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The local structure of gadolinium vanado-tellurite glasses

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Abstract In this work we report on a vibrational spectroscopic, X-ray diffraction, and density measurement study of the structural properties of the ternary $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ systems for various x values up to 70 mol%. Structural changes, as recognized by analyzing band shapes of X-ray diffraction and IR spectra, revealed that Gd_2O_3 causes a higher extent of network polymerization as far as $x \leq 40$ mol%, while for x between 40 and 50 mol% showed a drastic structural modification which lead to the apparition of the $GdVO_4$ crystalline phase.

Introduction

Tellurite glasses are of technical interest because of their low melting points and absence of the hygroscopic properties which limit application of phosphate and borate glasses. Previous works showed that vanadium tellurite glasses are semiconductor 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 binary and ternary V_2O_5 glasses is well established, the structure of vanadate glasses remains a subject of interest because there is not available a clear picture of the exact nature of the oxygen polyhedra surrounding the vanadium atoms or of 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 to that of the network modifiers.

In the present study we investigated the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ vitreous system, where $0\% \leq x \leq 70\%$, by using X-ray diffraction, infrared spectroscopy, and density measurements. Since a small amount of a secondary glass former/modifier is necessary to stabilize the TeO_2 glass, a content of 30 mol% V_2O_5 was chosen for the glasses to be studied. In addition, to follow the structural and behavioral effect of the incorporation of rare earth ions in the host vitreous matrix, samples with different contents of Gd_2O_3 ($5\% \leq x \leq 70\%$) were prepared and investigated. We note that the compositional range of the host matrix was not reported till now [4]. In the same time, the effect of the addition of Gd_2O_3 to vanadium tellurate glasses up to such high contents (60%) was not reported till now [5]. In the present study, the upper Gd_2O_3 content of the studied vitreous system was established and information was collected concerning the crystallization process that

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appears at this compositional range. Taking into account these aspects, the present study provides interesting information concerning a new vanadium tellurate vitreous system. The experimental data permitted the identification of the base structural units in the studied glasses as well as to follow their interconversion as function of composition.

Experimental

Glasses with the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ composition where $x = 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70$ mol% were prepared by mixing appropriate amounts of tellurium dioxide, vanadium pentoxide, and gadolinium trioxide. The mixtures were melted at 850 °C for about 10 min in corundum crucibles in an electric furnace and after that were rapidly quenched at room temperature.

The samples were analyzed by means of X-ray diffraction using an XRD-6000 Shimadzu diffractometer, with a monochromator of graphite for the Cu Kα radiation ($\lambda = 1.54$ Å) at room temperature. The pattern obtained did not reveal any crystalline phase in the samples up to 50 mol%.

The structure of the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ glasses was investigated by IR spectroscopy using the KBr pellet technique. The IR spectra were recorded in the 400–1100 cm^{-1} range using a JASCO FTIR 6200 FT-IR spectrophotometer.

Density measurements were performed using the picnometric method with water as the reference immersion liquid.

Results and discussion

X-ray diffraction

The X-ray diffraction patterns did not reveal any crystalline phase in the prepared samples up to 50 mol% $\mathrm{Gd_2O_3}$ (Fig. 1). By increasing the concentration of gadolinium ions from 60 to 70 mol% $\mathrm{Gd_2O_3}$ the $\mathrm{GdVO_4}$ crystalline phase was detected in the samples (Fig. 2).

FTIR spectroscopy

The observed FTIR bands for the investigated $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ ternary glasses are assigned to the Te–O linkage vibration in [$\mathrm{TeO_4}$], [$\mathrm{TeO_3}$] units and the V–O linkage vibration in [$\mathrm{VO_4}$], [$\mathrm{VO_5}$] units (Figs. 3 and 4). We note that the addition of rare earth oxide modifier up to 20 mol% does not cause significant spectral changes, and therefore does not induce important structural changes.

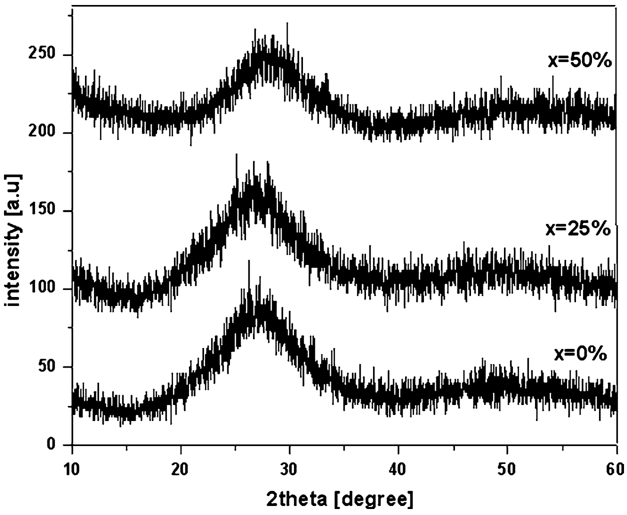

Fig. 1 X-ray diffraction patterns for $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ samples with $x = 0, 25, 50$ mol%

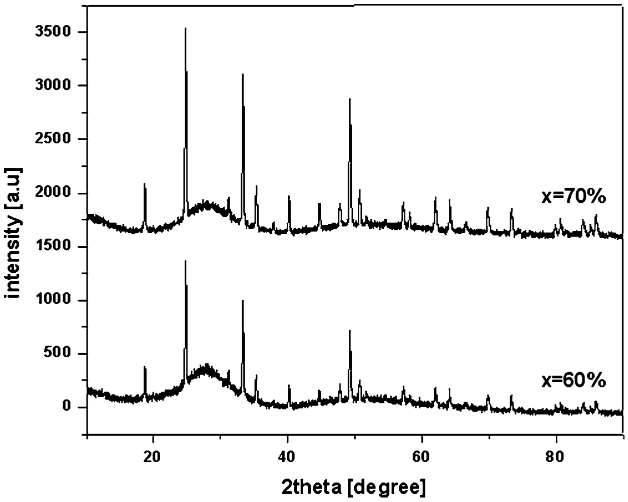

Fig. 2 X-ray diffraction patterns for $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ samples with $x = 60, 70$ mol%

The bands located around 460 cm^{-1}, in the range of 610–680 cm^{-1}, and 720–780 cm^{-1} are assigned the bending mode of Te–O–Te or O–Te–O linkages, the stretching mode [$\mathrm{TeO_4}$] trigonal pyramidal with bridging oxygen, and the stretching mode of [$\mathrm{TeO_3}$] trigonal pyramidal with non-bridging oxygen, respectively [6, 7].

In the case of pure $\mathrm{V_2O_5}$ glass it was reported [8] that $\mathrm{V^{5+}}$ ions exhibit both four- and five-fold coordination states, depending on the sample preparation conditions. The IR spectrum of both the pure crystalline and amorphous $\mathrm{V_2O_5}$ is characterized by the intense band in the range 1000–1020 cm^{-1}, assigned to the vibration of isolated V=O vanadyl groups in [$\mathrm{VO_5}$] trigonal bipyramids

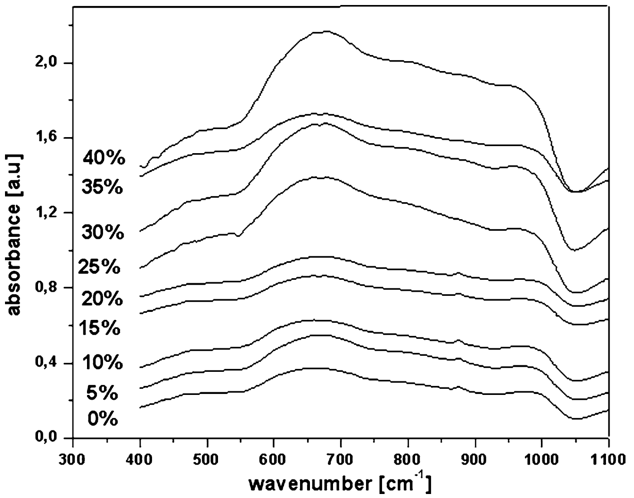

Fig. 3 FTIR spectra of the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ glasses for $x = 0$–40 mol% $\mathrm{Gd_2O_3}$

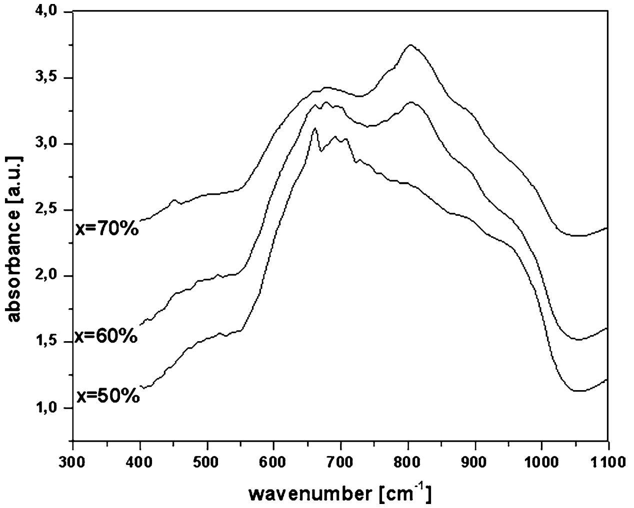

Fig. 4 FTIR spectra of the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ glasses for $x = 50$–70 mol% $\mathrm{Gd_2O_3}$

[9–11], the peak around 850–910 cm^{-1} assigned to the vibrations of $[\mathrm{VO_5}]$ units, and the band located about 950–970 cm^{-1} assigned to $[\mathrm{VO_4}]$ units [12–14].

The examination of the FTIR spectra of the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ glasses with $x = 0$–40 mol% (Fig. 3) and $x = 50$–70 mol% (Fig. 4) shows that the increase of $\mathrm{Gd_2O_3}$ content strongly modifies the characteristic IR bands as follows:

(i) The peak located at about 875 cm^{-1} increases with the increasing concentration of the gadolinium ions. As was previously mentioned, the presence of this band indicates the presence of $[\mathrm{VO_5}]$ units. By increasing the concentration of gadolinium ions from 25 to 70 mol% a prominent absorption appears at 882 cm^{-1}.

(ii) The intensity of the band from ~667 cm^{-1} increases with the increasing of the $\mathrm{Gd_2O_3}$ content up to 40 mol% and after that splits into three components located at ~663, 694, and 709 cm^{-1}. All these bands are attributed to the stretching vibrations in $[\mathrm{TeO_4}]$ units.

(iii) The intensity of the band centered at ~792 cm^{-1} increases slowly with the increase of the gadolinium ions, content up to 40 mol%, while for higher contents the band splits into four components located at 734, 744, 757, and 794 cm^{-1}.

(iv) The intensity of the band from ~975 cm^{-1} increases with the increasing content of $\mathrm{Gd_2O_3}$ and shifts to ~954 cm^{-1}. This band is due to the V–O stretching vibrations in $[\mathrm{VO_4}]$ units.

The IR data show that by increasing the $\mathrm{Gd_2O_3}$ content up to 40% causes a higher extent of vitreous network polymerization. After that, the significantly different shape of the IR spectrum for $x = 50\%$ $\mathrm{Gd_2O_3}$ compared to that for $x = 40\%$ reveals a drastic structural change occurring between these compositions due to the apparition of the $\mathrm{GdVO_4}$ crystalline phase, in agreement to the X-ray data.

In brief, the FTIR spectra of the studied glasses consist of four main bands and their structure is made up of $[\mathrm{TeO_3}]$, $[\mathrm{TeO_4}]$, tetrahedral $[\mathrm{VO_4}]$, and $[\mathrm{VO_5}]$ units, respectively. The presence of gadolinium cations in the glass structure lead to the appearance of a structural ordering process around the vanadium atoms as well as to an increase of the number of linked tellurium polyhedra.

Density

Figure 5 shows the variation of the density as function of the gadolinium oxide content of studied glasses. The estimated error for the determined density values was less than 0.2 g/cm^3.

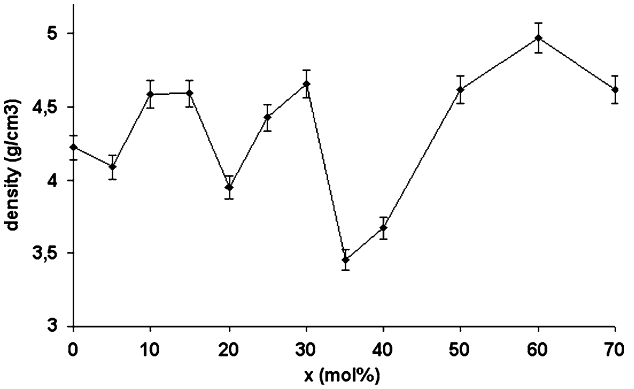

Fig. 5 The composition dependence of the density of the $x\mathrm{Gd_2O_3}(100-x)[7\mathrm{TeO_2}\cdot 3\mathrm{V_2O_5}]$ system where $x = 0$–70 mol% (the line is only a quide for the eye)

Note that the relation between the density and the gadolinium ions content is not linear and shows important variation between 3.5 and 5 g/cm^3. Such large density values were previously reported for the zinc–tellurite glasses dopped with samarium [15].

The density decreases abruptly when up to 5 mol% gadolinium oxide was added showing the formation of Gd–O–Te or Gd–O–V linkages, with strong Gd–O ionic bond [16, 17]. This modification of the density is due to a weakening of the cross-linking within the glass network [18].

The density increases from 3.45 to 4.97 g/cm^3 when the gadolinium oxide contents of the samples modify from 35 to 60 mol%. This could be explained by considering that the excess of oxygen may be accommodated in the glass network by the conversion of some [VO_4] to [VO_5] structural units, and of some [TeO_3] into [TeO_4] units.

Conclusions

FTIR spectroscopy and X-ray diffraction have been utilized to study structural changes produced by the variation of the Gd_2O_3 content in ternary $x Gd_2O_3(100-x)[7TeO_2 \cdot 3V_2O_5]$ glasses.

Structural changes produced by varying the Gd_2O_3 content of the samples consist in an increase of the extent of network polymerization up to 40 mol% and a drastic structural modification for $40 \leq x \leq 50\%$ leading to the apparition of the $GdVO_4$ crystalline phase. These results are supported by the density data when the density increases from 3.67 g/cm^3 for 40 mol% Gd_2O_3 to 4.61 g/cm^3 for 50 mol%. This compositional evolution of the structure could be explained by considering that the excess of oxygen may be accommodated by the conversion of some [VO_4] to [VO_5] structural units and of [TeO_3] into [TeO_4] units.

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