Comparative Study of Optical and Spectroscopic Properties of Lead and Bismuth on Borosilicate Glasses

N. Srisittipokakun\textsuperscript{a,b*}, J. Kaewkhao\textsuperscript{a,b,c}, W. Chewpraditkul\textsuperscript{d}, P. Limsuwan\textsuperscript{c,d}

\textsuperscript{a}Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand
\textsuperscript{b}Science Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand
\textsuperscript{c}Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, Thailand
\textsuperscript{d}Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi, Bangkok, 10140, Thailand

Abstract

The aim of this paper is comparative study of lead and bismuth on optical and spectroscopic properties of borosilicate glass. Glasses samples were prepared from reagent grade powders of SiO\textsubscript{2}, H\textsubscript{3}BO\textsubscript{3}, CaO, Na\textsubscript{2}O, Bi\textsubscript{2}O\textsubscript{3} and PbO. The glasses containing in formula (50-x)SiO\textsubscript{2}:xRmOn:30B2O\textsubscript{3}:10CaO:10Na\textsubscript{2}O (where x = 2 to 10 mol\% and RmOn = Bi\textsubscript{2}O\textsubscript{3} and PbO). It has been found that the properties of Bi-glass such as refractive index, density are better than Pb-glass. Moreover, in visible region, Bi-glass show good transparent more than Pb-glass. From the molar volume result, indicate that more average atomic spacing of Bi-glass compared with Pb-glass under same glass formula and preparing condition.

Keywords: borosilicate glass, lead, bismuth, optical transmission spectra

1. Introduction

There has been an increasing interest in the synthesis, structure and physical properties of heavy metal oxide (HMO) glasses due to their high refractive index, high infrared transparency and high density. Glasses based on heavy metal oxide such as Bi\textsubscript{2}O\textsubscript{3} have wide applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, etc. [1]. Bismuth oxide cannot be considered as network former due to small field strength of Bi\textsuperscript{3+} ion. However,
in combination with B₂O₃, glass formation is possible in a relatively large compositional range. It is now well known that lead oxide (PbO) is unique in its influence on the glass structure and is widely used in glasses because it enhances the resistance against diversification, improves the chemical durability and lowers the melting temperature. It can act both as a glass network former or modifier, depending on its concentration in the glasses [2, 3].

A large number of commercial glasses are based on alkali borosilicate systems, with a majority of these glasses primarily containing soda instead of any of the other alkali oxides. Most of the commercial glasses, while transparent, are actually phase separated with very fine scale morphology. The soda lime borosilicate glass consists of Na₂O, CaO, B₂O₃ and SiO₂ and widely studied and investigated in many field [4]. The addition of B₂O₃, which forms a network structure, creates a glass with a higher melting point and a greater ability to withstand temperature changes [5]. Therefore, the aim of the present study is to prepare the lead and bismuth doped in borosilicate glass with different concentrations of PbO and Bi₂O₃ and the effect of PbO and Bi₂O₃ content on the density, molar volume, refractive index and optical absorption have been studied.

2. Experimental

2.1 Glasses preparation

PbO and Bi₂O₃ doped borosilicate glass were prepared in composition (50-x)SiO₂: xRₘOₙ: 30B₂O₃: 10CaO: 10Na₂O (where x = 2 to 10 mol% and RₘOₙ = Bi₂O₃ and PbO). All chemical compositions were finely powder and then mixed in whole of composite. Each batch composition (about 30 g) was filled in high purity alumina crucibles. All glasses were melted in an electrical furnace for 3 hours, at 1,200°C. Afterwards, the melts were quickly poured onto a preheated stainless steel mould, annealed at 500°C for 3 hours, and cooled down to room temperature, respectively. Finally, the glass samples were cut and finely polished to a thickness of 3 mm. The PbO doped glasses are show colorless, but the Bi₂O₃ doped glasses show light yellow color after 8.0 mol%. Fig. 1 presents the photographs of PbO and Bi₂O₃ doped glass samples.

![Photographs of PbO and Bi₂O₃ doped borosilicate glass](a)

![Photographs of PbO and Bi₂O₃ doped borosilicate glass](b)

Fig. 1. PbO (a) and Bi₂O₃; (b) doped borosilicate glass
2.2 Measurements

The density ($\rho$) of each sample was calculated by the Archimedes’s method using xylene as immersion liquid. The molar volume ($V_M$) was calculated using the relation [6]

$$V_M = \frac{M_T}{\rho}$$

where $M_T$ is the total molecular weight of the multicomponent system given by

$$M_T = x_{B_2O_3}Z_{B_2O_3} + x_{Na_2O}Z_{Na_2O} + x_{CaO}Z_{CaO} + x_{SiO_2}Z_{SiO_2} + x_{RmOn}Z_{RmOn}$$

where $x_{B_2O_3}$, $x_{Na_2O}$, $x_{CaO}$, $x_{RmOn}$ and $x_{SiO_2}$ are the mole fractions of the constituent oxides, and $Z_{B_2O_3}$, $Z_{Na_2O}$, $Z_{CaO}$, $Z_{RmOn}$ and $Z_{SiO_2}$ are the molecular weights of the different oxides.

The optical absorption spectra were recorded at room temperature using a UV-visible spectrophotometer (Cary-50), working in 200-1,100 nm at room temperature. The refractive indices were measured at room temperature using an Abbe refractometer (ATAGO-3T) and mono-bromonaphthalene as an adhesive coating.

3. Results and discussions

It is seen from Fig. 2, the density of borosilicate glass samples increases with the increasing of Bi$_2$O$_3$ and PbO concentration. The density increases with additional content of Bi$_2$O$_3$ and PbO into the network. This result indicates that replacing SiO$_2$ by addition of a small amount of Bi$_2$O$_3$ and PbO results in the increase in the average molecular weight of oxide ions in the glass. The density of Bi-glass is more than that of Pb-glass due to a higher density of Bi$_2$O$_3$ with respect to PbO.

In 0-4 mol% of PbO concentration, the molar volume ($V_M$) of Pb-glass was decreased, so the Pb-glass was compacted. The increase of $V_M$ was obtained from 4 - 10 mol% of PbO concentrations, which is attributed to the increase in the number of non-bridging (NBOs). In case of Bi-glass, the $V_M$ increased in 0-2 %, due to increase of NBOs and is not changed in the range of 2-4 mol% of Bi$_2$O$_3$ concentration. However, between 4-10 mol%, the molar volume of Bi-glass was rapidly increased compared with Pb-glass.

These results indicate that, since 4 mol%, the PbO and Bi$_2$O$_3$ enter the glass network as a modifier by occupying the interstitial space in the network and generating the NBOs to the structure. It can also be observed that the addition of PbO and Bi$_2$O$_3$ may accordingly result in an extension of glass network [3]. Moreover, the molar volume of Bi-glass more than Pb-glass, reflecting that more average atomic spacing of Bi-glass compared with Pb-glass under the same glass formula and preparing condition. The plot of molar volume with Bi$_2$O$_3$ and PbO concentration are illustrated in Fig. 3.
The refractive indices were measured by an Abbe refractometer, which permits the measurement of refractive indices up to 1.7 with an accuracy of 0.0002. A sodium lamp (D line = 589.3 nm) was used as the light source and mono-bromonaphthalene was used as the contact liquid between the surface of the apparatus prism and the test piece. The refractive index of soda lime borosilicate glasses doped with Bi$_2$O$_3$ are between 1.5300-1.6482. In the case of glass doped with PbO, the refractive index are between 1.5300-1.5912. It is observed that the refractive index increases with increasing Bi$_2$O$_3$ and PbO concentration. This result is show similar trend with density. Moreover, the refractive index of soda lime borosilicate glasses doped with Bi$_2$O$_3$ are higher than soda lime borosilicate glasses doped with PbO (see Fig. 4).
Optical absorption spectra of undoped and different Bi$_2$O$_3$ doped soda lime borosilicate glasses in wavelength range 300-1,100 nm are shown in Fig 5a. The absorption edge of undoped glass occurred at a wavelength of around 325 nm. It can be observed that the absorption edge was slightly shifted to the longer wavelength with increasing of Bi$_2$O$_3$ concentration. In the case of PbO, the result is similar trend with case of Bi$_2$O$_3$ result. It can be observed that the absorption edge was slightly shifted to the longer wavelength with increasing of PbO concentration (Fig. 5b).

Fig. 5c shows the typical transmission spectra of Bi-glass and Pb-glass at 6 mol% concentration in borosilicate glasses samples. It was observed that the absorption edge of Bi-glass (365 nm) shows a little shifted to longer wavelength compared with Pb-glass (350 nm). In the range of visible region (400-700 nm), the transmission of Bi-glass is better than that of Pb-glass.
Fig. 5. Comparison optical absorption spectra of Bi$_2$O$_3$ (a) PbO; (b) doped in soda lime borosilicate glasses and (c) Comparison optical transmission spectra of Bi$_2$O$_3$-PbO doped 6 mol% in soda lime borosilicate glasses.
4. Conclusions

Bi$_2$O$_3$ and PbO doped in soda lime borosilicate glass samples were prepared with chemical composition (50-x)SiO$_2$:xR$_{m}$O$_n$:30B$_2$O$_3$:10CaO:10Na$_2$O (where x = 2 to 10 mol% and R$_{m}$O$_n$ = Bi$_2$O$_3$ and PbO) and investigated their properties. The results found that the density and refractive index of glass samples were increased along with increasing the concentration of Bi$_2$O$_3$ and PbO, due to high molecular weight of Bi$_2$O$_3$ and PbO compared with SiO$_2$. From the molar volume result, an average atomic spacing of Bi-glass is larger than that of Pb-glass under the same glass formula and preparing conditions. In the range of visible region (400-700 nm), the transmission of Bi-glass is better than that of Pb-glass.

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