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Effect of alkali metal on properties of aluminium barium phosphate glasses system

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Abstract

The physical and optical properties of aluminum barium phosphate glass were investigated. The glass was prepared using the melt-quenching technique at 1200 °C. Alkali oxide (R_2O-Al_2O_3-BaO-P_2O_5, where R = Li, N, K) content was varied and it's affect on the properties of the glass were analyzed. The results show that the experiment created glass samples that were clear and transparent. It was observed that the KABP, Potassium Aluminum Barium Phosphate, glass had a higher density and molar volume than the NABP, Sodium Aluminum Barium Phosphate, glass and the LABP, Lithium Aluminum Barium Phosphate, glass. Direct and indirect energy band gaps (E_{opt}) were determined to be in the range of 3.760 - 3.817 eV and 3.130 - 3.292 eV for the NABP and LABP samples respectively.

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1. Introduction

Glasses have gained much attention in recent years because of their properties which make them very useful in a wide variety of applications. They are low cost, easy to prepare, have high transparency at room temperature, have hardness along with sufficient strength, excellent electrical resistance, physical isotropy, absence of the grain boundaries, and continuously variable composition for optical applications [1-3]. Among oxide glasses, phosphate glass has several advantages over conventional silicate and borate glasses. This is because of its superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures and high ultraviolet transmission [4-8]. However, its chemical durability has limits. The addition of different types of metal oxides like Al_2O_3 to binary phosphate glasses has been found to improve their chemical durability [8-10]. Alkali elements (e.g. K^+, Na^+ and L^+) are becoming essential for improving glasses materials with a greater focus on end-user application requirements and a reduction of development costs [11-12]. Mixed alkali effect (MAE) refers to maintaining the total content of alkali metal ions in the glass, replacing one alkali ion with another alkali ion gradually until an optimum is reached. In the process of substitution, some properties related to ion migration characteristics like ion diffusion, chemical durability, electrical conductivity, dielectric loss, viscosity, glass transition temperature and thermal expansion coefficients deviate from linearity in a large way and some properties like density, refractive index and microhardness deviate in a smaller way [13-14]. MAE is useful in manufacturing low loss electrical glass [15]. Maass *et al.* developed the dynamic structure model to explain the mixed alkali effect [12]. Lithium is considered to be one of the best modifiers of the glass network. Glasses which contain lithium are more sensitive to neutrons and can therefore be used as neutron detection materials [16]. The addition of metal oxides such as Na_2O reduces the viscosity of the melted glass and lowers the melting temperature [17]. K_2O improves stability and optical quality of the glasses even under high temperature treatment (with optical losses lower than 0.02 cm^{-1}) [18].

This paper presents the effects of the addition of alkali oxide (Li_2O, Na_2O and K_2O) on the properties of aluminium barium phosphate glass. A discussion of the results and conclusions of this work are given providing details about the density, molar volume, optical

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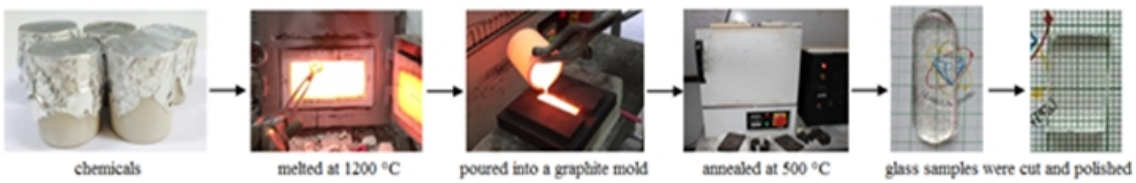

Figure 1: Photograph of the glass production process.

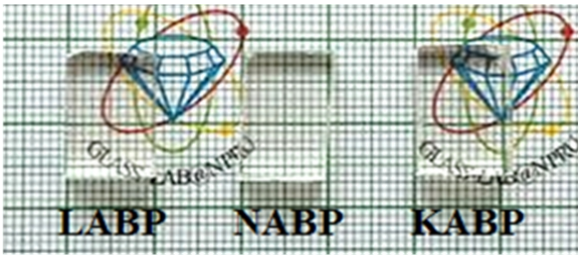

Figure 2: Photograph of the glass samples.

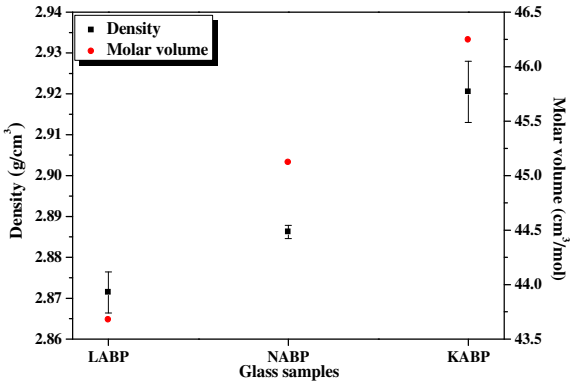

Figure 3: Density and molar volume of glass samples.

absorption spectra and energy bandgap of glasses prepared by melt quenching technique. A discussion is presented of the results of the addition of various alkali elements to aluminum barium phosphate glass.

2. Experimental Details

2.1. Preparation technique

The chemical compositions of various alkali, mixed alkali and aluminium barium phosphate that were studied in the work were as follows:

LABP : $15Li_2O : 5Al_2O_3 : 20BaO : 60P_2O_5$

NABP : $15Na_2O : 5Al_2O_3 : 20BaO : 60P_2O_5$

KABP : $15K_2O : 5Al_2O_3 : 20BaO : 60P_2O_5$

Carefully measured quantities of chemicals were placed into a gate mortar and were pounded well to obtain a homogeneous mixture. The mixed powders were melted at 1200 °C and were kept in the molten form for 3 h. The melted glass samples were quickly poured into a graphite mold and annealed at 500 °C for 3 h as shown in Fig. 1. Finally, the glass samples were cut and polished to obtain highly transparent surfaces for optical measurements. The resulting glass samples can be seen in Fig. 2.

2.2. Density and molar volume

The densities of the samples produced were calculated by using Archimedes method. This is shown in Eq. (1). In order to obtain accurate results, all measurements were repeated three times at room temperature [19].

$$\rho = \frac{w_a}{w_a - w_w} \times \rho_w \qquad (\mathrm{g/cm^3}) \tag{1}$$

where w_a is weights of the glass simple in air, w_w is weights of the glass simple in water and ρ_w is density of water.

The molar volumes of the glass samples that were produced were measured by the density values according to the following equation [19]

$$V_m = \frac{M_T}{\rho} \qquad (\mathrm{cm^3/mol}) \tag{2}$$

where V_m is the molar volume, ρ is the calculated density of the glass and M_T is the total molecular weight of the multicomponent glasses systems given by.

$$M_T = x_{R_2O}Z_{R_2O} + x_{Al_2O}Z_{Al_2O} + x_{BaO}Z_{BaO} + x_{P_2O_5}Z_{P_2O_5} \tag{3}$$

where x_{R_2O}, x_{Al_2O}, x_{BaO} and $x_{P_2O_5}$ (R_2O = Li_2O, Na_2O and K_2O) are the mole fractions of the constituent oxides, and $Z_{R_2O}, Z_{Al_2O}, Z_{BaO}$ and $Z_{P_2O_5}$ Z are the molecular weights of the constituent oxides. The physical properties of all of the glass samples were calculated and presented in Table 1.

2.3. Optical absorption

Measurements of the absorption spectra of the samples were made in ultraviolet (UV) and visible (Vis) regions at room temperature. The measurements were made using UV-Vis spectrophotometer (Cary 50) at wavelengths in the range 200-1100 nm.

2.4. Energy band gap (Eg)

The optical band gap energy (Eg) is an important parameter for describing solid-state materials. The optical absorption coefficient, α(v) was calculated for the glass samples using the following equation:

$$\alpha(v) = \frac{A}{d} \tag{4}$$

Table 1. The physical properties of glass samples

Physical Properties	LABP	NABP	KABP
ρ (g/cm^3)	2.8714±0.0050	2.8862±0.0016	2.9205±0.0075
M_T	123.9181	127.1279	130.3495
V_m (cm^3/mol)	43.6762±0.0614	45.1205±0.0199	46.2453±0.0936

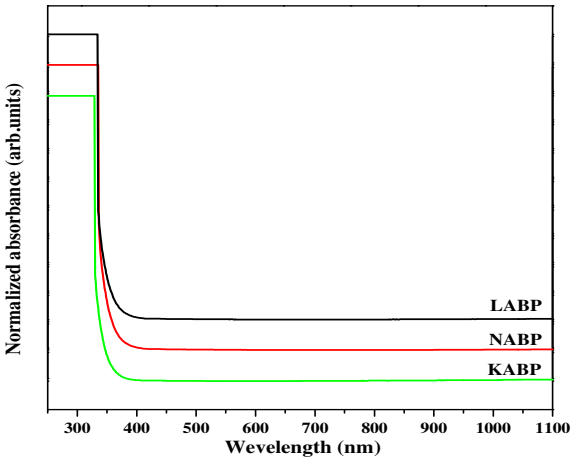

Figure 4: Absorption spectra of glass samples.

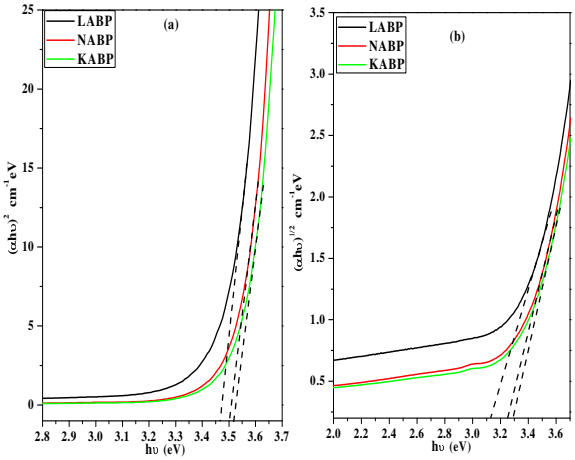

Figure 5: Tauc's plot as a function of energy (eV) for (a) direct and (b) indirect allowed transitions of glass samples.

Table 2. Optical band gap of direct and indirect transition and cutoff wavelength (λ_c) of glass samples

Glass Samples	E_{opt}^{ind} (eV)	E_{opt}^{dir} (eV)	λ_c (nm)
LABP	3.130	3.463	329
NABP	3.247	3.503	327
KABP	3.292	3.518	325

where B is a constant and hv is the photon energy, E_{opt} is the optical energy gap and n is an index. The exponent n takes different values depending on the mechanism of the inter-band transition and the nature of the material, whether it is crystalline or amorphous [21]. The values of n are 1/2 and 2 for direct and indirect transitions, respectively. Using Eq. (5) and by plotting $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ as a function of photon energy hv, the optical energy band gaps (E_{opt}) can be found. This is done for direct and indirect transitions by extrapolating the linear region of the curve to the hv axis. The results of this are shown in Fig. 3.

3. Results and Discussion

3.1. Physical properties

The density and molar volume of glass samples with difference alkali oxide is shown in Fig. 3 and Table 1. It can be seen that the density of the glasses depended on the atomic weight of the alkali oxide cation used to make the sample ($Li^{1+} < Na^{1+} < K^{1+}$). The molar volume of the glass samples was seen to increase with the increase in ionic radii of alkali metals oxide cations in the following order $Li^{1+} < Na^{1+} < K^{1+}$.

The change in the V_m is a result of the creation of a number of non-bridging oxygens (NBOs), which break the bonds in the glass and increase space in the glass network [23-25]. This result indicates that the glass structure becomes more loosely packed.

3.2. Optical absorption properties

Fig. 4 shows the absorption spectra of glass samples with different compositions. The results did not find an absorption spectra in the samples nor did they exhibit any detectable peak that would affect the clear color of glass samples. The cutoff wavelength (λ_c) of glass samples was found to be lower than 400 nm. This results indicated that the glass was colorless. It was observed from the absorption spectra that, the λ_c of the prepared alkali aluminium barium phosphate glasses slightly shift towards the blue region (329-325 nm) due to the change in alkali elements in the host matrix. It was thought that this may be due to the change in the structural rearrangement of the network former and modifier in the glass matrix.

The optical band gap (E_{opt}) values were determined by extrapolating the linear region of the Tauc's curve plotted between $(\alpha hv)^n$ and photon energy (hv) at $(\alpha hv)^2 = 0$ for direct allowed and at $(\alpha hv)^{1/2} = 0$ for indirect allowed transitions respectively. The result of this extrapolation is shown in Fig. 5. The values of the Eg for the glass samples are presented in Table 2. It can be seen from the table that, the E_{opt} values for the glass samples were found to be in the range 3.130-3.292 eV for the indirect allowed transitions and

3.463-3.518 eV for the direct allowed transitions. It can be seen that they increase in the order Li_2O < Na_2O < K_2O for the changes to the alkali elements in the glass samples. This increase can be understood in terms of structural changes that take place in the glass after alkali addition.

4. Conclusions

The density and molar volume of glass samples was found to increase with the increase in ionic radii of alkali metals oxide cations. It was found that this increase followed the order Li^{1+} < Na^{1+} < K^{1+}. In terms of the optical properties of the samples, there was no absorption spectra detected nor was there any detectable peak that would affect to the opacity of the glass samples. The cutoff wavelength (λ_c) of KABP glass showed a large transmission window when compared to NABP and LABP samples. Both direct and indirect optical band gap energies were found to increase with atomic weight of the alkali oxide cations. This confirmed that the cations act as network modifiers for the glasses that were produced. The variations in the band gap values are due to the change in alkali metal oxides in the host matrix. It is observed from studying the band gaps that the LABP glass possesses relatively fewer defects when compared with other glasses. It is also probable that LABP glass exhibits a better luminescence output when compared to the other glass samples.

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