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Experimental and theoretical studies of the structure of tellurate-borate glasses network

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Abstract The structural properties of the $xTeO_2 \cdot (1-x)B_2O_3$ glasses (x=0.6; 0.7) were investigated by FT-IR spectroscopy. From the analysis of the FTIR spectra, it is reasonable to assume that by the increasing of boron ions content, the tetrahedral $[BO_4]$ units are gradually replaced by the trigonal $[BO_3]$ units. The increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network and will yield the depolymerization of the borate chains. The molecular structure and vibrational frequencies of the proposed structural models have been studied by exploring the density functional theory (DFT) calculations. The FTIR spectra of the $xTeO_2 \cdot (1-x)B_2O_3$ vitreous systems were compared with the calculated spectrum. This procedure allowed us to assign most of the observed IR bands.

Keywords DFT calculations · FT-IR spectroscopy · Tellurate-borate glasses

Introduction

Tellurate glasses have recently gained wide attention because of their potential as hosts of rare earth elements for the development of fibres and lasers covering all the main telecommunication bands [1] and promising materials for optical switching devices [2]. Recently, tellurate glasses

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doped with rare earth oxides [3] have received great scientific interest because these oxides can modify the optical and physical properties of the tellurate glasses.

It is of fundamental importance in glass science to understand the structural forms that arise in glasses composed of network formers of intermediate strength [4]. The field strength of Te^{+4} ions is intermediate between the good glass formers and the modifiers. Tellurita (TeO_2) is only a conditional glass former and requires fast-quenching techniques to form a glass [5].
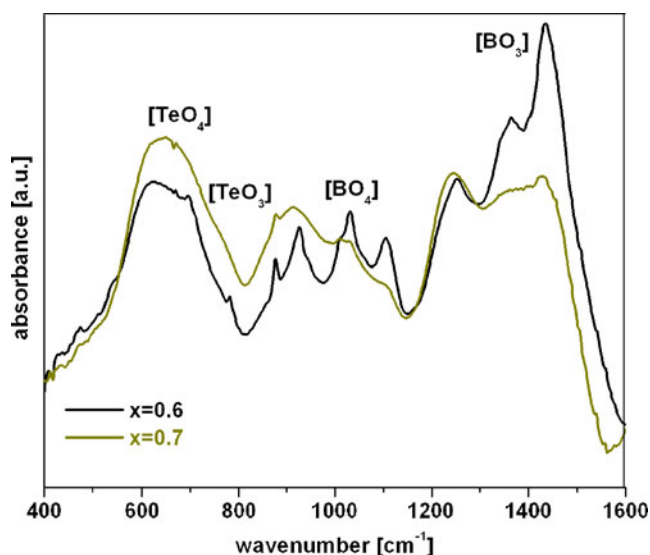
On the other hand, anomalous behavior in properties as a function of composition can usually be explained on the basis of the glasses structure. For example, the initial increase in glass transition temperature with the addition of modifier in borate glasses is due to the formation of $[BO_4]$ structural units. Similarly, modification of GeO_2 glass proceeds initially by formation of $[GeO_6]$ octahedral structural units. The glass transition temperature and molar volume in tellurates do not show similar anomalies, but the resistance to devitrification does [6].

Most tellurate glasses systems require at least 50 mol% TeO_2 for glass formation [7]. The building units of these materials include $[TeO_4]$ trigonal bipyramidal units with lone pair of electrons and $[TeO_3]$ pyramidal structural units [8].

The main objectives of the present work are to study structural properties of the borate-tellurate glasses induced by the modification of the $TeO_2:B_2O_3$ stoechiometry using the FT-IR spectroscopy and DFT calculations. The experimental data permitted to identification of the basic structural units in the studied glasses as well as to follow their interconversion as function of composition. At the same time, the present study provides interesting information concerning a new theoretical model of the $xTeO_2 \cdot (1-x)B_2O_3$ glasses network.

Fig. 1 FT-IR spectra of $xTeO_2 \cdot (1-x)B_2O_3$ glasses

Table 2 The total energy/atom of the $xTeO_2 \cdot (1-x)B_2O_3$ system

System	Total energy/atom [a.u/atom]
$0.7TeO_2$	-39.92
$0.6TeO_2 \cdot 0.4B_2O_3$	-45.91
$0.7TeO_2 \cdot 0.3B_2O_3$	-49.57

(DFT). The DFT computations were performed with B3PW91/3-21G* method using the Gaussian'03 program package [9]. Dangling bonds of outer atoms of the models were saturated with hydrogen atoms. The structural geometry of borate-tellurate glasses network was completely optimized. The vibrational frequencies and IR intensities were calculated for the equilibrium geometry.

Experimental

The binary $xTeO_2 \cdot (1-x)B_2O_3$, $x=0.6$ and 0.7 glasses were prepared by mixing together specific weights of tellurium dioxide and boric acid, in a ceramic crucibles. The crucible was transferred to a furnace for 60 minutes at 800 °C.

The FT-IR spectra of the glasses in the 400–1600 cm^{-1} spectral range were obtained with a JASCO FTIR 6200 spectrometer using the standard KBr pallet disc technique. The spectra were carried out with a standard resolution of 2 cm^{-1}.

The densities of the glass samples were measured accurately to the third decimal ($\pm 0,03$ gcm^{-3}) by the displacement method using water as an immersion liquid.

The geometry optimization of the proposed structural model was carried out using the density function theory

Results and discussion

The density of glasses is of special importance, especially in the context of the studies of the structural changes. Thus, the abrupt changes of density of the glasses suggest important structural modifications of the vitreous network.

Density measurements show that the density increases by increasing of the molar fraction, x from 3.91 gcm^{-3} to 4.96 gcm^{-3}. This dependence of the density on composition is in agreement with the weight and size of the constituent oxides. On the other hand, the increase in density could be explained considering that the atomic weight of B atom is smaller than Te atom and the network may be accommodation by conversion of some $[TeO_3]$ to $[TeO_4]$ structural units and $[BO_3]$ trigonal to $[BO_4]$ tetrahedral structural units yielding the open structure of glasses.

The FTIR spectra of the tellurate-borate glasses are presented in Fig. 1. IR bands are related directly with the nature and quantity of chemical bonds of the vitreous network. The examinations of these spectra show that by

Table 1 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
Tellurium ions	400–500	the bending mode of Te-O-Te or O-Te-O linkages
	620–680	Te–O bonds in $[TeO_4]$ structural units
	720–780 cm^{-1}	Te-O bonds in $[TeO_3]$ structural units

Fig. 2 **a.** Optimized structure of the 0.6TeO2·0.4B2O3 glasses network. **b.** Optimized structure of the 0.7TeO$_2$·0.3B$_2$O$_3$ glasses network
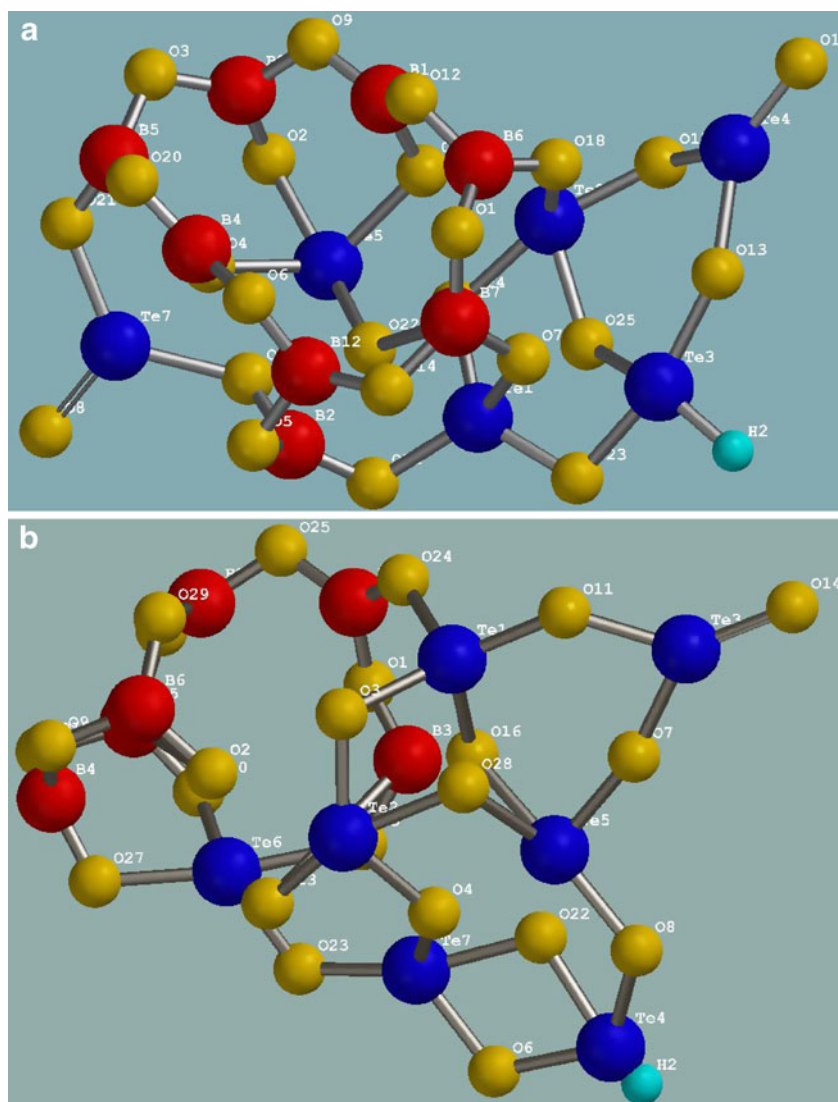
increasing of the molar fraction, x, the characteristic IR bands are modified, namely:

i) The broader band located at about 622 cm^{-1} increases and shifts to bigger wavenumber (645 cm^{-1}), then

shoulder situated at about 780 cm^{-1} disappears. These bands are attributed to the stretching vibration between tellurium and nonbridging oxygen atoms of [TeO$_3$] trigonal bipyramidal or polyhedral [TeO$_{3+1}$] structural units, Table 1 [10–13]. Some authors consider that the

Table 3 Some characteristics of the 0.6TeO$_2$·0.4B$_2$O$_3$ glass network

0.6TeO$_2$·0.4B$_2$O$_3$

B-O distance (Å)	Te-O distance (Å)	Calculated IR spectrum	Experimental IR spectrum
B1: 1.35, 1.36, 1.44	Te1: 1.79, 1.86, 1.94, 1.95	445	470
B2: 1.36, 1.40, 1.44	Te2: 1.81, 1.88, 1.91, 1.92	614, 676, 707	624, 669, 694
B12: 1.42, 1,42, 1.46	Te3: 1.84, 1.88, 1.96	738, 785	757, 783
B4: 1.34, 1.35, 1.44	Te4: 1.70, 1.83, 1.85	836, 919	877, 923
B5: 1.36, 1.41, 1.46	Te5: 1.88, 1.91, 1.94, 1.97	980, 1082	1007, 1028
B6: 1.35, 1.39, 1.40	Te7: 1.70, 1.90, 1.97	1116, 1258	1103, 1253
B7: 1.37, 1.38, 1.40, 2.41		1295, 1340, 1473	1363, 1433
B8:1.36, 1.36, 1.38			

Table 4 Some characteristics of the $0.7TeO_2 \cdot 0.3B_2O_3$ glass network

$0.7TeO_2 \cdot 0.3B_2O_3$

B-O distance (Å)	Te-O distance (Å)	Calculated IR spectrum	Experimental IR spectrum
B1: 1.34, 1.38, 1.40	Te1: 1.82, 1.86, 1.89, 2.03	454	475
B2: 1.38, 1.38, 1.39	Te2: 1.82, 1.83, 1.88, 1.92	521, 524, 576	510, 535
B3: 1.35, 1.40, 3.27	Te3: 1.69, 1.82, 1.83	650, 675, 678	650, 671, 680
B4: 1.36, 1.41, 1.42	Te4: 1.85, 1.87, 1.92	738, 767	722, 767
B5: 1.36, 1.39, 1.41, 3.05	Te5: 1.85, 1.87, 1.94, 2.02	865, 876	877, 914
B6: 1.37, 1.38, 1.40	Te6: 1.82, 1.88, 1.90, 1.98	966, 1020, 1099	961, 1010, 1031
	Te7: 1.84, 1.84, 1.89, 1.93	1165, 1285	1110, 1243
		1316, 1351, 1393	1335, 1358, 1398
		1428, 1506	1430, 1538

shoulder located at 780 cm^{-1} can be due to the fact that there are more distorted [TeO$_4$] structural units in the glasses than in TeO$_2$ reference crystals [14] or the benefit of the one of [TeO$_3$] entities [15].

ii) For sample with x=0.6, the larger bands centered in the 820–1150 cm^{-1} spectral region split in four components located at ~875, 975, 1025 and 1120 cm^{-1}. All these bands are attributed to the B-O stretching vibration in the [BO$_4$] structural units [16–19].

iii) The band centrated at ~1255 cm^{-1} is attributed to the B-O stretching vibrations in [BO$_3$] structural units from boroxol rings and shifts to 1243 cm^{-1}.

iv) The intensities of the intense bands located at about 1360 and 1435 cm^{-1} decrease showing the transformation of the [BO$_3$] structural units with varied types of borate groups to the [BO$_4$] structural units and the [BO$_3$] structural units from boroxol rings [16–19].

In brief, the increase of fraction molar, x yields the modification of coordination number of the Te and B atoms. The contain in [BO$_4$] structural units increases because some [BO$_3$] structural units with varied types of borate units were transformed in [BO$_3$] structural units from boroxol rings and [BO$_4$] structural units. Then, the tellurium coordination can be changed progressively from 3 through 3+1 to 4.

These experimental IR results were used to develop the theoretical models for binary $xTeO_2 \cdot (1-x)B_2O_3$ glasses network. Table 2 shows the dependence of the total energy (per atom) of the $xTeO_2 \cdot (1-x)B_2O_3$ system with molar fraction, x. It comes out that the borate-tellurate glasses are thermodynamicly stable with the increase of molar fraction, x. The total energy/atom of the TeO$_2$ glass are smaller than the borate-tellurate glasses which might explain the difficulty in synthesizing of the pure tellurate glasses without other formers and modifiers.

The simulation method used is able to provide a realistic description of the borate-tellurate network structure, which consist of four types of structural units: (i) [TeO$_4$] trigonal

bipyramidal structural units (all of the oxygen atoms are involved in bridged bonds and the tellurium atoms are three-coordinated), (ii) [TeO$_3$] pyramidal structural units (in which the oxygen involved in the double bond Te=O is nonbridging and the other two oxygens are involved in
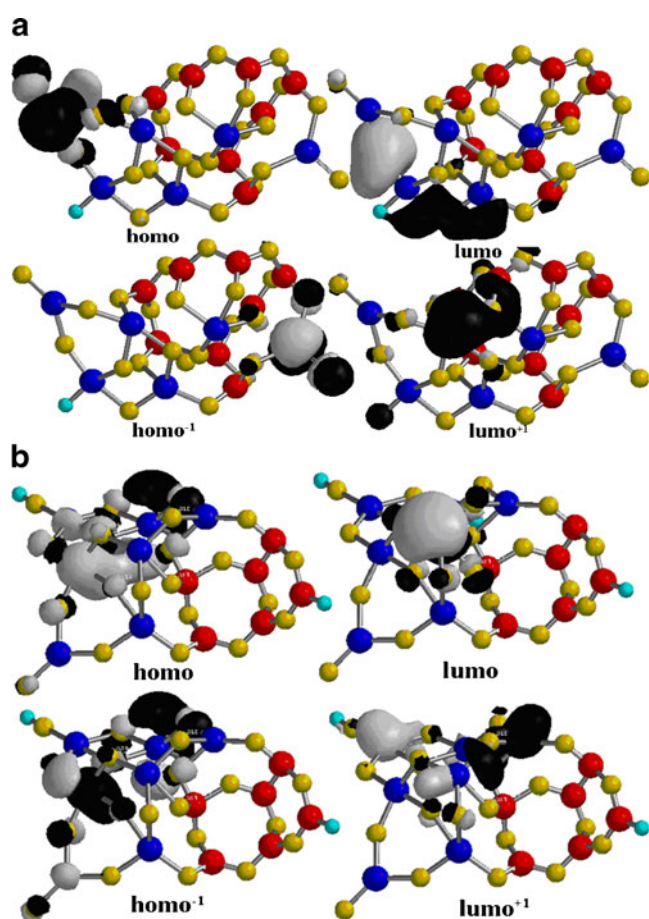
Fig. 3 a. The distribution of the electronic states of the HOMO, HOMO^{-1}, LUMO and LUMO^{+1} of the proposed model for $0.6TeO_2 \cdot 0.4B_2O_3$ glasses network. **a.** The distribution of the electronic states of the HOMO, LUMO^{-1}, LUMO and LUMO^{+1} of the proposed model for $0.7TeO_2 \cdot 0.3B_2O_3$ glasses network

bridged bonds, (iii) [BO$_3$] structural units (containing three-coordinated boron atom from boroxol rings or/and from varied types of borate units) and (iv) [BO$_4$] structural units (all of the oxygen are involved in bridged bonds).

The study of structural modifications of the network and the equilibrium geometry was performed by optimization. Figure 2 illustrates the result obtained form a Gaussian/B3PW91/3-21G* simulation.

It is known that tellurate structures containing tetravalent Te atoms could contain [TeO$_3$] trigonal pyramidal units, TeO$_{3+1}$ polyhedra with three short distances ranging from 1.86 to 1.95 Å, or [TeO$_4$] disphenoids, each having a well defined $5s^2$ lone pair. Te^{+4} ions are the lone-pair cation and lone-pair electrons occupy a non-bonding orbital that is stereochemically active and can be regarded as an additional ligand completing the coordination polyhedron. In addition to the lone-pair cations, oxygen ions have low coordination numbers also help to open up the crystal structures.

There are two types of atoms in our models (Fig. 2, Tables 3 and 4), namely:

i) Tellurium is in tetragonal and trigonal coordination. The Te-O bond lengths in the TeO$_n$ polyhedron of our models are ranged from 1.69 to 2.03 Å. The mean Te-O distances (1.88–1.95 Å) are comparable to that of the Te-O covalent bond distance (2.15 Å) and the tellurium atoms are strongly bonded to four oxygen atoms giving a trigonal bipyramidal arrangement. This geometry of the Te^{+4} ions show an asymmetric coordination due to the stereochemically active lone-pair electrons.

ii) The B-O bond distances from the [BO$_4$] structural unit are somewhat longer than the B-O covalent bond (1.51 Å) but significantly shorter than the sum of the van der Waals radii (3.52 Å). This leads to an unsymmetrical coordination in the structural [BO$_4$] units. Such irregular coordination polyhedron of the boron ion was found in bismuth borate compounds [20] and boro-bismuthate glasses [21, 22].

The vibrational properties of these glasses inferred from quantum chemical simulation are interpreted through a comparison with the experimental spectra (Tables 3 and 4). The evolution of vibrational spectrum of the proposed model is important for understanding the broadening-effect of the glasses from the experimental FTIR spectrum. Our results show that the Te-O and B-O stretching vibration region of the proposed model is similar to the same region of the glass. A good agreement was found between the theoretical and experimental IR absorption data. Comparing the theoretical and experimental data, we conclude that the performance of the method and basic set used for the prediction of the structural data and vibrational modes for the xTeO$_2$·(1-x) B$_2$O$_3$ glasses is good.

The massive vibrations of the [BO$_3$] structural units can be coupled each other *via* [TeO$_3$] and [TeO$_4$] structural units. This leads to the splitting of the bridge modes and a multiplication of the number of these bands.

The distribution of the electronic states of the HOMO, HOMO^{-1}, LUMO and LUMO^{+1} can be seen in Fig. 3. An interesting finding in these systems is that:

i) The HOMO and HOMO^{-1} give character of electron donor for the [TeO$_3$] structural units of the tellurate network.

ii) The LUMO and LUMO^{-1} give the character of electron acceptor for the [TeO$_4$] structural units of the tellurate network and some [BO$_n$] structural units (n=3, for sample with x=0.6 and n=3, 4 for sample with x=0.7) of the borate network.

There is a charge transfer between the tellurium atoms coordinated +3 and +4. Also, a charge transfer was yielded between tellurium atom and borate network. This can be explained considering that the tellurate network are flexible to form the appropriate coordination environments with structural units of opposite charge such as [BO$_4$]$^-$ tetrahedral structural units where change of the tellurate network provides the needed number of oxygen neighbours.

Conclusions

Glasses of the xTeO$_2$·(1-x)B$_2$O$_3$ vitreous system were obtained for x=0.6 and 0.7. The FT-IR studies show that the increase of molar fraction, x of the tellurate-borate network yield the formation of some [BO$_4$] and [TeO$_4$] structural units interconnected through Te-O-B bridges and the open of structure of the glasses.

Main results of the DFT calculations show that the thermodynamic stability of the vitreous systems increases by increasing of the molar fraction, x. There is a powerful charge transfer between tellurium atoms coordinated +3 and +4. The evolution of vibrational spectrum of the proposed models show that the Te-O and B-O stretching vibration region of the proposed model is similar to the same region of the glasses.

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