



Analyses of intrinsic inhomogeneity and metal segregation in samples of Ag–Ge–Se glasses

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ABSTRACT

$\text{Ge}_y\text{Se}_{(1-y)}$ glasses are semiconductors but when Ag is added above certain threshold concentration, $\text{Ag}_x[\text{Ge}_y\text{Se}_{(1-y)}]_{(100-x)}$ glasses behave as fast ionic conductors [Ureña et al., Solid State Ionics 176 (2005) 505]. This peculiar behavior may be attributed to the intrinsically inhomogeneous nature of these glasses where zones rich in metals coexist with zones of the host material. The conductivity transformation may be ascribed to the percolation of the Ag rich phase [Pradel et al., J. Phys.: Condens. Matter 15 (2003) S1561].

$\text{Ag}_x[\text{Ge}_{0.25}\text{Se}_{0.75}]_{(100-x)}$ glasses either massive or as films were obtained by melt quenching and pulsed laser deposition (PLD), respectively, in compositions belonging to the Se rich corner of the ternary phase diagram. Their amorphous nature and intermediate range order was checked employing X-ray diffractometry (XRD), the short range order was characterized by extended X-ray absorption fine structure (EXAFS) (Ge and Se K absorption edge) and their microstructure was characterized by scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS).

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1. Introduction

$\text{Ge}_y\text{Se}_{1-y}$ system has a broad glass forming range, which is $y \leq 0.43$ atomic fraction [3]. Ag can be introduced in high concentrations in the composition of these chalcogenide glasses (up to 30 at% Ag) and strongly modifies their properties. In particular, their electric properties change. Although, $\text{Ge}_y\text{Se}_{(1-y)}$ glasses are semiconductors, when Ag is added above certain threshold concentration (8 at% for $y = 0.25$), $\text{Ag}_x[\text{Ge}_{0.25}\text{Se}_{0.75}]_{(100-x)}$ glasses behave as fast ionic conductors [1]. This interesting result is attributed to the intrinsically inhomogeneous nature of these glasses where zones rich in metals coexist with zones of the host material. The conductivity transformation may be ascribed to the percolation of the Ag rich phase [2,4,5]. The crystallization processes are also strongly modified when Ag is added to $\text{Ge}_y\text{Se}_{1-y}$ glasses. Previous studies performed by differential scanning calorimetry (DSC) and X-ray diffractometry (XRD) (at room temperature) indicate that the glass transition temperature of $\text{Ag}_{25}[\text{Ge}_{0.25}\text{Se}_{0.75}]_{75}$ glasses heated at a constant rate $\beta = 10\text{K/m}$ is 223°C , the first crystallization product is the ternary phase Ag_8GeSe_6 (at 322°C for the same heating rate) and the second is GeSe_2 (at 379°C). An exothermic process in between (at 342°C) is also observed but could not be attributed to a stable crystallization phase [6]. Recent studies suggest that the intermediate

peak could be attributed to the crystallization of a metastable phase that decomposes on cooling [7].

The aim of this work is to analyze the intrinsically inhomogeneous nature of these glasses by employing scanning electron microscopy (SEM) and X-ray techniques (XRD, EXAFS and SAXS) and to obtain information (using temperature EXAFS measurements) about how the environments of certain atoms change on the crystallization process.

2. Experimental procedure

$\text{Ag}_x[\text{Ge}_{0.25}\text{Se}_{0.75}]_{100-x}$ glasses with $x = 0, 5, 10, 20$ and 25 (at%) were obtained by the joint melting of the elemental constituents (5 N purity) in previously evacuated (10^{-6} mbar) and sealed quartz ampoules. After 8 h at 910°C the ampoules containing the liquid samples were quenched in an ice–water mixture. These samples are named Ag_x .

Morphology characterization of these glasses was performed in a scanning electron microscope Philips XL 30CP with a back scattering electron detector employing an acceleration voltage of 25 kV.

Small angle X-ray scattering (SAXS) measurements of these glasses were performed in the D11A-SAXS beamline at the Laboratório Nacional de Luz Síncrotron (LNLS) in Campinas, Brazil. Powder samples obtained of bulk glasses were mounted between two Kapton foils and measured with $\lambda = 1.488 \text{ \AA}$. Information was analyzed in the q range $\sim 0.01\text{--}0.30 \text{ \AA}^{-1}$ ($q = 4\pi/\lambda \sin(\epsilon/2)$, with ϵ

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the scattering angle). Before the analysis, the scattered intensity curves were corrected to discard instrumental effects as well as incoherent scattering produced by the samples.

Ge and Se surroundings of $\text{Ag}_x[\text{Ge}_{0.25}\text{Se}_{0.75}]_{100-x}$ bulk glasses were studied by extended X-ray absorption fine structure (EXAFS) technique at different temperatures. EXAFS experiments were carried out on the D04B beamline at the LNLS. Ge and Se K-edges (12 658 and 11 104 eV, respectively) were studied in transmission mode. For room temperature (RT) experiences the samples were finely ground ($\varnothing \geq 25 \mu\text{m}$) and uniformly spread onto a Millipore membrane. For higher temperature experiences (262, 282 and 312 °C) the samples were mixed with boron nitride and pressed into compacted pellets.

3. Results and discussion

Ag containing bulk glasses with x from 7 to 20at% are intrinsically inhomogeneous as is shown in Fig. 1. On the contrary, glasses with lower or higher Ag concentration present a homogeneous aspect in the scale of observation. This phase separation in glasses is a consequence of a liquid miscibility gap [8] and obeys to a continuous transformation on cooling (without nucleation) so, the interfaces are diffuse and a composition profile cannot be accurately defined.

3.1. SAXS results

The scattered intensity for $\text{Ag}_x[\text{Ge}_y\text{Se}_{1-y}]_{100-x}$ powdered bulk glasses with $x = 0-25$ do not satisfy Guinier approximation [9] in any zone of the analyzed q range. Moreover, the scattered intensity $I(q)$ depends on q as q^{-m} in all q range and presents two different power law regimes. For lower q values ($q < 0.10 \text{ \AA}^{-1}$), $m \approx 4$ in agreement with the dependence proposed by Porod [9] for structures with smooth interfaces. This can be associated to the inhomogeneous nature of these glasses (two phases) that may be considered non-particulate at least for particles smaller than the maximum accessible size. The final slope of the scattered intensity as can be seen in the logarithmic graphs depicted in Fig. 2, changes to lower absolute values corresponding to $1.4 \leq m \leq 2.1$ that may be associated to a mass fractal structure of dimension $D_m = m$ [10]. This fact may be correlated to the lack of coherence of the interface, with compositional fluctuation on a small scale [11]. The above mentioned behavior is common to all the glasses analyzed, containing Ag or not. The value of q at which the exponent of the power law regime changes from $m = 4$ to $1.4-2.1$ decreases as Ag content increases (see Fig. 2).

3.2. Ge K-edge EXAFS analysis

For the EXAFS analysis, the β' - Ag_8GeSe_6 crystalline phase [8] was used as structural reference. In this structure, the Ge

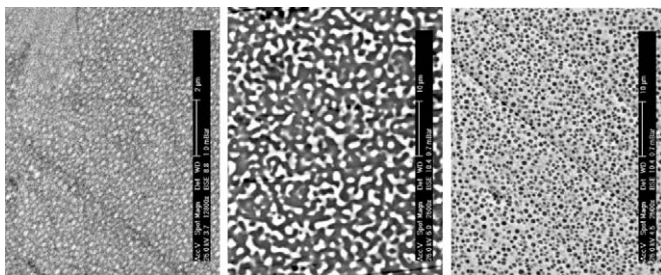


Fig. 1. SEM images employing back scattering electron detection. From left to right: $\text{Ag}_7(\text{Ge}_{0.25}\text{Se}_{0.75})_{93}$, $\text{Ag}_{10}(\text{Ge}_{0.25}\text{Se}_{0.75})_{90}$, $\text{Ag}_{20}(\text{Ge}_{0.25}\text{Se}_{0.75})_{80}$.

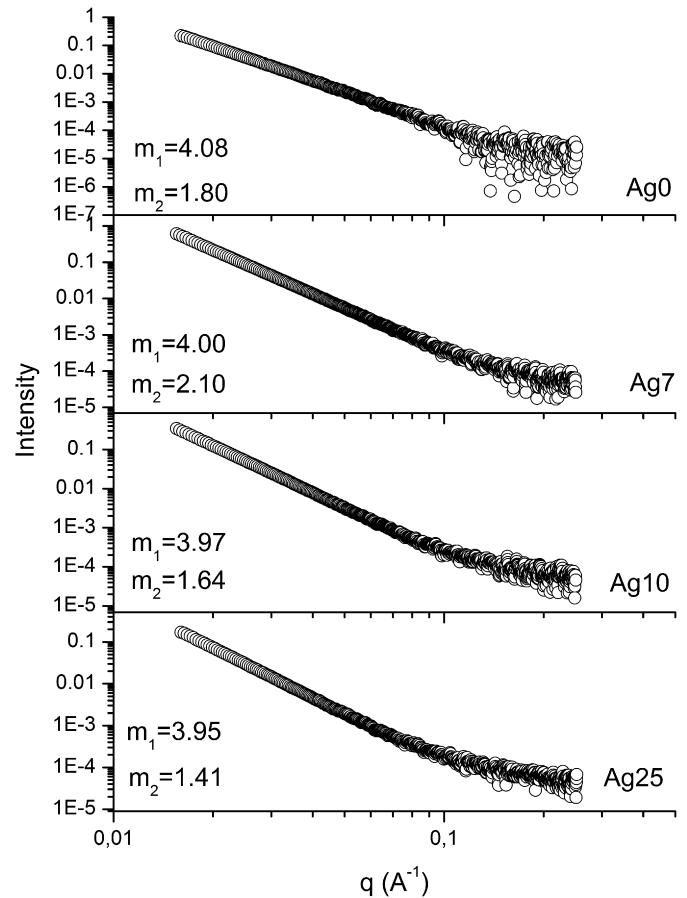


Fig. 2. Scattered radiation on powders of $\text{Ge}_{0.25}\text{Se}_{0.75}$ (Ag0), $\text{Ag}_7(\text{Ge}_{0.25}\text{Se}_{0.75})_{93}$ (Ag7), $\text{Ag}_{10}(\text{Ge}_{0.25}\text{Se}_{0.75})_{90}$ (Ag10) and $\text{Ag}_{25}(\text{Ge}_{0.25}\text{Se}_{0.75})_{85}$ (Ag25) bulk glasses. m_1 and m_2 are the absolute values of the slope for lower and higher q values.

surrounding is similar to the one in $c\text{-GeSe}_2$. The $c\text{-GeSe}_2$ crystalline phase possesses a layer structure made up of chains of $\text{GeSe}_{4/2}$ corner sharing tetrahedrons connected through links of two $\text{GeSe}_{4/2}$ edge sharing tetrahedrons [12]. In the β' - Ag_8GeSe_6 crystalline phase, the average Ge–Se distance of the elemental structure of $\text{GeSe}_{4/2}$ tetrahedrons is 2.34 Å.

Due to the thermal mobility of the atoms (Debye–Waller factor, σ), only the first coordination sphere could be identified in the EXAFS experiments, with four Se atoms surrounding a Ge atom ($\text{GeSe}_{4/2}$). The Fourier transform shows a main peak around 2 Å (see Fig. 3). The pseudo-radial distance between the absorber and the first coordination sphere (uncorrected for phase shifts) of the glass at RT and at higher temperatures are rather similar to that in the crystalline reference β' - Ag_8GeSe_6 . Taking this crystalline phase as structural reference, the first coordination shell distances $R_{\text{Ge–Se}}$ are reported in Table 1 (corrected for phase shifts with β' - Ag_8GeSe_6 as structural reference).

3.3. Se K-edge EXAFS analysis

EXAFS measurements at RT of the Ag_x ($x = 0, 5, 10$ and 25) samples allowed the characterization of the Se first coordination sphere. The β' - Ag_8GeSe_6 crystalline phase was used as structural reference. However, in this structure there are several different surroundings for Se, some with Ge as first neighbor ($\text{GeSe}_{4/2}$ tetrahedron) and some with Ag as first neighbor. In the sites where Ge is the first neighbor, the Se–Ge distance is 2.34 Å and in the sites where Ag is the first neighbor, the Se–Ag distance is higher (between 2.53 and 2.59 Å). The Fourier transforms of the

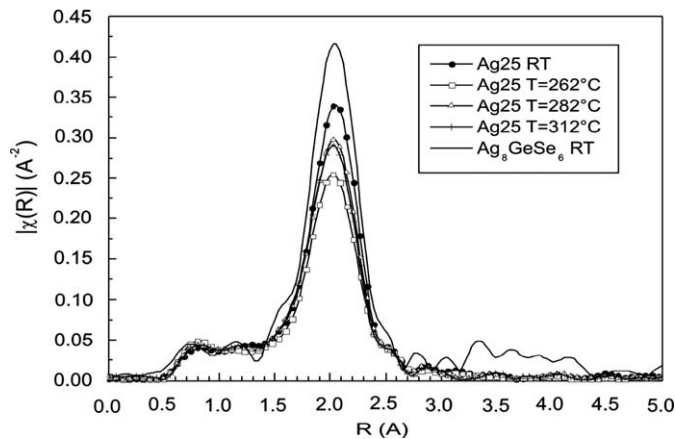


Fig. 3. $\chi(k)$ Fourier transform moduli obtained from the Ge K-edge EXAFS study for Ag25 at room temperature (RT) and at $T = 262, 282$ and 312 °C. Also included is β' -Ag₈GeSe₆ at RT.

Table 1

The first coordination shell distances $R_{\text{Ge-Se}}$ of the amorphous sample Ag25 obtained for Ge K-edge EXAFS measurements at different temperatures.

Sample	$R_{\text{Ge-Se}}$ (Å)
Ag25 RT	2.355
Ag25 $T = 262$ °C	2.33
Ag25 $T = 282$ °C	2.34
Ag25 $T = 312$ °C	2.33

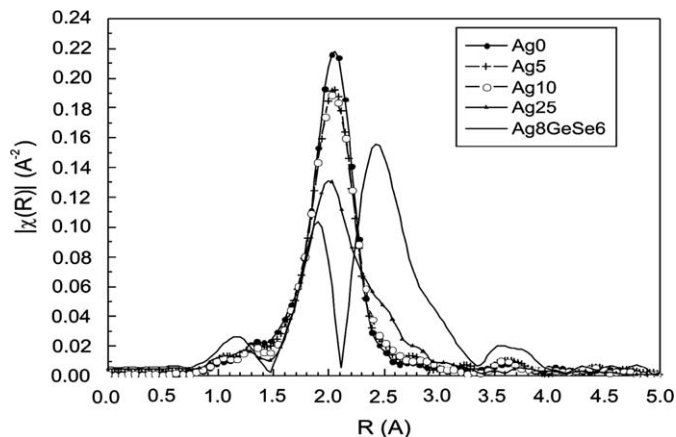


Fig. 4. $\chi(k)$ Fourier transform moduli obtained from the Se K-edge EXAFS study at room temperature (RT) for Ag $_x$ ($x = 0, 5, 10$ and 25). Also included is β' -Ag₈GeSe₆ crystalline reference at RT.

amorphous samples show a principal peak around 2 \AA (Fig. 4). In the β' -Ag₈GeSe₆ crystalline reference, two peaks at 1.96 and 2.48 \AA can be identified and associated with Se–Ge and Se–Ag surroundings correspondingly. The peak of the Ag25 amorphous sample has a deformation at higher distances that could be attributed to a contribution of the Se–Ag bonds. Average distances $R_{\text{Se-Ge}}$ and $R_{\text{Se-Ag}}$ for the amorphous samples (corrected for phase shifts with β' -Ag₈GeSe₆ as structural reference) are reported in Table 2.

4. Conclusions

Bulk glasses of composition Ag $_x$ [Ge_{0.25}Se_{0.75}]_{100-x} with $x \leq 25$, were analyzed employing SEM, SAXS and EXAFS techniques. The microstructure of these glasses (SEM) evidences phase separation

Table 2

Average distances $R_{\text{Se-Ge}}$ and $R_{\text{Se-Ag}}$ (corrected for phase shifts with β' -Ag₈GeSe₆ as structural reference) of the amorphous samples Ag $_x$ obtained for Se K-edge EXAFS measurements.

Sample	$R_{\text{Se-Ge}}$ (Å)	$R_{\text{Se-Ag}}$ (Å)
Ag0	2.43	–
Ag5	2.43	–
Ag10	2.43	–
Ag25	2.37	2.57

for $7 \leq x \leq 20$ that may be attributed to a spinodal transformation. SAXS reveals, for all samples, two power law regimes. For lower q ($q < 0.14 \text{ \AA}^{-1}$ for Ag7, $q < 0.10 \text{ \AA}^{-1}$ for Ag25) the power law exponent corresponds to intrinsic inhomogeneity with smooth interfaces whereas for higher q , the corresponding exponent may be attributed to a mass fractal structure that can be correlated to a lack of coherence of the interface. Metallic precipitates have not been detected.

Ge K-edge EXAFS experiments show that the Ge–Se distance in the amorphous samples is very similar (slightly higher) to that of the crystalline one. The experiments carried out at temperatures higher than RT do not present substantial differences and did not allow the observation of the crystallization of the metastable phase reported by Ref. [7].

The $R_{\text{Se-Ge}}$ values of Ag25 bulk glass obtained from the Ge K-edge are slightly smaller than those obtained from the Se K-edge. This could be due to thermal agitation or to the fact that these samples are ionic conductors and the movement of the Ag ions affects more directly the Se surroundings than the Ge surroundings. To investigate these contributions, low temperature measurements will be carried out in the future. On the other hand, it can be concluded, that the Se surroundings in the Ag25 amorphous sample have a closer resemblance to the Se surroundings of the β' -Ag₈GeSe₆ crystalline reference than those of the glasses with poorer Ag content (see Fig. 4).

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