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Spectroscopic characterisation of local structure in Y_2O_3–B_2O_3–Bi_2O_3 glasses doped with gadolinium

S. Simon · D. Eniu

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Abstract Gadolinium doped bismuth borate glasses containing up to 30 mol% Y_2O_3 were prepared by fast melt quenching method. The effect of yttrium on the local order in $3B_2O_3 \cdot Bi_2O_3$ and $B_2O_3 \cdot Bi_2O_3$ glass matrices, particularly on the bismuth sites, was investigated by infrared (IR) spectroscopy and electron paramagnetic resonance (EPR) of Gd^{3+} ions. The IR results show that the local structure is more ordered in the glass system with higher bismuth content and the progressive addition of yttrium increases the local disorder in both bismuth–borate glass matrices. The EPR results indicate that Gd^{3+} ions occupy both bismuth and yttrium sites and reflect the same structural disorder like that suggested by IR results.

Introduction

Bismuthate glasses are interesting because their properties are exploited in applications such as wave-guides in non-linear optics, scintillation detectors in high-energy physics, reflecting windows and layers for optoelectronic devices [1–4]. The properties of glasses are mainly determined by the degree of local order/disorder, so that investigations giving information about the local structure are important in order to understand the correlation between properties and structure. Vibrational spectroscopy has proven to be powerful and effective tool for characterizing the structure of local arrangements in glasses [5–7]. Electron paramagnetic resonance (EPR) spectroscopy is one of the most efficient methods for the characterisation of local order and of magnetic interactions in non-crystalline systems in general and in glasses in particular [8]. The non-linear properties of bismuthate glass systems can be controlled by addition of strontium [9, 10]. Considering the proximate element after strontium, yttrium, that has a relative large cationic radius, 1.04 Å, we investigated by IR and EPR the changes induced by yttrium oxide in the local order of bismuth borate glass matrices $3B_2O_3 \cdot Bi_2O_3$ and $B_2O_3 \cdot Bi_2O_3$, particularly on the bismuth sites, having in view that the non-linear properties are firstly related to the heavy metal ions.

Experimental

Samples belonging to $xY_2O_3(100 - x)[yB_2O_3 \cdot Bi_2O_3]$ glass systems, where $0 \le x \le 30$ mol% and $y = 1$ and 3, were doped with 0.5 mol% Gd_2O_3 in order to use Gd^{3+} EPR centres for investigation of structural changes in their vicinity. The glass samples under investigation were prepared by mixing appropriate amounts of H_3BO_3, Bi_2O_2-CO_3, Y_2O_3 and Gd_2O_3, all analar grade chemicals. A homogeneous mixture of powders was prepared and fired in sintercorundum crucibles at 1,300 °C for 30 min in an automatically temperature controlled furnace. The glass samples were prepared by splat-cooling technique, by quenching and pressing the melt between steel plates at room temperature. With respect to samples colours one remarks that the glass matrix $3B_2O_3 \cdot Bi_2O_3$ ($x = 0$) is dark brown-reddish while the glass matrix $B_2O_3 \cdot Bi_2O_3$ is

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S. Simon (✉)
Faculty of Physics, Babes-Bolyai University,
400084 Cluj-Napoca, Romania
e-mail: simons@Phys.ubbcluj.ro

D. Eniu
Faculty of Pharmacy, University of Medicine and Pharmacy,
400010 Cluj-Napoca, Romania

yellowish. By adding yttrium to 3:1 matrix the glasses with low Y_2O_3 content ($x \le 10$) become brighter and further, for high Y_2O_3 content ($20 \le x \le 30$) the samples become yellowish. Contrary the glasses formed with $B_2O_3 \cdot Bi_2O_3$ matrix are yellowish for low Y_2O_3 content ($0 \le x \le 10$) and become brown-reddish for high Y_2O_3 content ($20 \le x \le 30$).

The glass state of the as-quenched samples was attested by X-ray diffraction analysis. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded with a resolution of 2 cm^{-1} on a Bruker spectrophotometer at room temperature. Electron paramagnetic resonance spectra were recorded on powder samples at room temperature in X band on an ADANI spectrometer. DPPH (DiPhenil-Picryl-Hydrazyl radical) with a g value of 2.0036 was used as a standard field marker.

Results and discussion

The non-crystalline state of all samples was confirmed by X-ray diffraction analysis. The XRD patterns consist of a large structureless line typical for structural disordered systems.

B_2O_3 is one of the most common glass former. Pure vitreous B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B–O–B linkages (bridging oxygen atoms). The addition of other oxides causes a progressive change of the boron atom coordination from 3 to 4 and results in the formation of various cyclic units (diborate, triborate or tetraborate groups) [11]. At higher concentrations of network modifier the number of tetracoordinated boron atoms is decreasing [12].

Glass formation was reported even with unconventional Bi_2O_3 as unique network former despite the fact that Bi_2O_3 does not form glass by itself [13, 14]. The high ability of bismuth borate systems inclusively for high Bi_2O_3 contents to form glass samples is due to the high polarisability of Bi^{3+} ions [3]. It was shown by ^{11}B NMR studies [15] that the fraction of tetracoordinated boron decreases from 30% for 3:1 matrix to 20% for 1:1 matrix.

In the presence of conventional glass-forming cations, like P, Si, B, the network of bismuthate glasses can be built up of BiO_3 pyramidal units and in multicomponent bismuthate glasses may occur both BiO_3 pyramidal and BiO_6 octahedral units [16–18]. In the low wavenumber region, wherein are preponderantly located the heavy metals IR bands, the IR absorption bands for boron units are recorded at 730 cm^{-1}, assigned to bending vibration of the B–O–B, in the 800–1,000 cm^{-1} spectral region, most probably due to $[BO_3]$ or isolated diborate group vibrations and in the 900–1,100 cm^{-1} spectral range, assigned to pentaborate group vibrations [19–22]. For bismuthate glasses IR bands are reported around 678 cm^{-1} and 875 cm^{-1}, typical for the normal vibrations of $[BiO_6]$ groups, and around 830 cm^{-1}, typical for $[BiO_3]$ pyramidal units [3, 20, 23].

The absorption band at 678 cm^{-1} is recorded in $3B_2O_3 \cdot Bi_2O_3$ matrix only for the glasses with $x \ge 10$ (Fig. 1) and for all glasses in $B_2O_3 \cdot Bi_2O_3$ matrix (Fig. 2), suggesting that for these compositions the bismuth surrounding is better organised. The IR absorptions occurring in 800–1,000 cm^{-1} spectral range from $[BO_3]$ group vibration are larger in the case of $3B_2O_3 \cdot Bi_2O_3$ matrix glasses than for $B_2O_3 \cdot Bi_2O_3$ matrix glasses. Considering that the broader is the absorption line the higher is the disorder in the glass structure, we can conclude that the local structure is more ordered in the glass system with higher bismuth content. The 830 cm^{-1} band related to the symmetrical stretching vibration of the Bi–O bonds in the $[BiO_3]$ groups, if exists, is masked by the lines occuring in 800–1,000 cm^{-1} spectral range from the vibrations of $[BO_3]$ units. Nevertheless, it is very likely that the bands around 860 cm^{-1} in the IR spectra of $B_2O_3 \cdot Bi_2O_3$ matrix glasses with $x < 10$ arise from vibrations of $[BiO_3]$ units, which are destroyed by higher Y_2O_3 contents. The IR band around 860 cm^{-1} is shifted to lower wavenumbers as x increases up to 10 mol% Y_2O_3, showing that for these compositions bismuth can play glass network former role.

Taking into account that ionic radius of Gd^{3+} (1.08 Å) is a bit higher than of Y^{3+} (1.04 Å), but smaller than Bi^{3+} ionic radius (1.17 Å) it is expected that gadolinium ions are most probably disposed in sites corresponding to bismuth without to exclude the possibility to occupy also yttrium sites. The spectra of Gd^{3+} ions can reflect if their surroundings, and by extension the surrounding of bismuth

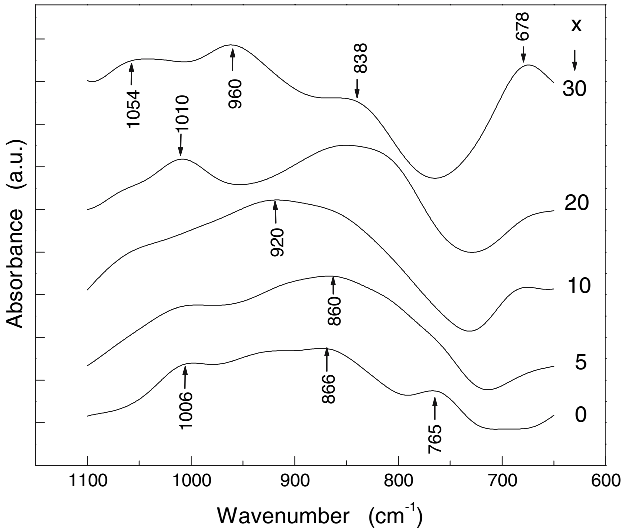

Fig. 1 ATR-FTIR spectra of $xY_2O_3(100-x)[3B_2O_3 \cdot Bi_2O_3]$ glasses

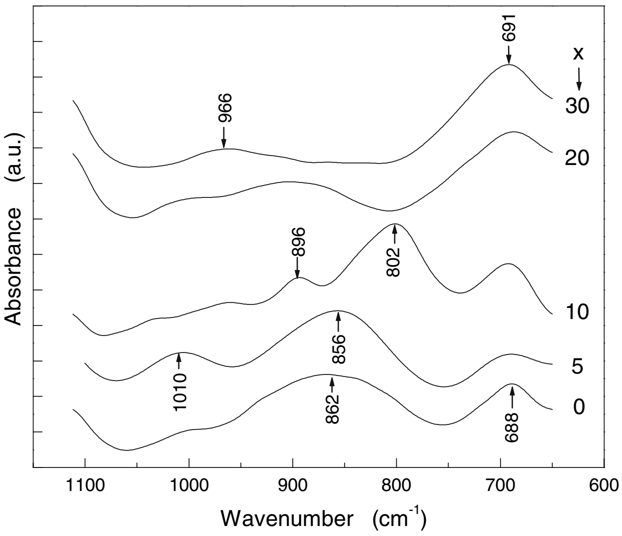

Fig. 2 ATR-FTIR spectra spectra of $xY_2O_3(100 - x)[B_2O_3 \cdot Bi_2O_3]$ glasses

ions in the investigated samples, are distorted by yttrium addition.

The Gd^{3+} EPR spectra of the samples formed in the system with lower bismuth content are shown in Fig. 3 and that corresponding to glasses formed in the system with higher bismuth content, having B_2O_3 to Bi_2O_3 ratio 1:1, are shown in Fig. 4. For all compositions are recorded resonance signals around $g \approx 2.0$, 2.8, 4.3, 4.8 and 5.9. The Gd^{3+} EPR spectra are the superposition of the well known U type spectrum [24–27], with lines at $g \approx 5.9$, 2.85 and 2.0 and of a weak resonance line at $g \approx 4.8$, that is unusual in X band for the vitreous samples [28]. The signal with $g \approx 4.3$ is assigned to Fe^{3+} impurities.

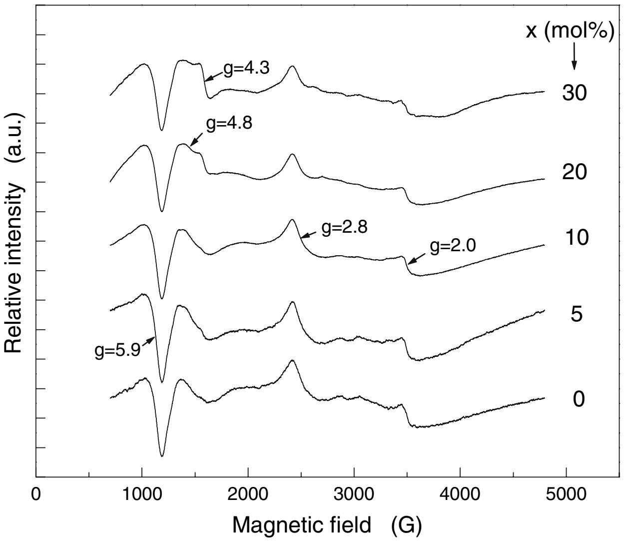

Fig. 3 Gd^{3+} EPR spectra recorded from $xY_2O_3(100 - x)[3B_2O_3 \cdot Bi_2O_3]$ glasses

The energy levels of these ions in an external magnetic field $\vec{B}$ are described, in a first approximation, by the spin Hamiltonian [24]:

$$H = g_o \beta \vec{B}\vec{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right)$$

where the first term is the Zeeman term and the following second order terms describe the crystal field effects, D and E are the axial and rhombic constants of the energy level splitting in zero magnetic field, respectively. Although, in particular for Gd^{3+}, higher order terms can, in general, not be neglected, Gd^{3+} EPR spectra in glasses are well described by this Hamiltonian. The lines at $g \approx 2$ are assigned to paramagnetic ions in sites characterised by relatively weak crystalline fields, for which Zeeman term dominates. The lines with $g > 2$ are attributed to paramagnetic ions in sites of relatively strong crystal field, where the crystal field terms are comparable or larger than the Zeeman term [25].

The well known fact that the line widths of EPR spectra of glass samples with low paramagnetic ions concentration are broader than those of crystalline samples reflects much larger inhomogeneities in the local structure of glasses and consequently the linewidth can be used as a measure of the local disorder in different non-crystalline materials.

The U type Gd^{3+}-EPR spectrum is characteristic for Gd^{3+} ions in structurally disordered systems [24]. The lines from U spectrum with $g \approx 5.9$, 2.8 and 2.0 are assigned to Gd^{3+} ions in sites with intermediate crystal fields having coordination numbers higher than six [29], while the $g \approx 4.8$ line is characteristic for Gd^{3+} ions in sites of strong crystal fields having a lower coordination number [30]. Such species with unsaturated coordination usually occur only at the surface of oxide systems and they are particularly an important presence in porous materials [25, 30].

The intensity of the resonance lines was computed as product of amplitude and peak-to-peak linewidth square. Considering the line intensity proportional to the number of resonance centres giving rise to a certain resonance line, it was appreciated that the doped gadolinium ions are preferentially disposed in sites of intermediate crystal field having coordination numbers equal or higher than six. Such coordinations are very plausible for gadolinium ions disposed in a larger hole of replaced bismuth ions. The distribution of gadolinium ions on sites of different crystal field strength in $3B_2O_3 \cdot Bi_2O_3$ glass matrix is comparable as yttrium oxide is added up to 10 mol%, but for $x \geq 20$ mol% the gadolinium ions are preponderantly disposed in sites with stronger crystal field giving rise to the resonance signal at $g \approx 5.9$. In contrast, in the samples formed with $B_2O_3 \cdot Bi_2O_3$ glass matrix by addition of yttrium oxide the gadolinium ions preferentially occupy the

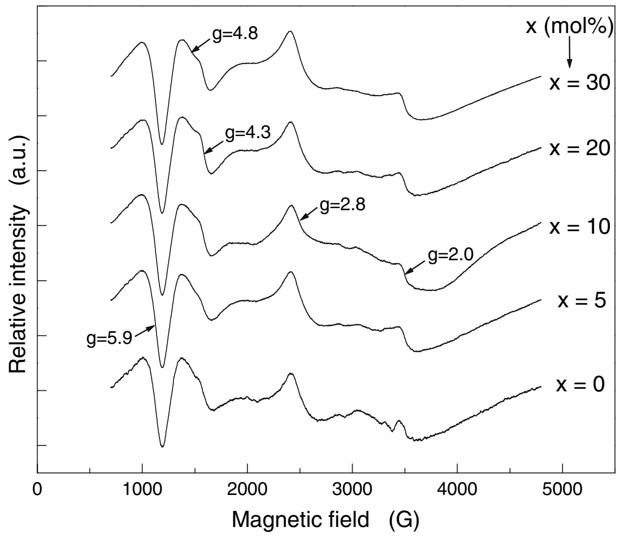

Fig. 4 Gd^{3+} EPR spectra recorded from $xY_2O_3(100 - x)[B_2O_3 \cdot Bi_2O_3]$ glasses

sites with lower crystal field strength that are related to the resonance lines with low g values. The relative independence on yttrium content of Gd^{3+} EPR spectra shape supports the assumption that Gd^{3+} ions are disposed in the bismuth sites.

The dependence of the linewidths on yttrium content is shown in Figs. 5, 6, 7 for the lines with g ≈ 5.9, 2.8 and 2.0, respectively. One remarks that in the samples without yttrium the linewidth of all resonance signals is sensibly narrower then in yttrium containing samples and, in general, it increases with Y_2O_3 content, showing that yttrium ions have a distortional effect on their environments.

The resonance lines for samples with higher bismuth content (1:1 matrix) are narrower than the corresponding ones for the glass samples with lower bismuth content (3:1 matrix) and similar yttrium concentration, denoting a diminished structural disorder degree around bismuth sites by increasing the bismuth oxide content. In this case beside boron also bismuth can play a glass network former role.

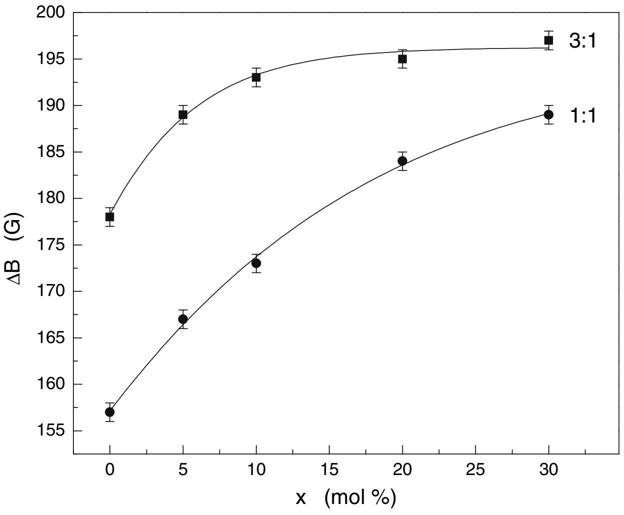

Fig. 5 Composition dependence of linewidth for the resonance lines occurring at g ≈ 5.9 The line is guide to the eyes

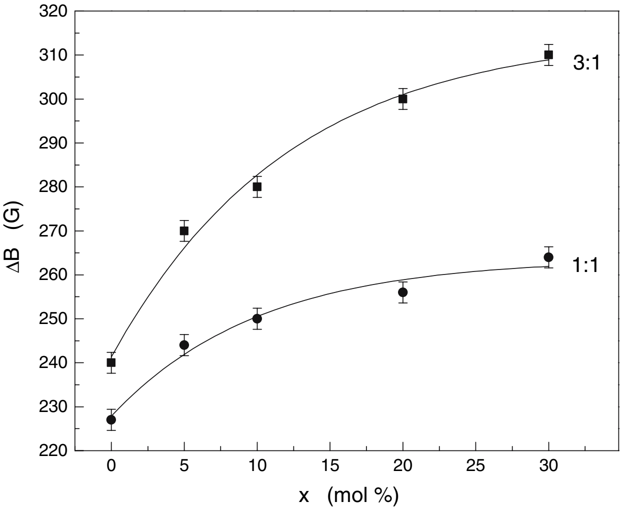

Fig. 6 Composition dependence of linewidth for the resonance lines occurring at g ≈ 2.8. The line is guide to the eyes

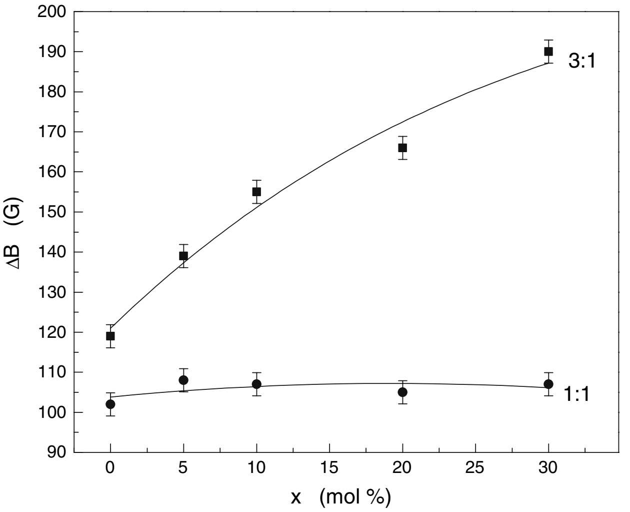

Fig. 7 Composition dependence of linewidth for the resonance lines occurring at g ≈ 2.0. The line is guide to the eyes

Conclusions

The composition dependence of IR absorption bands in the investigated yttrium–bismuth–borate glasses points out that in these glass samples structural disorder degree is increased by progressive addition of yttrium. An opposite effect on the local order is caused by increasing bismuth content. In the investigated samples bismuth acts also as a glass network former.

The evolution of Gd^{3+} EPR parameters shows that in these glass samples Gd^{3+} ions mainly occupy bismuth sites. The structural disorder degree is diminished in the glass system with higher bismuth content, but the progressive addition of yttrium has an opposite effect on the local order. The addition of yttrium oxide into $3B_2O_3 \cdot Bi_2O_3$ glass matrix increases the number of gadolinium ions disposed on sites of stronger crystal field strength while in $B_2O_3 \cdot Bi_2O_3$ glass matrix is noticed the tendency to increase the number of gadolinium ions in sites of lower crystal field strength.

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