OPTOELECTRONİCS AND ADVANCED MATERİALS – RAPID COMMUNICATIONS Vol. 6, No. 1-2, January-February 2012, p. 331 - 334

Structural changes induced by MnO addition in barium-borate oxide glass matrix

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In order to evidenced the structural changes induced by MnO in the barium-borate network, the following glass system was prepared and investigated by FT-IR and Raman spectroscopies: $x\mathrm{MnO}\cdot(100-x)[3\mathrm{B_2O_3}\cdot\mathrm{BaO}]$ with $0 \le x \le 50$ mol%. The results have shown that borate ions take part in the network of studied glasses. For our system both BO_3 and BO_4 units was detected, the first being dominant in all concentration range. By Raman spectroscopies were detected new structural units, boroxol rings and chain and/or ring type metaborate groups.

(Received January 18, 2012; accepted February 20, 2012)

Keywords: Barium-borate oxide glasses, Manganese ions, FT-IR, Raman

1. Introduction

The analysis of vibrational spectra of glasses can be applied to the solution of both industrial and basic research problems. In an applied study, the vibrational spectra can be used to identify the specific groups which are present in the glasses [1].

B_2O_3 is one of the most common glass former and is present in almost all commercially important glasses. It is often used as a dielectric and insulating materials and because of the occurrence of boron anomaly [2]. Barium borate glasses are important because of their use as a non-volatile flux in the crystal growth of garnets and ferrites [3]. The addition of iron oxide to borate glasses makes them electrically semiconducting and superparamagnetic [4].

The borate glasses are very often investigated by a lot of methods because they are relatively easy to obtain and moreover because in their structure appear a large variety of structural units over a wide range of modifier concentration [5, 6].

The structure of borate glasses was studied by X-ray [7,8] and neutron [9,10] diffraction, IR [11], Raman [11-14] and NMR [15-16] spectroscopies. All investigations report that B_2O_3 is composed essentially of boron atoms 3-coordinated, the basic structural units consisting in a boroxol rings. The addition of glass modifier oxide changes the coordination of boron from 3 to 4 as a result of BO_4 units formation. The introduction of the metal ions such as MnO in glasses produces other changes in glass structure.

In this study, $x\mathrm{MnO}\cdot(100-x)[3\mathrm{B_2O_3}\cdot\mathrm{BaO}]$ glasses were prepared and investigated by means of IR and Raman spectroscopies in order to determine the structure of these glasses.

2. Experimental

Glasses of the system $x\mathrm{MnO}\cdot(100-x)[3\mathrm{B_2O_3}\cdot\mathrm{BaO}]$ were prepared using reagent grade purity $MnCO_3$, H_3BO_3 and $BaCO_3$ in suitable proportions. The mechanically homogenized mixtures were introduced and melted in sintered corundum crucibles at 1250°C, in an electrical furnace. The mixtures were put into the electrical furnace direct at this temperature. After 30 minutes, the molten material was quenched at room temperature by pouring onto a stainless steel plates. The samples were analyzed by means of X-ray diffraction. The patterns of the investigated samples are characteristic for the vitreous systems. No crystalline phase was observed up to 50 mol% MnO.

The FT-IR absorption and the Raman spectra of these glasses were obtained with an Equinox 55 Bruker spectrometer. The IR absorption measurements were obtained in the 400 – 2000 cm^{-1} spectral range using the KBr pellet technique. The samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture. The Raman spectra have been recorded in the 70 – 1500 cm^{-1} spectral range for bulk glass samples using an integrated FRA 106 Raman module in a 180^0 scattering geometry, at room temperature, using for excitation 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

FT-IR study

The experimental IR spectra of the $x\mathrm{MnO}\cdot(100-x)[3\mathrm{B_2O_3}\cdot\mathrm{BaO}]$ glass system, with $0 \le x \le 50$ mol% , are presented in Fig. 1. The obtained absorption bands and their assignments are summarized in Table 1.

For the interpretation of the results we used the Tarte [17, 18] and Condrate [19, 20] methods. They interpreted the experimental date obtained for oxide glasses using date obtained for similar crystalline compounds. In our studied we used the absorption bands of the crystalline MnO_2, Mn_3O_4 and BaO [21], and of the vitreous B_2O_3 [22-27].

In the glass matrix ($3B_2O_3 \cdot BaO$) spectrum, the following bands are evidenced: ~ 474 cm^{-1}, ~ 710 cm^{-1}, ~ 770 cm^{-1}, ~ 930 cm^{-1}, ~ 1015 cm^{-1}, ~ 1200 cm^{-1} and ~ 1390 cm^{-1}.

The band centered at ~ 474 cm^{-1} is due to bending vibrations of various borate segments, [24, 28] and specific vibrations of Ba-O and Mn-O bonds, the intensity of the band is approximately the same for all compositional range. The presence in the spectrum of band at ~ 624 cm^{-1} starting with x = 0.5 mol% (Fig. 1) confirms the presence of manganese ions in our glasses (Table 1). The intensity of the band at ~ 624 cm^{-1} increases with the increase of MnO content up to 1 mol% and for higher concentrations of MnO almost disappears, probably being covered by the band from ~ 710 cm^{-1}. In all the IR spectra appears a band at ~ 710 cm^{-1} relative to the band at ~ 720 cm^{-1} from the spectrum of vitreous B_2O_3, which is due to B-O-B bonds bending vibrations from pentaborate groups [22, 26-30]. The intensity of this band increases with the increase of MnO content up to 10 mol% and for higher concentrations, the amplitude of this band decreases. The shoulder centered at ~ 770 cm^{-1} is assigned to the O_3B-O-BO_4 bonds bending vibrations [24] and has approximatively the same intensity for all the compositional range. It is already know that for borate glasses the broad FT-IR band structure in the region 800-1200 cm^{-1} is attributed to the B-O bonds stretching vibrations in tetrahedral BO_4 units while in the 1200-1700 cm^{-1} range the absorption bands profile is attributed to the B-O bonds stretching vibrations in borate units were boron atoms are coordinated with three oxygen atoms (BO_3) units [24]. Concerning our glasses in the 800-1200 cm^{-1} range we have observed the presence of a large band centered at ~ 930 cm^{-1} which is characteristic for the stretching vibration of B–O bonds in BO_4 tetrahedra from diborate groups and two bands centered at ~ 1015 and ~ 1054 cm^{-1} assigned to B-Ø bonds stretching vibrations of BØ$_4^-$ (Ø : oxigen atom bridging two boron atoms) tetrahedra from tri-, tetra- and penta- borate groups [24, 26, 31]. These bands are modifying with the increasing of MnO content, decreasing their intensity so at x=50 mol% they disappear. Regarding the absorption bands situated in 1200-1700 cm^{-1} range, they are situated for the glass matrix at ~ 1200 cm^{-1} and respectively at ~ 1390 cm^{-1} and are determinate by the presence of asymmetric stretching vibrations of B-O bonds from orthoborate groups respectively borate triangles BØ$_3$ and BØ$_2$O$^-$. These bands are the most intense from the spectra, they increase in intensity with the increasing of MnO up to x= 1 mol%, after that they decrease and disappear for x=50 mol%.

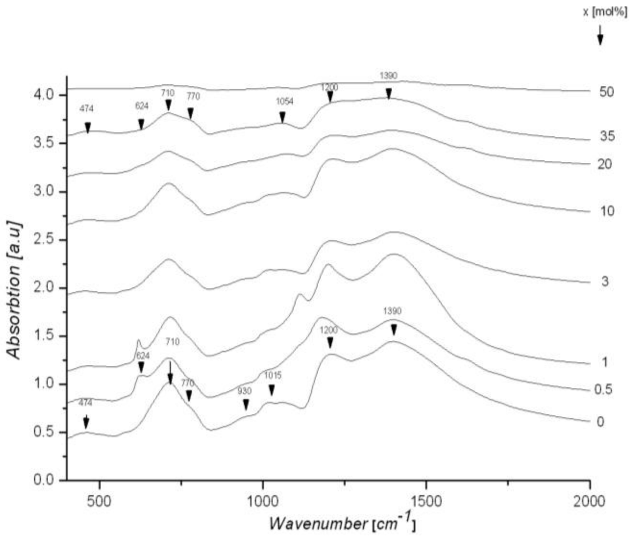

Fig. 1. Infrared absorption spectra of xMnO·(100-x)[$3B_2O_3 \cdot BaO$] glasses.

It is remarked that the presence of high content of MnO (x=50 mol%) in $3B_2O_3 \cdot BaO$ glass matrix determine strong structural disorder of glass network, behavior which is specific only for manganese ions.

Table 1. Frequencies and their assignments for FT-IR spectra of xMnO·(100-x)[$3B_2O_3 \cdot BaO$] glasses.

Wavenumber [cm^{-1}]	**Assignment**
~ 474	Bending vibrations of B-O-B bonds, Specific vibrations of Ba-O bonds, Specific vibrations of Mn-O bonds;
~624	Specific vibrations of Mn-O bonds;
~ 710	B-O-B bonds bending vibrations from pentaborate groups;
~ 770	O_3B-O-BO_4 bonds bending vibrations;
~ 930	B–O bonds stretching vibrations in BO_4 units from diborate groups;
~ 1015 ~ 1054	B-Ø bonds stretching vibrations of BØ$_4^-$ from tri-, tetra- and penta-borate groups[*];
~ 1200	Asymmetric stretching vibrations of B–O bonds from orthoborate groups;
~ 1390	Asymmetric vibrations of borate triangles BØ$_3$ and BØ$_2$O$^-$[*] ;

[*] Ø represents an oxygen atom bridging two boron atoms and O$^-$ a non- bridging oxygen

The structural changes involved by the MnO content addition have been analyzed on the basses of $A_r = A_4 / A_3$ ratio (where A_4 and A_3 were calculated as the integral of the absorption signal in the 800 – 1200 cm^{-1} (A_4) and 1200

– 1550 cm^{-1} (A_3) spectral ranges) [32]. The A_4 and A_3 indicate the relative content of tethraedral (BO_4) and triungular (BO_3) borate species, respectively. The dependence of A_r ratio by MnO content is shown in Fig. 2.

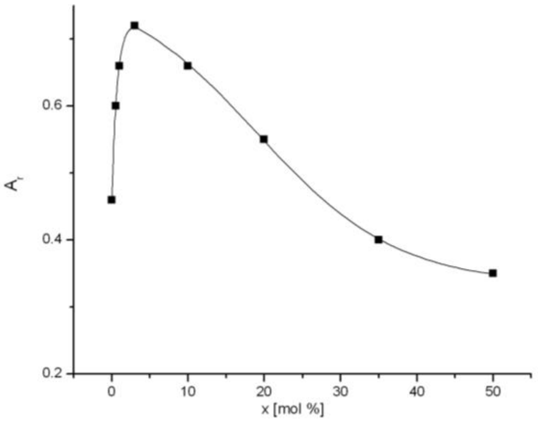

Fig. 2. Ar ratio evolution with the MnO content for xMnO·(100-x)[3B$_2$O$_3$·BaO] glasses.

It can be noticed that for all glasses the A_r values are lower than one, showing the predominance of BO_3 units in these borate glasses. The increasing of A_r ratio for $x \leq 3$ mol% indicates a progressively changes of boron coordination from three to four. For $x > 3$ mol% a descendent behavior was observed for A_r values with the manganese addition, which suggest the structures depolymerization tendency along with the increasing of nonbridging oxygen atoms.

Raman study

The experimental Raman spectra of $xMnO\cdot(100-x)[3B_2O_3\cdot BaO]$ glass system with various content of manganese oxide ($0 \leq x \leq 20$ mol%) were presented in figure 3. The bands obtained and their assignments are summarized in Table 2.

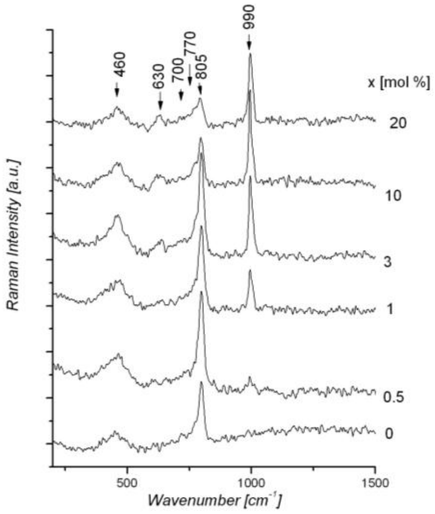

Fig. 3. Raman spectra of xMnO·(100-x)[3B$_2$O$_3$·BaO] glasses.

Table 2. Frequencies and their assignments for Raman spectra of xMnO·(100-x)[3B$_2$O$_3$·BaO] glasses.

Wavenumber (cm^{-1})	**Assignment**
~ 460	Deformation vibrations of B-O-B bonds;
~630	Vibrations of ring and chain – type of meta- and penta- borate groups;
~ 700	Vibrations of chain and/or ring-type metaborate groups;
~ 770	Symmetric breathing vibrations of six member borate rings with one or two $BØ_3$ triangle replaced by a $BØ_4^-$ tetrahedral;
~ 805	Symmetric breathing vibrations of boroxol rings;
~ 990	Vibration given by ortho-borate groups;

In the glass matrix spectrum, the following bands are evidenced: ~ 460 cm^{-1}, ~ 770 cm^{-1}, ~ 805 cm^{-1} and ~ 990 cm^{-1}. The band from ~ 460 cm^{-1} is assigned to deformation vibrations of B-O-B bonds [30, 33, 34]. The band situated at ~ 770 cm^{-1} has been attributed to the symmetric breathing vibrations of six member borate rings with one or two $BØ_3$ triangle replaced by $BØ_4^-$ tetrahedra. The band situated at ~ 805 cm^{-1} was assigned to symmetric breathing motion of the oxygen atoms inside the boroxol rings [24, 35, 36]. The band situated at ~ 990 cm^{-1} indicates the presence of ortho-borate groups in the structure [24, 37].

With the addition of manganese ions the band from ~ 460 cm^{-1} is increasing up to x=3 mol% then decreases. Also two new bands can be observed at ~ 630 cm^{-1} and ~ 700 cm^{-1}. The band at ~ 630 cm^{-1} was assigned to vibration of ring and chain – type of meta- and penta-borate groups and the band at ~ 700 cm^{-1} is characteristic to vibrations of chain and/or ring- type metaborate groups [25]. These bands are increasing with the increasing of MnO content. The band from ~ 770 cm^{-1} is increasing up to x=3 mol% then decreases. The band situated at ~ 805 cm^{-1} is increasing for x=3 mol% then decreases. The intensity of this band is higher than the intensity of the band at ~ 770 cm^{-1}, which means the number of boroxol rings is bigger than the number of BO_4 units. The band centered at ~ 990 cm^{-1} increases with the increasing of MnO content.

Raman spectroscopy has proved to be a more sensitive technique for the changes that appear in the glasses structure with the addition of manganese oxide.

4. Conclusions

Homogeneous glasses of the xMnO·(100-x)[$3B_2O_3$·BaO] system were obtained within $0 \le x \le 50$ mol% concentration range and investigated by IR and Raman spectroscopies.

The IR spectra revealed the presence of the boron atoms in different coordination states (three and four coordinated). In the investigated glass system the threefold boron atoms are dominated compared with the fourfold ones. The shape of the spectra revealed a significant disordered in our glasses for higher content of MnO.

The values of A_r ratio indicate the specific variations of BO_4 and BO_3 units function of MnO addition. The presence of MnO is not directly evidenced in Raman spectra, but it is involved in the appearance and variation of BO_4 structural units in studied glass system.

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