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Effect of the introduction of gadolinium ions in Boro-tellurite glasses

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Structural studies were investigated of glasses in the $xGd_2O_3\cdot(100\text{-}x)$ $[0,6TeO_2\cdot 0,4B_2O_3]$ ($0\leq x \leq 30$mol%) system. The variations observed in the FTIR spectra were correlated with density measurement. The structural results show that these glasses present characteristic tellurium and boron environments which vary with chemical composition of gadolinium oxide. So that at a small content of gadolinium oxide increase the intensity bands assigned to the $[TeO_4]$ and $[BO_4]$ units, thus transform the $[BO_4]$ units into the $[BO_3]$ units and changes progressively the coordination of tellurium from 4 through 3+1 to 3 when the quantity of gadolinium ions increases.

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1. Introduction

Rare-earth doped glasses have generated a great deal of interest as potential materials for optical devices in laser technology [1, 2]. Among them, tellurite-based glasses are the most promising for different applications due to their low dispersion, good transparency, and extended transmission from UV to the infrared region [3, 4].

It is of fundamental importance in glass science to understand the structural forms that arise in glasses composed of network formers of intermediate strength, [5]. The building units of these materials include trigonal bipyramidal $[TeO_4]$ groups with lone pair of electrons and tetrahedral $[TeO_3]$ groups, [6]. This assortment of species should provide a significant variety of structural sites for the incorporation of dopant species such as rare earth ions.

Keeping in view these features, our aim is to characterize the structural properties of the $xGd_2O_3\cdot(100\text{-}x)[0,6TeO_2\cdot 0,4B_2O_3]$ vitreous system ($0\leq x\leq 30$mol%) in view determination of local geometries around tellurium and boron.

2. Experimental

Glasses with composition $xGd_2O_3\cdot(100\text{-}x)$ $[0.6TeO_2\cdot 0.4B_2O_3]$ ($0\leq x \leq 30$mol%) were prepared by conventional melt-quenching method, melting mixtures of TeO_2, H_3BO_3 and Gd_2O_3 reagents of p.a purity grade in a corundum crucibles at 800^0C for 60 minute. The samples were analyzed by means of X-ray diffraction using a Bruker D8 ADVANCE X-ray Diffractometer.

The structure of the glasses was investigated by infrared transmission spectra in KBr matrices were recorded in the range 400-1600 cm^{-1} using a JASCO FTIR 6200 spectrometer and density measurements were performed using the picnometric method with water as the reference immersion liquid.

3. Results and discussion

The FTIR spectra for the $xGd_2O_3\cdot(100\text{-}x)$ $[0.6TeO_2\cdot 0.4B_2O_3]$ ($0\leq x \leq 30$mol%) glass system are presented in figure 1. A very broad shoulder is observed between 600 and 700cm^{-1} whose intensity increases with Gd_2O_3 content. By analogy with the work of Wang and Osaka [7], the first band is assigned to stretching vibrations of $[TeO_4]$ bypiramids characteristic of TeO_2, while the latter is assigned to stretching vibrations of the $[TeO_3]$ groups created during the glass-forming process. The increases of Gd_2O_3 content modify the characteristic bands of the tellurium ions in two proceeding. At a content of to 25%mole the coordination of the tellurium atom should be changed progressively from 3 though 3+1 to 4, thus at a content of 30%mole gadolinium ions the intensity of the $[TeO_3]$ band increases with the displacement to higher frequencies and the decreases of the band are observed around 600cm^{-1}. This is considered an indication that $[TeO_4]$ units were transformed into $[TeO_3]$ or polyhedra $[TeO_{3+1}]$ groups.

In the case of glass sample having 30mol% Gd_2O_3 a new band is observed at 1222cm^{-1} which becomes intense and is attributed to B-O stretching vibrations in $[BO_3]$ groups from boroxol rings [8]. Thus, the bands are assigned to the $B\text{-}O^-$ stretching vibrations in $[BO_3]$ units from varied types of borate groups in the range from 1222 to 1500cm^{-1} becomes intense and shifts from 1425 to 1410cm^{-1}. These results show that some $[BO_4]$ groups were transformed in [BO_3] units with varied types of borate groups and boroxol rings.

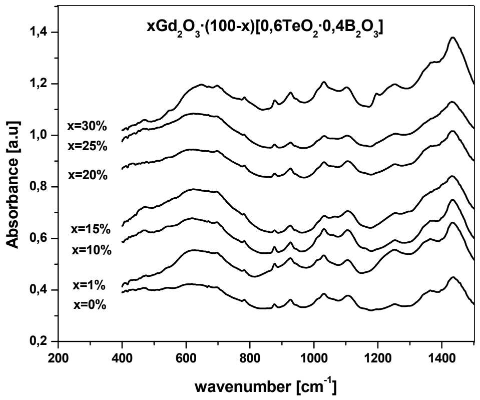

Fig. 1. FT-IR spectra of $xGd_2O_3\cdot(100-x)$ $[0,6TeO_2\cdot 0,4B_2O_3]$ $(0\leq x\leq 30 mol\%)$ *glasses.*

In all these glasses a small number of chain-type metaborate and pentaborate groups are also present because the apparition of the band at 770cm^{-1} and the band around 930cm^{-1} can be taken as a clear evidence for the presence of pentaborate groups in the studied glasses and the 670cm^{-1} band is assigned to metaborate units [9].

For this system, the increase of Gd_2O_3 content does strongly modify the characteristic bands and these could be explained in two proceedings: (i) at a small content of Gd_2O_3 as for as 25mole% increase the contain of [TeO_4] and [BO_4] units (ii) thus a content of 30%mole gadolinium ions concur transformation of the [BO_4] units into the [BO_3] units from boroxol rings and into [BO_3] units with varied types of borate groups and also, the coordination of the tellurium atom should be changed progressively from 4 though 3+1 to 3. The FTIR spectra for these glasses with increasing Gd_2O_3 content show unambiguous evidence of an increase in the number of [TeO_3] and [BO_3] groups in the glass structure and the vitreous network becomes more tightly packed.

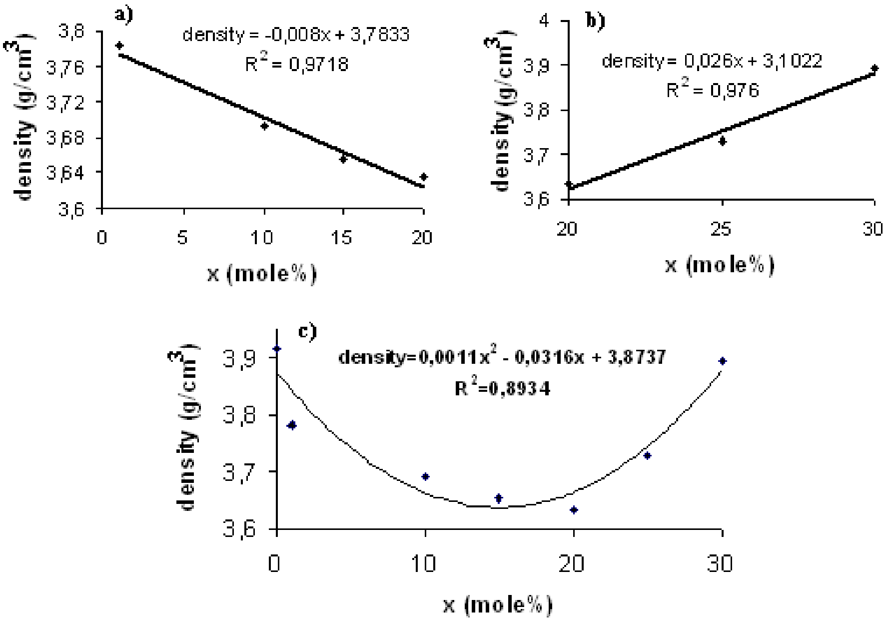

Fig. 2. Gadolinium oxide composition dependence on density, d, for $xGd_2O_3\cdot(100-x)$ *[] (0≤x ≤30mol%) glasses.*

Accordingly, the content of gadolinium ions exerts a particular influence on the homogeneity and stability of the glasses and in accommodating the vitreous network with the excess of oxygen.

In the view of the confirmation validity of these results we were investigated of the density measurements. Figure 2 shows the compositional variation of the density with the increase of gadolinium oxide content of the studied samples. As seen in figure 2c) that the density-composition dependence is a parable.

The change with composition of the density can be approximated to two linear regions with a change around 20mol% Gd_2O_3. Above 20mol% gadolinium oxide causes the formation of nonbridging oxygen ions in the tellurite matrix implying the increased of fraction of [BO_4] units (Fig. 2a).

The increase of the gadolinium ion concentration (figure 2b) in the studied glasses increases the density suggesting that it converts to [BO_4] units into [BO_3] groups and the vitreous network become more tightly packed.

FTIR spectra of the initial crystalline compounds (H_3BO_3, TeO_2 and Gd_2O_3) are presented in figure 3. The structure of TeO_2 crystalline is a three-dimensional network of [TeO_4] trigonal bypiramids (625cm^{-1}) and [TeO_3] groups (730cm^{-1}). We mention that Raman spectrum for TeO_2 crystalline previously reported show the structure of TeO_2 to be alone formatted from [TeO_4] trigonal bipyramids groups [10].

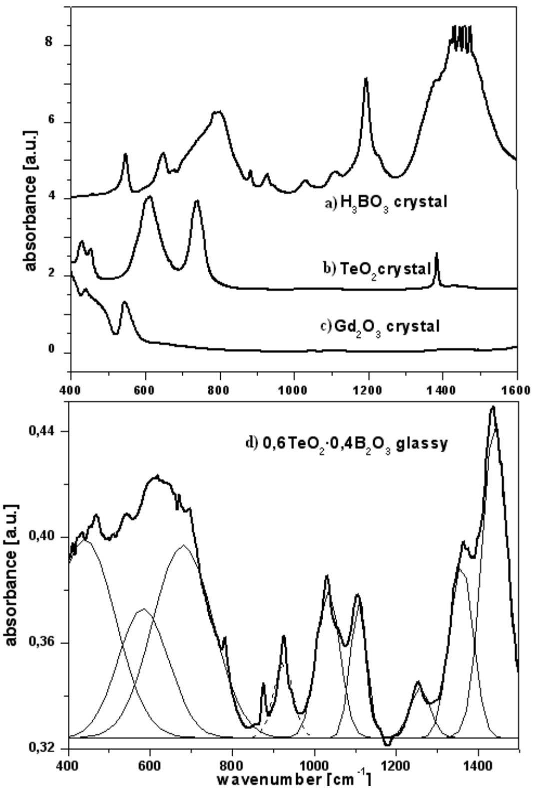

Fig. 3. FT-IR spectra of a) H_3BO_3 crystals, b) TeO_2 crystals, c) Gd_2O_3 crystals d) 0,6TeO_2·0,4B_2O_3 glassy.

Upon glass formation are presented the [TeO_3] and [TeO_4] groups and the spectral modifications could observed on local arrangement of the boron ions. So that, the intensity of the [BO_4] bands increases (800-1200cm^{-1}) in the glassy and the number of the [BO_3] units from boroxol rings decrease in favor of the [BO_3] units with varied types of borate groups (1200-1500cm^{-1}).

4. Conclusions

The structure of xGd_2O_3·(100-x) [0.6TeO_2·0.4B_2O_3] glasses prepared by melt-quenching method (for x=0-30mol% Gd_2O_3) was studied by FTIR spectroscopy and density measurement. With increasing gadolinium oxide content a part of boron atoms changes from tetrahedral [BO_4] to trigonal [BO_3] units, the tellurium atoms transforms from [TeO_4] to [TeO_3] groups and the vitreous network becomes more tightly packed.

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