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# The double role played by the $Gd_2O_3$ in the gadolinium–aluminum–borate–bismuthate quaternary glass forming tendency. $GdBO_3$ crystalline phase

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ABSTRACT

Glasses and glass–ceramics in the $xGd_2O_3\cdot(100-x)[2Bi_2O_3\cdot B_2O_3\cdot Al_2O_3]$ system with $x$ = 0, 1, 5, 10, 15, 20, 25, 30, 35, 50 mol% $Gd_2O_3$ have been prepared by the melt quenching method. The changes of the IR spectral features suggest that the formation of $[BO_4]$ tetrahedra is reduced because the modified $[BO_3]$ units containing one or more B–O–Gd bonds are unable to accept the fourth oxygen.

Based on our results, we conclude that the accommodation of the networks with the excess of oxygen is possible by the deformation of Bi–O–Bi linkages, the participation of aluminum atoms as network formers and the intercalation of $[BiO_6]$ and $[AlO_4]$ entities in the $[BO_4]$ chain network.

When high $Gd_2O_3$ content is introduced, more $[BO_3]$ structural units are coupled with gadolinium ions and the accumulation of oxygen can be supported by the formation of new $[BO_3]^{-3}$ structural units as ortho-borate units. These yield the formation of $GdBO_3$ crystalline phase which has been confirmed by XRD investigations.

Comparing the theoretical and experimental IR spectral characteristic features, we conclude that the prediction of the structural data is good.



## 1. Introduction

Despite the fact that $Bi_2O_3$ is not a classical glass former, due to its high polarizability and to the small field strength of $Bi^{+3}$ ions, in the presence of conventional glass formers (such as $B_2O_3$) it may build a glass network of $[BiO_n]$ pyramids [1–5]. Some authors [6,7] suggested that the bismuth ions form $[BiO_3]$, $[BiO_5]$ and $[BiO_6]$ units in the glasses similar to those in $\alpha$-$Bi_2O_3$ crystal. The problem is complex because the $[BiO_n]$ polyhedra are highly distorted due to lone pair electrons.

Glasses in the $Gd_2O_3$–$Bi_2O_3$–$B_2O_3$–$Al_2O_3$ quaternary systems are interesting subjects for structural investigations from two motives:

(i) The addition of network modifier oxides generate the appearance of the broken network bridges accompanied by the formation of non-bridging oxygen sites.
(ii) In the case of the structure of quaternary glasses there is no clear picture concerning the exact nature of the oxygen polyhedra surrounding the metallic atoms or of the role played by the other glass components or of their unusual glass forming tendency. The shortage of oxygens becomes more serious in quaternary glasses and it is expected that a fraction of the oxygens to be three-coordinated. Then, the presence of $[AlO_4]$ can indicate that $Al_2O_3$ behaved as a glass former in this system.

In brief, the structure of the $2Bi_2O_3\cdot B_2O_3\cdot Al_2O_3$ ternary glass is still a subject of discussion. The aim of the present study was to determine, by means of FTIR spectroscopic results and density functional theory (DFT) calculations, the influence of $Gd_2O_3$ on the structure of the aluminum–borate–bismuthate glasses with a special interest on the ability of gadolinium ions to produce the crystallization. The presence of three glass forming oxides, the classical $B_2O_3$ and the unconventional $Bi_2O_3$ and $Al_2O_3$, increase the interest of the present study.

## 2. Experiment

The quaternary glasses with the $xGd_2O_3\cdot(100-x)[2Bi_2O_3\cdot B_2O_3\cdot Al_2O_3]$ composition were prepared by mixing appropriate amounts of $Bi_2O_3$, $H_3BO_3$, $Al_2O_3$, $Gd_2O_3$. The mixtures were melted at 1200 °C for about 15 min in corundum crucibles in an electric furnace. After that the melts were rapidly quenched at room temperature.

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

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The FTIR spectra were recorded in the 400–1600 $cm^{-1}$ range using a JASCO FTIR 6200 FT-IR spectrometer.

The DFT (density functional theory) computations were performed with B3PW91/CEP-4G/ECP method using Gaussian 03 program package [8].

## 3. Results and discussion

The X-ray diffraction patterns reveal the $GdBO_3$ crystalline phase (Table 1) in the sample with 50 mol% $Gd_2O_3$ (Fig. 1).

### 3.1. FTIR spectroscopy

In the FTIR spectra of the $xGd_2O_3{\cdot}(100-x)[2Bi_2O_3{\cdot}B_2O_3{\cdot}Al_2O_3]$ glasses, the main absorption bands in the 1200–1500 $cm^{-1}$ range are due to B–O symmetric stretching of $[BO_3]$ groups. The strongest absorption bands that lie in the 900–1100 $cm^{-1}$ range are assigned to B–O stretching of $[BO_4]^-$ units. The absorption bands in the 600–800 $cm^{-1}$ regions are due to the bond-bending motion of B–O–B units [9–11], Table 2. This assignment of the IR bands agree with those reported in previous IR studies on alkali borate [12,13] and lead alumino-borate glasses [14,15].

Moreover, according to the authors [16,17], the intense absorption bands around 660 and 810 $cm^{-1}$ may be assigned to the stretching vibrations of the Al–O in $[AlO_4]$ units. The band centered at about 450 $cm^{-1}$ is attributed to the bending vibrations of the Al–O–Al bonds.

The existence of the absorption bands in the 820–850 and 860–890 $cm^{-1}$ spectral regions shows the presence of the $[BiO_3]$ pyramidal and $[BiO_6]$ octahedral units [18–20]. Thus, the band at 495 $cm^{-1}$ was assigned to the Bi–O bending vibration in $BiO_6$ units [21–24].

The examination of the FTIR spectra of the $xGd_2O_3{\cdot}(100-x)[2Bi_2O_3{\cdot}B_2O_3{\cdot}Al_2O_3]$ glasses with $x = 0$–50 mol% (Figs. 2 and 3) shows that the increase of the $Gd_2O_3$ content strongly modify the characteristic IR bands as follows:

(i) The band located at about ~495 $cm^{-1}$ attains two maximum values for 10 and 20 mol%, while decreases with the further increasing the concentration of gadolinium ions and shifts to ~468 $cm^{-1}$. The IR analysis of the $Bi_2O_3$ shows a frequency region extended from 400–606 $cm^{-1}$, which is assigned to the Bi–O in $[BiO_6]$ octahedral structural units [18]. This can be due to the replacement of the $[BiO_6]$ units by the $[BiO_3]$ units.

The shoulder at 602 $cm^{-1}$ can be attributed to $Bi–O^-$ stretching vibrations in distorted linked $[BiO_6]$ units modified in the presence of gadolinium oxide. It attains maximum values at $x = 10$, 20 and 50 mol% $Gd_2O_3$.

(ii) The intensity of the shoulder near ~660 $cm^{-1}$ modifies with increasing the $Gd_2O_3$ content as follows: for $x = 10$ and 20 mol% attains maximum values, while for $5 < x < 10$, $10 < x \leqslant 15$ and $x \geqslant 25$ decreases. These IR data show that by increasing the $Gd_2O_3$ content up to 5% causes a higher extent of vitreous network polymerization and the presence of $[AlO_4]$ structural units shows the glass former character of the $Al_2O_3$. After that, the significantly different shape of the IR spectrum for $x = 50\%$ $Gd_2O_3$ compared to that for $x = 35\%$ reveals a drastic structural change occurring between these compositions due to the apparition of the $GdBO_3$ crystalline phase, in agreement to the X-ray data.

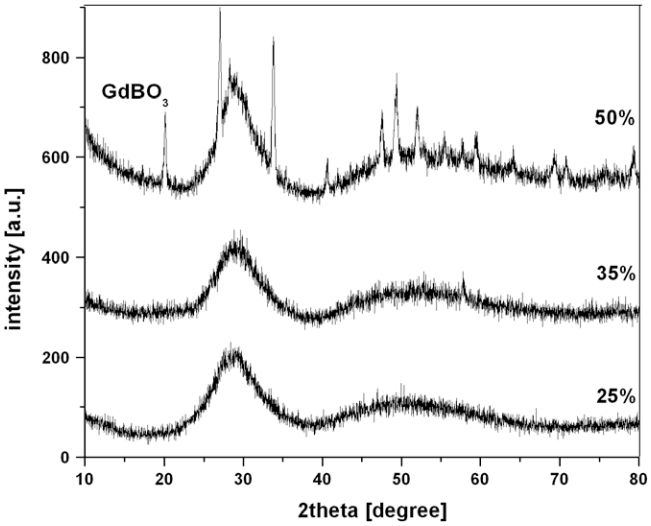


**Fig. 1.** X-ray diffraction patterns for the $xGd_2O_3{\cdot}(100-x)[2Bi_2O_3{\cdot}B_2O_3{\cdot}Al_2O_3]$ glass samples with $x = 25\%$, 35%, 50% $Gd_2O_3$.

**Table 1**
The indexing data of the $GdBO_3$ crystals at room temperature.

| 2 theta | Int-*f* | *h* | *k* | *l* |
|---|---|---|---|---|
| 19.952 | 50 | 0 | 0 | 2 |
| 26.853 | 100 | 1 | 0 | 0 |
| 28.704 | 10 | 1 | 0 | 1 |
| 33.693 | 100 | 1 | 0 | 2 |
| 40.639 | 14 | 0 | 0 | 4 |
| 41.025 | 6 | 1 | 0 | 3 |
| 47.476 | 40 | 1 | 1 | 0 |
| 49.310 | 50 | 1 | 0 | 4 |
| 51.954 | 25 | 1 | 1 | 2 |
| 55.415 | 14 | 2 | 0 | 0 |
| 59.481 | 20 | 2 | 0 | 2 |
| 64.185 | 10 | 1 | 1 | 4 |
| 69.410 | 16 | 1 | 0 | 6 |
| 70.848 | 16 | 2 | 0 | 4 |
| 75.939 | 12 | 2 | 1 | 0 |
| 79.310 | 16 | 2 | 1 | 2 |

**Table 2**
Infrared absorption bands and their assignment.

| Peak position ($cm^{-1}$) | | Assignment |
|---|---|---|
| $[BO_4]$ units | 550–630 | Bending vibrations of the $BO_3^{3-}$ isolated borate units |
| | 690–720 | Oxygen bridges between two trigonal atoms |
| | 720–780 | Oxygen bridges between one tetrahedral and one trigonal boron atom |
| | 900–1100 | Di-, Tri-, tetra- and penta-borate groups |
| $[BO_3]$ units | 1190–1240 | Boroxol rings and ortho-borate groups |
| | 1240–1350 | Boroxol rings |
| | 1350–1400 | B-O vibration of various borate rings |
| | 1420–1550 | Penta-, meta- and pyro-borate units |
| $[BiO_3]$ and $[BiO_6]$ units | 450–495 530 | Bi-O bonds in $[BiO_6]$ structural units |
| | 820–850 | Bi-O symmetric stretch in $[BiO_3]$ units |
| | 860–890 | Bi-O bonds in $[BiO_6]$ units |
| $[AlO_4]$ units | 450 | The bending vibrations of the Al–O–Al bonds |
| | 660 810 | The stretching vibrations of the Al–O bonds in $[AlO_4]$ units |