Physical, optical and gamma-ray shielding properties of BaO-La$_2$O$_3$-B$_2$O$_3$ and BaO-Na$_2$O-B$_2$O$_3$ glass systems at 662 keV

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Abstract. In this work, glasses with composition xBaO : 20La$_2$O$_3$: (80-x)B$_2$O$_3$ and xBaO : 20Na$_2$O: (80-x)B$_2$O$_3$ (where x= 15, 20,25 and 30 mol%) were prepared using melt-quenching method. Physical, optical and gamma-ray shielding properties were investigated and compared with theoretical calculations. $^{137}$Cs was used as $\gamma$-source for investigating experimental mass attenuation coefficient at 662 keV energy. The theoretical mass attenuation coefficient was calculated using WinXcom program. The density and the molar volume show increasing trend with increase in BaO concentration. Transmission spectra shows dissimilarity in their transmittance for BaO-Na$_2$O-B$_2$O$_3$ and BaO-La$_2$O$_3$-B$_2$O$_3$ glasses. BaO-Na$_2$O-B$_2$O$_3$ glasses show higher transmittance in the visible region than compared to BaO-La$_2$O$_3$-B$_2$O$_3$ glasses. Mass attenuation coefficients, $Z_{eff}$ show increasing trend whereas HVL at 662 keV show decreasing trend with increase in BaO concentration for these both these glasses. Theoretical and experimental mass attenuation results are in good agreement with each other. The synthesized glasses show potential use for radiation shielding material applications.

1. Introduction

Gamma ray absorbance can be enhanced by using higher Z element from the periodic table therefore, inclusion of heavy metals like Bi and Pb in the glass network can lead to increase the absorption of $\gamma$-rays. Such characteristic can be used in nuclear waste management and high energy physics for replacement of conventional $\gamma$-rays shielding material concrete. Concrete is opaque to visible light but glasses can substitute concretes due to their transparency in visible range and they can act as an effective $\gamma$-ray shielding transparent materials [1]. Glass is one of the materials that can be used as radiation shielding material, because of its advantages like good homogeneity and excellent transparency [2]. Radiation shielding properties can be enhanced by addition of oxides in glass formula [3]. Borate glasses are one of the most popular and excellent glass forming materials. Boric acid (B$_2$O$_3$) is one of the most popular and excellent glass former known to form glass at lower melting point with good transparency, high chemical durability [4]. Sodium oxide (Na$_2$O) is used to expand the glass-forming region and facilitate ion exchange and provide low melting glass [5]. Barium oxide (BaO) are expected to enhance the gamma-ray attenuation due to their higher atomic numbers. BaO can also replace the bismuth due to their low transparency in visible region and also extensively explored in radiation shielding purpose when...
fabricated in glass [6]. Glasses containing rare earth also tend to have higher hardness, elastic modulus, glass transition temperature (Tg) and chemical stability. Consequently, rare earth is widely introduced to improve the properties of glass, among which La$_2$O$_3$ is the most common oxide [7]. In the present work, we have investigated on physical optical and γ-rays shielding properties of BaO-La$_2$O$_3$-B$_2$O$_3$ and BaO-Na$_2$O-B$_2$O$_3$ glass system for radiation shielding material applications.

2. Experiment

2.1. Glasses preparation

The chemical compositions of lanthanum oxide and sodium oxide, mixed with barium borate glasses are as follows:

\[
\begin{align*}
\text{xBaO : 20La}_2\text{O}_3 &: (80-x)\text{B}_2\text{O}_3 \quad (\text{where } x = 15, 20, 25 \text{ and } 30 \text{ mol}%) \\
\text{xBaO : 20Na}_2\text{O} &: (80-x)\text{B}_2\text{O}_3 \quad (\text{where } x = 15, 20, 25 \text{ and } 30 \text{ mol}%) 
\end{align*}
\]

Glass systems with their composition were prepared by melt-quenching technique. Analytical reagent grade of H$_3$BO$_3$, BaCO$_3$, La$_2$O$_3$ and Na$_2$O were mixed thoroughly. Each batch of formulas were weighted to 20 gram and melted in porcelain crucible at 1200 °C for 3 h for homogeneous mixture was obtained. The prepared glasses were then annealed in a muffle furnace at 500 °C for 3 h and cooled to room temperature. The obtained glass samples were cut in 1.5×1×0.3 cm$^3$ dimension with rectangular shape.

2.2. Density and molar volume

By applying the Archimedes principle, the weights of the prepared glass samples were measured in air and water using a 4-digit sensitive microbalance (AND, HR200). Then the density ($\rho$) was determined from the relation [8].

\[
\rho = \frac{w_a - w_w}{w_a - w_w} \times \rho_w \quad \text{(g/cm$^3$)}
\]

(1)

where $w_a$ is weights of the glass sample in air $w_w$ is weights of the glass sample in water and $\rho_w$ is density of water. The corresponding molar volume was calculated using the relation [8].

\[
V_m = \frac{M_T}{\rho} \quad \text{(cm$^3$/mol)}
\]

(2)

where $V_m$ is the molar volume, $M_T$ is the total molecular weight and $\rho$ is the calculated density of the glass.

2.3. Optical transmission measurement

The optical transmission spectra of the prepared glass samples in the UV–VIS-NIR region in the wavelength from 200-1100 nm were recorded at room temperature using a double-beam spectrophotometer (Varian cary-50).

2.4. Radiation Shielding properties

The mass attenuation coefficient is written as [8]
\[ \mu_m = \ln \left( \frac{I_0}{I} \right) \left( \frac{\text{cm}^2}{\text{g}} \right) \]  

(3)

where \( \mu_m \) is the density of material (g/cm\(^3\)), \( I_0 \) and \( I \) are the incident and transmitted intensities, respectively, and \( t \) is the thickness of absorber (cm). Theoretical values of the mass attenuation coefficients of mixture or compound have been calculated by WinXCom, based on the mixture rule [8].

\[ \mu_m = \sum_i w_i (\mu_{m_i}) \left( \frac{\text{cm}^2}{\text{g}} \right) \]  

(4)

where \( w_i \) is the weight fraction of each element in mixture, \( (\mu_{m_i}) \) is the mass attenuation coefficient for individual element in mixture. The basic relation for calculating the effective atomic number (\( Z_{\text{eff}} \)) for all types of materials, compounds as well as mixtures can be written in terms of the fraction abundance as [8]:

\[ Z_{\text{eff}} = \frac{\sum_i f_i A_i (\mu / \rho)_i}{\sum_j f_j Z_j (\mu / \rho)_j} \]  

(5)

where \( f_i = n_i / \sum_j n_j \) is the fractional abundance of constituent element \( i \) (\( n_i \) is the number of atoms, \( \sum_j n_j \) is the total number of atoms present in the molecular formula), \( A_i \) is the atomic weight and \( Z_i \) is the atomic number. The following mass attenuation coefficient relates half value layer to linear attenuation coefficient [8].

\[ \text{HVL} = 0.693 / \mu \]  

(6)

The experimental setup for mass attenuation coefficient determination is shown in Figure 1. The source and absorber system were mounted on a composite of adjustable stands. This setup can move in the transverse direction for proper beam alignment. \(^{137}\)Cs radioactive source of 15 mCi (555 MBq) strength was obtained from the Office of Atom for Peace (OAP), Thailand. The incident and transmitted gamma-rays intensity were measured for a fixed preset time in each experiment by recording the corresponding counts, using the 2 in × 2 in NaI(Tl) detector having an energy resolution of 8% at 662 keV (BICRON model 2M2/2), with CANBERRA photomultiplier tube base model 802-5. The dead time in this experiment was 0.73–1.37%. The pulse shaping time was 0.5 µs. An optimum sample thickness (0.5 ≤ \( \mu x \) ≤ 5.0) was selected in this experiment on the basis of the Nordfors criteria. The statistical error in this experiment calculated from the standard error of 3 items (i) ray-sum measurement, which calculated from experiment, ray-sum is product of linear attenuation coefficient (\( \mu \)) with thickness (\( x \)); (ii) density measurement and (iii) thickness measurement. Finally, the total standard error has been determined by combining errors for the ray-sum measurement, density measurement and thickness measurement in a quadrature. The spectra were recorded using a CANBERRA PC-based multi-channel analyzer. In this experiment, the validity of the mass attenuation measurement was confirmed by measuring a lead slab.
3. Results and discussions

3.1. Physical properties

The density and molar volume results are shown in Table 1. These results show that the density of BaO-La$_2$O$_3$-B$_2$O$_3$ and BaO-Na$_2$O-B$_2$O$_3$ glass increases with increasing in BaO concentration due to the replacement of B$_2$O$_3$ (2.460 g/cm$^3$) by BaO (5.72 g/cm$^3$) which have lower densities than BaO. The density value for the BaO-La$_2$O$_3$-B$_2$O$_3$ and BaO-Na$_2$O-B$_2$O$_3$ glass system varies from 3.371-3.469 g/cm$^3$ and 2.385-2.385 g/cm$^3$ respectively with increase in the concentration of BaO. As well as lanthanum borate based glass show higher than the sodium borate glass due the density of La$_2$O$_3$ (6.51 g/cm$^3$) is higher than Na$_2$O (2.27 g/cm$^3$) as shown in Figure 4.

Figure 5, the molar volume of both these glass systems increased with increasing BaO concentration. This clearly indicates that the number of non-bridging oxygens (NBOs) increases in the glass resulting in expansion of their glass network by loose packing inside [9]. Such loose packing network is due to the bond length of BaO is higher compared to other oxides in the glass network as well as the ionic radii and Atomic radius of BaO is 1.35 Å and 270 pm respectively [10]. The result of molar volume showed similar trend to that of density as shown in the Table 1.

![Figure 1](image1.png)

**Figure 1.** Experimental setup for mass attenuation coefficient determination.

3.2. Optical property

Figure 2 shows that these glasses are colorless transparent glasses, such criteria being the suitability window applications. Figure. 3 shows the transmission spectra recorded for all the compositions of glass samples prepared for investigation. The transmission spectra shows that these glasses exhibits high transparency. The cut-off wavelength of the glass samples are lower than 300 nm. The glass system BaO-La$_2$O$_3$-B$_2$O$_3$, show higher transmission for 15 mol% of BaO concentration while BaO-Na$_2$O-B$_2$O$_3$ glass system show at 20 mol% BaO concentration. Whereas sodium content glass showed better transmittance compared with lanthanum glass. This may be due to the higher homogeneity of sodium glass than lanthanum glass. The cut-off wavelength or the absorption edge shows higher wavelength region with increase in BaO content. This is due to pale yellow colouration in the glass samples with addition of BaO content hence one could observe shift in the absorption edge from Figure 3.

![Figure 2](image2.png)

**Figure 2.** (A) Glass samples of BaO-La$_2$O$_3$-B$_2$O$_3$ glass system and (B) BaO-Na$_2$O-B$_2$O$_3$ glass system.
3.3. Gamma-ray shielding properties

The mass attenuation coefficients of glass samples are as shown in Figure 6. The experimental mass attenuation coefficients were evaluated from incident ($I_0$) and transmitted ($I$) gamma-ray intensities and theoretical values were calculated using winXCom program at 662 keV. It has been found that the mass attenuation coefficient values were increased with increasing of BaO concentration in both glass system, which indicates the better shielding properties.

The increase in photon interaction probability at this energy (662 keV) leads to the decrease of gamma-ray transmission with increasing amount of BaO. The experimental values of mass attenuation coefficient are in good agreement with the theoretical values with %RD less than 2 %. In this case, the mass attenuation coefficients of BaO-La$_2$O$_3$-B$_2$O$_3$ glass system were greater than BaO-Na$_2$O-B$_2$O$_3$ glasses. This shows that there is more photon attenuation in BaO-La$_2$O$_3$-B$_2$O$_3$ glass system than in BaO-Na$_2$O-B$_2$O$_3$ glasses, BaO-La$_2$O$_3$-B$_2$O$_3$ glass system has shielding properties that is better than BaO-Na$_2$O-B$_2$O$_3$ glass system.

Figure 7 presents the effective atomic number ($Z_{eff}$) of glass samples calculate by equation (5). It was found that both these glass system increased with increasing BaO concentration. The $Z_{eff}$ value increased from 9.47 to 12.22 electrons/atom and 14.27 to 17.17 electrons/atom for BaO-Na$_2$O-B$_2$O$_3$ and BaO-La$_2$O$_3$-B$_2$O$_3$ glasses respectively. The theoretical values of $Z_{eff}$ were found to be the same trend which are in good agreement with the experimental values. Increasing in BaO (153.33 g/cc) show increasing trend of $Z_{eff}$ while the lanthanum barium borate glasses show larger values due to higher molecular weight of La$_2$O$_3$ (325.8 g/cc) as compared to sodium barium borate glasses due to lower molecular weight of Na$_2$O (61.97 g/cc). This statement can be confirmed by correlating the density measurements as discussed in the section 3.1 where density of La$_2$O$_3$ glasses show higher values than Na$_2$O glasses.

![Figure 3. UV-Vis-NIR transmission spectra of glass samples.](image)

Half value layers of these glass system at 662 keV have been compared with some standard references such as concretes and commercial window as shown in Figure 8. The half value layers of both these glass system decreased with increasing BaO concentration. Such decrease results in the increase in mass attenuation coefficient. From these results, it has been observed that both glass system has better shielding properties than commercial window and some reference concretes. In this case the result found that BaO-La$_2$O$_3$-B$_2$O$_3$ glass system has been found to have better shielding properties than BaO-Na$_2$O-B$_2$O$_3$ glass system. The HVL properties of the glasses in this work has been found better than all mentioned materials, indicating the potential candidate for shielding applications of the prepared glasses.
Table 1. The Composition, density and molar volume of glass system.

| Composition (mol%) | Density (g/cm$^3$) | Molar volume (cm$^3$/mol) |
|-------------------|--------------------|--------------------------|
|                   |                    |                          |
| B$_2$O$_3$        | La$_2$O$_3$        | BaO                      |
| 65  20  15        | 3.34               | 39.87                    |
| 60  20  20        | 3.37               | 40.82                    |
| 55  20  25        | 3.42               | 41.43                    |
| 50  20  30        | 3.47               | 42.07                    |
| B$_2$O$_3$        | Na$_2$O            | BaO                      |
| 65  20  15        | 2.78               | 28.94                    |
| 60  20  20        | 2.82               | 30.04                    |
| 55  20  25        | 2.85               | 31.23                    |
| 50  20  30        | 2.90               | 32.11                    |

Figure 4. Density of glass samples.

Figure 5. Molar Volume of glass samples.

Figure 6. The mass attenuation coefficients of glass samples at 662 keV.
Figure 7. Effective atomic number of glass samples

Figure 8. Half value layer of glass samples at 662 keV compared with commercial window, serpentine, ordinary and hematite concretes.
4. Conclusions

In this work, the focus is been signified to understand the effect of barium oxide in lanthanum borate and sodium borate glass system. Glass composition BaO-La$_2$O$_3$-B$_2$O$_3$ and BaO-Na$_2$O-B$_2$O$_3$ glass system have been fabricated and investigated for their, physical, optical and radiation shielding properties. The results found that the density of the glasses increased with increasing BaO concentration, due to higher molecular weight of BaO than B$_2$O$_3$. The molar volume of both systems increased with increasing BaO concentration. Loose packing of glass network increases due to BaO which acts as a modifier providing more non-bridging oxygen (NBOs) in the glass system. The transmission spectra results shows the high transparency. It has been found that the mass attenuation coefficient values were increased with increasing of BaO concentration in both glass system. The experimental values of mass attenuation coefficient are in good agreement with the theoretical values with %RD less than 2 %. In this case, the mass attenuation coefficients of BaO-La$_2$O$_3$-B$_2$O$_3$ glasses were greater than BaO-Na$_2$O-B$_2$O$_3$ glasses. $Z_{eff}$ values shows higher for La$_2$O$_3$ doped barium borate glass compared to sodium borate glasses. The half value layers of both glass system decreased with increasing BaO concentration which results in half value layers of both glass system at 662 keV. The investigated glasses show HVL values lower than some standard shielding materials like ordinary concretes and commercial window, indicating that the potential use in radiation shielding materials due their transparency.

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