Synthesis and Structural Properties of Sm³⁺ doped Sodium Lithium zinc Lead Borate Glasses

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Abstract. Sodium lithium zinc-lead borate glasses co-activated with Sm³⁺ ion were prepared by melt and quenching method. The glass composition regarding to (65 – x)B₂O₃ : 5ZnO : 5Li₂O : 15 Na₂O : 10PbO : x Sm₂O₃ chemical formula is synthesized with x = 0.0; 0.05; 0.1; 0.5; 1.0; 2.0 and 4.0 mol.%. These samples which are labeled as Sm_0.0; Sm_0.05; Sm_0.1; Sm_0.5; Sm_1.0; Sm_2.0 and Sm_4.0 respectively. The structural characteristic was investigated and analyzed by using the FTIR and XRD. Moreover, physics properties such as molar weight, density, molar volume, refractive index, etc were calculated with the standard equations. From the measurement and calculation, the density was found to increase slightly by showing linear trends with Sm₂O₃ content in the glass network structure. It was happened due to the compactness level of glass structure and geometrical arrangement have modified in the glass network. The molar volume of the glass samples also gradually increases from 28.185 cm³/mol to 29.613 cm³/mol. From the FTIR and XRD analysis can be confirmed that the present samples are amorphous without the presence of the crystalline peak.

1. Introduction
The glass materials doped rare-earth (RE⁺) ions have been very interesting due to have broad application and potential in the design and development of photonic devices [1-3]. Commonly trivalent RE components have entirely stable discharges, because of the 4f electrons which are profoundly covered and henceforth all around protected from the external shells. This characteristic makes it suitable to integrate the RE components into different hosts with various cross-sections and still save the normal RE luminescence [4]. Host glass with low energy phonon was exactly had luminescence efficiency of RE⁺ ions [5-6]. Several famous research related to alkali-borate glasses utilization to improve optical and structural properties of glasses have been reported through the placement of several metal oxides into the glass network [7-9]. The intensity and sharpness of emission cross-section of RE-doped glasses enable the observer to investigate free atoms interaction in
a solid optical material with a kind degree of accuracy [10]. RE-doped glass formers especially inorganic borate with additional suitable modifiers were being studied. The compositions can be applied at several devices such as new lasing materials upconverters, light-emitting diodes (LEDs), fiber amplifiers, memory devices, fluorescent display, etc [11-12]. One of the most popular types of RE ions is the Samarium oxide (Sm$^{3+}$) ion due to its high density in optical storage devices, corrosion-free when doped into glasses, and is an essential component in a solid-state laser. Besides that, the Sm-doped Borate glasses system is capable to produce $G_s$→$H_{5/2}$, $G_s$→$H_{7/2}$, $G_s$→$H_{9/2}$, $G_s$→$H_{11/2}$ transitions with full red or orange color that used as solid-state lighting and display devices [12]. The red and orange luminescence from Sm$^{3+}$ clearly can be used in the cathode-ray tube (CRT) and plasma display. Glass material like borate oxide (B$_2$O$_3$) is suitable as a host matrix type due to high transparency, good thermal stability, low melting point and make a glass network to be stable [15]. Furthermore, zinc borate glasses were increasingly interesting because of their produced large stimulated emission cross-section and quantum efficiency [16].

In our previous studies on structural and spectroscopic properties of sodium-lead-zinc-lithium-borate glasses doped several RE ions among them are Neodymium [7]; Europium [8]; Erbium [7] and Dysprosium [17] have been reported. In the present work, we report the Sm$^{3+}$ doped borate glass system and the extended investigation is related to the optical properties of glasses system.

2. Method
The Sm$^{3+}$-doped sodium-lead-zinc-lithium-borate glasses with Sample composition of (65 – x)B$_2$O$_3$ : 5ZnO : 5Li$_2$O : 15Na$_2$O : 10PbO : x Sm$_2$O$_3$ (where x = 0.0; 0.05; 0.1; 0.5; 1.0; 2.0 and 4.0 mol.%) were prepared by melted and quenched method with the chemical reagents purity more than 99.99 % in 20 g batches. The glass samples were labelled with the following codes Sm_0.0; Sm_0.05; Sm_0.1; Sm_0.5; Sm_1.0; Sm_2.0; Sm_4.0 code respectively. The nomenclature of chemical compounds and details composition were showed in Table 1. After composed and mixture in crucible alumina, the powdered sample was melted in a furnace at 1100°C and held on 3 h. The pouring process was done on stainless steel and extended to the annealing process at 500°C for 3 h. Then, the furnace was decreased to room temperature. Glasses sample were cut and polished in dimensions size of 20 x 10 x 5 mm$^3$. The structural properties were investigated by using X-Ray Diffractometer (XRD) and Fourier Transform Infrared (FTIR) respectively. Moreover, physics properties were calculated with a kind equation such as molar weight, density, molar volume, refractive index, etc.

### Table 1. The initial and details composition of doped sodium-lead-zinc-lithium-borate glasses

| No | Glass initial | B$_2$O$_3$ (mol%) | Na$_2$O (mol%) | PbO (mol%) | ZnO (mol%) | Li$_2$O (mol%) | Sm$_2$O$_3$ (mol%) |
|----|---------------|------------------|---------------|-----------|-----------|-------------|-------------------|
| 1  | Sm_0.0        | 65.00            | 15.0          | 10.0      | 5.0       | 5.0         | -                 |
| 2  | Sm_0.05       | 64.95            | 15.0          | 10.0      | 5.0       | 5.0         | 0.05              |
| 3  | Sm_0.1        | 64.90            | 15.0          | 10.0      | 5.0       | 5.0         | 0.10              |
| 4  | Sm_0.5        | 64.50            | 15.0          | 10.0      | 5.0       | 5.0         | 0.50              |
| 5  | Sm_1.0        | 64.00            | 15.0          | 10.0      | 5.0       | 5.0         | 1.00              |
| 6  | Sm_2.0        | 63.00            | 15.0          | 10.0      | 5.0       | 5.0         | 2.00              |
| 7  | Sm_4.0        | 61.00            | 15.0          | 10.0      | 5.0       | 5.0         | 4.00              |

3. Results and Discussion
3.1. Glasses Display
The appearance of six glass samples after a cut and polished treatment were displayed in Figure 1. The glasses take placed on millimeter paper and photographed to see the transparency level of samples. Figure 1 can be seen that the light yellow color dominates the glasses color and appears to high transparency. The sample is placed on millimeter paper and photographed to see the level of transparency. Glass with 0.05 mol% label was seen most transparency and is almost clear. This sample has almost the same transparency with the un-doped sample as the previously reported [7-10]. The addition of a small amount of Sm$^{3+}$ ion to the glasses system can be increasing the color change of the sample towards orange. This phenomenon is seen starting from 0.10 mol% to 4.00 mol% sample. As we have known that the Sm$^{3+}$ ion has a characteristic color leading to a bright orange color [18-20].

![Figure 1: The view of Sm$^{3+}$ doped sodium-lead-zinc-lithium-borate glasses with varied concentration dopant from 0.05 mol% to 4.00 mol%.](image)

3.2. Physical Properties
The Physical Properties such as molar weight, density, molar volume internuclear distance as well as field strength and optical band gap of Sm$^{3+}$ doped borate glasses were displayed in Table 2. From Table 2 can be seen that the Sm$^{3+}$ ion concentrations are varied and affect the others parameters like polaron radius ($r_{p}$). As we known that the ion concentration number will be increased with the addition of Sm$^{3+}$ concentration however will decrease the polaron radius. The same trend also happened at internuclear distance $r$, where the highest value was achieved for Sm_0.05 and the lower for Sm_4.0.

| Physical properties | Glass samples |
|---------------------|---------------|
|                     | Sm 0.05 | Sm 0.1 | Sm 0.5 | Sm 1.0 | Sm 2.0 | Sm 4.0 |
| Molar weight, $M$ (g) | 82.573 | 82.713 | 83.829 | 85.224 | 88.015 | 93.597 |
| Density, $\rho$ (g/cm$^3$) | 2.930 | 2.933 | 2.941 | 2.968 | 3.048 | 3.161 |
| Molar volume, $M_V$ (cm$^3$/mol) | 28.185 | 28.198 | 28.508 | 28.717 | 28.875 | 29.613 |
| Thickness (cm) | 0.285 | 0.315 | 0.340 | 0.305 | 0.335 | 0.310 |
| Ion concentration, $N$ (x10$^{22}$ ion/cm$^3$) | 0.107 | 0.214 | 1.056 | 2.097 | 4.171 | 8.134 |
| Polaron radius, $r_{p}$ (Å) x10$^{-8}$ | 3.942 | 3.129 | 1.836 | 1.461 | 1.162 | 0.930 |
| Internuclear distance, $r_{n}$ (Å)x10$^{-8}$ | 9.782 | 7.765 | 4.558 | 3.626 | 2.883 | 2.308 |
| Field strength, $F$ (x10$^{17}$ cm$^{-2}$) | 0.399 | 0.633 | 1.838 | 2.904 | 4.593 | 7.169 |
| Refractive index, $n$ | 1.573 | 1.585 | 1.609 | 1.599 | 1.610 | 1.608 |
| Optical band gap (indirect), $E_{G}(eV)$ | 3.27 | 3.35 | 3.37 | 3.38 | 3.39 | 3.49 |
| Optical band gap (direct), $E_{G}(eV)$ | 3.77 | 3.70 | 3.80 | 3.79 | 3.46 | 3.78 |
| Dielectric constant, $\varepsilon$ | 2.474 | 2.511 | 2.59 | 2.555 | 2.591 | 2.584 |
| Molar refractivity, $R_{m}$ (cm$^{-3}$) | 9.285 | 9.446 | 9.873 | 9.804 | 10.009 | 10.233 |
| Polarizability of oxide ions, $\alpha_{o}$ (x10$^{-24}$ cm$^3$) | 3.683 | 3.747 | 3.916 | 3.889 | 3.970 | 4.059 |
| Metallization criteria, $M$ | 0.671 | 0.665 | 0.654 | 0.659 | 0.653 | 0.654 |
| Reflection loss, $R$ (%) | 4.597 | 5.117 | 5.451 | 5.305 | 5.46 | 5.428 |

The Practically, density parameters $\rho$ (g/cm$^3$) were measured by using the Archimede’s principle with water used as the immersion liquid. Moreover, the density and molar volume trends have been obtained and shown in Figure 2. As shown in Figure 2 both of molar volume and density were started
from below values 28.185 cm/mol and 2.930 g/cm$^3$ respectively. The density was increased slightly by showing linear trends with Sm$_2$O$_3$ content in the glass network structure. It was happened due to the compactness level of glass structure and geometrical arrangement have modified in glass network [18]. With the increasing of Sm$^3+$ concentration, the molar volume of the glass samples gradually increases from 28.185 cm/mol to 29.613 cm/mol. The change in the borate network from Sm$_{0.05}$ to Sm$_{1.0}$ causes the molar volume to increase slightly. However, it has been increased drastically from Sm$_{1.0}$ to Sm$_{4.0}$ glasses when doped for the higher content of Sm$^3+$. The addition of Sm$^3+$ contents to borate glass might cause several changes in the glass network, as a result, is the molar volume showing an increment trend [2,19].

![Figure 2. Molar volume and density pattern of Sm$^3+$ doped sodium-lead-zinc-lithium-borate glasses](image)

3.3. Structural Properties

The interpretation of Fourier Transform Infrared Spectrum (FTIR) has been carried out with the presumption that B – O bonds are the constituent of the B.O. glass structure. The FTIR spectra of the Sm$^3+$ doped sodium-lead-zinc-lithium-borate glasses are recorded from 650 to 4000 cm$^{-1}$ as shown in Figure 3. All the studied glass samples shows the active modes characteristic of borate network vibrations. The borate network is generally built up from the coordination dividing of BO$_4$ tetrahedral units [20]. The units of BO$_4$ tetrahedral were made network features in the glass structure that always has a negative charge ([BO$_4$]$^-$) [20]. The transmission bands of present glasses are clear at three fundamental bands. The first band occurs between 650 and 834 cm$^{-1}$ reflects to the B-O-B bending vibrations of borate ion various in BO$_3$ triangles units. The second transmittance at 850-1200 cm$^{-1}$ band corresponds to the B-O stretching of BO$_4$ tetrahedral units. Moreover, the third transmittance broad band centered at 1200 – 1500 cm$^{-1}$ corresponds to the vibration of asymmetric stretching of the borate ion in BO$_3$ triangles units [21].
The X-ray diffraction spectra were recorded in the theta range of 10 to 80 degrees for Sm\textsuperscript{3+} doped sodium-lead-zinc-lithium-borate glasses is shown in Figure 4. The diffraction pattern for six glass samples shows two broad humps at around $2\theta = 27^\circ$ and $43^\circ$. Generally, the XRD spectrum as shown in Figure 4 were not appear diffraction or crystallization peaks which confirms the amorphous nature for all glass samples. Based on this investigation, the same pattern also obtained with our previous report for some rare-earth dopant [18-20].

**4. Conclusion**

Transparent glasses based on Samarium oxide (Sm\textsubscript{2}O\textsubscript{3}) doped sodium-lead-zinc-lithium-borate have been successfully prepared by melt and quenching principle. The chemical composition of $(65 - x)\text{B}_2\text{O}_3 : 5\text{ZnO} : 5\text{Li}_2\text{O} : 15\text{Na}_2\text{O} : 10\text{PbO} : x\text{Sm}_2\text{O}_3$ with $x = 0.0; 0.05; 0.1; 0.5; 1.0; 2.0$ and $4.0$ mol.\%
were cut, polished and characterized to observe physical and structural properties. The density as a part of physical parameters was found to increase slightly by showing linear trends with Sm₂O₃ content in the glass network structure. It was happened due to the compactness level of glass structure and geometrical arrangement have modified in the glass network. The molar volume of the glass samples also gradually increases from 28.185 cm/mol to 29.613 cm/mol. From the FTIR and XRD analysis can be confirmed that the present samples are an amorphous nature without the presence of the crystalline peak.

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