FTIR spectroscopic study of some lead germanate glasses

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Abstract. The structures of two lead germante glasses – yGeO$_2$·(100-y)PbO and xNd$_2$O$_3$(100-x)[GeO$_2$·PbO] – are investigated by the Fourier transform infrared (FTIR) spectroscopy. The structural role of germanium, lead and neodymium ions is discussed. The presence of GeO$_4$, GeO$_6$ and PbO$_4$ structural units was evidenced in the studied glass networks. In the case of the xNd$_2$O$_3$(100-x)[GeO$_2$·PbO] glasses it was shown that the ratio of the mentioned structural units depends on the Nd$_2$O$_3$ content of the samples. Therefore Nd$_2$O$_3$ play the network modifier role in studied glasses.

1. Introduction

In last years the need to find out new methods and materials for electronics, laser or nuclear technology in order to support the global economy became very important. It is known that, in general, the oxide glasses present interesting electrical, magnetic and optical properties as well as a good chemical stability and mechanical resistance. Among the oxide glasses, lead germanate are of interest because of several characteristics that make them promising materials for applications as new lasing materials and upconverters. Recently, more and more researchers have been started to study such glasses due their good mechanical strength, high thermal stability, good chemical durability and high refractive index (~2) [1-5]. Also, germanate glasses doped with rare-earth ions have been investigated extensively because their physicochemical, optical and spectroscopic properties are advantageous for optoelectronic applications [6-8].

The purpose of this paper was to obtain information on the basic structural polyhedra which form the glass network in the GeO$_2$-PbO and the GeO$_2$-PbO-Nd$_2$O$_3$ glass systems with the aid of FTIR spectroscopy.

2. Experimental

The glass samples having the general chemical formula yGeO$_2$·(100-y)PbO, with y=10, 20, 30, 40, 50, 60, 70 mol% and xNd$_2$O$_3$(100-x)[GeO$_2$·PbO] with x = 0, 1, 3, 5, 7, 10 mol% have been prepared by the melt quenching technique. Required quantities of analyer grade GeO$_2$, PbO and Nd$_2$O$_3$ were mixed and milled together with the aim to obtain a fine powder. The mixture was melted in sintered corundum crucibles in an electric furnace a temperature of 1100°C for 15 min.

X-ray diffraction investigation was performed by a XRD-6000 SHIMADZU diffractometer using the Cu K$_\alpha$ radiation ($\lambda$ = 1.54056 Å), a working voltage of 40 kV, a working current of 30 mA and the scanning speed of 2°/min.
The FTIR spectra of the studied glasses were registered 400-2000 cm\(^{-1}\) wave number range with a resolution of 4 cm\(^{-1}\) at room temperature using a JASCO FTIR 6200 type spectrometer and the KBr pellet technique.

3. Results and discussion

X-ray diffraction patterns of all the studied glasses have shown broad halo patterns with no crystalline peaks. Thus, for example, figure 1 presents the X-ray diffractograms for the \(x\text{Nd}_2\text{O}_3(100-x)\text{[GeO}_2\cdot\text{PbO]}\) glass system and shows only broad humps typical of amorphous materials.

![Figure 1. XRD patterns of the xNd\(_2\)O\(_3\)\((100-x)\)[GeO\(_2\)·PbO] glass system.](image)

Figure 2 shows the FTIR spectra of \(y\text{GeO}_2\cdot(100-y)\text{PbO}\) (left) and \(x\text{Nd}_2\text{O}_3(100-x)\text{[GeO}_2\cdot\text{PbO]}\) (right) glass systems.

![Figure 2. FT-IR spectra of yGeO\(_2\)·(100-y)PbO (left) and xNd\(_2\)O\(_3\)·(100-x)[GeO\(_2\)·PbO] (right) glass systems.](image)
summarized in table 1. The assignments were made based on data from the literature and comparing the experimental data of glasses with those of the related crystalline compounds [9-16]. Note that there were some absorption features located at 1300 and 1540 cm\(^{-1}\), but based on the present data it was not possible to assign them.

**Table 1.** FTIR bands and there assigned in case of the yGeO\(_2\)·(100-y)PbO glass system.

| Wavenumber [cm\(^{-1}\)] | y = 10 | y = 70 | Assignments |
|-------------------------|-------|-------|-------------|
| 472                     | 465   |       | symmetric bending vibration mode of Pb–O in PbO\(_4\) units [15, 16] |
| 625                     | 570   |       | asymmetric bending mode of Ge–O–Ge bonds [9, 12, 13] |
| 705                     | 695   |       | stretching mode of Ge–O–Ge bonds in GeO\(_6\) units [11, 14] |
| 823                     | 755   |       | asymmetric stretching mode of Ge–O–Ge bridges connecting GeO\(_4\) units [12, 13] |
| 892                     | 830   |       | asymmetric stretching mode of Ge–O–Ge bonds from GeO\(_4\) units [9, 12] |
| 1015                    | 954   |       | symmetric stretching vibration modes of Pb–O bonds [15, 16] |
| 1100                    | 1075  |       | asymmetric stretching vibration modes of Pb–O bonds [15] |
| 1300                    | 1365  |       | - |
| 1410                    | 1430  |       | asymmetric stretching vibration modes of Ge–O–Ge bonds [9] |
| 1540                    | 1545  |       | - |
| 1630                    | 1630  |       | OH bending mode of vibration |

In the case of the yGeO\(_2\)·(100-y)PbO glass system, a simple inspection of the spectral features (figure 2) shows that the bands characteristic of the lead oxide decrease with increasing the germanium oxide content. It was shown that the germanium ions appear in the glass network in both the GeO\(_4\) and GeO\(_6\) polyhedra. On the other hand, the lead ions are incorporated in the glass network in the PbO\(_4\) structural units for all the investigated glasses.

The xNd\(_2\)O\(_3\)(100-x)[GeO\(_2\)·PbO] glasses spectra (figure 2) show that no dramatic changes occur with increasing the Nd\(_2\)O\(_3\) content in the samples. In this glass system a new band was observed around 585 cm\(^{-1}\). This band increases in intensity with x and was attributed to the Nd–O stretching vibrations [10]. In addition, the intensity of the peak assigned to germanium oxide increases with the increase of the Nd\(_2\)O\(_3\) content. This suggests that the presence of Nd\(_2\)O\(_3\) favours the GeO\(_4\) and GeO\(_6\) units while the Pb–O vibration mode is affected.

The structural changes observed by varying the Nd\(_2\)O\(_3\) content in the xNd\(_2\)O\(_3\)(100-x)[GeO\(_2\)·PbO] glass system by using the FTIR investigation suggest that the neodymium ions play a network modifier role in these glasses.

### 4. Conclusions

Glasses of the yGeO\(_2\)·(100-y)PbO and xNd\(_2\)O\(_3\)(100-x)[GeO\(_2\)·PbO] systems were obtained within y = 10÷70 mol% and x = 0÷10 mol%. The FTIR spectra of these glasses were registered. It was shown that for all the samples the glass matrix consists on GeO\(_4\), GeO\(_6\) and PbO\(_4\) structural units. In the glasses containing Nd\(_2\)O\(_3\), the proportion of the mentioned structural units depends on the neodymium ions content. Therefore, we can conclude that the neodymium ions play the network modifier role in the studied glasses.

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