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Structural investigation of bismuth germanium system doped with gadolinium

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The local structure of the glasses and vitroceramics belonging to the $0.5Gd_2O_3 \cdot 99.5$ [xBi_2O_3 (1-x) GeO_2] system, with 0.12<x<0.875 were studied by differential thermal analyses (DTA), X-ray diffraction (XRD) technique electron paramagnetic resonance (EPR) and infrared spectroscopy (IR). Differential thermal analyses were used in order to investigate the thermal behavior of the vitreous samples and to establish much appropriate the heat treatment temperature for obtaining vitroceramic samples. The crystalline phases developed in the glass matrix by heat treatment were identified by X-ray diffraction. Was identified five structural phases in heat-treated samples $Bi_2Ge_4O_{11}$, $Bi_4Ge_3O_{12}$, Bi_2GeO_5, Bi_4GeO_8 and $Bi_{12}GeO_{20}$. EPR data show that the Gd^{3+} ions are homogeneously distributed in the host matrices and the presence of small antiferromagnetic interactions between the Gd^{3+} ions. IR measurements show the presence of GeO_4, GeO_6, BiO_6 and BiO_4 structural units.

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1. Introduction

Bismuth germanates are intensively investigated for applications in optical devices. The sillenite crystals, $Bi_{12}GeO_{20}$ are interesting for applications such as optical memories, holography or optical phase conjugating devices [1,2]. The eulytite crystals, $Bi_4Ge_3O_{12}$ are used as scintillators or, when doped with rare-earth elements, as laser materials [3,4]. The study of glassy systems, having properties similar to those of crystals, is of high interest because of the lower cost and easier production of glasses with respect to crystals. Vitreous germanates have been proposed as materials for optical waveguides, due to their transmission characteristics in the infrared region. In addition, the high Raman scattering cross-section makes these glasses good candidates for devices such as fiber-optic amplifiers [5]. In recent years, many studies on bismuth germanates and mixed crystals have been performed in order to understand their properties [6,7]. An attractive reason in studying these glasses also lies in the fact that they contain non-conventional glass formers such as Bi_2O_3.

In order to extend the available information concerning glasses containing gadolinium ions, in this work we performed a systematic investigation of the $0.5Gd_2O_3 \cdot 99.5(xBi_2O_3 \cdot (1-x)GeO_2)$ system with 0.12<x<0.875 using DTA, X-ray diffraction, IR and EPR methods.

2. Experimental

Bismuth germanate glasses were obtained by oxide mixtures melting, starting from the pure Bi_2O_3, GeO_2 and Gd_2O_3. The powder components were mixed and then melted in an electric furnace in air atmosphere at temperature 1250 °C for 15 minutes. The time at the melting temperature was chosen to have good mixing of the components while preventing the evaporation of the highly volatile bismuth oxide. The glasses were obtained by quenching onto a brass plate at room temperature.

All the samples were heat treated at the 600 °C for 24 hours in order to obtain crystalline phases in the glass matrix. The heat treatment temperature was established by DTA. The DTA traces of the glassy samples were recorded using MOM thermal analysis system in the temperature range 30–800 °C. The heating rate was 10°C/ min.

The vitreous phase was ascertained from the X-ray diffraction pattern of the as prepared samples using a Bruker X-ray diffractometer. Powder samples were used for the X-ray diffraction measurements. The crystalline phases obtained after heat treatment were identified by the same method.

The IR spectra of the samples were recorded in the wavenumber range 400-2000cm^{-1} at room temperature. The measurements were made by IR Equinox 55 spectrometer using "KBr pellet" technique, with the maximum resolution of 0.16 cm^{-1}.

The local structural order in the obtained samples was investigated by infrared spectroscopy and around Gd^{3+} ions by electron paramagnetic resonance, before and after heat treatment.

The EPR measurement was made using an EPR spectrometer ADANI PS 8400 system, in the magnetic field range of 700-4700 Gauss, in the X-band, at room temperature on powder samples.

3. Results and discussion

Fig. 1 shows the DTA, TG and DTG traces of the sample with x=0.67. The T_g temperature is assigned to the glass transition and characterises the beginning of the structural transformation. The first exothermic peak, around at 575 °C, corresponds to the exothermic effect of first crystallization process. This peak for other samples are located between 575 and 660 °C. No weight loss of the samples was observed from the TG curve. The heat treatment temperature at 600 °C favors partial crystallization of the investigated samples.

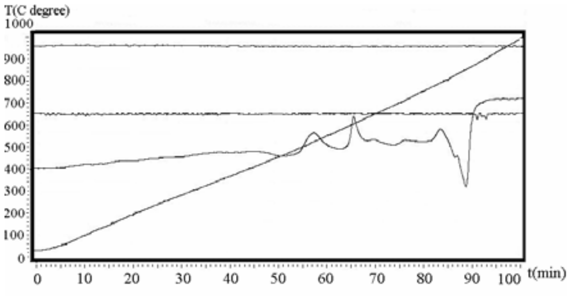

Fig. 1. DTA curves for x=0.67 sample.

Using the X-ray diffraction measurements was tested the vitreous nature of the glass matrices. All untreated samples were finded to be non-crystalline. In the heat-treated samples were identified some crystalline phases (Fig. 2).

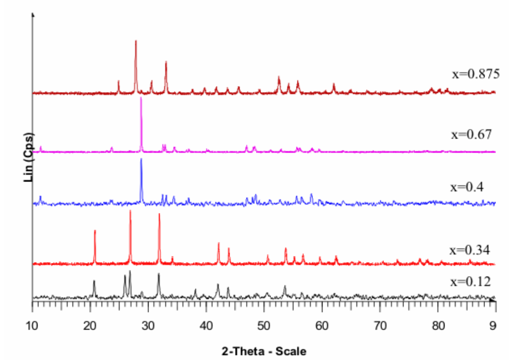

Fig. 2. X-ray diffractions function of x for vitroceramic samples.

The sample with x=0.12 is a mixture of $Bi_4Ge_3O_{12}$ (4:3), Bi_2GeO_5 (2:1) phases and a small amount of germanium oxide. For the sample with x=0.2 the $Bi_2Ge_4O_{11}$ (1:2) phase was observed.

The sample with x=0.34 contains the $Bi_4Ge_3O_{12}$ (4:3) phase with a cubic structure and the following parameters: a=b=c=10.497 Å and $\alpha=\beta=\gamma=90^0$. This phase is formed from GeO_4 and BiO_4 structural units.

The sample with x=0.4 contains the Bi_2GeO_5 (2:1) phase with a orthorhombic structure and the following parameters: a=15.69Å, b=5.492Å c=5.383Å and $\alpha=\beta=\gamma=90^0$.

For the sample with the x=0.67 was identified the structural phase Bi_4GeO_8 (4:1), phase that contains the BiO_6 and GeO_4 structural units [8].

The sample with x=0.875 crystallize in a new structural phase $Bi_{12}GeO_{20}$ (12:1). This phase is a cubic one, having the following parameters: a=b=c=10.147 Å and $\alpha=\beta=\gamma=90^0$ and containing the BiO_6, GeO_4 and BiO_4 structural units [8]. The BiO_4 structural unit was explained using a pyramidal model by Hudon [9]. This structure was suggested also by Takeda and Omote [10,11]. The electronic configuration of Bi^{3+} is particular: 2+ cation with a lone pair of electrons, this lone pair is located at the apex of a square pyramid bounded by four oxygen. The lone pair of electrons is located on the opposite side of the plane formed by the four oxygens and effectively shields the top of the pyramid [12]. On the apex of the pyramid is realized the Bi-Bi binding, with the next BiO_4 unit (Fig. 3). The same type of pair was proposed for Bi^{3+} in binary germinate [10,11].

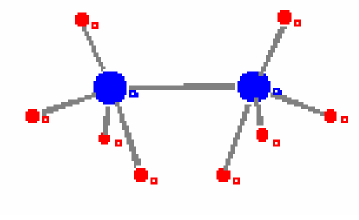

Fig. 3. The pair of BiO_4 structural units.

Fig. 4 present the IR spectra of studied glass samples. The IR spectra of the vitreous system contains two major absorption bands in the wavenumber range 440-560 cm^{-1}, 725-875 cm^{-1} and also a small band located at 1637 cm^{-1}.

In the first wavenumber range 440-560 cm^{-1} were observed three different values at 430, 445, 470cm^{-1} for the samples with high bismuth oxide x=0.5, 0.67 and 0.875 respectively. The band at 430 cm^{-1} is assigned to the stretching vibration of $Bi-O^-$ bonds in distorted BiO_6 octahedra [13]. The shift to higher wavenumber for samples with x=0.67 and 0.875 is due to the structural relaxation of BiO_6 units [14].

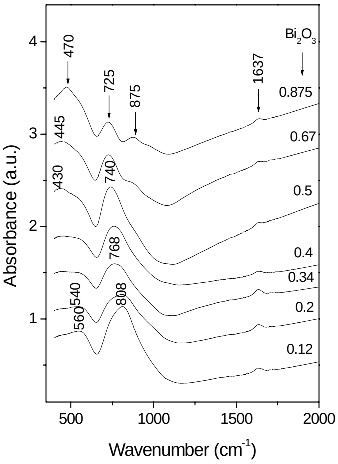

Fig. 4. IR spectra of glass samples function on x.

The absorption band situated at 470 cm^{-1} is much better evidenced compared with the bands 430, 445 cm^{-1} and is assigned beside to the $Bi-O^-$ bonds vibration into

BiO_6 units [13] also to the $Bi-O^-$ total symmetric bending vibration in the BiO_4 units [15]. In these samples the number of BiO_6 units is higher compared with the BiO_4 units. For the sample with low bismuth oxide was identified two absorption bands at 560 cm^{-1} and 540 cm^{-1} absorption bands present as a shoulder in all IR spectra where the Ge-O-Ge and O-Ge-O stretching and deformation mode are active in GeO_4 units [16,17]. Also in this wavenumber range are active the $Bi-O^-$ double degenerate stretching vibration in BiO_4 units [16].

The second strong absorption band was identified in the wavenumber range 725-875cm^{-1}. In this range the asymmetric Ge-O-Ge stretching vibration mode in GeO_4 units is present. For this range was observed a decrease in intensity of the absorption with the increasing of the bismuth oxide content in the glass. For the sample with lower concentration of bismuth was observed a strong absorption band at 808 cm^{-1} with a shoulder at 730cm^{-1}. By increasing of bismuth content was observed a shift of this band to low wavenumbers. This shift could be explained through local structural distortion around germanium with increasing of bismuth content in the matrix. For the sample with x=0.875 the disappearance of the 740 cm^{-1} band assigned to the asymmetric Ge-O-Ge straching vibration in GeO_4 tetraedra in which germanium assumes fourfold coordination and the appearance of two maximum at 725 cm^{-1} and 875 cm^{-1} indicate important modification in the germanium environment. At these wavenumber values are presented the Ge-O-Ge and O-Ge-O stretching and deformation mode in GeO_4 and GeO_6 units respectively [13,16].

In the higher wavenumber region over 1000 cm^{-1} was observed one band at 1637 cm^{-1} that corresponds to the vibrations of the Bi-O-Bi and Bi-O-Ge binding.

In Fig. 5 are presented the IR spectra of the samples after heat treatment. The IR spectra for the heat-treated samples exhibit some changes, those illustrated by the narrowing of previous band and appearance of the new bands in the spectra.

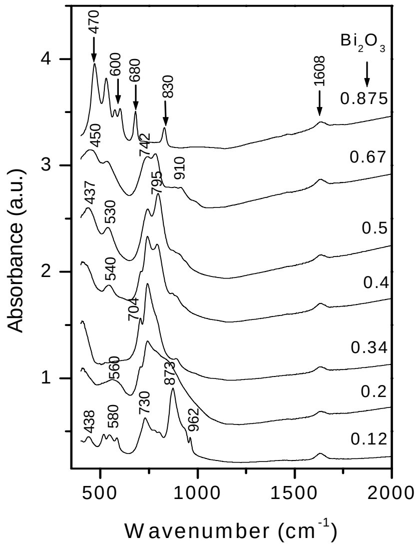

Fig. 5. IR spectra of vitroceramic samples function of x.

For the samples with x=0.12 the band situated at 438 cm^{-1} are assigned to the $Bi-O^-$ bond vibration in BiO_6 structural units[14,15]. The infrared bands situated at 730 and 873 cm^{-1} are more intense and correspond to the Ge-O-Ge and O-Ge-O stretching and deformation modes in GeO_4 and GeO_6 units respectively [13]. By comparing with the IR spectrum of the corresponding glass sample we can assume that band centred at 808 cm^{-1} is due to the presence of the same type of structural units, much distorted, but the ratio between them are changes. While in the glass sample preponderant are the GeO_4 units in the crystallized sample the majority is formed by GeO_6 units due to the crystalline GeO_2 phase[16] evidenced by X-ray diffraction data in this sample. For x=0.2 and 0.34 are present two infrared band situated at 560 and 742 cm^{-1} where are active the Ge-O-Ge stretching and deformation mode in GeO_4 units [14]. The shoulders at 870 cm^{-1} show that the GeO_6 units are still present in a relatively large amount.

The sample with x=0.4, 0.5 and 0.67 present one strong absorption in the wavenumber range 742-795 cm^{-1} indebt to the Ge-O-Ge stretching and deformation mode in GeO_4 units.

The new bands at 540 and 530 cm^{-1} where the $Bi-O^-$ double degenerate stretching vibration are active in BiO_4 and 437 cm^{-1} stretching vibration of $Bi-O^-$ bonds in BiO_6 octahedra are also present in the IR spectra of these samples[13]. The band at 430-450 cm^{-1} assigned to $Bi-O^-$ bonds in BiO_6 octahedra and 530-540 cm^{-1} $Bi-O^-$ bonds in BiO_4 are resolved.

For the sample with x=0.875 the bands situated in 742-782 cm^{-1} range disappear and the new band situated at 830 cm^{-1} assigned to the Ge-O-Ge stretching vibration in GeO_4 units are present. Are more intense for this sample the spectral region 470-680 cm^{-1} where the bismuth structural units are present. The band at 470 cm^{-1} assigned to the vibration of $Bi-O^-$ bonds in BiO_6 units[13] and the $Bi-O^-$ total symmetric bending vibration in the BiO_4 units and the band at 530 cm^{-1} where the $Bi-O^-$ double degenerate stretching vibration in BiO_4 are active[15] and are in agreement with the presence of phase $Bi_{12}GeO_{20}$. The bands at 600 and 680cm^{-1} are due to the Ge-O-Ge bridge bending vibration in GeO_4 units.

Due to their relatively large ionic radius it is more probable that Gd^{3+} ions (r_{Gd} =1.20Å) will occupy in these matrices Bi^{3+} ions sites (r_{Bi} =1.20Å) than in Ge^{4+} ions sites (r_{Ge} =0.52Å). Both sites of Bi^{3+} ions from BiO_6 and BiO_4 are possible sites for Gd^{3+} ions but taking into account the preference of gadolinium for higher coordination we assume that Gd^{3+} ions occupy sites with six oxygen's. The EPR spectra for the glass samples with low concentration of Bi_2O_3 (x ≤0.4) are illustrated in Fig. 6 and for with high bismuth content in Fig. 7.

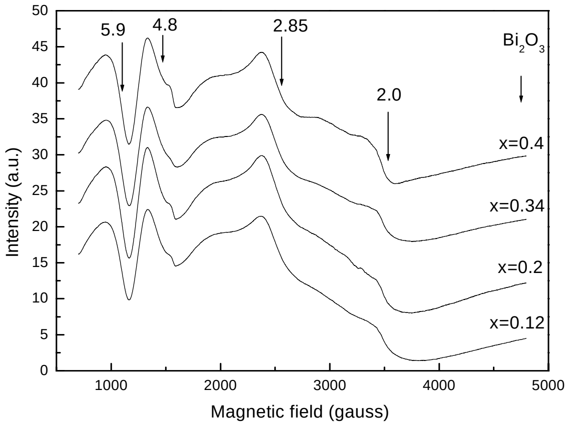

Fig. 6. EPR spectra of glass sample with x=0.12, 0.2, 0.34 and 0.4.

The relative correspondence of EPR spectra on glass composition shows that the Gd^{3+} environment is quite the same. The changes in the local structure of the matrix by the increasing of bismuth oxide content are reflected in the shape evolution of the Gd^{3+} ions EPR spectra. The EPR spectra of these glasses show the resonance lines at g ~2; 2.85; 4.8 and 5.9 being typical for Gd^{3+} ions uniform distributed in disordered matrices [18]. The two EPR lines having almost the same intensity and corresponding to the g ~ 4.8; 5.9, are observed at low magnetic field. The line with g ~4.8 corresponds to the Gd^{3+} ions with a coordination number lower than six ($N_c \leq 6$), located in sites with intense crystal fields [18-20].

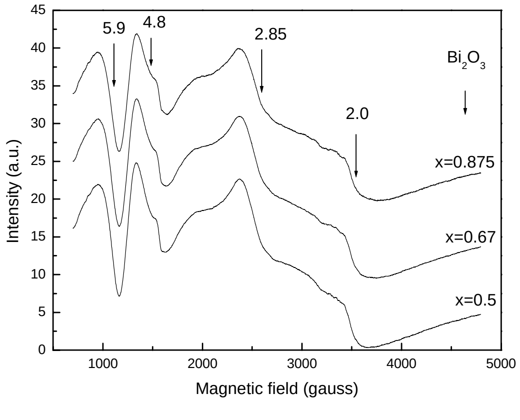

Fig. 7. EPR spectra of glass sample with x=0.5, 0.67 and 0.875.

The width of the lines, particularly the line with g ~5.9 show that some Gd^{3+} ions dimmers are experiencing antiferomagnetic exchange interaction[21].

The EPR spectra for the crystallized samples after 24 hours heat treatment at 600 °C are presented in Fig. 8 and Fig. 9. In the EPR spectra of these samples beside other line narrowing and several changes appear.

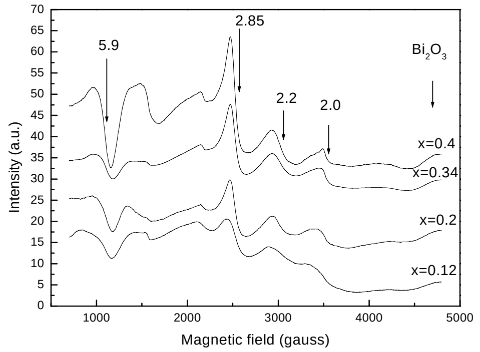

Fig. 8. EPR spectra of vitroceramic sample with x=0.12, 0.2, 0.34 and 0.4.

For the first three samples (x=0.12; 0.2; 0.34) where according to XRD results, the 1:2 and 4:3 crystalline phases have been observed the intensity of the resonance lines at g ~5.9; 4.8 is attenuated in comparison with that corresponding to untreated samples, while for sample with x= 0.4 only the intensity of the line at g ~4.8 decreases.

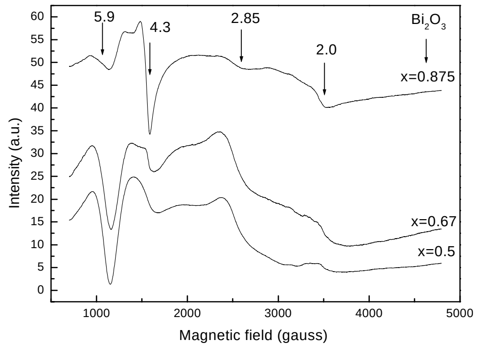

Fig. 9. EPR spectra of vitroceramic sample with x=0.5, 0.67 and 0.875.

The intensity of the line with g ~2.85 increases with increasing of the bismuth oxide concentration and in according with the simulated Gd^{3+} ions spectrum function on the crystal field[22] show that a fraction of Gd^{3+} ions are experiencing stronger crystalline field that in the corresponding glasses. For these samples with small concentration of the Bi_2O_3 an additional resonance line with g ~2.2 can be observed.

For vitroceramic samples with high bismuth oxide content the line at g ~2.85 become larger and almost disappeared for sample with x=0.875. The lines at g ~4.8, 2.2 and 2 decrease in intensity for samples with x = 0.5 and 0.67. but the intensity of the line with g~4.3 increase. The sample with x=0.875 reveals a strong absorption at g ~4.3 showing that Gd^{3+} ions we occupying new sites in developed crystalline phase. This new phase was identified as $Bi_{12}GeO_{20}$ (12:1) phase by X-ray diffraction. The EPR results confirm that in majority Gd^{3+} ions occupy the sites of cubic symmetry with strong crystalline field [20], specific for this phase.

The analyse of the EPR spectra for investigated glasses and vitroceramic samples confirm that Gd^{3+} ions are occupying hexacoordinated Bi^{3+} ions sites but their environment is quite distorted even in a very well crystallized samples.

4. Conclusions

The structure of glasses and vitroceramics belonging to the GeO_2 -Bi_2O_3 system prepared by the melting technique as was proved by IR results is mainly form from GeO_4 and BiO_6 but also the GeO_6 and BiO_4 have been identified.

For the glass sample with low content of bismuth the GeO_4 units are predominant but with increasing of the bismuth in the matrix are present also the BiO_6, GeO_6 and in small amount the BiO_4 units.

In the vitroceramic samples the $Bi_2Ge_4O_{11}$, $Bi_4Ge_3O_{12}$, Bi_2GeO_5, Bi_4GeO_{11} and $Bi_{12}GeO_{20}$ phases have been identified. The structure of these phases is formed the same type of structural units as compositional corresponding glasses but these are less distorted.

The Gd^{3+} EPR spectra for the glass samples are almost independent of composition with resonance lines at g ~2; 2.85; 4.8 and 5.9 and are attributed to the Gd^{3+} ions situated in the sites with relatively large crystalline field. This support the assumption that Gd^{3+} ions occupy the same type of sites hexacoordinated with oxygen's, like Bi^{3+} ions in octahedral BiO_6 units. Beside these sites that are present in glass and vitroceramic samples, new sites are evidenced for Gd^{3+} ions, particulary in the vitroceramic sample with highes bismuth content where the majority of gadolinium ions are placed in sites of cubic symmetry with strong crystalline field.

These EPR results show also that the Gd^{3+} ions are homogeneously distributed in the host glass but some Gd^{3+} dimmers are formed dimmers that are experiencing dipolar interactions.

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