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Structural characteristics of terbium - lead - bismuthate glasses

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Fourier transform infrared (FT-IR) spectra and Fourier transform Raman (FT-Raman) spectra of the $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glass system with $0.01 \leq x \leq 0.12$ were recorded and analyzed with the aim of determining some of its structural characteristics. The FT-IR spectra of the samples were recorded for the 400-1300 cm^{-1} range using an Equinox 55 Bruker spectrometer. The FT-Raman spectra were recorded for the 70-1000 cm^{-1} region using the same equipment. The observed IR and Raman features were assigned to various vibration modes of the studied vitreous network.

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1. Introduction

Glasses consisting of rare-earth oxides and heavy metal oxides have attracted attention for their excellent optical properties such as high refractive index, infrared transmission and non-linear optical properties. On one hand, heavy metal oxides like Bi_2O_3 and PbO are of great interest because they form glasses without traditional network formers such as B_2O_3, SiO_2, P_2O_5, GeO etc and on the other hand, rare-earth ions can be incorporated easily into several glass matrices. [1-5]

In this context, Raman and infrared spectroscopy have proven to be powerful and effective tools for characterizing the structure of local arrangements in glasses [6–8].

The effect of the terbium ions on the glass structure are studied on this paper. Therefore, we report structural characterization of $[3Bi_2O_3 \cdot PbO]$ glass system for different concentration of Tb_4O_7, based on IR and Raman spectroscopy.

2. Experimental

Samples of the $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glass system, with $0 \leq x \leq 0.12$, were prepared by mixing Bi_2O_3, PbO and Tb_4O_7 of reagent grade purity. The mentioned oxides were mixed in suitable proportions to obtain the desired compositions. The mixtures were milled in an agate ball mill for 30 minutes and then were melted at 1200^{o}C for 15 minutes. The glass samples were obtained by pouring the melts on a stainless steel block.

X-ray diffraction was performed using a D8 Advance D8 Discover equipment in order to check the vitreous character of the samples.

The FT-IR absorption spectra of the glasses were recorded using an Equinox 55 spectrometer in the 400-1300 cm^{-1} wave number range at room temperature. Sample pellets were prepared by mixing and grinding a small quantity of glass powder with spectroscopic grade dry KBr powder and then compressing the mixtures to form thin pellets for testing. All measurements were run at a 2 cm^{-1} resolution. The FT-Raman spectra of these glasses were recorded using the same spectrometer like in case of IR spectroscopy but with a FRA 106/S FT-Raman attache, in the 70-1000 cm^{-1} wave number range, at room temperature. The spectral resolution was about 4 cm^{-1}.

3. Results

According to X-ray diffraction patterns, which do not reveal any crystalline phase, the as prepared samples are amorphous from structural point of view.

The FT-IR spectra of $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glass system are presented in figure 1. The seven absorption bands and shoulders clearly visible around 473, 581, 724, 846, 880, 980 and 1120 cm^{-1} dominate the infrared spectra of the investigated glasses. These bands have been assigned to the stretching frequencies of the Bi-O and Pb-O bonds.

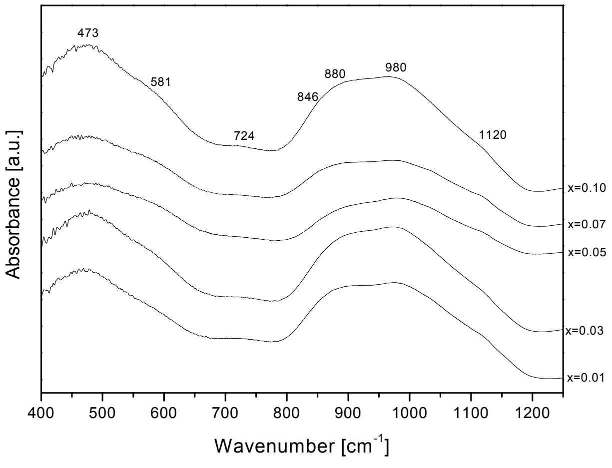

Fig. 1. FT-IR spectra of $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses.

Fig. 2 presents the FT-Raman spectra of the $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses. By looking at the FT-Raman spectra we can see that the band located at 138 cm^{-1} dominates all the spectra of the glass system. Other bands characteristic of these spectra appear around 253, 400, 552 and 910 cm^{-1} at higher Tb_4O_7 contents. All these bands increase in intensity with the increasing of terbium oxide content.

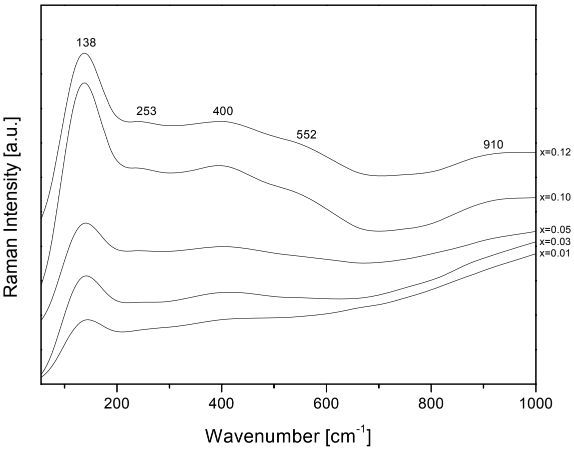

Fig. 2. FT-Raman spectra of $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses

4.Discussion

The assignment of the IR absorption bands for the $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses is discussed by comparing the experimental data obtained for this vitreous system with the absorption spectra of the Bi_2O_3 and PbO crystalline compounds [9, 10].

The IR spectral features characteristic of lead bismuthate glasses show the presence of two types of environments associated to structural units involving Bi^{3+} and Pb^{2+} ions. Thus, the bands and shoulders located around 473, 581, 846 and 880 cm^{-1} are associated with the presence of BiO_6 and BiO_3 units [13-17], while those located around 473, 724, 980 and 1120 cm^{-1} suggest the presence of PbO_3 and/or PbO_4 units [15-23] (see Table 1).

The most important absorption feature present in the studied IR spectra is located around 846 cm^{-1} and indicates the presence of the BiO_3 units in the glass network. This shoulder is more intense for higher terbium oxide content. Therefore, the presence of terbium ions influences the surrounding of the Bi^{3+} ions, favouring the formation of BiO_3 units. In this view we mention two important facts that were previously reported [11]: (i) the bonding strength of Bi-O is higher in the BiO_3 units than in the BiO_6 units and (ii) the degree of the connectivity of the glass network increases with increasing the number of BiO_3 polyhedra.

In bismuthate glasses the BiO_3 polyhedra play the glass network former unit role while the BiO_6 play the glass network modifier unit role [12].

Based on the IR spectra obtained for the terbium – lead - bismuthate glasses, we assumed that the structure of these glasses is built up of both BiO_3 and BiO_6 structural units. The analysis of these IR spectra suggests that PbO_n structural units (where n= 3 and/or 4) are present, too, in the glass network of the studied glasses.

Table 1. IR absorption features and their assignment for the of $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses.

Wavenumber [cm^{-1}]	Assignment
~ 473	Bi-O bending vibrations in BiO_6 units Pb-O bonds vibrations in PbO_4 units
~ 581	Bi-O stretching vibrations in BiO_6 units
~ 724	Pb-O bonds vibrations from PbO_n pyramidal units (n = 3 and/or 4)
~ 846	Bi-O stretching vibrations in BiO_3 units
~ 880	Bi-O stretching vibrations in BiO_6 units
~ 980, ~ 1120	Pb-O vibration from Pb-O-Bi connections

Raman spectra of the Bi_2O_3 and PbO crystalline compounds were used for the identification of the specific structural groups in the corresponding vitreous systems [24, 25]. Based on the experimental Raman spectra obtained for the heavy metal based glasses a classification of the Raman vibrations modes is given: (i) heavy metal ion vibration at 100–180 cm^{-1}; (ii) bridging anion modes in various cation – anion - cation or anion – cation - anion configurations at 180–600 cm^{-1}; (iii) non-bridging anion vibrations modes which correspond to higher wavenumbers and appear as a consequence of the cation - anion motions [26,27].

Therefore, the band situated around 138 cm^{-1} in the Raman spectra of $xTb_4O_7(1-x)[3Bi_2O_3 \cdot PbO]$ glasses (Fig. 2) was attributed to vibrations modes involving the Bi^{3+} and Pb^{2+} ions motion [19].

By comparing the FT-Raman spectra of the low content terbium oxide samples to the spectra with high content terbium oxide samples, remarkable structural changes can be seen as a consequence of the variation of the terbium ion content. These structural changes are related to the rearrangement of the surroundings of the bismuth and lead ions. The most important spectral evidence is represented by the appearance of new Raman bands around 253, 552 and 910 cm^{-1} that show a new structural arrangement in the glass network. This result proves again that terbium ions favour the formation of BiO_3 units in the glass network. Consequently, terbium ions play the network-modifier roll in this glass system. The assignment of all bands which appear in FT-Raman spectra was presented in Table 2.

Table 2.Raman features and their assignment for the $xTb_4O_7(1-x)[3Bi_2O_3{\cdot}PbO]$ glasses.

Wavenumber [cm^{-1}]	Assignment
~ 138	Bi^{3+} ions vibrations in BiO_6 and BiO_3 units Pb^{2+} ions vibrations in PbO_4 or/and PbO_3 units
~ 253	Bi-O-Bi stretching vibrations in BiO_6 and BiO_3 octahedral units Pb-O bonds vibrations in PbO_4 or PbO_3 units
~ 400	Pb-O stretching vibrations from PbO_n pyramidal units
~ 552	Bi-O-Bi stretching vibrations in BiO_6 and BiO_3 units Pb-O bonds vibrations in PbO_4 units
~ 910	Vibrations of Pb-O bonds in different structural units

5. Conclusions

FT-IR and FT-Raman spectral investigation of the $xTb_4O_7(1-x)[3Bi_2O_3{\cdot}PbO]$ glasses evidenced the roll of terbium ions in determining the structural characteristics of the glass network. Thus, the terbium ion content of these glasses determines the ratio of BiO_3/ BiO_6 structural units, respectively that of the PbO_3/ PbO_4 structural units.

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