ORIGINAL RESEARCH

The local structure of gadolinium vanadate–tellurate glasses and glass ceramics: Te$_2$V$_2$O$_9$ crystalline phase

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Abstract Glasses in the system xGd$_2$O$_3$ · $(100 - x)$ [0.7TeO$_2$ · 0.3V$_2$O$_5$] with $0 \leq x \leq 20$ mol% have been prepared from melt quenching method. Influence of gadolinium ions on structural behavior in vanadate–tellurate glasses has been investigated using FTIR spectroscopy, X-ray diffraction (XRD), and magnetic susceptibility measurements. The structural changes have been analyzed with increasing rare earth concentration. The structural changes, as recognized by analyzing band shapes of XRD and FTIR spectra, revealed that Gd$_2$O$_3$ causes a higher extent of network polymerization as far as 20 mol%. The structure of the heat-treated glasses was found to consist mainly of the Te$_2$V$_2$O$_9$ crystalline phase. These vitreous systems were investigated by magnetic susceptibility measurements. From the paramagnetic susceptibility χ was calculated at different temperature and from the $1/\chi(T)$ graph, the Curie temperature of the glass has been evaluated. Magnetic susceptibility data show the presence of small antiferromagnetic interactions between the Gd^{+3} ions.

Keywords Gadolinium vanadate–tellurate glasses and glass ceramics · FTIR spectroscopy · XRD diffraction · Magnetic susceptibility

Introduction

Tellurate glasses have more advantages over silicate and borate glasses because of their physical properties such as low-melting temperature, high-refractive index, high-dielectric constant, and good infrared transmissivity. Demonstrating a wide range of unique properties, tellurate glasses have potential applications such as pressure sensors, data storage, optical displays, optical amplifiers or as new laser hosts, optical modulators, and optical memory storage systems [1]. Previous studies showed that vanadium tellurate glasses are semiconducting and that they switch when a high electrical field is applied [1, 2].

Tellurium dioxide, like vanadium pentoxide, is a conditional glass former. It is very difficult to form pure vitreous TeO$_2$ and it has been suggested [3] that this is due to the lone pair of electrons in one of the equatorial positions of the [TeO$_4$] polyhedron. The repulsive forces in this zone hinder the free movement of the polyhedra in space during the cooling of the melt. In a binary tellurite composition, the effect of the free electron pair is limited by the introduction of the new structural units which are compatible with the [TeO$_4$] polyhedra.

Although the existence of vanadate glasses is well established, their structure remains a subject of interest because there is no clear picture as to the exact nature of the oxygen polyhedra surrounding the vanadium atoms or the role played by the other glass components. Moreover, the structure of the vanadate glasses can be related to the nature of the network formers as well as on the network modifiers.

The potential use of the glass materials to design a fiber laser requires no crystallization in the matrix. Hence, it is vital to understand the crystallization behavior by studying the thermal properties and the microstructure for these applications.

This study includes the investigation of structural, magnetic properties of the glass, and the crystallization behavior of the xGd$_2$O$_3$(100 − x)[0.7TeO$_2$ · 0.3V$_2$O$_5$]

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ternary glass system. The structural changes have been analyzed with increasing rare earth concentration using FTIR spectroscopy, X-ray diffraction (XRD), and magnetic susceptibility measurements.

Experimental

Glasses containing $x\text{Gd}_2\text{O}_3(100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ composition with $x = 0, 5, 10, 15, 20$ mol% were prepared by mixing appropriate amounts of tellurium dioxide, vanadium pentoxide, and gadolinium trioxide. After melting at 850 °C for about 10 min in a corundum crucibles and introduce in an electric furnace, the melt was quenched rapidly to room temperature. Then, the glassy sample was subjected to heat treatment applied at 400 °C for 48 h.

The samples were analyzed by means of XRD using a XRD-6000 Shimadzu diffractometer, with a monochromator of graphite for the Cu-Kα radiation ($\lambda = 1.54$ Å) at room temperature. The position and intensity of diffraction peaks of the crystalline powder $x\text{Gd}_2\text{O}_3(100 - x)$ $[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ systems are consistent with that of the powder diffraction file, which indicates that the sample crystalized well.

The structure of the glasses and glass ceramics was investigated by infrared spectroscopy in KBr matrices and was recorded in the range 400–1100 cm^{-1} using a JASCO FTIR 6200 spectrometer. The density measurements were performed using the pycnometric method with water as the reference immersion liquid.

Magnetic susceptibility measurements were performed using a Weiss-type magnetic balance in the temperature range 80–300 K. The accuracy of the temperature control was better than ±0.1 K over the whole temperature range and the overall accuracy of the measurements of the magnetic moment was less than ±3%.

Results and discussion

FTIR spectroscopy

The XRD patterns did not reveal any crystalline phase in the prepared glass samples up to 20 mol% Gd$_2$O$_3$ (Fig. 1).

The observed FTIR bands for the presently investigated ternary gadolinium telluro-vanadate glasses are assigned to the Te–O linkage vibration in [TeO$_4$], [TeO$_3$] units and the V–O linkage vibration in [VO$_4$], [VO$_5$] units (Fig. 2).

The bands appear around 460 cm^{-1}, in the range 610–680 and 720–780 cm^{-1}, are assigned the bending mode of Te–O–Te or O–Te–O linkages, the stretching mode [TeO$_4$] trigonal pyramidal with bridging oxygen and
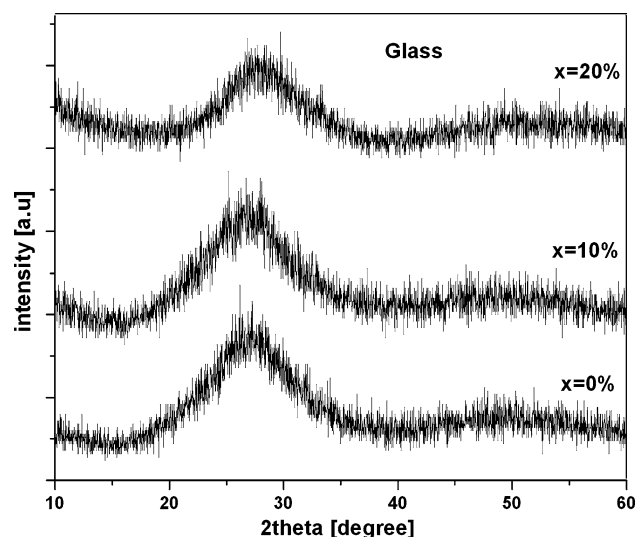

Fig. 1 XRD patterns for $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glasses with $x = 0, 10$, and 20 mol% Gd$_2$O$_3$
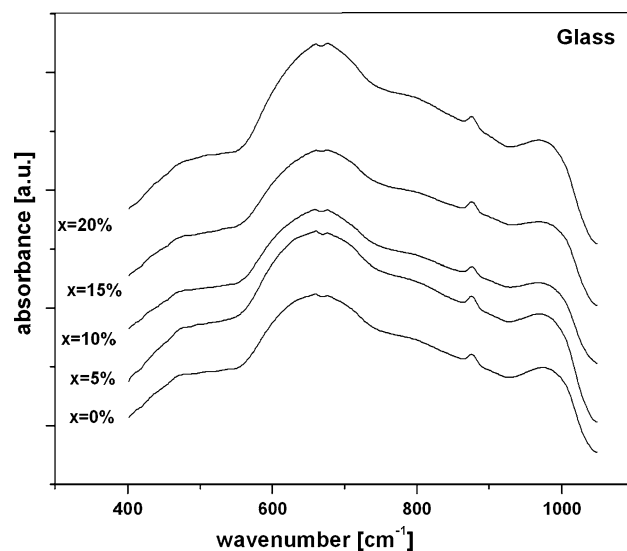

Fig. 2 FTIR spectra of the $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glasses for $x = 0$–20 mol% Gd$_2$O$_3$

the stretching mode of [TeO$_3$] trigonal pyramidal with non-bridging oxygen, respectively [4–6].

In the case of pure V$_2$O$_5$ glass it has been reported [7] that V^{+5} ions exhibit both four and fivefold coordination states, depending on the sample preparation conditions. The IR spectrum of pure crystalline and amorphous V$_2$O$_5$ is characterized by the intense band in the range 1000–1020 cm^{-1}, related to vibration of isolated V=O vanadyl groups in [VO$_5$] trigonal bipyramids [8–10]; the peak around 850 and 910 cm^{-1} to the vibrations of [VO$_5$] units, whereas the band in range 950–970 cm^{-1} was attributed to [VO$_4$] units [11–14].

The examination of the FTIR spectra of the $x\text{Gd}_2\text{O}_3(100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glasses with $x = 0$–20 mol% (Fig. 2) shows that the increase in Gd_2O_3 content weakly modify the characteristic IR bands as follows:

(i)   The intensity of the band centered at about $\sim 470 \text{ cm}^{-1}$ increases with the increasing of the content of Gd_2O_3 up to 20 mol%. This band is assigned to the bending mode of the Te–O–Te or O–Te–O linkages [15].

(ii) The intensity of the band from $\sim 655 \text{ cm}^{-1}$ increases with the increasing of the Gd_2O_3 content and shifts to $\sim 658 \text{ cm}^{-1}$. This band is attributed to the stretching vibrations in $[\text{TeO}_4]$ units [16].

(iii) The intensity of the band centered at $\sim 792 \text{ cm}^{-1}$ increase slowly with the increasing of the gadolinium ions content up to 20 mol%. This band is corresponding to the stretching vibrations in $[\text{TeO}_3]$ structural units [17].

(iv) The intensity of the band from $\sim 985 \text{ cm}^{-1}$ increases with the increasing the content of Gd_2O_3 and shifts to $\sim 979 \text{ cm}^{-1}$. This band is due to the V–O stretching vibrations in $[\text{VO}_4]$ structural units.

So that when the Gd_2O_3 content increases the coordination of the Te atom can be changed progressively from 4 through 3 + 1 to 3 and the contain in $[\text{VO}_4]$ units increases because some $[\text{VO}_5]$ groups were transformed in $[\text{VO}_4]$ units, respectively. The IR data show that the increase in Gd_2O_3 content up to 20% causes a higher extent of vitreous network polymerization.

Taking into account these changes of the IR spectral features, we assume that the increase in the number of gadolinium cations in the glass structure leads both to the appearance of a structural ordering process around the vanadium atoms as well to the increase in the number of linked tellurium-based polyhedra. Such a behavior, namely the increase in the polymerization degree of the structural units with increasing the rare earth ion content, was previously reported for other glasses [18, 19].

Glass ceramics

After heat treatment some structural changes were observed and a new $\text{Te}_2\text{V}_2\text{O}_9$ crystalline phase appeared in the structure of the samples with 15 mol% Gd_2O_3. In the glass sample with 20 mol% Gd_2O_3, $\text{Te}_2\text{V}_2\text{O}_9$ crystalline phase appears very small (Fig. 3). The intensities of the peaks corresponding to these glass ceramics are reduced by increasing the concentration of gadolinium ions from 5 to 15 mol% Gd_2O_3. After that, the addition of rare earth oxide modifier up to 20 mol% causes significant changes, respectively, induce structural changes, namely the gradual disappearance of crystalline phase and a high extent of
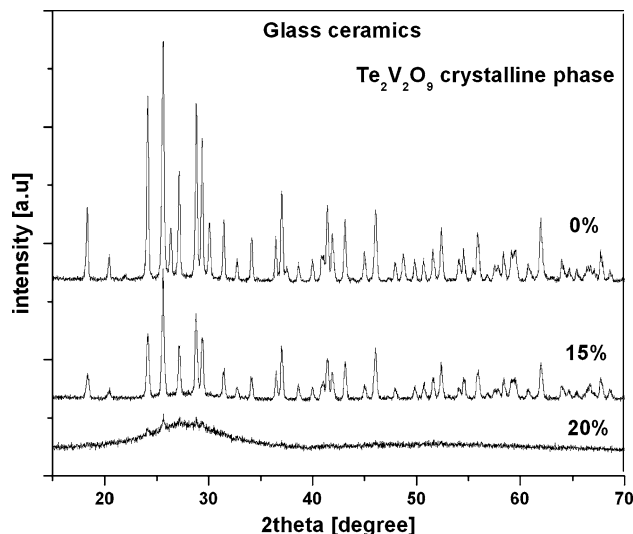

Fig. 3 XRD patterns for $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glass ceramics with $x = 0$, 15, and 20 mol%

glass network polymerization. This result shows a relaxation of the glass network and the increase in the content of vitreous phase by increasing gadolinium oxide content.

The examination of the FTIR spectra of the $x\text{Gd}_2\text{O}_3(100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glass ceramics with $x = 0$–20 mol% (Fig. 4) shows that the increase in Gd_2O_3 content strongly modifies the characteristic IR bands as follows:

(i)   The prominent band centered at about $\sim 478 \text{ cm}^{-1}$ (Fig. 2) splits into four components located at ~ 420, 446, 490, and 525 cm^{-1} for x between 0 and 15 mol% Gd_2O_3 (Fig. 4). After that, the intensity of this band increases with increasing the Gd_2O_3 content up to
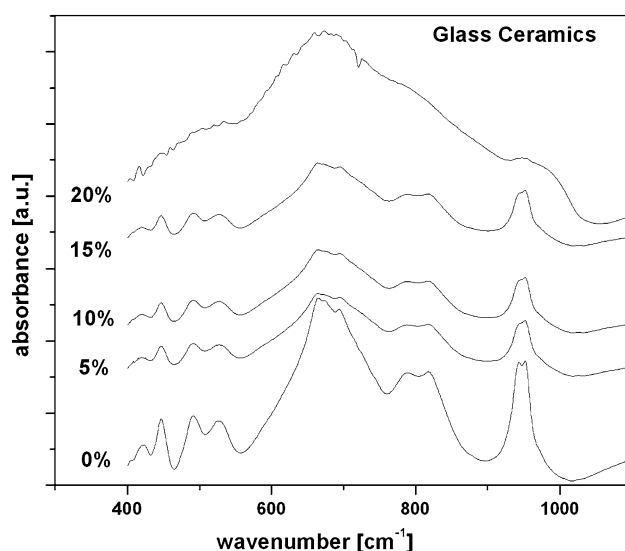

Fig. 4 FTIR spectra of the $x\text{Gd}_2\text{O}_3 \cdot (100 - x)[0.7\text{TeO}_2 \cdot 0.3\text{V}_2\text{O}_5]$ glass ceramics for $x = 0$–20 mol% Gd_2O_3

20 mol%. All these bands are assigned to the bending mode of Te–O–Te or O–Te–O linkages [4, 16, 20].

(ii)   The intensity of the bands centered from ∼653 and 678 cm^{-1} in glass decreases with the increase in the Gd_2O_3 composition and shift to ∼663 and 693 cm^{-1} for glass ceramics. For $0 \leq x \leq 15$ mol% Gd_2O_3 these bands split into some components located at about ∼665, 675, and 695 cm^{-1}, whereas 20 mol% Gd_2O_3 becomes the dominant features of the spectrum. These bands are attributed to the stretching vibrations in $[TeO_4]$ units [21].

(iii) The intensity of the band centered at ∼795 cm^{-1} increase slowly with increasing the gadolinium ions content up to 20 mol%, whereas for small contents ($0 \leq x \leq 15$ mol%) the band splits into two components located at ∼785 and ∼820 cm^{-1}. All these bands correspond to the stretching vibrations in $[TeO_3]$ structural units [12].

(iv) The band centered at about ∼970 cm^{-1} splits into two components located at 942 and 953 cm^{-1} at a small content of Gd_2O_3 ($0 \leq x \leq 15$ mol%). After that, these bands shift to higher wavenumbers at ∼950 and 983 cm^{-1}. All these bands are due to the V–O stretching vibrations in $[VO_4]$ units [9, 11, 22].

Structural changes in $xGd_2O_3(100 - x)[0.7TeO_2 \cdot 0.3V_2O_5]$ glass ceramics, as recognized by analyzing band shapes of XRD and IR spectra, reveal that the gadolinium ions play an essential network modifier role. For x between 15 and 20 mol% Gd_2O_3 showed a drastic structural modification which leads to the gradual disappearance of the $Te_2V_2O_9$ crystalline phase. This result shows a relaxation of the glass network, an accommodation of the network with the excess of oxygen and the increase in the vitreous phase content by heat treatment. This could be explained considering that the excess of oxygen may be accommodated by the conversion of some $[TeO_3]$ into $[TeO_4]$ structural units and $[VO_4]$ into $[VO_5]$ structural units and/or the formation of covalent Gd–O bonds lead to the open structure of the glass.

Thus, heat-treated glasses occur to the apparition of the $Te_2V_2O_9$ crystalline phase for x between 0 and 15 mol% Gd_2O_3. The content of $Te_2V_2O_9$ crystalline phase decreases drastically with the increase in the gadolinium oxide composition up to 20% Gd_2O_3. Accordingly, the gadolinium oxide plays a particular role on the homogeneity of the glasses and in accommodation of the network with the excess of oxygen.

In conclusion, the structural changes observed by increasing the Gd_2O_3 content in $xGd_2O_3(100 - x)$ $[0.7TeO_2 \cdot 0.3V_2O_5]$ glass ceramics and evidenced by the XRD and FTIR investigation suggest that the gadolinium ions play an essential network modifier role.

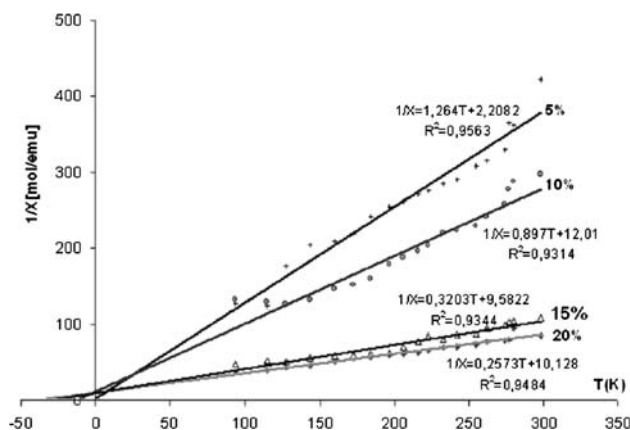**Fig. 5** Temperature dependence of the inverse magnetic susceptibility of $xGd_2O_3 \cdot (100 - x)$ $[0.7TeO_2 \cdot 0.3V_2O_5]$ glasses with $x = 5$, 10, 15, 20 mol% Gd_2O_3

Magnetic susceptibility

The paramagnetic susceptibility was calculated for vanadate–tellurate glasses doped with x mol% Gd_2O_3 ($x = 5$, 10, 15, 20 mol%) at different temperatures. Plots of reciprocal susceptibility $(1/\chi)$ as a function of absolute temperature (T) of the glass are shown in Fig. 5.

For all glasses the inverse of the paramagnetic part of the magnetization is described of Curie–Weiss law and a linear extrapolation of this yields, respectively, $\theta_p = -3$, -12, -30, and -40 K (Table 1). The paramagnetic Curie temperature (θ_p) is a rough indicator of magnetic interaction between Gd^{+3} ions. The small negative values of θ_p $(\theta_p < 7$ K) suggest the presence of weak antiferromagnetic interaction between the Gd^{+3} ions [23]. The absolute magnitude of the paramagnetic Curie temperature values increases with the Gd_2O_3 content for the studied glasses and denotes the intensification of the exchange interactions as the concentration of the gadolinium ions rises [24].

Note that at higher of Gd_2O_3 contents, isolated Gd^{+3} ions can coexist with clusters and actual paramagnetic Curie temperature (θ_p) can differ from those obtained by fitting the experimental $1/\chi(T)$ dependence [25]. Usually, glasses containing gadolinium ions have negative paramagnetic Curie temperature [26–28], similar to Gd_2O_3 [22]. However, some gadolinium compounds have positive paramagnetic Curie temperature [28], attributed to a strong influence of the environment on the exchange interaction between the Gd^{+3} ions.

The lower paramagnetic Curie temperature and the features observed in the field dependence of the magnetization for these glasses can be tentatively ascribed to the antiferromagnetic nature of some clusters. This fact suggests that the participation of gadolinium ions at superexchange magnetic interactions being antiferromagnetic coupled.

Table 1 The paramagnetic Curie temperature (θ_p), molar Curie constants (C_M), effective magnetic moments of gadolinium ions (μ_{eff})

x (mol%)	θ_p (K)	C_M (emu/mol)	μ_{eff} (μ_B/ion)
5	−4	0.72	7.60
10	−12	1.5	7.74
15	−30	3.02	7.76
20	−40	4.66	7.88

From the temperature dependence of inverse magnetic susceptibility, the effective magnetic moments μ_{eff} of Gd^{+3} are determined as 7.60, 7.74, 7.76, and 7.88 μ_B/ion (μ_B is the Bohr magneton) for the studied glasses (Table 1). For all the glasses experimental values obtained for molar Curie constant, C_M, and consequently for μ_{eff} are lower than those which correspond to the Gd_2O_3 content. Because the value of the effective magnetic moment for the free gadolinium ion is 7.98 μ_B [29], indicating a weak influence of the crystal field on the magnetic moments.

However, the assumption of the antiferromagnetic nature of the interaction between the Gd^{+3} ions also supported by the fact that the effective magnetic moment per gadolinium is less than the magnetic moment of the free gadolinium ions.

Conclusions

The FTIR spectra for glass containing xGd$_2$O$_3$(100 − x) [0.7TeO$_2$ · 0.3V$_2$O$_5$] composition with $x = 0$, 5, 10, 15, 20 mol% have been investigated in order to understand their structural properties. The IR data show that increasing the Gd$_2$O$_3$ content up to 20% causes a higher extent of vitreous network polymerization.

The structure of the heat-treated glasses was found to consist mainly of the Te$_2$V$_2$O$_9$ crystalline phase. Structural changes in xGd$_2$O$_3$(100 − x)[0.7TeO$_2$ · 0.3V$_2$O$_5$] glass ceramics, as recognized by analyzing band shapes of XRD and IR spectra, revealed that increasing Gd$_2$O$_3$ composition up to 20 mol% causes a drastic structural modification which leads to the gradual disappearance of the Te$_2$V$_2$O$_9$ crystalline phase. In brief, the gadolinium oxide played a particular role on the homogeneity of the glasses, in accommodation of the network with the excess of oxygen and to going strong as network modifier.

The paramagnetic susceptibilities of the vanadate–tellurate glasses, doped with x mol% gadolinium ions, are calculated at different temperatures. Plots of $1/\chi$ and T are found to be in accordance with the Curie–Weiss law. From plots, Curie temperatures, molar Curie constants, and, the effective magnetic moments per gadolinium ion were evaluated. All glasses are indicated a behavior of antiferromagnetic nature of some clusters.

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