# Experimental Report

24/02/2014

**Proposal:** **6-03-429** **Council:** 10/2012

**Title:** Study of the miscible character inthe liquid state on the Ag-Ge-Se system

**This proposal is resubmission of: 6-03-421**

**Researh Area:** Physics

**Main proposer:** **PIARRISTEGUY Andrea Alejandra**

**Experimental Team:** PIARRISTEGUY Andrea Alejandra
LE PARC ROZENN

**Local Contact:** CUELLO Gabriel Julio
CRISTIGLIO Viviana

**Samples:** Agx(Ge0.25Se0.75)100-x, with x=0, 5, 15 and 25

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D33 | 4 | 3 | 05/03/2013 | 08/03/2013 |

**Abstract:**

A new type of electrical memory based upon Ag–Ge–Se thin films was recently proposed. The Programmable Metallization Cell is a nanometric Ni/AgGeSe/Ag cell which electrical characteristics undergo drastic changes (resistive/conductive) upon electrical polarisation. A clear understanding of the phenomenon underlying such a change is still lacking. Our team has recently carried out a series of investigation on the Agx(Ge0.25Se0.75)100–x bulk glasses (x < 30 at.%). Their conductivity changed suddenly by 7-8 orders of magnitude for x ~ 10 at.%. Phase separation has been evidenced by electrical force microscopy and field emission scanning electron microscopy. Different Ag-Ag correlations depending on Ag content in the glasses were shown by combined neutron scattering (D4) and ab initio molecular dynamic simulations.

In order to go further in the understanding, we now propose to elucidate the miscible character in the liquid state at different

# Experimental Report

EXPERIMENT TITLE

**Study of the miscible character in the liquid state on the Ag-Ge-Se system**

PROPOSAL NUMBER

**6-03-429**

EXPERIMENTAL TEAM (names and affiliation)

**PIARRISTEGUY Andrea Alejandra, ICG, Montpellier**

**LE PARC Rozenn, L2C, Montpellier**

INSTRUMENT D33 Local contacts : Isabelle Grillo, Gabriel Cuello, Viviana Cristiglio

For many years chalcogenide glasses have been widely investigated since several of their properties make them very attractive materials. They possess a large ionic conductivity – 2 to 3 orders of magnitude larger than that of the oxide glasses with the same mobile ion content. For example, Ag-Ge-Se glasses evolve from semiconductors to superionic conductors when the Ag concentration is increased ($\sigma = 1 \times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$ for $Ag_{25}Se_{56.25}Ge_{18.5}$ glass at room temperature) [1]. Moreover thin layers of chalcogenide glasses, deposited by thermal evaporation or RF sputtering, exhibit photoinduced phenomena which are at the basis of many interesting applications [2]. In particular, Ag photodissolution or photodeposition in a chalcogenide layer can be used to produce diffraction gratings, microlenses or optical memories.

More recently a new type of electrical memory based upon the high mobility of silver in chalcogenide glasses has been proposed [3]. A Programmable Metallization Cell -PMC- memory typically comprises a silver-photodoped glassy thin film of composition ~ $Ge_{0.25}Se_{0.75}$ placed between two electrodes, a silver one and a nickel one for example. The conductivity of the film is reversibly changed by several orders of magnitude when a weak positive/negative bias is applied (~ 0.3 V). The assumption that a phase separation with the presence of silver-rich domains would exist in the film has been proposed to explain the fast reversible switching (~10 ns) between ON (conductor) and OFF (resistive) states [3]. However no clear understanding of the phenomenon is known to date.

Different investigations focusing on bulk $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with $1 < x < 30$ at.% were performed during the last two decades. On the one hand, the combined investigation of electrical conductivity and microstructure by field emission scanning electron microscopy (FE-SEM) and electric force microscopy (EFM) helped in understanding the difference of seven to eight orders of magnitude in the conductivity of the system: the glasses were phase separated with the co-existence of Ag-rich and Ag-poor regions which sizes ranged from 100nm to few microns. The percolation of the Ag-rich phase was at the origin of a sudden jump in conductivity at ~ 8 -10 at.% Ag.[4] On the other hand, neutron diffraction and molecular dynamic simulations showed that the local structure of the glasses comprised $Ge(Se_{1/2})_4$ tetrahedra connected by single or multiple Se–Se bonds. Moreover, it was shown that the Ag–Ag distances changed strongly with silver introduction in the $Ge_{25}Se_{75}$ matrix suggesting that aggregation of the Ag atoms occurred in the percolating Ag-rich phase [5].

*During this beam team allocation we would like to elucidate the miscible character in the liquid state on the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ system by exploring the small angle neutron scattering (SANS)*

## Experimental Details

The investigated samples were glasses and liquids of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ system with x = 0, 5, 15 and 25 at.%. Bulk glasses were prepared from high-purity (4 N) elements by the melt-quenching technique. The materials were synthesized by placing the powdered elements in stoichiometric proportions in a cylindrical quartz ampoule that was evacuated up to a pressure of $\approx 10^{-5}$ mbar and then sealed. After synthesis and homogenization for 8h at T=950°C in a furnace, the ampoules were quenched in a mixture of ice and water to obtain the glassy materials. Then, powders were placed in Hellma cells (110-QS) and quenched again in order to obtain a bulk material inside the cell.

The SANS experiments were performed using the small momentum transfer diffractometer D33. The incident neutron wavelength was 8 Å (nominal) with a beam diameter of 7 mm. Experimental conditions used for large and small angles were ($D_2$=2m, $D_1$=1.2m) and ($D_2$=2m, $D_1$=1.2m), respectively. Measurements were carried out on samples with x=5, 15 and 25 at.%, under the melting point (room temperature, 300°C, 400°C), just above the melting point (500°C, 550°C) and well above the melting point (600°C and 700°C). For $Ge_{25}Se_{75}$ (x=0) only one experiment was performed at room temperature.

## Results

Figures 1a and 1b show normalised SANS scattering intensities I(*Q*) with the three samples of the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ system. At room temperature, we can observe that all the curves are practically superimposed. At 600°C, the shape of the curves is still similar but we can notice a significant shift in intensities at the *Q*-low range.

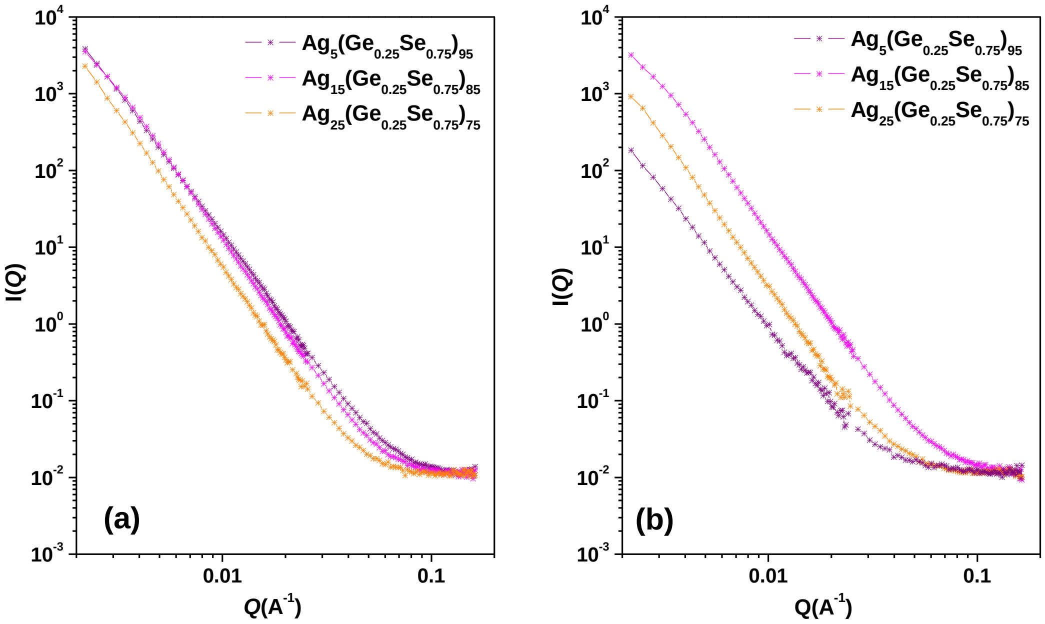

**Figure 1**: Normalised SANS scattering intensity I(Q) for (a) glasses at room temperature and (b) liquids at 600°C of the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ system.

Figures 2a, 2b and 2c compare the lnI(*Q*) vs. ln(*Q*) of the samples (x=5, 15, and 25 at.%, respectively) at two different temperatures (room temperature and 600°C). For both temperatures, the same slope very close to - 4 was obtained with two Ag-rich samples (x=15 and x=25 at.%). This corresponds to a Porod law ($I(Q) \approx S\,Q^{-4}$) characteristic of a two-phase sample with well-defined phase boundaries, which has already been observed with other heterogeneous chalcogenide glass ($(Ag_2S)_x(As_2S_3)_{100-x}$ with x=11.1) studied by SANS [6]. The Ag-poor sample (x=5) exhibits a different behaviour: the slope is below - 4 and decreases when the temperature increases.

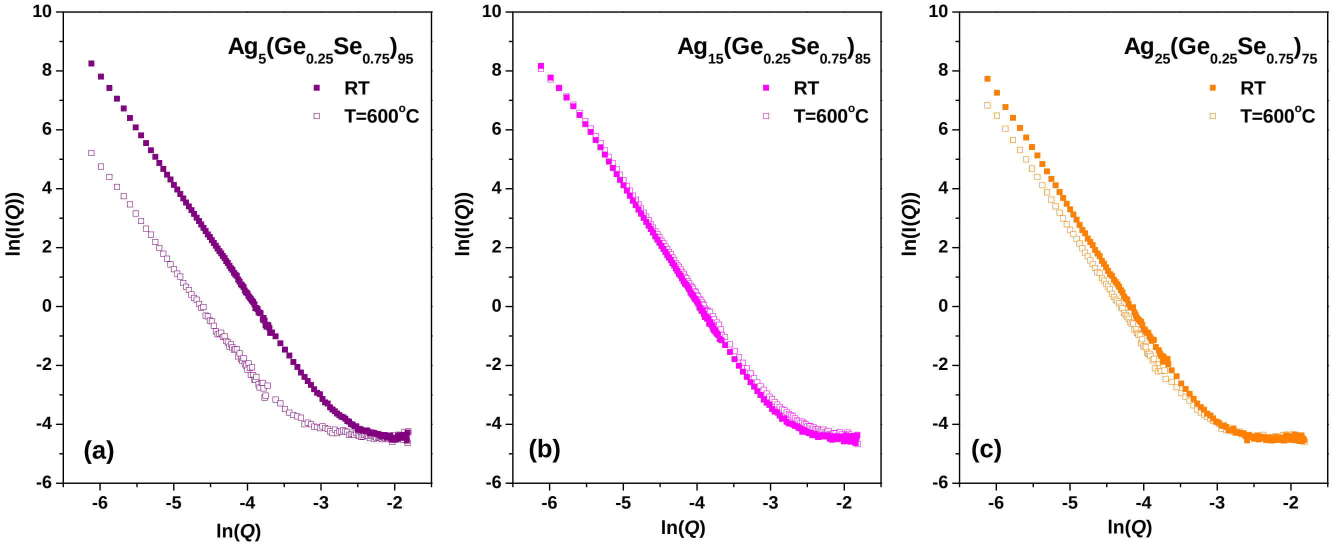

**Figure 2**: Ln I(Q) vs ln(Q) for (a) x=5, (b) x=15 and (c) x=25 at two different temperatures.

*A thorough analysis is currently in progress for a better understanding of the phase separation phenomenon (size, shape…).*

## References

[1] M. Kawasaki, J. Kawamura, Y. Nakamura, M. Aniya, J. Non-Cryst. Solids 123, 259 (1999).
[2] A. Kolobov and K. Tanaka, Handbook of Advanced Electronic and Photonic Materials and Devices, ed .S.Nalwa, vol 5.
[3] M. N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan, Superlattices Microstructures 34, 459 (2003).
[4] V. Balan, A.A. Piarristeguy, M. Ramonda, A. Pradel, M. Ribes, J. Optoelectronic and Advance Material Vol.8 ISS.6, 2112 (2006).
[5] A.A. Piarristeguy, G.J. Cuello, A. Fernández-Martínez, V. Cristiglio, M.R. Johnson, M. Ribes, A. Pradel, Physica Status Solidi B 249 (10), 2028 (2012).
[6] E. Bychkov, D.L. Price, A. Lapp, J. Non-Cryst. Solids 293-295, 211 (2001).