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# Phase separation in Ag–Ge–Se glasses

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**Abstract**

Field emission-scanning electron microscopy (FE-SEM) and electric force microscopy (EFM) measurements were carried out on bulk $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with $x = 5$ and 15 at.%. The presence of chemical contrasts and electrical inhomogeneity throughout the samples indicated that the glasses were phase separated. Moreover it appears that while silver-rich nodules of ~1 μm were embedded in a silver-poor connecting phase in the glass containing 5 at.% Ag, it was the opposite that occurred in the glass containing 15 at.% Ag. Such an inversion explains the large difference of seven orders of magnitude in the conductivity of the two glasses.
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## 1. Introduction

Ion conductive chalcogenide glasses have been extensively studied since they are potential candidates for use as solid electrolytes in all solid state batteries [1]. Conductivity as high as $10^{-2}$ S/cm and $10^{-3}$ S/cm at room temperature can be achieved for $Ag^+$-conducting chalcogenide glasses [2] and for $Li^+$-conducting one [3], respectively.

Recently a new type of electrical memory, i.e. the Programmable Metallization Cell (PMC), based upon the high mobility of silver in chalcogenide glasses has been proposed [4]. It takes advantage of a sudden increase in conductivity by several orders of magnitude when an increasing amount of silver is forced by polarization to diffuse inside a silver-photodoped glassy thin film of composition $Ge_{25}Se_{75}$ for example. Assumption that a phase separation with the presence of silver-rich domains would exist in the film was proposed to explain the phenomenon [5].

Bulk Ag–Ge–Se glasses have already been widely studied for their electrical, structural and thermal properties [6–12]. In particular it was shown that the conductivity of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with $1 < x < 30$ at.% changed suddenly by seven orders of magnitude for $x = 10$ at.%. Gutenev et al. indicated that the glasses were phase separated according to optical microscopy data [8]. Later, thermal analysis studies were carried out and, depending upon the authors, one or two vitreous transition temperatures were found [11,12]. None of these results gave a clue to understand the sudden jump in the conductivity data.

A series of experiments were recently carried out on $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with $1 < x < 30$ at.% in order to get new information. A neutron thermodiffraction study helped in getting insight in the crystallization process in the glasses [13]. We present here a study of $Ag_5(Ge_{0.25}Se_{0.75})_{95}$ and $Ag_{15}(Ge_{0.25}Se_{0.75})_{85}$ glasses by field emission-scanning electron microscopy and electric field microscopy which

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recently proved to be an efficient method to show the electrical inhomogeneity in glasses [14].

## 2. Experimental details

Two glasses with compositions $Ag_5Ge_{23.75}Se_{71.25}$ and $Ag_{15}Ge_{21.25}Se_{63.75}$, hereafter named Ag5 and Ag15 respectively, were prepared from high-purity (4 N) elements by the melt-quenching technique using an ice-water bath as previously described [10].

Fresh fractures of the two glasses were observed by field emission-scanning electron microscopy (FE-SEM) and electric force microscopy (EFM). FE-SEM measurements were carried out using a HITACHI S5400 instrument with an acceleration voltage of 20 kV and a magnitude of 3000×–30 000×. The EFM experiments were performed with a Nanoscope Dimension 3100 from Veeco Instruments operating in the Lift-Mode in ambient conditions. During an EFM measurement, an electric field between the tip of the cantilever (PtIr5) and the sample is induced by applying a voltage. The frequency of the cantilever oscillation depends upon the tip-sample interaction which in turn depends upon the electrical state of the sample surface. The frequency changes are detected and used to create an EFM image in the plane $(x, y)$. In practise two sweepings are necessary to create each scan line. A first sweeping

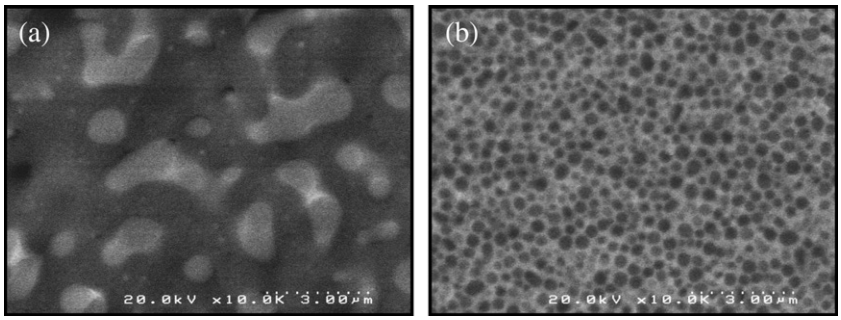


Fig. 1. FE-SEM micrographs of the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses: (a) $x = 5$ at.% and (b) $x = 15$ at.%.

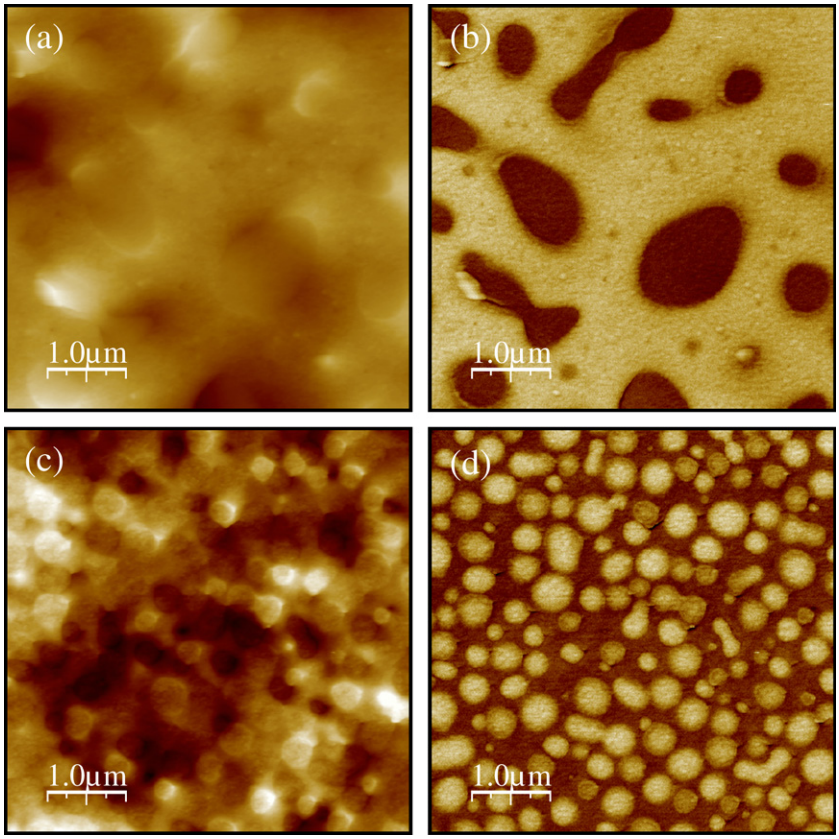


Fig. 2. EFM micrographs of the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses: (a) $x = 5$ at.%, topography, (b) $x = 5$ at.%, applied voltage $= -5$ V, (c) $x = 15$ at.%, topography, (d) $x = 15$ at.%, applied voltage $= -5$ V.

in the tapping mode without any voltage applied helps in recording a topography data and in evaluating the height at each point of the surface. During the second sweeping when the voltage is applied, the tip is lifted above the surface to an adjustable 'lift height' and the EFM data are generated. Dark regions in the diagrams represent strongly attractive zones between the tip and the sample. EFM images for both Ag5 and Ag15 samples were recorded using four different voltages, i.e. ±5 V and ±6 V.

## 3. Results

FE-SEM images of Ag5 and Ag15 samples are shown in Fig. 1(a) and (b), respectively. The strong chemical contrasts observed for both samples indicate that the glasses are phase separated with a connecting phase that includes nodules of a second phase. Interestingly enough it appears that the connecting phase for Ag5, i.e. the dark one, is the embedded one in sample Ag15 while the clear phase which was the embedded one for Ag5 becomes the connecting one for Ag15.

EFM images of Ag5 and Ag15 samples are shown in Fig. 2. Fig. 2(a) and (c) refer to the topography images for sample Ag5 and Ag15, respectively while Fig. 2(b) and (d) correspond to their EFM images when the voltage applied equals −5 V. Note that similar images were obtained when other voltages were applied. While the topography of sample Ag5 is rather flat, that of sample Ag15 shows stronger fluctuations. On the other hand EFM images show strong electrical inhomogeneity at the surface of both samples. The data point towards a phase separation for both glasses with a reversing of the connecting phase, i.e. from the clear phase to the dark one when changing from sample Ag5 to sample Ag15.

## 4. Discussion

The images obtained for Ag5 and Ag15 glasses by both experimental techniques, i.e. FE-SEM and EFM are in complete agreement between one another. They indicate a phase separation for both glasses and give similar indication on the size and nature of the two co-existing phases. For Ag5 glass the silver-rich phase (clear area for FE-SEM and dark one for EFM) corresponds to nodules of ~1 μm embedded in a connecting silver-poor phase. For Ag15 the silver-rich phase is the connecting phase while the silver-poor phase corresponds to nodules of 250–500 nm. The presence of a phase separation is in agreement with the former optical microscopy study by Gutenev et al. [8] and the conclusion of the modulated differential scanning calorimetry (MDSC) study reported by Wang et al. [12]. In the last case the authors based their conclusions on the presence of two vitreous transition temperatures ($T_g$) that are observed on MDSC for glasses with $10 \leqslant x < 25$. Compared to the optical microscopy measurement, our data give the signature of the phase separation not only on topology basis (presence of inclusions) but also on the basis of chemical contrast and electrical inhomogeneity. The additional information is decisive to understand the evolution of the conductivity when the silver content increases, i.e. the jump of seven orders of magnitude in the conductivity for $x \sim 10$ at.%. Clearly such a jump is related to the fact that the silver-rich phase that was first embedded in the silver-poor phase becomes the connecting one for $x > 10$ at.% and becomes the one that controls the silver diffusion.

## 5. Conclusions

The FE-SEM and EFM images of $Ag_5Ge_{23.75}Se_{71.25}$ and $Ag_{15}Ge_{21.25}Se_{63.75}$ glasses helped in understanding the difference of seven orders of magnitude in the conductivity of the two materials. The materials are phase separated and while a silver-rich phase is embedded in a silver poor phase for the first glass, the reverse is true for the second with the silver-rich phase controlling the silver diffusion throughout the material.

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