Immobilization of gadolinium in borate-tellurate glasses

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Abstract. Glasses in the $xGd_2O_3\cdot(100-x)[6TeO_2\cdot4B_2O_3]$ system, where $x = 0, 5, 10, 15, 25$ and $30$ mol%, have been prepared from melt quenching method. The structural changes were studied by FTIR spectroscopy and DFT calculations. The FTIR spectroscopy data for these systems show that the gadolinium ions have a strong affinity towards the structural units containing non-bridging oxygens, which are negative-charged, because they are readily available for charge compensation. So that, it seems that the content of $[BO_4]$ structural units cannot become higher, because the modified $[BO_3]$ units containing one or more $B-O-Gd$ bonds are unable to accept a fourth oxygen atom. On the other hand, the gadolinium ions have also an affinity pronounced towards $[TeO_3]$ structural units yielding the deformation of the Te-O-Te linkages. The compositional evolution of the network was accommodated with excess of oxygen by the formation of orthoborate structural units, disintegration of some boroxol rings and radical rearrangement of the network formed by the $[TeO_6]$ octahedral units.

1. Introduction

Immobilization of high level nuclear wastes by vitrification is a well established process that has been studied extensively over last 40 years. A suitable glass host is used to dissolve the high level nuclear waste to form a glassy (vitreous) homogeneous product that can be cast into suitable forms, including large glass blocks. Under suitable conditions, it is possible to incorporate up to 25-30 wt% high level waste into a glass [1-4].

The future is directed towards the identification of similar glasses and glass ceramics with improved durability and processing characteristics, which will mainly be achieved through compositional modifications of existing waste forms. Then, other types of glasses and glass ceramics waste forms with lower manufacturing temperature and easier processing route also offer potential for further study.

The present contribution investigates the borate-tellurate glasses as possible candidate for the immobilization of nuclear wastes. We propose than needful for alternative vitrification processes the borate glasses formulations because they appear to offer advantages of reduced process temperature and improved chemical durability compared to other glasses. Although there are many reports in the literature about glass ceramics, these were undesirable due to high processing temperature ($>1400^\circ$C) and poor chemical durability [4, 5]. This new formulation differs in the type and quantity of network modifiers added, resulting in a glass matrix with improved chemical durability and reduced melting temperature.
2. Experimental

Glasses with composition xGd$_2$O$_3$(100-x)[6TeO$_2$-4B$_2$O$_3$] (0 ≤ x ≤ 30 mol%) were prepared by conventional melt-quenching method, melting mixtures of TeO$_2$, H$_3$BO$_3$ and Gd$_2$O$_3$ reagents of purity grade in a corundum crucibles at 800°C for 60 minutes.

The samples were analyzed by means of X-ray diffraction using a XRD-6000 Shimadzu diffractometer. The FTIR absorption spectra of the studied glasses were measured for each glass sample over the range 400-1600 cm$^{-1}$ of wavenumbers.

The proposed model for borate-tellurate glass network was performed by direct optimization of the geometry with help of the B3PW91/CEP-4G/ECP method using Gaussian 03 program. Dangling bonds of outer atoms of the models were saturated with hydrogen atoms.

3. Results and discussion

3.1. FTIR spectroscopy

We performed X-ray diffraction investigation of the samples and these data indicated unambiguous the amorphous character of the samples.

FTIR spectrum of the 6TeO$_2$·4B$_2$O$_3$ glass for the 400 and 1400 cm$^{-1}$ wavenumber range is shown in figure 1. Obtained bands and their assignments can be summarized as follow:

i. The large band centered at ~625 cm$^{-1}$ is assigned to the stretching mode of [TeO$_4$] trigonal bipyramidal with bridging oxygens [7, 8]. The shoulder located at about ~780 cm$^{-1}$ indicates the presence of [TeO$_4$] units [9, 10].

ii. The broad bands in the region 800-1200 cm$^{-1}$ are due to the stretching of B-O bonds of [BO$_4$] units [11, 12]. The feature of band centered in the region ~1030 cm$^{-1}$ is due to the pentaborate, tetraborate, triborate and diborate vibrations. The IR absorption band at about 1263 cm$^{-1}$ was attributed to the B-O stretching vibrations of the [BO$_3$] units from the boroxol rings [13, 14].

iii. The bands centered in the region between ~1200 and 1600 cm$^{-1}$ can be attributed to the [BO$_3$] units stretching vibrations, which are associated with the vibrational mode inside the various borate rings and the non-bridging B–O bonds, respectively [12-15].

The addition of Gd$_2$O$_3$ in the 6TeO$_2$·4B$_2$O$_3$ glass matrix (figure 1), gives some drastically changes in the FTIR spectra of these glasses as follows:

i. The intensity of the band centered at ~780 cm$^{-1}$ increase with increasing the gadolinium ions concentration. This observation is consistent with the destruction of the [TeO$_4$] structural units.

ii. By increasing the Gd$_2$O$_3$ content between 5% and 25%, the characteristic features of the four absorption bands were included. The decreasing trends in wavenumber of the bands located at 1256 and 1384 cm$^{-1}$ imply an inter-conversion process of the [BO$_3$] ↔ [BO$_4$] structural units and the transformation of the large number of boroxol rings [13-15]. The increasing trend in wavenumber of the band centered in the regions ~680 cm$^{-1}$ can be explained considering a conversion process of the [TeO$_4$] structural units into [TeO$_3$] structural units.

iii. The decreasing trend of the bands located in the region between 900 and 1150 cm$^{-1}$ (1020 cm$^{-1}$) can be due to the formation of bridging bond of Te–O–B. Since the stretching force constant of Te-O bonding is substantially lower than that of the B–O, the stretching frequency of Te–O–B might trend to be lower.

iv. The responsible for this attack of the gadolinium ions seems to be the partial disappearance of the small band located in the range between 450 cm$^{-1}$. This band is assigned the bending mode of Te–O–Te or O–Te–O linkages. The effect suggests that the doped with gadolinium ions deforms the Te–O–Te linkages and generate their destruction.
v. With the increase of Gd$_2$O$_3$ content up to 30 mol%, a new peak was observed at about ~1200 cm$^{-1}$, which was assigned to B–O asymmetric stretching vibrations in BO$_3$ units from orthoborate groups. This may be attributed to the electrostatic field of the strongly polarizing Gd$^{3+}$ ions. It seems that upon addition of the rare earth ions to the glass, some free B–O bonds are also generated. These simpler units containing a large number of non-bridging oxygen and boroxol rings (the band located at about 1254 cm$^{-1}$ becomes sharper and pronounced), are expected to be created if Gd$_2$O$_3$ behaves as a glass modifier.

It seems that the content of [BO$_4$] structural units cannot become higher, because the modified [BO$_3$] units containing one or more B–O–Gd bonds are unable to accept a fourth oxygen atom [13]. Accordingly, the borate-tellurate glasses may be good hosts for the incorporation of high gadolinium ions contents at low temperature.

![Figure 1. FTIR spectra of xGd$_2$O$_3$·(100-x)[6TeO$_2$·4B$_2$O$_3$] glasses where 0 ≤ x ≤ 30 mol%.

For this reason, it is assumed that the framework of glasses is built up of [BO$_4$] tetrahedra, [BO$_3$] triangles, trigonal bipyramids [TeO$_5$], pyramidal [TeO$_4$] and accidentally at a high B$_2$O$_3$ content of [TeO$_6$] octahedral units. Accordingly, the increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network and would necessity quite a radical rearrangement of the network formed by the [TeO$_6$] octahedral. Our results show the role of the gadolinium ions as a modifier on the glass network [14].

3.2. DFT calculations
The IR data were used in the present research in order to compute a possible structural model of the 6TeO$_2$·4B$_2$O$_3$ glass network. Similar methodology has previously been reported to study other glasses [10, 13, 15, 16]. The tellurium atom in our model has six oxygen atoms in vicinity and the Te–O distances are 1.99, 2.01, 2.02, 2.05, 2.09 and 2.15 Å. Acceding to the data from this study, the Te–O distances vary from 1.99 to 2.15 Å and this octahedron is distorted [17]. Tellurate networks are flexible to form the appropriate coordination environments for groups of opposite charge such as [BO$_4$]$^-$ tetrahedra where change of the TeO$_6$ network units provides the needed number of oxygen neighbours. This result, namely the existence of the distorted [TeO$_6$] structural units was previously reported based on neutron and X-ray diffraction experiments for the P$_2$O$_5$-TeO$_2$ glasses [18].

Our DFT calculations show that the increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, would depolymerize of borate chains and would necessity quite a radical rearrangement of the network formed by the [TeO$_6$] octahedral. This is possible considering that tellurium dioxide brings stoechiometrically with two oxygen atoms in [TeO$_5$] and needs an additional oxygen atom for the formation of [TeO$_6$] octahedrons. This additional oxygen atom can be taken off also from the boron coordination and thus boron atoms transfer their [BO$_4$] coordination into [BO$_3$] coordination.
In these conditions, the compositional evolution of the network was accommodated with excess of oxygen by the formation of orthoborate structural units, disintegration of some boroxol rings and radical rearrangement of the network formed by the [TeO$_6$] octahedral units. The reduced processing temperature makes borate-tellurate glasses suitable for the use of immobilization of high level hazardous waste, as well as for many alternative commercial glass and glass ceramic products.

4. Conclusions
Glasses with composition xGd$_2$O$_3$·(100-x)[6TeO$_2$·4B$_2$O$_3$] (0 ≤ x ≤ 30 mol%) were prepared by conventional melt-quenching method. The investigations of FTIR spectroscopy show that the content of [BO$_4$] structural units cannot become higher, because the modified [BO$_3$] units containing one or more B–O–Gd bonds are unable to accept a fourth oxygen atom. The FTIR spectroscopy and DFT investigations show that the increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, would depolymerize of borate chains by the formation of orthoborate structural units and disintegration of some boroxol rings, respectively and would necessity quite a radical rearrangement of the network formed by the [TeO$_6$] octahedral units.

References
[1] Kehagias Th, Komninou Ph, Kavouras P, Chrissafis K, Nouet G and Karakostas Th 2006 J. Eur. Ceram. Soc. 26 1141
[2] Jantzen C M 1986 J. Non-Cryst. Solids 84 215
[3] Sales C B and Boatner A L 1984 Science 226 45
[4] Sales C B and Boatner A L 1986 J. Non-Cryst. Solids 79 83
[5] Donald W, Metcalfe B L and Taylor R N J 1997 J. Mater. Sci. 32 5851
[6] Frisch M J et al 2003 Gaussian 03, Revision A.1 (Pittsburgh PA: Gaussian, Inc)
[7] Kozhukharov V, Nikolav S, Marinov M and Troev T 1979 Mater. Res. Bull 14 735
[8] Rada S, Culea E, Rus V, Pica M and Culea M 2008 J. Mater. Sci 43 3713
[9] Rada S, Culea M, Rada M and Culea E 2008 J. Mater. Sci. 43 6122
[10] Rada S, Culea M and Culea E 2008 J. Phys. Chem. A 112 11251
[11] Konijnendijk W L, Stevels J M 1975 J. Non-Cryst. Solids 18 30
[12] Bhargava A, Snyder R L and Condrate R A 1987 Mater. Res. Bull. 22 1603
[13] Rada S, Culea M, Neumann M and Culea E 2008 Chem. Phys. Lett. 460 196
[14] Coroiu I, Borodi G, Vida-Simiti I, Darabont A, Culea E and Jumate N 2006 J. Optoelectron. Adv. Mater. 8 529
[15] Rada S, Culea M and Culea E 2008 J. Non-Cryst. Solids 354 5491
[16] Rada S, Pascuta P, Bosca M, Culea M, Pop L and Culea E 2008 Vib. Spectrosc. 48 255
[17] Ciceo Lucacel R, Marcus C, Timar V and Ardelean I 2007 Solid State Sci. 9 850
[18] Hope U, Gugov I, Burger H, Jovari P and Hannon A C 2005 J. Phys: Condens. Matter 17 2365
[19] Hoppe U, Yousef E and Russel C 2002 Solid State Commun. 123 407.