Characterization of Ag-Ge-Se bulk glasses by means of Mössbauer effect on $^{57}$Fe and $^{119}$Sn atomic nuclei.

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Abstract. In this work, the structure of Fe and Sn doped Ag$_{x}$(Ge$_{0.25}$Se$_{0.75}$)$_{100-x}$ ($x=0$ to 25 at.%) intrinsically inhomogeneous glasses is analyzed employing $^{119m}$Sn and $^{57}$Fe Mössbauer spectroscopy, X-ray diffractometry and scanning electron microscopy. $^{119m}$Sn enters in the glass as a substitutional impurity for Ge whereas $^{57}$Fe enters as an interstitial impurity. Mössbauer spectra obtained with $^{119m}$SnO$_3$Ca source, from samples containing about 1% $^{119}$Sn reveal that the local order of Ge in both amorphous phases is basically the same whereas Mössbauer spectra obtained with $^{57}$Fe(Rh) source, from samples containing about 0.5% $^{57}$Fe, evidence the differences between both phases.

1. Introduction

The GeSe$_2$-Se system presents an extensive glass forming composition range by the melt quenching technique. These glasses can be easily obtained either as massive glasses or as films and present great stability and resistance to water and corrosive media.

The fundamental structural unit of pure chalcogen glasses, e.g. Se, is based on a single atom, therefore the short range order is rather straightforward and Se coordination number is $n=2$. [1] For binary glasses the situation is more complex. Their structure consists of tetrahedral units centered on the tathogen, e.g. GeSe$_{4/2}$. Ge coordination number is $n=4$. In GeSe$_2$-Se system glasses, Ge centered tetrahedra are connected by Se bridges whereas in glasses with higher Ge content the tetrahedra are either corner sharing or edge sharing. [2] Crystalline GeSe$_2$ has a layered structure formed by chains of tetrahedra whereas crystalline Se is formed by Se chains. [3] The binary glasses, as well as the corresponding crystalline phases, are semiconductors with a band gap above 2 eV. [4] However, it is possible to control their physicochemical properties by adding a third element even in a low concentration. When Ag is incorporated in the GeSe$_2$-Se system above certain threshold concentration ($\sim$8at.%) ternary glasses result in fast ionic conductors. [5]

The Ag-Ge-Se glass forming system [6] is dominated by liquid immiscibility. Glasses in the Se-GeSe$_2$-Ag$_2$Se triangle may have different morphologies according to their composition but, in general, they are intrinsically inhomogeneous [7]. The physical properties of these glasses are dependent on their composition and can be easily correlated to their morphology. Accordingly, the electric conductivity evolves from semiconducting to ionic conductivity whereas a percolation transition occurs in a narrow Ag concentration range. [5]

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In this work, the structure of Fe and Sn doped $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ ($x=0$ to 25 at.%) is characterized employing X-ray diffractometry. Their morphology is analyzed by means of scanning electron microscopy, and the local order about the $^{57}\text{Fe}$ and $^{119}\text{Sn}$, analyzed by means of Mössbauer spectroscopy, is employed to infer the physical characteristics of these glasses.

In section 2 is described the synthesis procedure of the samples as well as the characterization techniques. In section 3 are described and discussed the results obtained and, finally, the conclusions are stated in the last section.

2. Experimental Procedure

$\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ samples ($x=0$ to 25 at.%), named $\text{Ag}_x$, $\text{Ag}_2\text{Se}$, $\text{Ag}_8\text{GeSe}_6$ and GeSe$_2$, were synthesized in 10 mm diameter quartz tubes evacuated to $3.10^{-5}$ mbar and sealed. 1 at.% Sn (>90% $^{119}\text{Sn}$) or 0.5 at.% Fe (>90% $^{57}\text{Fe}$) were added to the components (which purity is 99.99% for Ge, Se and 99.9% for Ag) in the desired stoichiometry in the synthesis step. The batches were heated in a furnace at 910 ºC for 8 hrs and then, either quenched in a mixture of ice-water or slowly cooled. Either glasses or crystalline samples were obtained with these procedures.

The amorphous or crystalline nature of the samples was checked by X-ray diffractometry (XRD) using a $\theta-\theta$ diffractometer with monochromatised Cu (Kα) radiation. Samples morphology was analyzed by scanning electron microscopy (SEM), employing an acceleration voltage of 25 kV, and energy dispersive x-ray analysis (EDX). Microscopy images were obtained by means of a back scattering electron detector (BSED) to reveal the chemistry differences on the sample surface.

Mössbauer measurements (MS) were performed in transmission geometry at room temperature, employing $^{119m}\text{SnO}_3\text{Ca}$ or $^{57}\text{Co(Rh)}$ sources. The spectra were fitted employing sites or quadrupole splitting ($\Delta$) distributions with the Normos programs (Site or Dist) [8]. Isomer Shift ($\delta$) is reported either relative to $\text{SnO}_3\text{Ca}$ or to $\alpha\text{-Fe}$.

3. Results and Discussion

3.1. XRD characterization

Rapidly quenched $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ samples ($x=0$ to 25 at.%) doped either with $^{57}\text{Fe}$ or with $^{119}\text{Sn}$ resulted in completely amorphous samples. FeSe was segregated in $\text{Ag}_2\text{Se}$ doped with $^{57}\text{Fe}$ slowly cooled. Segregation of FeSe in other Fe doped crystalline samples cannot be ignored. However, no segregation was detected in samples cooled in air. The $\text{Ag}_8(\text{Ge}_{1-x}\text{Sn}_x)\text{Se}_6$ pattern evidenced the unlimited solubility of Sn in $\text{Ag}_8(\text{Ge}_{1-x}\text{Sn}_x)\text{Se}_6$.[9]

3.2. SEM and EDX analyzes

Bulk glasses resulted in homogeneous glasses for $x<7$. On the other hand, bulk glasses for $7\leq x\leq20$ present notorious inhomogeneity that denotes a spinodal decomposition for $8\leq x\leq10$ outflanked by two bi-nodal composition ranges (figure 1). For $5<x<8$ bright dots appear isolated embedded in a dark matrix. For $10<x<25$ dark dots appear embedded as a Ag rich matrix. According to EDX analyzes on glasses with $8\leq x\leq20$, bright zones composition are characterized by larger Ag and smaller Se concentration. Ge composition of both zones is very similar in agreement with the liquid miscibility gap reported in the ternary phase diagram.[6] Sample with $x=25$, in spite of being non-homogeneous as observed with a magnification of 48000x, does not present the same morphology as the above described glasses.

3.3. MS analyzes

Mössbauer spectra of $^{57}\text{Fe}$ doped $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ glasses for $x=5$, 10 and 25 at. % are shown in figure 2. The best fit was obtained with two Gaussian quadrupolar splitting ($\Delta$) distributions plus a single environment with $\delta=0.69$ mm s$^{-1}$ and $\Delta=1.40$ mm s$^{-1}$. Two types of Fe environments are present: high spin (HS) and low spin (LS) $\text{Fe}^{2+}$ in octahedral environments. The tendency of $\langle \Delta \rangle$ in the
Figure 1. SEM images of Ag$_7$(Ge$_{0.25}$Se$_{0.75}$)$_{93}$ (left) and Ag$_{20}$(Ge$_{0.25}$Se$_{0.75}$)$_{80}$ (right) glasses.

Figure 2. MS of $^{57}$Fe doped Ag$_x$(Ge$_{0.25}$Se$_{0.75}$)$_{100-x}$ glasses. The experimental points, the fitting (solid line) and each interaction are depicted.

Figure 3. MS of $^{119}$Sn doped Ag$_6$GeSe$_6$ and Ag$_x$(Ge$_{0.25}$Se$_{0.75}$)$_{100-x}$ glasses. The experimental points and the fitting (solid line) are depicted.

Gaussian distribution corresponding to HS environments is that it decreases as $x$ grows. These environments have already [7] been identified as corresponding to Ag rich zones and Ag depleted zones respectively and the Debye temperature ($\Theta_D$) for each phase had been determined being $\Theta_D$(bright zone) ~ 0.78$\Theta_D$(dark zone). This fact can be correlated with a different conducting regime in Ag rich and Ag depleted zones.

The local diffusion of Ag$^+$ in the neighborhoods of the impurity Fe atom in Ag rich zones modifies the electric field gradient (EFG) on the Fe atom, strongly dependent on the distortions of its octahedral environment. As a consequence, the effective value of the EFG is its average value calculated in the mean life of the 14.4 keV $^{57}$Fe excited level and, consequently, the effective value of $<\Delta>$ would be smaller as the ionic conductivity increases.
Figure 3 shows Mössbauer spectra of samples doped with $^{119}$Sn. The fittings were performed with a Gaussian $\Delta$ distribution. However, fittings with sites are not less satisfactory denoting a strong short range order around Sn (that is around Ge). Sn environments in the studied glasses are similar to those of Sn doped Ag$_8$GeSe$_6$

Isomer shift for Sn doped Ag$_x$GeSe$_6$ ($\sim$1.65 mm s$^{-1}$) corresponds to Sn$^{4+}$ tetrahedrally coordinated by 4 Se. This $\delta$ is larger than that of Ge (Sn) in Sn doped Ag$_8$GeSe$_6$. This fact could be attributed to an octahedral coordination [10]. However, as Sn is tetrahedrally coordinated by 4 Se in this phase this decrease in $\delta$ may be attributed to a decrease in Ge (Sn)-Se distances for Ag$_8$GeSe$_6$ (0.234 nm) [11] as compared to Sn-Se distances in glasses (0.236-0.239 nm) [12]. Sn doped Ag$_{25}$ presents in addition a Sn$^{2+}$ contribution.

A general trend is observed in the spectra fittings with sites mode, $\Delta$ and $\delta$ values increase with x as well as the linewidth ($\Gamma$) (0≤x<25 at. %). This fact together with the linear dependence of the diffusion coefficient of Ag$^+$ ions reported in [5] let us correlate the line widths with the diffusion coefficient (D) in agreement with the case described in [13] for the motion, governed by the diffusion equation, of the diffusive atom in the absorbent. In addition, the increase in $\delta$ can be attributed to the increase in Ge-Se average distances with x reported in [12]. In a similar manner the increase in Ag-Se correlation with x will be responsible for the increase of $\Delta$ as the EFG on $^{119}$Sn atoms is strongly dependent on the charge state of the near neighbor Se atoms and consequently on the ionicity of their bonds.

4. Conclusions

$^{57}$Fe and $^{119}$Sn doped Ag-Ge-Se glasses in the Ag$_2$Se-Se-GeSe$_2$ are intrinsically inhomogeneous in a wide range of composition. They are formed by a Ag rich phase (bright) and a Ag depleted one (dark). The balance of these phases volume controls the conductivity regime.

Se concentration in the bright phase is smaller than in the dark phase whereas Ge concentration is similar in both phases.

From MS on $^{57}$Fe a decreasing of the average value in the $\Delta$ distribution corresponding to HS Fe$^{2+}$ environment in the Ag rich phase, was found and explained as a relaxation effect, due to the diffusion of Ag ions, that distorts the EFG on Fe.

An increase in linewidths in MS on $^{119}$Sn with x is observed and attributed to the increase in the diffusion coefficient of Ag$^+$ in the samples. In addition, the increase of $\delta$ and $\Delta$ are attributed respectively to the increasing of Ge-Se distances and Ag-Se correlation with x.

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