

AGEING EFFECTS IN Ag-Ge-Se BULK GLASSES*

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Glasses of composition $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ and $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ doped with 0.5 at% of ^{57}Fe were analyzed with the aim to evaluate if their structure evidences any effect of ageing, for thousands of hours at room temperature and/or hundreds of hours for sub- T_g thermal treatments. Strong ageing effects were observed by means of Mössbauer spectroscopy whereas Raman spectroscopy contributed to identify the origin of these effects.

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1. Introduction

As well as other chalcogenide glasses, Ag-Ge-Se glasses have attracted much interest in recent years due to their actual or potential applications in fields such as solid electrolytes, electro/opto-chemical sensors, non-volatile memories, etc. As a consequence, the stability of these glasses is one aspect to be controlled. Several authors [1-5] have approached the study of relaxation and ageing of chalcogenide glasses and some of them even analyzed ageing and relaxation on glasses of composition $\text{Ge}_u\text{Se}_{1-u}$ from different points of view [3-5]. Among these authors J.M. Saiter et al. [3] reported an interesting result, that is, for $\text{Ge}_u\text{Se}_{1-u}$ samples with $u < 0.12$ at. Fraction, aged for 13 years, differential scanning calorimetric analyzes present two endothermic peaks associated to the glass transition (T_g) instead of the single endothermic peak observed at short ageing duration. On the other hand only one peak occurs for $u = 0.12$. The authors propose that it is needed a long time ageing at temperatures well below T_g for the occurrence of double endothermic peaks. They attribute these two peaks to a transformation of an initial homogeneous glass towards an inhomogeneous one during ageing. The fact that they only occur for low x is attributed to the coexistence, in the initial glass, of Se chains and $\text{GeSe}_{4/2}$ structural units in a model of local atomic arrangements, and the presence of only one relaxation peak for higher x values is attributed to the gradual disappearing of the Se chains as x increases. The authors propose that the first endothermic peak corresponds to the faster relaxation of Se chains whereas the $\text{GeSe}_{4/2}$ cells must relax with a slower kinetics and so they need larger ageing duration to be observed. This phenomenon corresponds to the second relaxation peaks in low u samples and to the single peak that appears in DSC patterns for Ge higher concentrations.

For higher Ge concentrations the structure of $\text{Ge}_u\text{Se}_{1-u}$ glasses is characterized by the presence of chains of tetrahedra centered on a Ge ($\text{GeSe}_{4/2}$) which are linked together either sharing vertices (CS) or edges (ES). [6] The presence of rings and chains of Se is also possible [7] whereas ethane type structures (Et) are reported for high Ge concentration [8]. The addition of Ag to the structure of these binary glasses does not alter substantially their structural units. However,

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due to the addition of Ag, a spinodal decomposition takes place and the glasses become intrinsically inhomogeneous.[9]

In the present work, the ageing of Ag-Ge-Se glasses as well as the effect of thermal treatments below T_g are analyzed employing Mössbauer effect spectroscopy and FT-Raman spectroscopy.

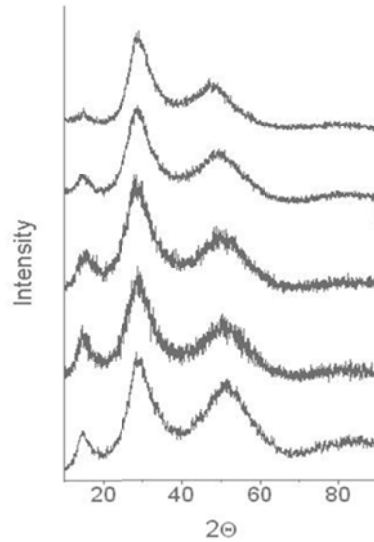


Fig. 1.a. XRD of Ag_x_0 samples. From bottom to top, $x = 0, 2.5, 5, 10$ and 25% .

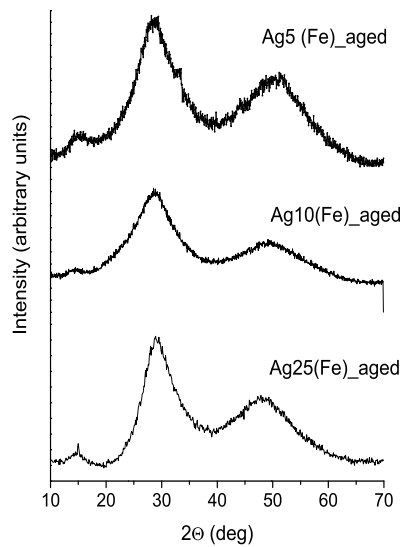


Fig. 1.b. XRD of (left) $Ag_5(Fe)$, (right) $Ag_{10}(Fe)$ aged.

2. Experimental

Samples of composition $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ (called Ag_x) and $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ doped with $0.5\% \text{ } ^{57}\text{Fe}$ ($x \leq 25\text{at. \%}$) (called $Ag_x(Fe)$) were prepared by the melt-quenching procedure. The elements in the desired stoichiometry were sealed in quartz ampoules evacuated to 10^{-6} mbar, heated to $950\text{ }^\circ\text{C}$ and then maintained, in liquid state, at that temperature for about 10 hours. After this time, the liquid samples were rapidly quenched in an ice/water mixture. Several series of samples were obtained with the same protocol for at least 15 years. These samples were analyzed and the obtained results were opportunely reported.[9-13] Some of these samples were kept at

ambient conditions in the dark (Agx_aged). A new series was prepared for this work (Agx_0). This series of samples was thermally treated at 110°C for different periods of time (t) and then cooled down to room temperature to be evaluated (Agx_t).

The atomic structure of the samples was characterized by means of X-ray diffractometry (XRD) in a Rigaku Θ - Θ goniometer, with monochromatized Cu K α radiation. The local structure was revealed by FT-Raman spectroscopy (RS) employing a Bruker 66 equipment with a Nd-YAG laser ($\lambda=1064$ nm). The employed parameters in Raman spectroscopy, in order to avoid crystallization, were: Current = 0.81A, Power \approx 4mW and Scans=100. The spectra were fitted with Voigt functions employing the Fityk 0.9.8 program [14]. Due to fluctuations on the laser power, normalization was performed with reference to the band at 197cm $^{-1}$.

Mössbauer spectroscopy was employed to evaluate local structure by means of a ^{57}Fe probe. Mössbauer spectra (MS) were obtained at room temperature in transmission geometry, from ^{57}Fe doped samples of the first series, employing a constant acceleration spectrometer with a ^{57}Co (Rh) source. The samples spectra were fitted with two distributions of electric field gradients corresponding to both ^{57}Fe environments, employing the Normos-Dist program, whereas calibration spectra were fitted employing the Normos-Site program. [15]

3. Results

XRD of both as quenched samples (Figure 1a) and aged samples Agx and Agx(Fe) (Figure 1.b) present wide peaks characteristic of an amorphous structure together with a first scattering peak (FSP) at $2\Theta \approx 15^\circ$. The intensity of this FSP decreases with increasing Ag concentration x.

The MS of fresh samples show two Fe environments, one of them corresponding to high spin (HS) Fe^{2+} whereas the other one corresponds to low spin (LS) Fe^{2+} . Each Fe environment is attributed to a different amorphous phase, HS Fe^{2+} to the Ag-rich phase and LS Fe^{2+} to the Ag-poor phase. [9] MS of aged samples evidence the presence of strong effects of long-term relaxation in the phase containing LS Fe^{2+} (Figure 2). After aging, the relative absorption of HS Fe^{2+} does not vary whereas the relative absorption of Fe^{2+} (LS) increases substantially.

These effects are inversely proportional to the Ag concentration of the samples, that is, they depend on the relative amount of Ag poor phase as can be seen in Figure 2.

In all tested samples, the most important contributions to the Raman spectra (Figure 3) are the bands centered at 197 cm $^{-1}$ and 213 cm $^{-1}$ and those centered at 240 cm $^{-1}$ and 261 cm $^{-1}$. The first bands are attributed (see Table 1) to Ge-Se-Ge vibrations in tetrahedra that share corners (CS) and Se-Se vibrations in tetrahedra that share edges (ES) respectively. The other bands are attributed to chains (CM) and rings (SeN) of Se atoms.

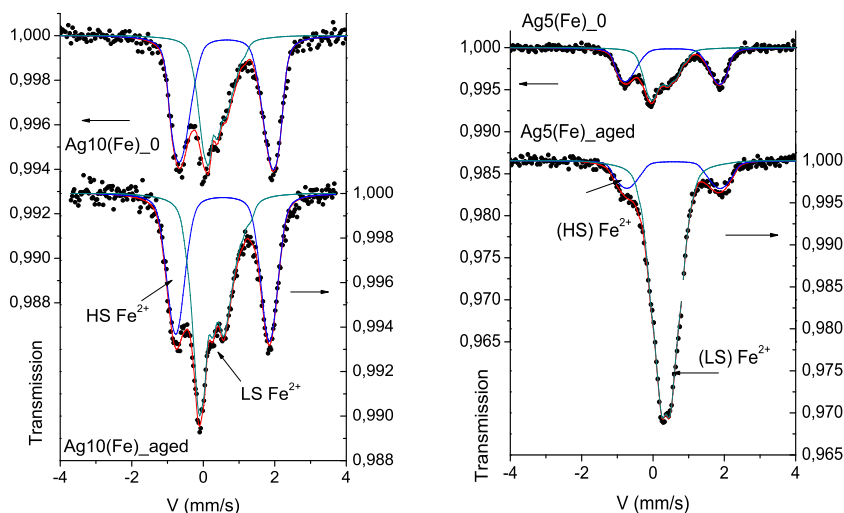


Fig. 2. MS of samples Agx(Fe) $_0$ and Agx(Fe) $_aged$ for 8 years at ambient

conditions. Top $x=10$, bottom $x=5$.

The increasing of Ag concentration (x) in these glasses produces a relative decrease of the band corresponding to the vibration of Se-Se bonds (SeN rings) and an increase in the contribution from the chains of Se, which can be attributed to the Ag breaking of the Se-Se bonds. Moreover the band corresponding to the CS mode shifts slightly towards the red and an asymmetry is observed which can be attributed to the emergence of new environments. On the other hand, SeN bands present a blue shift as Ag concentration increases. This has already been seen in Ge-Se glasses on decreasing the concentration of Se. [5]

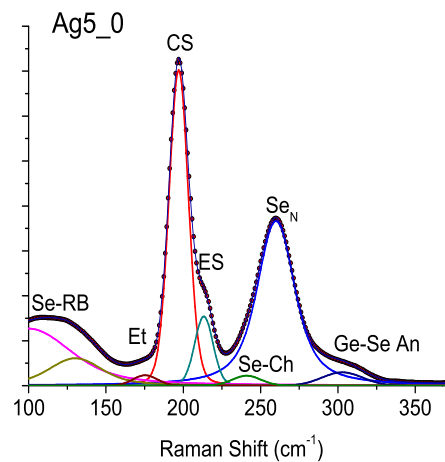


Fig. 3. Raman spectrum of simple Ag5_0

The most notable effects observed after the ageing of the sample, consist of the main band broadening, CS, on which there is an asymmetry that can be attributed to the emergence of new modes of vibration along with a decrease in the contribution of the ES mode. Additionally a sharper Et mode appears (Figure 4).

On the other hand, a decrease of the Se rings/chains contribution was detected after sub-T_g thermal treatments (Figure 5). From the comparison of the spectra of samples Ag5_0 and samples of the same composition, heat treated at T=110 °C for different times: 2 to 14 days it is evident a relative decrease and a blue shift of the band corresponding to SeN rings vibrations. It is observed, to a lesser extent, a decrease of the contributions of Se-RB and ES modes.

4. Discussion

Scanning electron microscopy (SEM) on samples Ag x and Ag x (Fe) evidenced the presence of two amorphous phases, where the main difference is the Ag concentration, in an intrinsically inhomogeneous morphology that is the key to the huge jump of ionic conductivity for $x \approx 8$ at.% [9]. MS analyzes [9,13] attributed LS Fe²⁺ to the Ag-poor amorphous phase and HS Fe²⁺ to the Ag-rich amorphous phase.

Table 1. Raman Spectroscopy. Identification of the bands.

Raman Shift (cm ⁻¹)	Description	Name	References
120	Rocking/Bending modes of Se	Se RB	[5]
180	Ethane-like mode Ge ₂ Se _{6/2}	Et	[16, 17, 18]
197	Symmetric stretching of Se in Ge-Se-Ge bondings (corner sharing GeSe _{4/2} tetrahedra)	CS	[16]
216	Breathing mode Se-Se (edge sharing GeSe _{4/2} tetrahedra)	ES	[16]
240	Se-Se stretching in Se chains. Ge-Se bondings different to Ge-Se-Ge.	SeCh	[19] [20]
260	Se-Se stretchings in SeN rings	SeN	[19]
310	Asymmetric vibrations of Ge-Se-Ge	Ge-Se As	[16, 21]

The ageing effect observed in Mössbauer spectra of samples Ag_x(Fe)_{aged} cannot be attributed to crystallization, in the light of the XRD patterns of these samples.

Long-term relaxation does not affect HS Fe²⁺ environments, i.e. Ag-rich amorphous phase but it does affect LS Fe²⁺ environments, i.e. Ag-poor amorphous phase which structure is very similar to that of Ge_uSe_{1-u} glasses.

The increasing of the absolute area corresponding to LS Fe²⁺ may be attributed to an increasing of the Lamb-Mössbauer fraction of the Ag-poor zones, i.e. a structure modification involving the Ge_uSe_{1-u} structural units.

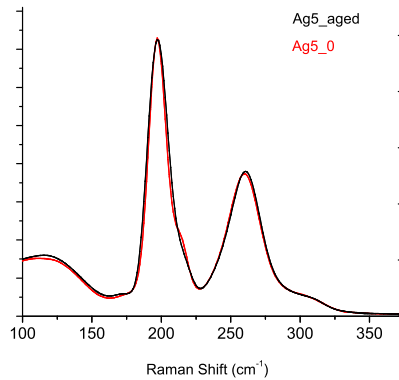


Fig. 4. Comparison of Ag_{5_0} spectrum and that of a sample of the same composition aged for 8 years at room temperature Ag_{5_aged}.

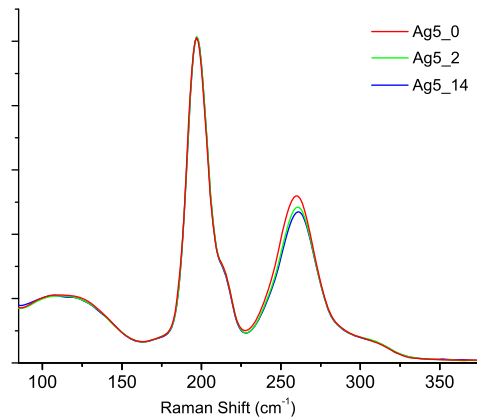


Fig. 5. Sub- T_g thermal treatments of sample Ag5_0.

As the overall effect of the increasing of Ag concentration in $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ glasses, as was observed by RS, was the decreasing of Se-Se bands (250 cm^{-1}) one may assume that the GeSe_{1-u} backbone in the Ag-poor phase mainly consists of $\text{GeSe}_{4/2}$ units. Thus, long term ageing involve as proposed by Saiter [3] the slower $\text{GeSe}_{4/2}$ units. In agreement with this, RS of samples Ag5_0 and Ag5_aged evidence no effect of long term ageing on the band at 260 cm^{-1} , but exhibit a broadening and an asymmetry on the main band (CS) at 197 cm^{-1} along with a decrease in the contribution of the ES mode that can obey to the emergence of new modes of vibration.

On the other hand, short time ageing at 110°C exhibits a decreasing of the chain mode contribution whereas the $\text{GeSe}_{4/2}$ structural units remain unaltered. This fact may be attributed either to a short time relaxation ($t \leq 336\text{ h}$) or to temperature dependence of the glass's structure below T_g as proposed by Edwards [5] except that in our case the structural units involved are those related to Se-Se bonds and not ES/CS fraction.

5. Conclusions

From the results of Raman spectroscopy it can be concluded that in the long term (thousands of hours) physical ageing of $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$ glasses, structural changes take place and involve the relative fraction of CS and ES modes or, in general, the $\text{GeSe}_{4/2}$ tetrahedral structural units. On the other hand, in short term ageing (hundreds of hours) the structural changes observed involve Se chains/rings.

The long term structural changes may account of an increased structural rigidity of the glass.

The evolution of Mössbauer spectra of these glasses on ageing may be attributed to their structural modification. However, further experiences are needed in order to determine whether the relaxation of the structure in the short range (the scope of Raman spectroscopy), i.e. the tetrahedral units, is enough to modify so significantly the Lamb-Mössbauer fraction of the amorphous phase with low Ag content.

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