Investigation of BaO reinforced TiO$_2$–p$_2$O$_5$–li$_2$O glasses for optical and neutron shielding applications

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The optical and radiation shielding characteristics of 15TiO$_2$–70P$_2$O$_5$ – (15 − x) Li$_2$O–x BaO x = (0 ≤ x ≤ 10 mol%) glasses were reported in this study. The glass status of the investigated samples was established by XRD. Although the molar volume decreases within 39.8–31.2 cm$^3$ mol$^{-1}$, the density was increased from 2.908 to 4.11 g cm$^{-3}$ with the addition of BaO. UV-Vis-NIR spectroscopy was utilized for the examination of the optical characteristics of all compositions. $E_{\text{opt}}$ and $E_{\text{dir}}^\text{opt.}$ both increased from 2.7 to 3.07 eV and 2.79 to 3.31 eV, while $E_{\text{u}}$ decreased from 0.368 to 0.295 eV. Furthermore, the Phy-X/PSD code was used to evaluate the gamma-ray shielding parameter. Within the energy range of 15 keV to 15 MeV, the equivalent atomic number, as well as the EBF and EABF parameters, was evaluated. Overall, excellent material properties were detected for a glass with a high BaO content, which could be useful for future optical, shielding, and fast neutron shielding properties.

1. Introduction

Glasses have unique characteristics like microhardness, optical, non-toxicity, and flexibility. The dominated incorporation of specialized transition metal oxides (TMO) into phosphate glasses allows them to be used in a variety of applications. Adding various intermediate oxides to phosphate glasses has been found to improve their low chemical durability, according to several investigations. ZnO, CaO, BaO, ZrO$_2$, TiO$_2$, PbO$_2$, Bi$_2$O$_3$, Al$_2$O$_3$, and Fe$_2$O$_3$ are the most widely recommended additions to P$_2$O$_5$. Due to their unique physical characteristics, such as ultraviolet (UV) emission, excellent moisture resistance, and a high thermal expansion coefficient, TiO$_2$–P$_2$O$_5$ glasses have attracted a lot of attention in the last few decades. The main fields of application for TiO$_2$–P$_2$O$_5$ glasses are microelectronics, photonic materials, optical amplifiers, and semiconductors. Regrettably, binary TiO$_2$–P$_2$O$_5$ glass creation is limited, and elucidating these glasses requires a significant amount of energy. Glasses based on TiO$_2$–P$_2$O$_5$ have been studied as semiconductor materials for a long time. Furthermore, because Ti$^{4+}$ has empty or unfilled d-shells, which can be attributed to polarizabilities, the presence of TiO$_2$ in P$_2$O$_5$ glasses may improve their optical and electrical characteristics. TiO$_2$–P$_2$O$_5$ based glasses have been considered as potential applicants for Raman applications because of all these distinctive optical characteristics.

Alkaline oxides, in specific, are found to lower the melting temperature of TiO$_2$–P$_2$O$_5$ systems. When Li$_2$O is added to TiO$_2$–P$_2$O$_5$, lithium titanophosphate glasses are formed, which can be used in micro-batteries and electric devices. The optical absorption of glass systems is affected by the presence of TiO$_2$ and BaO. To minimize thermal expansion and enhance mechanically, and thermal stability, metal oxides such as BaO were added to the glass system. BaO was doped in TiO$_2$–P$_2$O$_5$–Li$_2$O glasses in this investigation. Physical, optical, and radiation characteristics of BaO–TiO$_2$–P$_2$O$_5$–Li$_2$O glasses were developed and characterized.

The goal of this article was to develop BaO–TiO$_2$–P$_2$O$_5$–Li$_2$O glasses. This article can be used in the future for enhancing the optical requirements and to reduce the harmful effects of radiation on organisms. We have expanded our research into BaO in lithium titanophosphate glasses as a result of the above existing literature. As a result, we’ve developed lithium titanophosphate glasses with BaO substituted in a variety of compositions. In addition to the aforementioned studies, photons, neutrons, characteristics of BaO doped lithium titanophosphate glasses will be investigated using theoretical code in this work.

2. Materials and methods

The melt-quenching technique was utilized for manufacturing the glass system in Table 1 70P$_2$O$_5$–15TiO$_2$–(15 − x) Li$_2$O − xBaO,
where \( x = 0, 2, 4, 8, \) and 10 mol%. A digital electronic balance was used to weigh starting materials such as titanium oxide, TiO_2, barium oxide BaO, lithium oxide Li_2O, and phosphorous oxide P_2O_5 as (NH_4)_2HPO_4. The powder was put into the porcelain crucible and the mixture was preheated at 400 °C for 90 min. Then, the mixture was melted at 1150 °C. For the annealing procedure, the glasses were preheated at 375 °C to eliminate any thermal stress. The samples were cut to a thickness of 1 cm × 1 cm × 0.25 mm and polished on both sides before optical measurement.

The UV-Vis-NIR data were collected at room temperature using a JASCO V-670 spectrometer. The absorption coefficients \( \alpha \) and \( \chi \) were calculated as physical parameters related to optical energy:

\[
\alpha = \frac{2.303 \log R}{d}
\]

where \( d \) is the sample thickness in cm. The absorption coefficient was determined for different thicknesses to achieve a constant absorption coefficient of 0.1 to 0.2.

The molar polarizability \( \alpha_m \) was calculated using optical absorbance. Molar refractivity \( R \) was calculated as physical parameters related to optical energy:

\[
R_m = V_m(1 - \sqrt{E_{\text{opt}}/20}), \quad \alpha_m = \frac{3}{4\pi N} R_m, \quad R_L = \left( \frac{R_m}{V_m} \right)^{1/3}.
\]

The inter-ionic, polaron, and internuclear distances were calculated using the Archimedes Code, the density (\( \rho \)) of the investigated glasses is calculated. The following is the formula for calculating molar volume: \( V_m = M/\rho \).

The inter-ionic, polaron, and internuclear distances were calculated as follows:

\[
R_i = \left( \frac{1}{\text{concentration of Fe}_i} \right)^{1/3}, \quad r_p = \frac{1}{2}
\]

\[
(\pi/6N)^{1/3}, \quad \text{and} \quad r_i = \left( \frac{1}{N} \right)^{1/2}.
\]

Ba–Ba separation is calculated using

\[
(d_{Ba-Ba}) = \frac{V_m}{N^{1/2}} \quad \text{and} \quad V_m^B = \frac{V_m}{2(1 - 2X_n)}.
\]

Phy-X/PSD is a new software developed by Sakar et al.\(^{13}\) that can compute several shielding factors and parameters at any energies using a remote server with an Intel (R) Core(TM) i7-2600 CPU@3.40 GHz CPU and 1 GB installed memory.

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### Table 1: Glasses that have been prepared have the following chemical composition

| Code | \( P_2O_5 \) | \( TiO_2 \) | \( Li_2O \) | \( BaO \) |
|------|------------|------------|------------|---------|
| G 1  | 70         | 15         | 15         | 0       |
| G 2  | 70         | 15         | 13         | 2       |
| G 3  | 70         | 15         | 11         | 4       |
| G 4  | 70         | 15         | 7          | 8       |
| G 5  | 70         | 15         | 5          | 10      |

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Equivalent atomic number expected as

\[
Z_{eq} = Z_1(\log R_2 - \log R_1) + Z_2(\log R - \log R_1),
\]

where \( Z_1 \) and \( Z_2 \) are G–P fitting variables that correlate to the atomic numbers \( Z_1 \) and \( Z_2 \). G–P fitting was used to estimate EABF and EBF.

3. Results and discussion

3.1 Physical investigations

The XRD of the samples is depicted in Fig. 1, and they are all amorphous. The XRD showed a broad hump instead of peaks, demonstrating that the glasses are amorphous.\(^{14–21}\)

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**Fig. 1** XRD of 70P_2O_5–15TiO_2–11Li_2O–4BaO glasses.

**Fig. 2** Density & molar volume of glass system.
As a function of BaO content, the density ($\rho$) and molar volume ($V_m$) are shown in Fig. 2. As the BaO content rises, ($\rho$) increases, but ($V_m$) decreases. ($\rho$) values are affected by molecular weights and the density of oxide. Li$_2$O and BaO have densities (2.013 and 5.72 g cm$^{-3}$), as well as molecular weights (29.881 and 153.326). A change in molar volume was shown to be the inverse of the density. Consequently, as packing density ($V_i$) rises, molar volume values decrease. The packing density ($V_i$) values are obtained in Table 2. As BaO replaces Li$_2$O, ($V_m$) decreases and ($\rho$) rises, resulting in a more compact glass structure.

The Ba$^{2+}$ ion concentration increment as the ($V_m$) decline. The ($R_i$), ($r_i$), & ($r_p$) were predictable. These values decrease as Ba$^{2+}$ increments. This trend was associated with a decrease in the ($V_m$). Separation of Ba–Ba declines with Ba$^{2+}$ increment, because of decrement in ($V_m$). The data values are obtained in Table 2.

### Table 2: Optical properties of 15TiO$_2$-70P$_2$O$_5$-(15-x) Li$_2$O-x BaO glasses

| Samples | G1 | G2 | G3 | G4 | G5 |
|---------|----|----|----|----|----|
| $N_0$   | 3.95 | 3.95 | 3.95 | 3.95 | 3.95 |
| Ba$_{x}$x$^{1021}$ | — | 0.64 | 1.35 | 2.92 | 3.87 |
| ($R_i$) | — | 11.79 | 9.20 | 7.11 | 6.48 |
| ($r_i$) | — | 13.61 | 10.64 | 8.25 | 7.52 |
| ($r_p$) | — | 3.91 | 3.06 | 2.37 | 2.16 |
| $R_m$ (cm$^{-1}$ mol$^{-1}$) | 25.19 | 23.63 | 22.13 | 20.26 | 18.97 |
| $\sigma_m$ (Å$^3$) | 9.99 | 9.37 | 8.78 | 8.03 | 7.52 |
| ($\rho_i$) | 0.63 | 0.63 | 0.62 | 0.61 | 0.61 |
| ($M$) | 0.367 | 0.373 | 0.381 | 0.387 | 0.392 |
| ($\chi$) | 0.73 | 0.75 | 0.78 | 0.81 | 0.83 |
| ($\alpha^2$) | 2.85 | 2.83 | 2.80 | 2.77 | 2.76 |
| ($\gamma$) | 1.34 | 1.33 | 1.31 | 1.30 | 1.29 |
| $E_{\text{opt.in}}$ (eV) | 2.7 | 2.78 | 2.91 | 3 | 3.07 |
| $E_{\text{opt.dir}}$ (eV) | 2.79 | 2.99 | 3.09 | 3.19 | 3.31 |
| $E_u$ (eV) | 0.368 | 0.338 | 0.323 | 0.308 | 0.295 |
| $K_0$ | 61.4 | 77.4 | 103.4 | 121.5 | 135.5 |
| $T_{\text{g(thermo.)}}$ | 387 | 419 | 472 | 508 | 536 |
| $V_i$ | 0.7 | 0.74 | 0.778 | 0.847 | 0.9 |

### 3.2 Optical investigations

Fig. 3 shows the optical absorption data of glass samples at various BaO. ($\alpha$), $E_{\text{opt.in}}$, $E_{\text{opt.dir}}$, ($E_u$), & ($n_D$) have been estimated.
(α) calculated as: \( \alpha = (2.303 \log(f/d)) \times A \). (α) of these samples are displayed in Fig. 4. Increase \( \alpha \) to the increase in BaO concentration and light energy.\(^{26-35}\)

Using the Tauc plot, \( E_{\text{indir}}^{\text{opt}} \) & \( E_{\text{dir}}^{\text{opt}} \) was determined as \( a_{\text{hv}} = C(hv - E_{\text{opt}})^{2} \). Fig. 5 and 6 depict the correlation among both \( (a_{\text{hv}})^{1/2} \), \( (a_{\text{hv}})^{2} \), and \( (hv) \). The intercepts were used to estimate \( E_{\text{opt}}^{\text{indir}} \) & \( E_{\text{opt}}^{\text{dir}} \), \( E_{\text{indir}}^{\text{opt}} \), & \( E_{\text{dir}}^{\text{opt}} \) both increased in value as the BaO content raised. An increase in the bond length of the Ba (0.4347 nm) and Li (0.4347 nm) could explain this (0.3039 nm). The logarithm (α) is used to calculate \( E_{u} \) as a function of energy from the curve slope in Fig. 7. \( E_{u} \) decreases as BaO concentrations rise. As a function of BaO, the values of \( E_{\text{indir}}^{\text{opt}} \), \( E_{\text{dir}}^{\text{opt}} \), & \( E_{u} \) are included in Table 1. Bulk module (K) and glass transition temperature \( T_{g(\text{thero.})} \) are predictable in comparison to the optical bandgap \( K_{\text{th}} = -478.93 + 200.13 E_{\text{opt}}, T_{g(\text{thero.})} = -701.87 + 403.33 E_{\text{opt}}, K_{\text{th}} & T_{g(\text{thero.})} \) are increment as BaO, this is thought to be caused by an increase in the bandgap. The data values obtained are shown in Table 2.
\( n_D \) was determined as 
\[ n_D = \frac{1}{C_0 R} - k^2 \left( 1 + R \right) \] 
As Fig. 8, the \( n_D \) of the investigated samples increment. \( n_D \) is increment as BaO, this is thought to be caused by an increase in density. \( n_D \) & \( r \) have a similar relationship. 

\[ R_m, f_0^{2/C_0} \] was estimated as 
\[ n_D & \text{ exemplified in Fig. 9, 10, and 11. As the amount of BaO increases, these constructs deteriorate. This observation has been reduced due to the decrease in } V_m. \]

According to \( E_{\text{dir opt.}} \), the values of \( (R_m), (\nu_m), \) and \( (\lambda) \) decrease, although \( (\chi), M \) increment. This observation has been reduced due to the decrease in \( V_m. \) \( \chi \) and \( \lambda \) have different values of \( (\chi) \), so they both decline. The data values obtained are shown in Table 2. 

\[ E_{\text{opt}} \text{ and } E_{\text{indir opt.} \text{ are used to calculate the refractive index in Fig. 12 and 13. As an outcome, there is a minimal difference in the } (n_D). \] The dielectric and static dielectric constants \( (\varepsilon_\infty, \varepsilon_0) \) were estimated: \( \varepsilon_0 = -33.26876 + 78.61805E_g - 45.70795E_g^2 + 8.32449E_g^3, \varepsilon_\infty = n_{AV}^2. \) Table 3 shows the effects of \( E_{\text{opt}}, \) and \( E_{\text{indir opt.} \text{ on various optical constrictions. \] Dispersion \( E_\infty \) and \( E_d \) were calculated as 
\[ n^2 - 1 = \frac{E_\infty E_d}{E_\infty^2 - E_d^2}, \] 
\( E_\infty \) and \( E_d \) are calculated from the slope and intercept, as shown in Fig. 14 & Table 3. \( E_{\text{opt}} \) is the optical energy that represents \( E_{\text{opt}} = \frac{E_d}{2}. \) Refractive static index \( (n_0), \) oscillator’s wavelength \( (\lambda_0), \) static dielectric \( \varepsilon_\infty \) and strength \( (S_0) \)

\[
\begin{align*}
E_\infty &= 25.37, 26.58, 25.03, 23.89, 24.05 \\
E_d &= 6.020, 6.540, 6.65, 6.81, 7.150 \\
E_{\text{opt}} &= 3.01, 3.27, 3.324, 3.400, 3.573 \\
n_0 &= 1.10, 1.12, 1.125, 1.13, 1.13 \\
\varepsilon_\infty &= 1.24, 1.25, 1.27, 1.285, 1.297 \\
S_0 &= 1.952, 2.064, 2.078, 2.079, 2.084 \\
\lambda &= 415, 477, 498, 522, 558
\end{align*}
\]

Table 3 The dielectric and static dielectric \( (\varepsilon_\infty, \varepsilon_0) \) nonlinear parameter \( (\chi^{(1)}), (\chi^{(3)}) \) and average refractive index \( (n_2) \) value as a function of \( E_{\text{opt.}} \).

| Sample name | \( \varepsilon_\infty \) | \( \varepsilon_0 \) | \( \chi^{(1)} \) | \( (\chi^{(3)}) \) \( 10^{-12} \) | \( (n_2) \) \( 10^{-11} \) | \( E_{\text{opt}} \) | \( E_{\text{indir opt.}} \) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| G 1         | 6.45            | 9.64            | 0.438           | 6.25            | 9.24            | 25.37           | 26.58           |
| G 2         | 6.39            | 10.89           | 0.4297          | 5.76            | 8.59            | 26.58           | 25.03           |
| G 3         | 6.22            | 13.58           | 0.4155          | 5.07            | 7.66            | 25.03           | 23.89           |
| G 4         | 6.11            | 15.97           | 0.4059          | 4.64            | 7.08            | 23.89           | 24.05           |
| G 5         | 6.02            | 18.16           | 0.4             | 4.34            | 6.6             | 24.05           | 23.89           |

\[
\begin{align*}
\text{Value as a function of } E_{\text{opt}} & \\
G 1 & : 6.376, 11.1, 0.428, 5.71, 8.5 \\
G 2 & : 6.12, 15.68, 0.407, 4.69, 7.14 \\
G 3 & : 5.998, 18.84, 0.398, 4.26, 6.56 \\
G 4 & : 5.88, 22.62, 0.389, 3.88, 6.03 \\
G 5 & : 5.75, 28.06, 0.378, 3.47, 5.46
\end{align*}
\]

Table 4 The 4 values of the dispersion parameters for the glass system.

| Code | G1 | G2 | G3 | G4 | G5 |
|------|----|----|----|----|----|
| \( E_\infty \) | 25.37 | 26.58 | 25.03 | 23.89 | 24.05 |
| \( E_d \) | 6.020 | 6.540 | 6.65 | 6.81 | 7.150 |
| \( E_{\text{opt}} \) | 3.01 | 3.27 | 3.324 | 3.400 | 3.573 |
| \( n_0 \) | 1.10 | 1.12 | 1.125 | 1.13 | 1.13 |
| \( \varepsilon_\infty \) | 1.24 | 1.25 | 1.27 | 1.285 | 1.297 |
| \( S_0 \) | 1.952 | 2.064 | 2.078 | 2.079 | 2.084 |
| \( \lambda \) | 415 | 477 | 498 | 522 | 558 |
was expected as \( n_0 = \sqrt{1 + \frac{E_d}{E_0}} \), \( \epsilon_{\infty} = n_0 \lambda_0 \), (\( \lambda_0 \)) & (\( S_0 \)) & 
\( n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - \left( \frac{\lambda_0}{\lambda} \right)^2} \). The items available are listed in Table 4.

3.3 Radiation attenuation capacities

Fig. 15 depicts the \( Z_{eq} \) results graphically. When the incident photon energy was increased and \( \text{Li}_2\text{O} \) was replaced with \( \text{BaO} \), the \( Z_{eq} \) enhanced then decreased. Due to the photoelectric process, the \( Z_{eq} \) is smallest at low energy, then suddenly increases in the middle energy region due to Compton scattering, and finally, the \( Z_{eq} \) is reduced due to the pair production process. Because of the pair creation interaction, the \( Z_{eq} \) value decreases at energies higher than 1 MeV.\(^{36-45}\) As a result, glass with a higher \( \text{BaO} \) content has a higher \( Z_{eq} \) than others. In all photon energy, it was discovered that \( G_5 \) has the maximum values, while \( G_1 \) has the smallest.

Using the (G-P) fitting method, the (EBF) and (EABF) were calculated. Fig. 16 show EBF and EABF. The pattern of variation for both EAF & EABF is similar. Because of the different dominant interaction processes, the EBF and EABF rise, and decline. One common feature of the EAF & EABF spectra is that the Compton scattering (CS) dominated areas have relatively higher values when compared to both photoelectric effect (PE) and pair production (PP). This also confirms that a material’s EAF & EABF is determined by its photon energy and chemical structure. In addition, as \( \text{BaO} \) content increases, the EAF & EABF decrease. As a result, the EBF and EABF variance behaviors are primarily impacted by the three main interaction mechanisms discussed previously.\(^{38-45}\)

Fig. 15 Equivalent atomic number for glasses.

Fig. 16 EAF & EABF for \( 70\%\text{P}_2\text{O}_5-15\%\text{TiO}_2-15\%\text{Li}_2\text{O} \) & \( 70\%\text{P}_2\text{O}_5-15\%\text{TiO}_2-5\%\text{Li}_2\text{O}-10\%\text{BaO} \) glasses.
Finally, we investigate the neutron shielding behavior of glasses using effective removal cross-sections $\sum R$. The $\sum R$ of synthesized samples is shown in Fig. 17. $\sum R$ is a density-dependent parameter shown in Fig. 18a and b. Clearly, as the BaO content of the glasses increases, $\sum R$ increases. When the FNRC of glass samples is compared, G 5 is a better fast neutron absorber. As a result, the highest value is given to G 5. The glass sample G 5 is the best choice for neutron attenuation applications.38–45

4. Conclusions

Melt quenching performance was utilized to manufacture lithium titanophosphate glasses doped with different amounts of BaO for optics and radiation applications. The XRD analysis confirmed the amorphous state. The molar volume is the decline within 39.8–31.2 cm$^3$ mol$^{-1}$, the density was increment from 2.908 to 4.11 g cm$^{-3}$ with an increase of BaO. With increment BaO, the studied glasses’ linear and nonlinear optical properties improve significantly. $E_{\text{indir}}$ and $E_{\text{dir}}$ both increased from 2.7 to 3.07 eV, 2.79 to 3.31 eV, while $E_u$ decline from 0.368 to 0.295 eV. For all glasses, the metallization ranged from 0.367 to 0.392, and electronegativity ranged from 0.73 to 0.83. The (EFB and EABF) values reduced slightly as the BaO increased. Overall, excellent material properties were detected, which could be useful for future optical applications. Consequently, these glasses can be suggested and improved as shielding material for gamma-ray & neutrons.

Conflicts of interest

There are no conflicts to declare.

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