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FT-IR and EPR spectroscopic studies of B_2O_3–Bi_2O_3–Gd_2O_3 glasses

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Glasses from $xGd_2O_3·(100-x)[B_2O_3·Bi_2O_3]$ system with 0≤x≤10 mol% have been prepared and than studied by means of FT-IR absorption and electron paramagnetic resonance (EPR) measurements. FT-IR data indicate in the studied glasses the presence of the BO_3, BO_4, BiO_6 and BiO_3 units and its proportion dependence of the Gd_2O_3. The EPR spectra of these glasses reveal resonance sites with an unexpected high crystalline field in addition to the "U" spectrum, typical for Gd^{3+} ions in disordered systems. These absorption lines are due to the Gd^{3+} ions that can partially replace Bi^{3+} ions from the host glass matrix and could play the network unconventional former role in the studied glasses.

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1. Introduction

Heavy metal oxide glasses containing Bi_2O_3 are investigated for their special properties such as high refractive index, high nonlinear optical susceptibility, high density which make them suitable for potential applications as nonlinear optical materials, low loss optical fibers, thermal and mechanical sensors, IR transmitting windows, etc. [1-3]. Gadolinium ions in oxide glasses are investigated for their possible applications in luminescent devices [4].

The presence of two network forming oxides the classical B_2O_3 and unconventional Bi_2O_3, the possible participation in the glass structure of both boron and bismuth atoms with more than one stable coordination, as well as the presence of gadolinium ions increase the interest of the present study.

In ordered to extend the available information concerning the interesting class of the $B_2O_3·Bi_2O_3$ glass matrix containing gadolinium ions, in this work we investigated the $xGd_2O_3·(100-x)[B_2O_3·Bi_2O_3]$ vitreous system with 0≤x≤10 mol% by FT-IR and EPR measurements.

2. Experimental procedures

Glasses of the $xGd_2O_3·(100-x)[B_2O_3·Bi_2O_3]$ system were prepared using pure reagent grade chemicals, H_3BO_3, $Bi(NO_3)_3·5H_2O$ and Gd_2O_3 in suitable proportions. The mixtures were mechanically homogenized and melted in sintered corundum crucibles in an electric furnace. The mixtures were introduced directly at 1200°C in the pre-heated furnace. After 5 minutes the molten materials were quenched to room temperature by pouring on the stainless-steel plates. The structure of the samples was studied by means of X-ray diffraction and no crystalline phase was detected up to 10 mol % Gd_2O_3.

The Fourier-transform infrared (FT-IR) absorption spectra were recorded with an Equinox 55 Bruker spectrometer, at room temperature, in the 400-2000 cm^{-1} range, using the KBr pellet technique. The spectral resolution was 2 cm^{-1}.

EPR measurements were performed at room temperature using ADANI Portable EPR PS 8400 type spectrometer, in X frequency band (9.4 GHz) and a field modulation of 100 KHz. The microwave power used was 5 mW. To avoid the alteration of the glass structure due to the ambient condition, samples of equal quantities were enclosed immediately after preparation in the tubular holders of the same caliber.

3. Results and discussion

The experimental FT-IR spectra for the $xGd_2O_3·(100-x)[B_2O_3·Bi_2O_3]$ with 0≤x≤10 mol % are presented in Fig. 1.

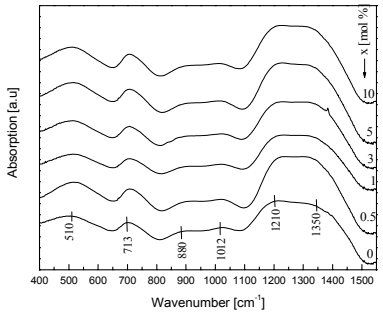

Fig.1. FT-IR spectra of $xGd_2O_3·(100-x)[B_2O_3·Bi_2O_3]$ glasses.

The FT-IR spectra bands of the glasses investigated in this paper and their assignments are summarized in the Table 1. These data have been discussed on the basis of the methods given by Tarte [5] and Condrate [6] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for the vitreous B_2O_3, Bi_2O_3 [7-9] and crystalline Gd_2O_3 [10] were used as a reference point in the results discussion.

The FT-IR absorption bands obtained for our glasses are centered at ~510, ~713, ~880, ~1012, ~1210 and ~1350 cm^{-1}.

The band centered at ~510 cm^{-1} represents a convolution of three absorption bands at ~457 cm^{-1}, ~520 cm^{-1} and ~592 cm^{-1} [7-12]. In this way, the first band situated at ~457 cm^{-1} represents a broad shoulder specific for the vibration mode of Gd-O bonds [10]. The deconvoluted band situated at ~520 cm^{-1} is most prominent and is typical for the stretching vibrations of Bi-O bonds in BiO_6 octahedral units [7]. The increase of the Gd_2O_3 content determines an increase of the contribution band centered at ~520 cm^{-1}, which suggest that the presence of gadolinium ions seems to influence the surrounding of the Bi^{3+} cations which can favor the formation of BiO_6 units. The last band deconvoluted is situated at ~592 cm^{-1} and is assigned to B-O-B bending vibrations and borate ring deformation [13].

The band at ~713 cm^{-1} is assigned to the bending vibrations of O_3B-O-BO_3 bonds [9,14] and also to the symmetric stretching vibration of Bi-O bonds in BiO_3 pyramidal units [15,16]. The intensity of this absorption band slowly increases with the concentration of the gadolinium ions.

It was shown that Bi_2O_3 appears in the bismuth-borate glasses networks as distorted BiO_6 units [8,17], both BiO_6 and BiO_3 polyhedra [18, 19] or only as BiO_3 pyramidal units [20]. Based on the IR spectra obtained for our samples, we assumed that the structure of these glasses is built up of both BiO_3 and BiO_6 structural units.

Table 1. The assignments of the FT-IR bands detected in the spectra of $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses.

Wavenumber (cm^{-1})	Assignment
~510	Specific vibrations of Gd-O bonds, Bi-O bonds stretching vibrations in BiO_6 octahedral units, B-O-B bending vibrations and borate ring deformation
~713	O_3B-O-BO_3 bending vibrations, Bi-O bonds symmetric stretching vibrations in pyramidal BiO_3 units
~880	B-O bonds stretching vibrations in BO_4 units from diborate groups, Symmetric stretching vibrations of Bi-O bonds in BiO_3 units
~1012	B-∅ stretching vibrations in $B∅_4^-$ units from tri- tetra- and penta-borate groups
~1210	B-O bonds stretching vibrations in BO_3 units from meta- and ortho-borate groups
~1350	Asymmetric stretching vibrations of B-O bonds in BO_3 and $B∅_2O^-$ units

In borate glasses the absorption in 800-1100 cm^{-1} range is assigned to B-O asymmetric stretching vibration of tetrahedral BO_4 units. The absorption band at ~880 cm^{-1} are assigned to the B-O stretching vibrations in BO_4 units from diborate groups over which can be superposed symmetric stretching vibrations of Bi-O bonds in the BiO_3 units [7,8,11,16]. The absorption band centered at ~1012 cm^{-1} is assigned to the B-∅ bonds stretching vibrations in $B∅_4^-$ units from tri-, tetra-, and penta-borate groups (∅=oxygen atom bridging two boron atoms) [7,21,22].

In the 1100-1500 cm^{-1} range the absorption is assigned to stretching vibrations of B-O bonds in BO_3 units. The band centered at ~1210 cm^{-1} is characteristic for stretching vibrations of B-O bonds in BO_3 units from meta- and ortho-borate groups [21]. The band centered at ~1350 cm^{-1} is assigned to asymmetric stretching vibrations of B-O bonds in BO_3 and $B∅_2O^-$ units [23-25]. On the addition of the gadolinium ions to the glass the bands from 1100-1500 cm^{-1} becomes more pronounced w hich means that the proportion of BO_3 units increase.

Comparing the intensity of bands situated in 800-1100 cm^{-1} range with the bands situated in 1100-1500 cm^{-1} range it can be shown that in our glasses the proportion of BO_3 units is predominant, therefore the BO_4/BO_3 ratio is sub-unit.

The EPR spectra obtained for the $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses are shown in Fig. 2. These spectra are due to the presence of Gd^{3+} ions in the $B_2O_3 \cdot Bi_2O_3$ glass matrix and are relatively close to those previously reported for other oxide glasses containing gadolinium ions [12, 26-34]. For low gadolinium ions concentrations in glass matrix the EPR spectra is characterized by prominent features with effective g_{eff} values of ≈6, ≈4.8, ≈2.87, ≈2 and at higher concentration being superimposed on a broad resonance line shape that encompasses the prominent g_{eff}≈2 feature.

The resonance signals at g_{eff}≈6, g_{eff}≈2.87 and g_{eff}≈2 are a characteristic of the so-called "U" spectrum of Gd^{3+} ions in disordered materials [32-35].

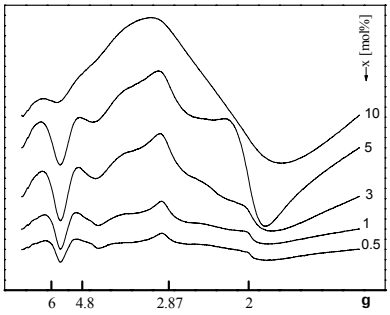

Fig. 2. EPR spectra of $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses.

EPR spectra of Gd^{3+} ions in glasses are generally very anisotropic and sensitive to variations in ligand field from site to site [35]. Most of the authors [12, 26-28] consider the mentioned absorption features (g_{eff}≈6, g_{eff}≈2.87, g_{eff}≈2) to be generated by Gd^{3+} ions disposed in tetrahedral, octahedral, or cubic sites with moderate distortions. In these sites the gadolinium ions experience a relatively weak crystalline field and they are characterized by a coordination number higher than six [32-34]. The difference between Gd^{3+} EPR spectra of $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses and the "U" spectrum is the occurrence of an asymmetric absorption line with g_{eff}≈4.8. This line indicates a relatively strong crystalline field with an orthorhombic symmetry and is associated with gadolinium ions with a coordination number lower than six. This location for Gd^{3+} is unusual being known the general tendency of the rare earth ions for locations associated with high coordination number. The Gd^{3+} ion

prefers to be 6 or 8 coordinated and can be more readily accommodated in a vitreous phase than in a crystalline state of higher symmetry. The vitreous structure offers the Gd^{3+} ions more preferred coordination sites to choose from and the EPR spectra reflect this preference [35]. Such a location for gadolinium ions with a coordination number lower than six may appear in the $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses when Gd^{3+} ions replace Bi^{3+} ions. Taking into account the radii of the involved ions r_{Bi3+} =1.20Å and r_{Gd3+}=1.20Å [36] the accommodation of gadolinium ions in the mentioned positions is perfectly possible.

Increasing Gd_2O_3 content first produces the dipole-dipole broadening of the spectra ($0<x\leq3$ mol %) and then their exchange narrowing ($3<x\leq10$ mol %). But for x=10 mol % the narrowing of the EPR signal can be balanced by the broadening effects due the progressive disordering of the vitreous structure. At higher gadolinium contents, isolated Gd^{3+} ions can coexist with clusters of Gd^{3+} ions linked with each other by exchange interaction through the oxygen bridges [12,27,29].

3. Conclusions

The infrared data revealed the presence of boron atoms in both, three and four coordination states, for all investigated glasses. All over the compositional range the four coordinated boron atoms number is lower than three coordinated. On the basis of the IR spectra investigation it was also found that Bi^{3+} cations are incorporated in the glass network as BiO_3 and distorted BiO_6 structural units. The presence of gadolinium ions and his influence in this vitreous system was shown.

The EPR study of $xGd_2O_3 \cdot (100-x)[B_2O_3 \cdot Bi_2O_3]$ glasses shown a structural distribution of gadolinium ions in different locations, such in high crystalline field where could act as network unconventional former because it can partially substitute the bismuth ions which has the same radius, and in weak crystalline field where could act as network modifier. From magnetically point of view, the EPR data obtained confirm the presence of the Gd^{3+} ions like isolated species, participating at dipole-dipole interactions and/or magnetic superexchange interactions.

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