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Structural investigation of Gd_2O_3–B_2O_3–Li_2O glasses by FT-IR and Raman spectroscopies

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Glasses of the $xGd_2O_3·(100-x)[B_2O_3·Li_2O]$ system with $0 \le x \le 10$ mol% were prepared and investigated by means of FT-IR absorption and Raman scattering. Acting as complementary spectroscopic techniques, both types of measurements, FT-IR absorption and Raman scattering, revealed that network structure of the studied glasses is mainly based on the BO_3 and BO_4 units. The structural changes have been analyzed with increasing of gadolinium oxide concentration. The N_{BO4}/N_{BO3} ratio values are under unit, which denote the predominance of BO_3 units in the structure of these glasses.

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1. Introduction

B_2O_3 is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems in order to attain the desired physical and chemical properties. Since the past several years, borate glasses have attracted much attention because of their electrochemical and optical applications, namely as solid-state batteries, optical waveguides and luminescent materials. Several previous works on borate glasses are devoted to studying the structure, magnetic and electrical properties [1-8]. The properties of the borate glasses are commonly attributed to the fact that the boron atom can assume trigonal and tetrahedral coordination and also to the different ways through which the borate buildings units can be linked together [1]. The concentration of various borate species in the glass structure is determined by the nature and concentration of modifier oxides. Oxide glass containing Li^+ ions is one of the promising candidate for the electrolyte materials of thin-film batteries because it exhibits an isotropic ionic conduction and stability at a high voltage [9]. Rare earth ions have often been used as a sensitive probe to study the structure of glasses as their optical properties [10-13].

In previous papers we studied various borate glasses containing BaO, Bi_2O_3, MnO, Fe_2O_3,TeO_2,As_2O_3, V_2O_5, CuO, PbO, Ag_2O [14-21].

The purpose of this paper is to establish aspects related to the structure of Gd_2O_3–B_2O_3–Li_2O glasses by means of two complementary spectroscopic methods: Fourier-transformed infrared (FT-IR) absorption and Raman scattering.

2. Experimental procedures

Glasses of the $xGd_2O_3·(100-x)[B_2O_3·Li_2O]$ system were prepared using pure reagent grade chemicals: H_3BO_3, Li_2CO_3 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 1150°C in the pre-heated furnace for 30 minutes. After then, 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 FT-IR absorption and Raman spectra of these glasses were recorded with an Equinox 55 Bruker spectrometer. The FT-IR absorption measurements were done using the KBr pellet technique, at room temperature, in the 400-2000 cm^{-1} range. The spectral resolution was 2 cm^{-1}. The Raman spectra have been recorded for bulk glasses using an integrated FRA 106 Raman module in a 180° scattering geometry, at room temperature and for excitation using the 1064 nm line of Nd-YAG laser with an output power of 500 mW. The spectral resolution was 1 cm^{-1}.

3. Results and discussion

The experimental FT-IR spectra for the the $xGd_2O_3·(100-x)[B_2O_3·Li_2O]$ with various content of gadolinium oxide ($0 \le x \le 10$ mol%) are presented in Fig. 1. The bands in all the spectra are broad, characteristic of vitreous structures. The absorption bands detected in the FT-IR spectra of these glasses and theirs assignments are summarized in Table 1. The results have been discussed on the basis of the method given by Condrate and Tarte [22, 23] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for the vitreous B_2O_3 [2-9] and crystalline Li_2O, Gd_2O_3 [24] were used as a reference point in the results discussion.

The FT-IR absorption bands obtained for our matrix ($B_2O_3·Li_2O$) are centered at ~500 cm^{-1}, ~720 cm^{-1}, ~780 cm^{-1}, ~870 cm^{-1}, ~1035 cm^{-1}, ~1270 cm^{-1}, ~1360 cm^{1} and ~1430 cm^{1}.

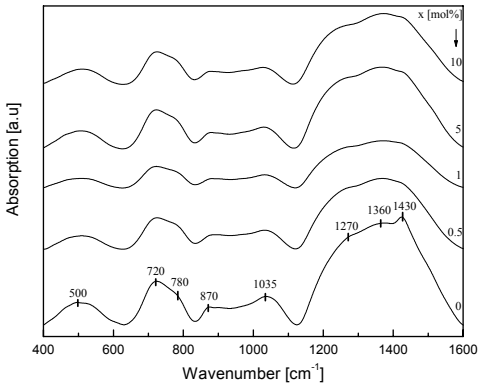

Fig. 1. FT-IR spectra of $xGd_2O_3{\cdot}(100\text{-}x)[B_2O_3{\cdot}Li_2O]$ glasses.

The band situated at ~500 cm^{-1} is assigned to the B-O-B bonds bending vibrations of various borate segments [25]. The next one centered at ~720 cm^{-1} is assigned to the O_3B-O-BO_3 bonds bending vibrations [25]. These two bands have similar variations in intensity once with the addition of gadolinium oxide: decreasing in intensity until x=1 mol% and increasing after it, up to x=10 mol%. The shoulder presented at ~780 cm^{-1} is a characteristic of the formation of metaborate rings and no noticeable changing occurs all over the composition range [10].

Table 1. The assignments of the FT-IR bands detected in the experimental spectra for $xGd_2O_3{\cdot}(100\text{-}x)[B_2O_3{\cdot}Li_2O]$ glasses.

Wavenumber [cm^{-1}]	FT-IR Assignments
~500	B-O-B bonds bending vibrations
~720	O_3B-O-BO_3 bonds bending vibrations
~780	vibrations of metaborate rings
~870	B-O bonds stretching vibrations in BO_4 tetrahedra from diborate groups
~1035	B-Ø bonds stretching vibrations in $BØ_4^-$ tetrahedra from tri-, tetra- and penta-borate groups
~1270	B-O bonds asymmetric stretching vibrations from pyro- and ortho-borate groups
~1360	asymmetric stretching modes of borate triangles ($BØ_3$ and $BØ_2O^-$)
~1430	stretching vibrations of borate triangles with NBO ($BØ_2O^-$)

It is already known that for borate glasses the broad FT-IR band structure in the region 850-1150 cm^{-1} is attributed to the B-O bonds stretching vibrations of tetrahedral BO_4 units while in the 1150-1600 cm^{-1} range the absorption bands profile is attributed to the B-O bonds stretching vibrations of borate units in which boron atoms are coordinated with three oxygen atoms (BO_3 units) [26]. Concerning our glasses in the 850-1150 cm^{-1} range we have observed the presence of the band centered at ~ 870 cm^{-1} which is characteristic for stretching vibrations of B-O bonds in BO_4 tetrahedra from diborate groups [2,3,6] and a band centered at ~1035 cm^{-1} assigned to B-Ø bonds stretching vibrations in $BØ_4^-$ tetrahedra (Ø: oxygen atom bridging two boron atoms) from tri-, tetra- and penta-borate groups [3,11,26]. In the 1150-1600 cm^{-1} range we have the band centered at ~1270 cm^{-1} characteristic for the B-O bonds asymmetric stretching vibrations from pyro- and ortho-borate groups, the band situated at ~1360 cm^{-1} characteristic for the asymmetric stretching mode of borate triangles ($BØ_3$, $BØ_2O^-$) [2,6,26] and the sharp band at ~1430 cm^{-1} assigned to the stretching vibrations of borate triangles with non-bridging oxygen NBO ($BØ_2O^-$) [26].

No characteristic vibrations mode of bonds from Li_2O and Gd_2O_3 oxides were directly detected in the FT-IR spectra.

The structural changes involved by the Gd_2O_3 content addition have been analyzed on the base of $A_r=A_4/A_3$ ratio (A_4 was calculated as the integral of the absorption signal in the 850-1150 cm^{-1} range and A_3 as integral of the absorption signal in the 1150-1600 cm^{-1} spectral ranges). The A_4 and A_3 reflect the relative content of tetrahedral (BO_4) and triangular (BO_3) borate species respectively. The Ar ratio versus Gd_2O_3 content is given in Fig. 2.

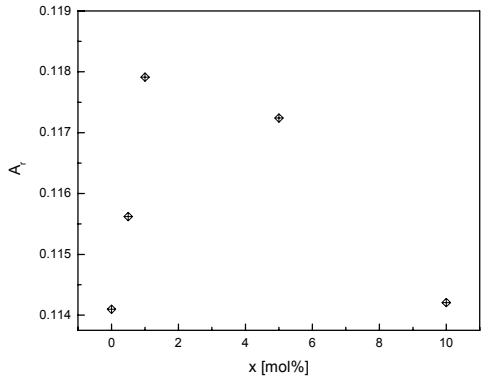

Fig.2. Ar ratio vs. x values.

For all the investigated glasses the Ar values are much lower than 1, showing the predominance of BO_3 units in these glasses structures. The ascending trend of the A_r ratio in the first part of the compositional range ($x \leq 1$ mol %) indicates a progressively changes of boron coordination from three to four. For $x > 1$ mol %, a descendent behavior was observed for A_r values with the gadolinium addition proving the increase of number of triangular units and the structures depolymerisation tendency along with the NBO atoms numbers increasing. Following the FT-IR spectra it can be said that in the analyzed glasses the controlled addition of Gd_2O_3 generates several rearrangements in the network structure

at short range order, so that gadolinium oxide played the vitreous network modifier role in these glasses.

The Raman spectra of $xGd_2O_3 \cdot (100\text{-}x)[B_2O_3 \cdot Li_2O]$ glasses with various content of gadolinium oxide ($0 \le x \le 10$ mol%) are presented in Fig. 3. The data obtained from the Raman bands assignments (Table 2) confirm the structure proposed by FT-IR results and moreover new structural groups were detected. The following bands are present in these spectra: ~490 cm^{-1}, ~650 cm^{-1}, ~700 cm^{-1}, ~764 cm^{-1}, ~900 cm^{-1}, ~1000 cm^{-1}, ~1150 cm^{-1}, ~1250 cm^{-1}, ~1325 cm^{-1}, ~1430 cm^{-1} and ~1480 cm^{-1}.

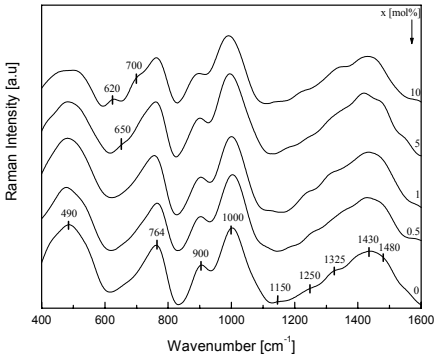

Fig. 3. Raman spectra of $xGd_2O_3 \cdot (100\text{-}x)[B_2O_3 \cdot Li_2O]$ glasses.

The bands situated in the region 400-600 cm^{-1} were assigned by Kamitsos et al. [6] to the symmetric stretching vibration of the BO_4 units connecting various segments without participating in the specific borate arrangements. In our case the characteristic band for this vibrations is the band centered at 490 cm^{-1} and it slowly decrease once with the addition of gadolinium oxide.

Table 2. The assignments of the Raman bands detected in the experimental spectra for $xGd_2O_3 \cdot (100\text{-}x)[B_2O_3 \cdot Li_2O]$ glases.

Wavenumber [cm^{-1}]	**Raman Assignments**
~490	symmetric stretching vibrations of the BO_4 units
~620	vibrations of ring type metaborate groups
~700	vibrations of chain type metaborate groups
~764	symmetrical breathing vibrations of six-member borate rings with one or two BO_4 tetrahedra
~900 ~1000	vibrations of diborate groups
~1150 ~1250	vibrations of pyro-borate groups
~1325	$B–O^-$ vibrations from various borate groups
~1430 ~1480	vibrations of chain type metaborate units

It can be seen the apereance of a band centered at 650 cm^{-1} for the x=5 mol%. This band is assigned to ring type metaborate groups [27]. It is clear evidence that the addition of Gd_2O_3 results in the increase in the number of ring-type metaborate groups (the intensity of this band rises for x=10mol% and is shifted to lower wavenumber ~620 cm^{-1}).

The presence of a shoulder at 700 cm^{-1} is assigned to chain type metaborate groups [6,28] and appears only for the highest concentration of gadolinium oxide.

The band situated at ~764 cm^{-1} has been attributed to the symmetrical breathing vibrations of six-member borate rings with one or two BO_4 tetrahedra [26].

The bands centered at ~900 cm^{-1} and ~1000 cm^{-1} have been attributed to the presence of diborate groups [6,7]. The intensity of the above bands doesn't vary much all over the compositional range.

The broad band in the region 1200–1600 cm^{-1} has been assigned to the stretching mode of $B–O^-$ bonds associated with a large number of borate groups [29,30]. This band convoluted the next few bands presented in our spectra for this region. The Raman spectra of figure 3 indicate that these bands are shifted to lower wavenumbers once with increasing the gadolinium oxide content. The bands situated at ~1150 cm^{-1} and ~1250 cm^{-1} can be assigned to the stretching vibration of terminal $B–O^-$ bonds of the pyroborate groups [2,8]. The 1325 cm^{-1} band was attributed to the $B–O^-$ vibrations occurring in a large borate network and not to a specific group [29,30]. The presence in our Raman spectra of the band at 1430 cm^{-1} and the shoulder at 1480 cm^{-1} is an indication that chain type metaborate units are present.

The non-bridging oxygen are weakly rising with increasing the content of gadolinium oxide denoting a depolymerization degree of the vitreous network.

4. Conclusions

By means of FT-IR and Raman spectroscopies, the local structure peculiarities of the glass system $xGd_2O_3 \cdot (100\text{-}x)[B_2O_3 \cdot Li_2O]$ were analyzed in order to identify the contribution of each component on the structure and to point out the role of the gadolinium ions as a modifier of the glass network.

Both types of spectroscopies revealed a structure based on di-, tri-, tetra-, penta-, pyro-, orto- and meta-borate groups. All over the compositional range the four coordinated boron atoms number is lower than that three coordinated. The values of A_r ratio indicate the specific variations of BO_4 and BO_3 units function of Gd_2O_3 addition. The presence of Gd_2O_3 is not directly evident in IR and Raman spectra, but it is involved in the appearance of BO_4 structural units in our glass system.

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