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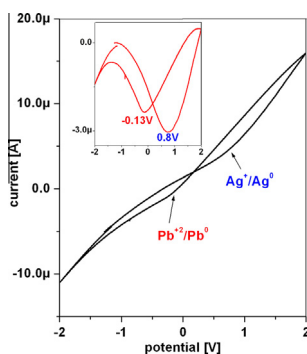
The network modifier and former role of the bismuth ions in the bismuth–lead–germanate glasses

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HIGHLIGHTS

- The increase of the Bi₂O₃ concentration affects the structural and optical properties of the host network.
- A intense UV–VIS absorption band shows the presence of Pb⁺² ions.
- The electrochemical performances of the glass system can be due to Pb⁺²/Pb⁰ system.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work is focused on the enhancement of network former environment in lead-germanate glasses by bismuth ions doping. A series of bismuth–lead–germanate glasses with the $x\text{Bi}_2\text{O}_3 \cdot (100 - x)[7\text{GeO}_2 \cdot 3\text{PbO}]$ composition glass where $0 \leq x \leq 30$ mol% Bi₂O₃ were synthesized by melt-quenching method. The FTIR, UV–VIS spectroscopy and cyclic voltammetry were conducted on these samples to evaluate the doping effect of structure of the host matrix network. Our results indicate that direct incorporation of Bi₂O₃ into the lead-germanate network modifies the lead-germanate network and the internal structure of glass network is rearranged. The structural flexibility of the lead-germanate network is possible due to its incapacity to accommodate with the excess of oxygen atoms and the creation of bridging oxygen ions. Optical gap energy and refractive index were obtained as a function of Bi₂O₃ content. Gap energy values decrease as Bi₂O₃ content increased from 0 to 10 mol%. Further increase of Bi₂O₃ concentration beyond 10 mol% increased the gap energy values. These behaviors of the glass system can be explained by two mechanisms: (i) for $x \leq 10$ mol% Bi₂O₃ – increase of degree of disorder of the host matrix because Bi₂O₃ is network modifier and (ii) for $x > 10$ mol% – Bi₂O₃ acts as a network former. Cyclic voltammetry measurements using the glass system with 10Bi₂O₃·90[7GeO₂·3PbO] composition as working electrode show the mobility of the lead ions, in agreement with UV–VIS data.

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Introduction

Glasses based on heavy metal oxides have always been an area of interest because of their characteristic structural and physical properties such as high refractive index, high thermal expansion, high density, low transformation temperature and excellent

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infrared transmission [1–4]. Glasses in the system $\text{Bi}_2\text{O}_3\text{--PbO--GeO}_2$ are interesting subjects for structural investigation since they form stable glasses by a conventional melt-quenching method even though none of the constituents is a traditional network-former [3]. Some authors reported that the network forming property of bismuth was greater than that of lead [5,6]. However, there has been no systematic structural analysis on this ternary heavy metal oxide glasses over the glass-forming region.

Bismuth containing glasses are also often compared with lead-glasses [7]. The Bi^{+3} and Pb^{+2} ions are the group of ions with lone-pair electron configurations. They have two electrons outside a closed shell which promotes pyramidal bonding [8]. The pyramidal geometry possesses a dipole moment which may result in spontaneous polarization [9,10].

Despite the fact that Bi_2O_3 is not a classical glass network former, due to its high polarizability, in the presence of conventional glass formers, it may build a glass network of $[\text{BiO}_n]$ pyramidal structural units (where $n = 3$ and 6).

However, the structural role played by Bi_2O_3 in glasses without or with low content of conventional glass formers, so called heavy metal glasses, is complicated and poorly understood. The problem is complex because the $[\text{BiO}_n]$ polyhedra are highly distorted due to lone pair electrons.

PbO -containing glass systems have become popular as synthesizable glasses at low temperature due to high structural stability, low glass transition temperature and electrical characteristics [11–15]. One of the advantages of PbO glasses is that they do not easily crystallize even when they contain 70% of PbO because systems form $[\text{PbO}_4]$ structural units easily since lead ions plays the role of an intermediate due to its own ionic field strength [16]. The investigation of the glasses containing divalent ions such as Pb^{+2} is particularly important due important role of the lead ions both in formation and modification of glass structure.

The current study is, therefore, aimed at the structural analyses on the ternary bismuth–lead–germanate unconventional glasses using FTIR, UV–VIS spectroscopy and cyclic voltammetry to find a model of the structural development in such glasses.

Experimental procedure

Glasses were prepared using reagent grade purity germanium (IV) oxide, lead (II) oxide and bismuth (III) oxide of high purity (99.99%) in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1000°C in an electric furnace. The samples were put into the electric furnace direct at this temperature. After 10 min, the molten material was quenched at room temperature by pouring onto a stainless-steel plate.

The samples were analyzed by means of X-ray diffraction using a XRD-6000 Shimadzu diffractometer, with a monochromator of graphite for the $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at room temperature.

The FT-IR spectra of the glasses in the $350\text{--}1200 \text{ cm}^{-1}$ spectral range were obtained with a JASCO FTIR 6200 spectrometer using the standard KBr pellet disk technique. The spectra were carried out with a standard resolution of 2 cm^{-1} .

UV–VIS absorption spectra of the powdered glass samples were recorded at room temperature in the $250\text{--}600 \text{ nm}$ range using a Perkin–Elmer Lambda 45 UV/VIS spectrometer equipped with an integrating sphere. These measurements were made on glass powder dispersed in KBr pellets. The validity of the band position is $\pm 2 \text{ nm}$.

The electrochemical properties were characterized by cyclic voltammetry using a VERSASTAT3 potentiostat and V3Studio software. Disks of glasses were used as working electrode, platinum

electrode as counter and calomel as reference electrode. The silver nitrate solution (10^{-5} M) was used as electrolyte solution.

Results and discussion

The X-ray diffraction patterns of glasses ($x = 10\%$ and $30\% \text{ Bi}_2\text{O}_3$) after and before cyclic voltammetry ($x = 10\% \text{ Bi}_2\text{O}_3$) illustrated in Fig. 1 did not reveal any crystalline phase in these samples.

FTIR spectroscopy

Bi_2O_3 is also known to occupy both network forming and network modifying positions in the glass matrix; however, when used as a modifier, the cation due to its highest valence state produces important structural effects. Ab initio calculations on the local structure of bismuth-borate glasses reported the instability and highly distorted of the $[\text{BiO}_6]$ octahedral structural units [17–19].

Therefore, the presence of three types of cations (germanium, lead and bismuth) in the matrix network produces a competition between these cations. The preference to attract the oxygen ions for compensation of electric charge will be decided by the electronegativity theory: the covalency of the bond will become stronger with the decrease of the difference of electronegativity between cation and anion ions. Since the values of electronegativity, for Ge, Pb, Bi and O elements are 2.1, 2.33, 2.2 and 3.5, respectively, the covalency of Pb--O are stronger than Ge--O and Bi--O , respectively. As a result, the covalency of Pb--O and Bi--O bonds is stronger than this of the Ge--O bond. Accordingly, the excess of non-bridging oxygen ions will coordinate with lead and bismuth ions.

FTIR spectra obtained for vitreous system with the following composition $x\text{Bi}_2\text{O}_3 \cdot (100 - x)[7\text{GeO}_2 \cdot 3\text{PbO}]$ where $x = 0, 1, 5, 10, 15, 20, 25$ and $30 \text{ mol}\%$ Bi_2O_3 are shown in Fig. 2. The stronger IR band centered at about 800 cm^{-1} was attributed to deformation vibrations of the Ge--O--Ge bonds in $[\text{GeO}_4]$ tetrahedral structural units. Band located at about 700 cm^{-1} corresponds to vibrations of the Ge--O bonds in the $[\text{GeO}_6]$ structural units [20–22].

The existence of the absorption bands in the $820\text{--}850$ and $860\text{--}890 \text{ cm}^{-1}$ spectral regions shows the presence of the $[\text{BiO}_3]$ pyramidal and $[\text{BiO}_6]$ octahedral units. Thus, the bands situated at about 495 and 630 cm^{-1} can be attributed to vibrations of the Bi--O bonds in $[\text{BiO}_6]$ structural units [23,24].

An analysis of the FTIR spectra in the $x\text{Bi}_2\text{O}_3 \cdot (100 - x)[7\text{GeO}_2 \cdot 3\text{PbO}]$ ternary system shows that the addition of high Bi_2O_3 content to glass matrix causes:

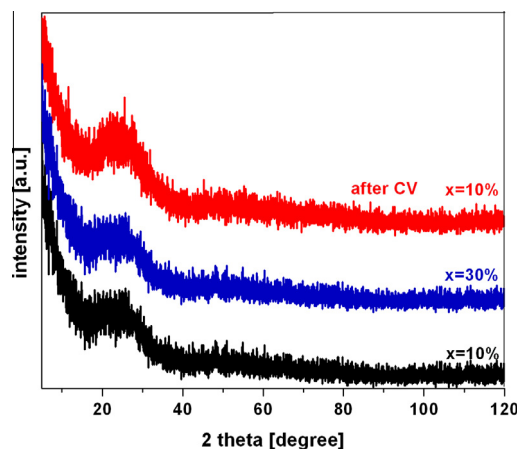


Fig. 1. X-ray diffraction patterns of $x\text{Bi}_2\text{O}_3 \cdot (100 - x)[7\text{GeO}_2 \cdot 3\text{PbO}]$ glass before and after cyclic voltammetry.

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