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Vibrational spectroscopic study on iron doped silica-bismuthate glasses and glass ceramics

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Fourier transform infrared (FTIR) and Raman spectroscopic data obtained for iron doped silica-bismuthate glasses were used to investigate the changes induced in the local structure of samples as the ratio between Bi_2O_3 and SiO_2 content changes from 9 to 0.66. The environment of constituent cations was investigated both in vitreous and partially crystallised samples of same composition. Progressive substitution of Bi_2O_3 by SiO_2 contributes to the structural relaxation of vitreous network and enhances glass stability. By crystallisation heat treatment the structural units appear to be more uniform as it results from the narrowing of corresponding IR and Raman bands. FTIR data show that more affected by composition and heat treatment is the environment of bismuth than that of silicon. Developing of polycrystalline phases in vitreous matrices was investigated also by X-ray diffraction.

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1. Introduction

Despite the fact that Bi_2O_3 is not a classical glass network former, due to its high polarizability, in the presence of conventional glass formers, it may build a glass network of [BiO_3] pyramids [1, 2]. In all optical switching and broadband amplification devices are used glasses based on bismuth oxide [3] characterised by high non-linear optical susceptibility. Bismuth-silicate glasses acquired special applications as low loss optical fibres, infrared-transmitting materials or as active medium of Raman-active fibre optical amplifiers and oscillators [4-7]. Bismuth based glasses are also used to produce after appropriate annealing high temperature superconductors with controllable microstructure [8-10].

However, the structural role played by Bi_2O_3 in glasses without or with low content of conventional glass formers, so called heavy metal glasses, is complicated and poorly understood. The problem is complex because the [BiO_n] polyhedra are highly distorted due to lone pair electrons and consequently the structural model for $xSiO_2 \cdot (100\text{-}x)Bi_2O_3$ glasses is still under discussion [11, 12].

Several techniques have been employed in the attempt to identify the local environment of the different elements in bismuthate glasses. Micro-Raman and infrared spectroscopy can provide important information on the local structure in vitreous and ceramic materials [13-22]. Due to the lack of structural long range order in amorphous materials a unambiguous assignment of the structural groups is not possible without comparing their spectra with those of corresponding crystalline counterparts.

This paper is focused on the structural changes induced in iron doped silica-bismuthate glasses by progressive replacing of Bi_2O_3 with SiO_2 and by crystallisation heat treatment.

2. Experimental

Glass samples belonging to $0.01Fe_2O_3 \cdot 0.99[xSiO_2 \cdot (100\text{-}x)Bi_2O_3]$ system ($10 \leq x \leq 60$ mol %) were prepared using $BiO(NO_3) \cdot H_2O$, SiO_2 and Fe_2O_3 of analytical grade purity. Corresponding amounts of reagents were mixed and melted in sintercorundum crucibles for 10 minutes at 1200°C. The samples were obtained by fast quenching of the melts cast and pressed between steel plates at room temperature. X-ray powder diffraction analysis did not reveal any crystalline phase. The vitreous samples were partially crystallised by heat treatment applied at 600°C for 24 hours.

The FTIR spectra were recorded with a resolution of 2 cm^{-1} on a Bruker FT-IR EQUINOX 55 spectrophotometer at room temperature using the KBr disk technique.

The micro-Raman spectra were recorded on a Bruker Raman FRA 106/S spectrophotometer at room temperature.

3. Results

The silica-bismuthate samples doped with 1 mol % Fe_2O_3 are transparent and coloured from yellow-brown to red-brown as SiO_2 content increases from 10 to 60 mol %. The X-ray diffraction patterns show a very large peak typical for glass systems and prove their vitreous state. The crystalline phases identified from X-ray diffractograms of heat treated samples (Fig. 1) are $Bi_{12}SiO_{20}$ and a δ solid solution $Bi_{5.6}Si_{0.5}O_{9.4}$ [23]. The

$Bi_{12}SiO_{20}$ phase is present in samples with $10 \leq x \leq 30$ and $Bi_{5.6}Si_{0.5}O_{9.4}$ phase in samples with $40 \leq x \leq 60$.

In Figs. 2 and 3 are shown the IR absorption spectra for glass and glass ceramic samples, respectively, recorded between 400 and 1000 cm^{-1}, the spectral range wherein the bands assigned to $[BiO_n]$ and $[SiO_4]$ structural units are located.

In Figs. 4 and 5 are shown the micro-Raman spectra of glass and glass ceramic samples, recorded between 0 and 2000 cm^{-1}, the spectral range where the bands assigned to $[BiO_n]$ and $[SiO_4]$ structural units are located.

4. Discussion

The crystalline phases $Bi_{12}SiO_{20}$ and $Bi_{5.6}Si_{0.5}O_{9.4}$ identified in X-ray diffractograms of heat treated samples with $x \leq 50$ (Fig. 1) evidence different configurations of the component atoms in phases of almost the same Bi/Si ratio and same oxygens number ($Bi_{12}SiO_{20}$ vs. $Bi_{11.2}SiO_{18.8}$).

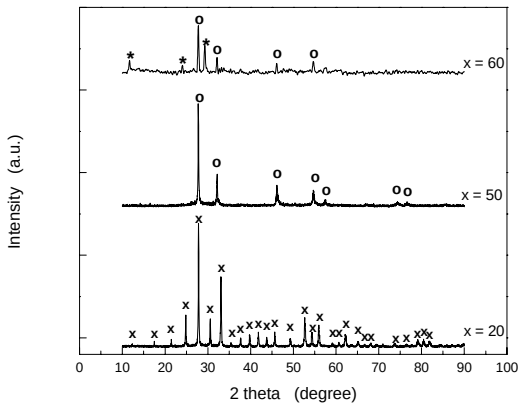

*Fig. 1. X-ray diffraction pattern of glass ceramics samples (**x**-$Bi_{12}SiO_{20}$, **o**-$Bi_{5.6}Si_{0.5}O_{9.4}$ and ***-Bi_2SiO_5).*

The expected crystalline phases with higher silicon content, like Bi_2SiO_5 [24], are observed, in a low amount, only for the sample with x=60. The development of 12:1 and δ type crystalline phases in glass samples with $x \leq 50$ shows that in these glasses, which appear macroscopic completely homogeneous, there are small regions rich in silicon, quite stable and regions rich in bismuth, that will easily crystallise in 12:1 and/or δ phase. It was suggested [12] that the structure of glasses with x = 50 is similar with that of Bi_2SiO_5 crystal, that is a structure formed from continuous $[SiO_n]$ chains placed between double layers of $[BiO_n]$ units. The growth of a δ crystalline phase in our sample with x = 50 instead of the expected Bi_2SiO_5 phase support the above invoked phase separation rather than a layered structure.

The IR spectra show structural changes both with composition and heat treatment. For the vitreous samples (Fig. 2) are recorded IR bands around 480 and 610 cm^{-1} and very large shoulders around 730 and 860 cm^{-1}.

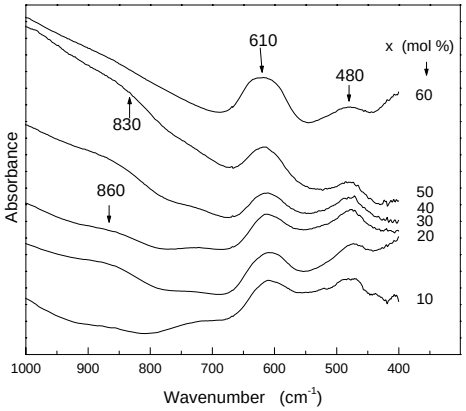

Fig. 2. FTIR spectra of glass samples.

The expected structural units building the glass network of the investigated samples are $[BiO_3]$ pyramidal, $[BiO_6]$ octahedral and $[SiO_4]$ tetrahedral units. The bands around 480 cm^{-1} can be assigned both to Si–O–Si bend vibrations and Bi-O bonds vibration in $[BiO_3]$ and $[BiO_6]$ units [13-17]. The IR absorption bands around 610 cm^{-1} can be assigned to internal vibration modes of $[SiO_4]$ structural units [19] while the shoulder at 860 cm^{-1} is related to vibrations of $[BiO_6]$ octahedral units [20-22]. It is also remarked that the position of the weak shoulder arising around 860 cm^{-1} for x = 10 and assigned to $[BiO_6]$ units shifts to lower wavenumbers as SiO_2 content increases and it appears around 830 cm^{-1} for x = 50. The shoulder related to a band at 830 cm^{-1}, that is assigned to $[BiO_3]$ units, points out that this low coordinated bismuth species are integrated in the glass matrix as network former [14].

By inspecting the IR spectra obtained from heat treated samples (Fig. 3) one observes the occurrence of new absorption bands around 530 and 830 cm^{-1} for the samples with x = 10, 20 and 30, where the main crystalline phase is $Bi_{12}SiO_{20}$. The band around 530 cm^{-1} is assigned to the Bi-O bond vibrations in $[BiO_3]$ and/or $[BiO_6]$ units while that around 830 cm^{-1} is associated to Bi-O bond vibrations only from $[BiO_3]$ units [14, 21, 22]. These new bands are not recorded for the partially crystallised samples with x = 40, 50 and 60, but for x = 60 a weak band appears around 855 cm^{-1} and is assignable to $[BiO_6]$ units.

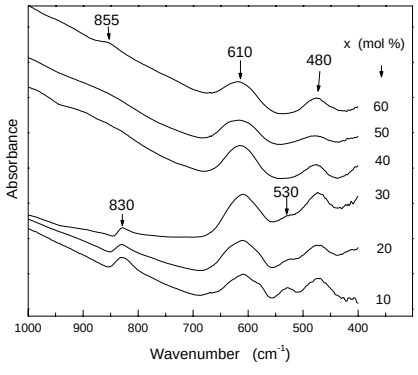

Fig. 3. FTIR spectra of glass ceramics samples.

For the vitreous samples (Fig. 4) are recorded Raman bands around 130 cm^{-1} , very large bands around 410 cm^{-1} and a week and broad band appears around 900 cm^{-1} for all samples.

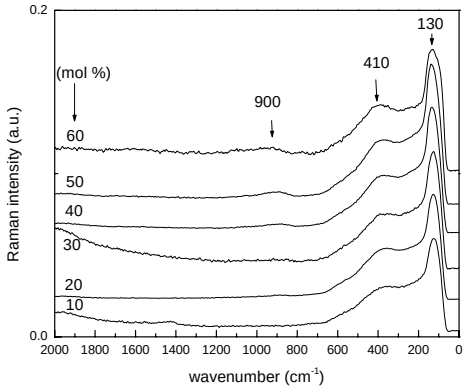

Fig. 4. Micro-Raman spectra of glass samples.

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 in [BiO_6] and [BiO_3] units. [21, 22, 25]. However, a very precise assignment of these vibrational modes becomes very difficult if the possible participation of silicium cations and the evolution of these bands for different concentrations are considered. To the band around 410 cm^{-1} which is assigned to the Bi-O-Bi and Bi-O stretching vibrations in [BiO_6] octahedral units [21, 22], a small contribution to its appearance could have the oxygen atoms vibration in the SiO_2 structure. According to the approach of P. McMillan [26] the vitreous silica shows weak bands near 1200-1060 cm^{-1}, a medium intensity band group near 800 cm^{-1} , and a strong polarized band near 430 cm^{-1}. Other silicate compositions show strong bands at 1100-1050 cm^{-1} , 1000- 950 cm^{-1} , near 900 cm^{-1} and near 850 cm^{-1} attributed to symmetric stretching vibrations of silicate tetrahedra with respectively one, two three and four non-bridging oxygens. The bands in the 700-400 cm^{-1} region have been associated with the presence of inter-tetrahedral Si-O-Si linkages.

In this approach we can conclude that the band near 410 cm^{-1} is assigned to the Bi-O-Bi and Bi-O stretching vibrations in [BiO_6] octahedral units and oxygen atoms asymmetric bend vibration Si-O-Si in [SiO_4] structural units. The position of this band shifts to higher wavenumbers as SiO_2 content increases.

The band around 900 cm^{-1} can be attributed to symmetric stretching vibrations of silicate tetrahedra. The position of this band shifts to higher wavenumbers as SiO_2 content increases.

The half-width of the band near 130 cm^{-1} increase with SiO_2 addition compared to the corresponding bands observed in the spectra recorded for the samples with smaller SiO_2 content. Being known [27] that the width of the Raman bands in disordered materials is a measure of the disorder in the local structure. We can assume that the vecinity of bismuth in glasses with high silicium content is more distorted.

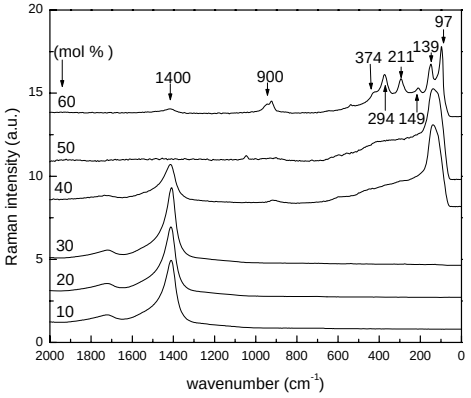

Fig. 5. Micro-Raman spectra of glass ceramics samples.

By inspecting the Raman spectra obtained from glass ceramic samples (Fig. 5) one observes the occurrence of new bands around 97, 139, 149, 211, 294, 374 cm^{-1} for the samples with $40 \leq x \leq 60$ and an unexpected silent region between 50 and 1300 cm^{-1} for glass ceramic samples with $x \leq 30$. Again unexpected intense are the bands located around 1400 cm^{-1}. The Raman bands and shoulders occurring in the 50-400 cm^{-1} spectral range of the heat-treated glasses indicate that Bi^{3+} cations are incorporated in the network as [BiO_6] octahedral units at all compositions [21, 22, 25].

The new intense Raman bands at 97, 139, 149, 211, 294 and 374 cm^{-1} are related with the well developed crystalline phase $Bi_{5.6}Si_{0.5}O_{9.4}$ that is present in the treated samples with $40 \leq x \leq 60$.

For the explanation of the unusual Raman spectra like for samples with $x \leq 30$, new Raman experiments with different wavelength radiation are necessary.

5. Conclusions

According to Raman and FTIR spectroscopic results the structure of the investigated $0.01Fe_2O_3 \cdot 0.99[xSiO_2 \cdot (100\text{-}x)Bi_2O_3]$ glass and glass ceramic samples is formed by [SiO_4] polymeric chains and [BiO_3] or/and [BiO_6] units connected or not with [SiO_4] units, in function of glass composition and thermal history of samples. The IR spectral investigations indicate that the environment of bismuth is more affected than that of silicon. In glasses the structural units of bismuth change with SiO_2 content from [BiO_6] to [BiO_3], while in glass ceramic samples the [BiO_3] units are better evidenced in the samples with lower SiO_2 content.

The development of only δ type solid solution crystalline phase in the heat treated samples with high SiO_2 content, $x \geq 40$, even though their composition is much closer to Bi_2SiO_5 phase, proves that in the corresponding precursor glasses there are small regions with high bismuth content that will easily crystallise in a δ

phase and regions rich in silica, more stable as non-crystalline phase.

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