

THE INFLUENCE OF MANGANESE AND IRON CATIONS ON Bi₂O₃-GeO₂ GLASS STRUCTURE

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Abstract: Samples belonging to 97% [xBi₂O₃(1-x)GeO₂]3%M (M = MnO and Fe₂O₃) glass systems with different Bi/Ge nominal ratios ($0.20 \leq x \leq 0.875$) have been investigated by means of micro-Raman spectroscopy. The influence of manganese and iron cations on vitreous Bi₂O₃ and GeO₂ networks as well as the structural changes around bismuth and germanate atoms have been evidenced by comparing spectra recorded on samples containing different dopants and the same concentrations of Bi₂O₃ and GeO₂. The structural units that built up the bismuthate and germanate networks in the case of both dopants have been also reported.

Key words: Glasses, micro-Raman spectroscopy, manganese cations, iron cations.

1. INTRODUCTION

Glasses containing bismuth have been investigated for their optical and physical properties [1-4], while glasses containing heavy metal oxides such as Bi₂O₃ in combination with GeO₂ have been studied for their possible use as optical waveguides in the infrared region [5]. Therefore, in order to extend the applicability area of glasses based on Bi₂O₃ and GeO₂, their doping with different cations together with their comparative structural characterization represent a research topic of major interest.

The goal of the present study was to obtain by means of micro-Raman spectroscopy specific data regarding the local structure of manganese and iron doped Bi₂O₃-GeO₂ glasses and to evidence the influence of the above-mentioned dopants on the Bi₂O₃ and GeO₂ structural units. The interest for this study is further increased by the presence of two network forming oxides, the classical GeO₂ and the unconventional Bi₂O₃, the possible participation in the glass structure of both germanate and bismuth oxides with two possible coordinations, i. e. tetrahedral [GeO₄] and octahedral [GeO₆] [6-9] and [BiO₃] pyramidal and [BiO₆] octahedral units [10-13].

2. EXPERIMENTAL

The samples were prepared in laboratory using as starting materials Bi₂O₃, GeO₂, MnO and Fe₂O₃ of reagent grade purity (99.9%). The components have been mixed in

proportions corresponding to the desired compositions, then they were melted in sintered corundum crucibles. The mixtures have been heated in an electric furnace at 1100°C and maintained at this temperature for 10 minutes, then they were quickly undercooled at room temperature by puring onto stainless steel plates. These glass systems are fairly hygroscopic, and therefore special care has to be taken for protection against hydrolysis. All the samples have been analyzed by X-ray diffraction and no crystalline phase was evidenced.

The Raman measurements were performed on a Dilor Labram system equipped with an Olympus LMPlan FI 50 microscope objective, an 1800 lines/mm grating and an external laser with an emission wavelength of 514 nm. In the recording of the micro-Raman spectra a power of 100 mW on the sample has been employed. The focal length of the spectrometer is 300 mm and the slit used for all measurements was 80 μm. Thus, the spectral resolution was about 4 cm⁻¹.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the Raman spectra of 97% [xBi₂O₃(1-x)GeO₂]3%M (M = MnO and Fe₂O₃) glasses with compositions in the range 0.20 ≤ x ≤ 0.875. Kamitsos et al. have pointed out in a study [8] on glasses containing GeO₂ that the formation of connected [GeO₆] octahedral units is evidenced in the Raman spectra as bands at ca. 315 and 590-630 cm⁻¹. On the other hand, the presence of [BiO₃] pyramidal units in glasses based on Bi₂O₃ is clearly revealed only when infrared investigations are done [6, 12, 13, 14]. Taking into account all these information concerning the structural units which built up the Bi₂O₃ and GeO₂ structure we can affirm that in the present study the Bi₂O₃-GeO₂ matrices consist preponderantly of [GeO₄] tetrahedra and [BiO_x] (x = 3 and/or 6) polyhedra. By comparing the Raman spectrum recorded on manganese doped Bi₂O₃-GeO₂ glass for x = 0.20 (Fig. 1) with the corresponding spectrum of the iron doped sample (Fig. 2) many similarities concerning the number and position of the bands can be seen. However, one can observe a clear difference between the above-mentioned spectra, namely, the increase in intensity of the Raman band at 420 cm⁻¹ attributed to the symmetric stretching vibration of the oxygen atoms [8], when MnO is present in the structure of the investigated glasses.

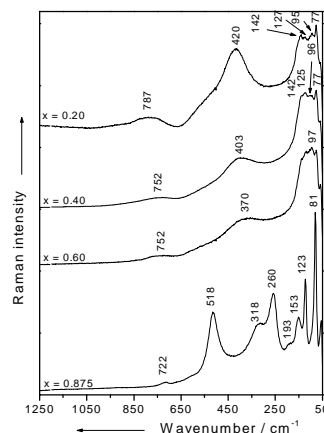


Fig. 1 - Micro-Raman spectra of 97% $[\text{xBi}_2\text{O}_3(1-\text{x})\text{GeO}_2]$ 3%MnO glasses.

This spectral behaviour could be interpreted as an influence of manganese cations expressed in terms of ordering of $[\text{GeO}_4]$ tetrahedra. It should be mentioned that the Raman bands that arise in the spectral region between 50 and 200 cm^{-1} are usually related to vibrations involving motions of the Bi^{3+} cations [10, 12, 13]. However, a very precise assignment of these vibrational modes becomes very difficult if the possible participation of germanium cations and the evolution of these bands for different concentrations are considered.

By increasing the Bi_2O_3 concentration, $x = 0.40$, one remarks that the structural arrangement of the $[\text{GeO}_4]$ tetrahedra is strongly distorted. Thus, for the iron doped glass the major structural change is given by the appearance of a new broad band at 380 cm^{-1} instead of that centered at 420 cm^{-1} for $x = 0.20$, which is assigned to the Bi-O-Bi stretching vibration, a small contribution to its appearance could have the above-mentioned oxygen atoms vibration in the GeO_2 structure.

In the case of the other dopant, the manganese cations seems to preserve better than the iron cations the structural arrangement of the $[\text{GeO}_4]$ tetrahedra. This supposition is demonstrated by the presence for $x = 0.40$ of a broad band at 403 cm^{-1} , which can be seen as a convolution of two bands centered around 380 and 420 cm^{-1} . However, the effect of the manganese cations on the germanium structural units is manifested by the increase of the non-bridging oxygen number, this fact being mirrored in the Raman spectrum by the shift of the band from 787 cm^{-1} for $x = 0.20$ to 752 cm^{-1} for $x = 0.40$.

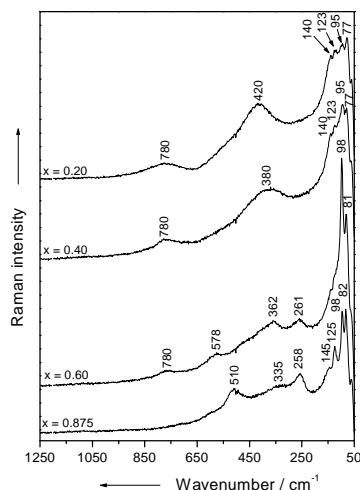


Fig. 2 - Micro-Raman spectra of 97%[xBi₂O₃(1-x)GeO₂]3%Fe₂O₃ glasses.

For $x = 0.60$ the majority of the bands observed in the Raman spectra of the doped glasses belong to the Bi₂O₃ structural unit vibrations, the only evidence of the GeO₄ stretching vibration being the bands at 752 and 780 cm⁻¹. Thus, while for the manganese doped glass the structural ordering process of the Bi₂O₃ structural units occurs slowly, only at this concentration appearing the broad band at 370 cm⁻¹ assigned to the Bi-O-Bi vibration, in the case of the iron doped glass an obvious order of bismuthate polyhedra can be evidenced both by the appearance of very sharp and intense bands in the 50-180 cm⁻¹ spectral region, in which the Bi³⁺ cations are preponderantly involved, as well as by the existence of new distinguished bands in the spectral range between 200 and 600 cm⁻¹, which are due to the Bi-O-Bi and Bi-O vibrations [14-16]. This conclusion is supported by the fact that the half-width of these bands is considerably reduced compared to the corresponding bands observed in the spectra recorded for the samples with smaller Bi₂O₃ content, especially of those observed in the first spectral domain, being also known [17] that the width of the Raman bands in disordered materials is a measure of the disorder in the structure.

For high Bi₂O₃ content, $x = 0.875$, the Raman spectra illustrated in Figs. 1 and 2 reveal very interesting and unexpected changes concerning the manganese doped glass structure relative to those observed for the samples discussed before. Thus, if the presence of all bands in the 50-180 cm⁻¹ and 200-600 cm⁻¹ spectral domains shown in Fig. 2 denotes the constant structural arrangement of the [BiO_x] ($x = 3$ and/or 6) polyhedra, a very intense ordering process of the structural units, which built up the Bi₂O₃ network, together with a depolymerization process of the [GeO₄] tetrahedra occur in the manganese doped glass structure (Fig. 1). These results are evidenced by the appearance of intense and distinguished bands in the above-mentioned regions and the relative significant shift towards lower wavenumbers of the band at 752 cm⁻¹ for $x = 0.60$. After a very careful analysis of the Raman spectra of the samples with $x = 0.875$ one can see the more pregnant influence of the manganese cations on the bismuthate polyhedra order compared to that of the iron cations. This influence is indicated by the appearance of strong and very strong Raman bands that arise at this concentration in the low wavenumber range (Fig. 1), their half-width showing the validity of the supposition made before. On the other hand, as it was related in a previous study [8], the increase of the amount of other oxide in the structure of germanate glass could produce an increase of the non-bridging oxygens number. This effect is present also in this study (Fig. 2) and is manifested by the appearance of the small band at 722 cm⁻¹ attributed to the symmetric stretching vibration of Ge-O bonds. The presence of this Raman band at a lower wavenumber value compared to its position at smaller Bi₂O₃ concentrations could be explained as a consequence of the appearance of a depolymerization process of the GeO₂ network, which is expected to relieve some of the network strain and to increase therefore the intertetrahedral angle in a Ge-O-Ge configuration. By inspecting the Raman spectrum of iron doped glass one observes the missing of a band between 700 and 800 cm⁻¹. Therefore, we affirm that despite the fact that the manganese dopant induces a higher influence on the bismuthate structural units arrangement compared to the iron dopant, the presence of the latter dopant leads to the appearance of a significant breaking of the [GeO₄] tetrahedral structure.

4. CONCLUSION

Micro-Raman spectroscopy has been used to study the manganese and iron dopant cations influence on the $\text{Bi}_2\text{O}_3\text{-GeO}_2$ matrices for different Bi/Ge nominal ratios ($0.20 \leq x \leq 0.875$). It was found that the germanium cations take part in the structure of these glasses as $[\text{GeO}_4]$ tetrahedra. The manganese cations favourize the occurrence of a structural ordering process of the GeO_2 structural units for small Bi_2O_3 concentration ($x = 0.20$) and of the $[\text{BiO}_x]$ ($x = 3$ and/or 6) polyhedra for high Bi_2O_3 concentration ($x = 0.875$). The iron cations participation leads to the appearance of a gradual ordering of the Bi_2O_3 structural units for $0.20 \leq x \leq 0.60$ compared to that caused by the manganese cations, which is a slow process. For high Bi_2O_3 content ($x = 0.875$) it was observed the depolymerization of the GeO_2 structure for both doped glass systems.

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