The local structure of gadolinium-borate-tellurate vitrocermics investigated by FTIR and EPR spectroscopy

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Abstract. The present study provides interesting information concerning devitrification behavior of xGd2O3·(100-x)[6TeO2·4B2O3] vitreous system with 0 ≤ x ≤ 30 mol%. The structural changes have been analyzed with increasing rare earth concentration. Two halos characteristic of the amorphous compounds can be observed in XRD diffraction pattern for sample with x ≥ 20 mol% Gd2O3. These changes can be explained only if we admit that the adding of gadolinium oxide now participate in the network as [GdO6] structural units yielding a change from the continuous borate-tellurate network to the continuous gadolinium-borate-tellurate network with interconnected through Gd–O–B and Gd–O–Te bridges. The EPR spectra of the studied glass ceramics reveal an increase of the content of Gd3+ ions in network former and modifier positions. Therefore, Gd3+ ions will coordinate more with non-bridging oxygens leading the decreased of the number of individual Gd3+ ions.

1. Introduction
Glasses containing rare earth ions have attracted a great deal of interest due to their important physical and chemical properties [1-5]. Glass ceramics based on partial crystallization of precursor glasses from the silicate or phosphate systems were developed for the possible solidification of fuel recycle waste or the immobilization of high level waste [6-9].

Design of the controlled crystallization process of gadolinium-borate-tellurate glasses in order to obtain glassy-crystalline materials has been the main goal of the work. Glass ceramics structural changes have been studied using the X-ray diffraction, FTIR and EPR spectroscopy.

2. Experimental
Glasses with composition xGd2O3·(100-x) [6TeO2·4B2O3] (0 ≤ x ≤ 30 mol%) were prepared by conventional melt-quenching method, melting mixtures of TeO2, H3BO3 and Gd2O3 reagents of purity grade in a corundum crucibles at 800°C for 60 min. Then, the glasses samples were subject to heat treatment applied at 475°C for 24 h, respectively.
The samples were analyzed by means of X-ray diffraction using a XRD-6000 Shimadzu diffractometer. The IR spectra were recorded in the range 400-1600 cm\(^{-1}\) using a JASCO FTIR 6200 spectrophotometer. EPR measurements were performed at room temperature using ADANI Portable EPR PS 8400-type spectrometer, in X frequency band (9.1 Hz) and a field modulation of 100 kHz.

3. Results and discussion

The X-ray diffraction patterns reveal that the composition of the glass ceramics with the Gd\(_2\)O\(_3\) concentration up to 10 mol% was found to consist mainly of the TeO\(_2\) and B\(_2\)O\(_3\) crystalline phases (figure 1). Surprising for samples with \(x \geq 20\) mol% Gd\(_2\)O\(_3\) can be observed two halos characteristic of the amorphous compounds. The role of such oxide in the geometrical arrangement of the building units of the glass ceramics network can be considered as follow (figure 2):

i. For low concentrations, \(0 \leq x \leq 20\) mol\%, 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. The band located at about \(~680\) cm\(^{-1}\) corresponds to the stretching vibrations in [TeO\(_3\)] structural units [10-12]. The content of three-coordinated tellurium attains its maximum values of 1 mol% Gd\(_2\)O\(_3\). This increase yields the apparition of the TeO\(_2\) crystalline phase. It seems that the content of [BO\(_3\)] structural units become higher, because results to transformation of some [BO\(_3\)] units into [BO\(_4\)] structural units.

\[
\begin{array}{c}
\text{20\%} \\
\text{10\%} \\
\text{1\%} \\
\text{0\%}
\end{array}
\]

\[
\begin{array}{c}
\text{TeO}_2 \\
\text{B}_2\text{O}_3 \\
\text{TeO}_2 \\
\text{B}_2\text{O}_3 \\
\text{B}_2\text{O}_3
\end{array}
\]

\[
\begin{array}{c}
475^\circ\text{C, 24h}
\end{array}
\]

**Figure 1.** X-ray diffraction patterns for \(x\text{Gd}_2\text{O}_3\cdot(100-x)[6\text{TeO}_2\cdot4\text{B}_2\text{O}_3]\) glass ceramics treated at 475\(^\circ\)C with \(x = 20, 25\) and 30 mol\%.

ii. The band centred at around 450 cm\(^{-1}\) is most often assigned to bending vibrations of Te–O–Te linkages [13]. The intensity of this band varies with the increasing amounts of gadolinium oxide. The effects suggest that doping with gadolinium ions deforms the Te–O–Te linkages and changes the distribution of ordered microregions within the glass ceramics [14, 15].

iii. The broad bands in the region 800-1200 cm\(^{-1}\) are due to the stretching of B–O bonds of [BO\(_4\)] units. The features of the bands presented in the region 1200-1600 cm\(^{-1}\) can be attributed to the [BO\(_3\)] structural units stretching vibrations, which are associated with the vibrational modes inside the various borate rings and the non-bridging B– bonds, respectively.

The gadolinium ions have a strong affinity towards these [BO\(_4\)] structural units containing non-bridging oxygens, which are negative-charged, because they are readily available for charge compensation. 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 changed of the distribution of ordered microregions of the TeO$_2$ crystalline phase and pursuant to the intercalation of [GdO$_4$] entities in the [TeO$_4$] chain network [16]. These observations can be related by modifies of characteristic features of the bands located in the region ranges between 500-800 and 1200-1600 cm$^{-1}$.

![FTIR spectra](image1)

**Figure 2.** FTIR spectra of xGd$_2$O$_3$·(100-x)[6TeO$_2$·4B$_2$O$_3$] glass ceramics treated at 475°C.

![EPR spectra](image2)

**Figure 3.** EPR spectra of xGd$_2$O$_3$·(100-x)[6TeO$_2$·4B$_2$O$_3$] glass ceramics.

With the increase of Gd$_2$O$_3$ content up to 20 mol%, a sharp decreasing trend was observed in strength on the bands centered at about 780 and 1200 cm$^{-1}$, which correspond to the TeO$_2$ and B$_2$O$_3$ crystalline phases. This may be attributed to the electrostatic field of the strongly polarizing Gd$^{3+}$ ions which will yield the apparition of amorphous compounds by increasing of gadolinium ions.

The EPR spectra of xGd$_2$O$_3$·(100-x)[6TeO$_2$·4B$_2$O$_3$] glass ceramics sample treated at 475°C show a significant increase of the resonance line attributed to the type of Gd$^{3+}$ ions which can be presented as network former in the glass ceramics (g $\approx$ 4.8) (figure 3). Moreover, we observed a weak resonance line attributed the g $\approx$ 2 due to formation of Gd$^{3+}$ clusters for all glass ceramics samples. The weak resonance line g $\approx$ 6 was considered to be a characteristic feature of intermediate crystal field sites of axial symmetry and have attributed the broadened general appearance of the U-spectrum to isolated rare earth ions in wide varieties of sites. The Gd$^{3+}$ ions in these glass ceramics can be considered as isolated in the sense of the absence of clustering. The weakening intensity of the clusters EPR line could be due to the Gd$^{3+}$ migrations inside the glass network. It should lead to the appearance of more Gd$^{3+}$ content in network former positions. It can be pointed that the Gd$^{3+}$ ions are generally suspected to improve their environment [17, 18].
In brief, the gadolinium ions have a strong affinity towards [BO$_3$] groups containing non-bridging oxygens yielding the disappearance of the B$_2$O$_3$ crystalline phase. Then, the Gd$_2$O$_3$ behaves as a glass-former by means of the intercalation of [GdO$_4$] entities in the [TeO$_4$] chain network.

4. Conclusions
The structure of $x$Gd$_2$O$_3$·(100-$x$)[6TeO$_2$·4B$_2$O$_3$] glass ceramics prepared by melt-quenching method (for $x = 0-30$ mol% Gd$_2$O$_3$) was studied by FTIR, EPR spectroscopy and X-ray diffraction. The increase of Gd$_2$O$_3$ content leads the disappearance of B$_2$O$_3$ and TeO$_2$ crystalline phases and causes a change from the glass ceramics network to the continuous gadolinium-borate-tellurate glass network with interconnected through Gd–O–B and Gd–O–Te bridges. The EPR spectra of the studied glass ceramics reveal the presence of line at $g \approx 4.8$ characterized for Gd$^{3+}$ ions in sites of strong crystal fields having a low coordination number. This type of Gd$^{3+}$ ions can be presented as network former in the glass.

References
[1] Simon S, Ardelean I, Filip S, Bratu I and Cosma I 2000 Solid State Commun. 116 83
[2] Ristoiu T and Culea E 2001 J. Non-Cryst. Solids 279 93
[3] Ristoiu T, Culea E and Bratu I 1999 Mater. Lett. 41 135
[4] Coroiu I, Borodi G, Vida-Simiti I, Darabont A, Culea E and Jumate N 2006 J. Optoelectron. Adv. Mater. 8 529
[5] Coroiu I and Cristea I 2005 J. Magn. Magn. Mater. 293 520
[6] Kim H. G and Komatsu T 1988 J. Mater. Sci. Lett. 17 1198
[7] Sitarz M and Szumera M 2008 J. Ther. Anal. Calorim. 91 255
[8] Lucaci P, Burzo E and Lupsa I 1996 J. Alloys. Compd. 14 238
[9] Donald W, Metcalfe B L and Taylor R N J 1997 J. Mater. Sci. 32 5851
[10] Wright A C, Vedischeheva N M and Shakmatahin B A 1995 J. Non-Cryst. Solids 192-193 92
[11] Rada S, Culea M and Culea E 2008 J. Phys. Chem. A 112 11251
[12] Pan A and Ghosh A 2002 Phys. Rev. B 66 012301
[13] Rada S, Culea M, Neumann M and Culea E 2008 Chem. Phys. Lett. 460 196
[14] Jha A, Shen S and Naftaly M 2000 Phys. Rev. B 62 6215
[15] Iton I E, Brodbeck C M, Suib S L, Stucky G D 1983 J. Chem. Phys. 79 1185
[16] S Rada and E Culea 2009 J. Mol. Struct. 929 141
[17] Culea E, Pop L and Simon S 2004 Mater. Sci. Eng. B 112 59
[18] Brodbeck C M and Iton I E 1985 J. Chem. Phys. 83 4285.