glassy samples were thus obtained in the form of thin pallets with an average thickness of 1 mm each.

2.2. Annealing. Samples were annealed at 300°C, 350°C, and 400°C for 2 hrs each. The samples obtained were then tested for optical properties.

2.3. Optical Characterization. Optical characterization was carried out in the wavelength range 200–1000 nm using Perkin-Elmer UV-Visible spectrophotometer at room temperature. Plots between the absorption and wavelength of incident radiations were obtained for further analysis.

3. Results and Discussion

3.1. Optical Analysis. A series of samples in $x$ZnO·$(40 - x)$LiF·60B$_2$O$_3$ compositions with $x = 0, 5, 10, 15,$ and 20 annealed at temperatures 300°C, 350°C, and 400°C are tested for UV-visible absorption at room temperature. The absorption profiles of annealed samples are depicted in Figures 1, 2, and 3, which are the plots of absorption coefficient $\alpha(\nu)$ versus wavelength of incident radiation.

The absorption coefficient $\alpha(\nu)$ is related to transmitted intensity ($I_t$), incident intensity ($I_i$), and the thickness of the sample ($t$) [15] as

$$\alpha(\nu) = \left(\frac{1}{t}\right) \ln\left(\frac{I_i}{I_t}\right).$$  \hspace{1cm} (1)

Absence of sharp absorption edge in all the plots given in Figures 1, 2, and 3 confirms that the samples are amorphous.
In nature. Optical bandgap energy is an important parameter which reflects the optical behavior of a sample in terms of its transparency towards electromagnetic radiations. The optical bandgap energy \((E_g)\) is related to the absorption coefficient \(\alpha(\nu)\) \[15\] as

\[
\alpha h \nu = B (h \nu - E_g)^r.
\]

In this equation \(\nu\) is the frequency of incident radiation and \(B\) is a constant named as band tailing parameter. The value of the index \(r\) suggests the nature of transitions taking place in the sample. For indirect allowed and forbidden transitions \(r\) equals 2 and 3, respectively, and for direct allowed and forbidden transitions \(r\) equals 1/2 and 2/3, respectively. Tauc’s plots \([\alpha h \nu]^{1/2}\) versus \(h \nu\), \(r = 2\) for the reported samples are shown in Figures 4, 5, and 6. Values of optical bandgap energy \(E_g\) are obtained by extrapolating the linear regions of Tauc’s plots. The variation of \(E_g\) against the composition for the samples annealed at different temperatures is listed in Table 1 and plotted in Figure 7.

At annealing temperature 300°C, optical bandgap energy increases from \(x = 0\) to \(x = 10\) with maximum at \(x = 10\) and then decreases for \(x = 15\) and \(x = 20\). This trend is followed for the annealing temperature 350°C with a decreased value of \(E_g\) for each sample. It is expected here that during annealing of the samples at 350°C, some of BO\(_4\) structural units get converted in BO\(_3\) units with one nonbridging oxygen atom (NBO) each. Therefore an increase in the number of NBOs decreases the value of \(E_g\). For annealing temperature 400°C there is a change in optical behavior of the samples. In this case the value of \(E_g\) increases for the samples with \(x = 0\) to \(x = 15\) and decreases for the sample with \(x = 20\) as compared to its value at annealing temperature 350°C. It is expected that in the samples with \(x = 0\) to \(x = 15\) BO\(_3\) units get connected to themselves to form boroxol rings. This phenomenon results in a decrease in the number of NBOs and in turn an increase in the optical bandgap energy. For the sample with \(x = 20\) the formation of BO\(_3\) units from BO\(_4\) units dominates over the phenomenon of the formation of boroxol rings, which results in a decrease in the value of \(E_g\). Although, the trend of variation of \(E_g\) in
Table 1: Cutoff wavelength (\(\lambda_{\text{cutoff}}\)), optical band gap energy \(E_g\), and Urbach energy \(E_U\) for the samples with \(x = 0, 5, 10, 15,\) and 20 in the compositions \(x\text{ZnO} \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3\).

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<th>Annealing temperature (°C)</th>
<th>(x) (mol%)</th>
<th>(\lambda_{\text{cutoff}}) (nm)</th>
<th>(E_g) (eV)</th>
<th>(B) (cm eV)^{-1}</th>
<th>(E_U) (eV)</th>
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Figure 7: Variation of \(E_g\) with composition for samples with \(x = 0, 5, 10, 15,\) and 20 in the compositions \(x\text{ZnO} \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3\).

Figure 8: Urbach plots for samples annealed at 300° C with \(x = 0, 5, 10, 15,\) and 20 in the compositions \(x\text{ZnO} \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3\).

The value of \(E_U\) for the reported samples is calculated from the inversus of the slopes of the linear parts of the urbach plots (\(\ln(\alpha)\) vs. \(hv\)), shown in Figures 8, 9, and 10. The values of \(E_U\) for samples annealed at different temperatures are listed in Table 1 and the variation of \(E_U\) is plotted against the composition in Figure 11.
At annealing temperature 350°C $E_U$ is more than that at annealing temperature 300°C for all the samples. It again decreases at annealing temperature 400°C as compared to that at annealing temperature 350°C, except for the sample with $x = 20$, which increases remarkably. It can be explained on the same ground that at annealing temperature 350°C more BO$_3^-$ units are formed as compared to those at annealing temperature 300°C and hence the number of NBOs increases. This results in more potential fluctuations to enter in the mobility gap which increases the value of $E_U$. At annealing temperature 400°C, the expected formation of boroxol rings decreases the number of NBOs and so the mobility gap fluctuations. Therefore the value of $E_U$ decreases for samples with $x = 0$ to $x = 15$ as compared to their respective values at annealing temperature 350°C. And due to the formation of more BO$_3^-$ units than boroxol rings, $E_U$ increases for the sample with $x = 20$ as compared to its value at annealing temperature 350°C.

4. Conclusions

(1) In the series of samples $x$ZnO·$(40 - x)$LiF·60B$_2$O$_3$, values of $E_g$ at annealing temperature 300°C increase from $x = 0$ to $x = 10$ and decrease for the samples with $x = 15$ and $x = 20$. This trend is followed by all the samples at annealing temperature 350°C with decreased values of $E_g$, due to the formation of more BO$_3^-$ units. Values of $E_U$ at annealing temperature 350°C are more than those at annealing temperature 300°C for all the samples. This is also due to the same reason as explained above.

(2) At annealing temperature 400°C values of $E_g$ again increase and values of $E_U$ decrease for the samples with $x = 0$ to $x = 15$ as compared to their values at annealing temperature 350°C, due to the formation of boroxol rings. For the sample with $x = 20$ the phenomenon of formation of BO$_3^-$ units dominates over the formation of boroxol rings. Therefore, value of $E_g$ again decreases and that of $E_U$ increases.
References


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