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Phase separation and ionic conductivity: an electric force microscopy investigation of silver chalcogenide glasses

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Electric Field Microscopy was used to characterise the electrical heterogeneousness existing in several chalcogenide glasses. While the $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses were shown to be homogeneous, sulphide $(Ag_2S)_x(GeS_2)_{100-x}$ and $(Ag_2S)_x(As_2S_3)_{100-x}$ and selenide $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses show heterogeneousness. Such a heterogeneousness is the electrical signature of a phase separation existing in the glasses. The obtained data helped us in identifying the phase separation and the subsequent percolation threshold as being responsible for the big jump occurring in the conductivity curve of these materials.

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1. Introduction

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, the latest developments of all solid state secondary batteries include Li_2S-based glasses or glass-ceramics as the electrolyte [1]. Chalcogenide glasses can be used as sensitive membranes for the development of chemical sensors for the detection of heavy ions in aqueous media [2]. They are transparent in the infrared (up to the far IR ~ 20µm for the telluride glasses) and have been used as glasses for night vision [3], as optical fibers [4] and when prepared in a thin film form as components for integrated optics [5, 6]. Because of an intrinsically metastability, structural modifications can be induced in some chalcogenide materials, in particular in telluride ones, by applying an external, *e.g.* optical or electrical, stimuli. It is the basis of the functioning of optical (CD, DVD, Rewritable DVD) or electrical (Unified Ovonic Memory-UOM) [7] devices for data storage. More recently a new type of electrical memory based upon the high mobility of silver in chalcogenide glasses has been proposed [8]. 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 voltage is applied (~ 0.3V). When applied to nanometric devices (when the thickness of the glassy film is typically 20-30nm), the phenomenon is characterized by a very short time for commutation (~10ns) and a very high cyclability ($>10^6$ cycles).

For many applications, *e.g.* solid state batteries, chemical sensors, PMC memories, the ionic mobility plays an essential role. Thus a survey of ionic transport in chalcogenide glasses is a topic of interest to the academic community as well as industries using these glasses. It might be of a particular interest to know the link that exists between the structure – at an atomic level as well as a microscopic level - and the electrical properties in these glasses, all the more that phase separations - which are a common phenomenon in glasses that they result from a spinodal decomposition or from a germination-growth process- can affect strongly the electrical properties. Very few authors dealing with the electrical properties of chalcogenide glasses have attempted to get an insight in the homogeneity of the materials. Might it be due to experimental difficulties or due to the need of specific equipment?

Since several years we had to face the problem when we attempted to get an insight in the laws that govern the evolution of the conductivity with the mobile ion content in chalcogenide glasses [9, 10]. The domain of composition had then to be widened from very few percents in cation up to several tenths of percents - typically from 0,01% to 20-30% in atomic fractions of cation - and the change in the glass homogeneity then revealed to be critical. A systematic investigation of the relationship existing between electrical conductivity and “structure” was then carried out in the Ag-Ge-S and Ag-As-S systems. While the investigation was first carried out on the basis of experimental data collected from complex impedance spectroscopy (CIS) and field-effect scanning electron microscopy (FE-SEM) [11] it has been recently extended to electrical force microscopy (EFM) [12]. Such a technique which can probe electrical heterogeneousness had never been used previously for the characterisation of inorganic glasses but it had been successfully used to visualise heterogeneous blends of polymers with different dielectric constants [13]. Finally a similar type of investigation, including CIS, FE-SEM and EFM characterisation, was performed in a selenide system, *i.e.* Ag-Ge-Se [14].

The paper will review the main results of the whole investigation. Those concerning the sulphide systems will be described first followed by those obtained with the selenide family.

2. Experimental

Synthesis and conductivity

Bulk glasses of composition $(Ag_2S)_x(GeS_2)_{100-x}$, $(Ag_2S)_x(As_2S_3)_{100-x}$, $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ and $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ with different silver contents were prepared by the melt-quenching technique as already described [11, 15]. The electrical conductivity measurements were performed on bulk samples using the impedance spectroscopy technique in the frequency range 5Hz - 2MHz and the temperature range 293-363 K [11, 16].

Field Emission-Scanning Electron Microscopy (FE-SEM)

The chemical contrasts at the glass surface were observed by field emission-scanning electron microscopy on a fresh fracture of the sample. FE-SEM measurements were carried out using either a LEO-982 instrument with an acceleration voltage varying from 1 to 5kV and a magnification of 5000x-20000x or a HITACHI S5400 instrument with an acceleration voltage of 20kV and a magnitude of 3000x-30000x.

Electrostatic Force Microscopy (EFM)

Electrical heterogeneousness at the sample surface was studied by EFM. The EFM experiments were performed with a Nanoscope Dimension 3100 from Veeco Instruments operating in the Lift-Mode in ambient conditions using fresh fractures of glasses. Several images of each glass were recorded while different voltages, from -6V to +6V, were applied between the tip (PtIr5) and the sample.

In fact, two sweepings were necessary to create each scan line. First, topographical data were taken in the *Tapping Mode* without any voltage applied. It helped in evaluating the height at each point of the surface. A second sweeping was then performed while maintaining a constant separation between the tip and the local surface. During the second sweeping a voltage was applied between the tip and the sample surface. Due to the electrostatic forces an electric field gradient was sensed which generated the EFM data. In this method the information is collected in the following way: the cantilever is vibrated by a small piezoelectric element near its resonant frequency. The resonant frequency changes in response to any additional force gradient. Attractive forces make the cantilever effectively “softer,” reducing the cantilever resonant frequency. Conversely, repulsive forces make the cantilever effectively “stiffer,” increasing the resonant frequency. Changes in cantilever resonant frequency were detected owing to the frequency modulation detection. In the EFM images, dark regions represent strongly attractive zones between the tip and the sample.

3. Results and discussion

Ag – Ge(As) – S systems

Glasses belonging to the pseudo-binary Ag_2S-GeS_2 and Ag_2S-As_2S_3 systems and to the glasses $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses with different content in silver have been studied from both electrical and microstructural point of view [9-11]. The main results are summarized in Figs. 1 and 2. Let us first concentrate on the first two systems. Fig. 1 shows a log-log plot of the conductivity at room temperature versus composition for the two glass systems. The data clearly show two different conductivity domains, with a strong increase of 4 to 5 orders of magnitude in the conductivity occurring at about 8 at. % in silver.

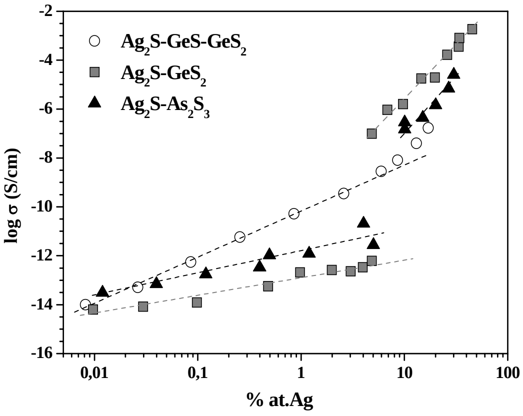

Fig. 1. Variation of the conductivity at room temperature with silver content (in at%) for $(Ag_2S)_x(GeS_2)_{100-x}$ [11]; $(Ag_2S)_x(As_2S_3)_{100-x}$ [10] and $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ [9] glasses.

A FE-SEM investigation performed on the glasses clearly showed phase separation. As an example Figs. 2a and 2b show the FE-SEM images of two $(Ag_2S)_x(GeS_2)_{100-x}$ glasses, the first one containing 5 at. % in silver and belonging to the low conductivity domain and the second one containing 15 at. % in silver belonging to the high conductivity domain [11]. While the Ag-poor regions, *i.e.* those corresponding to the dark areas in the micrographs, are connected in the glass with 5 at. % in silver, the Ag-rich regions corresponding to the clear areas in the micrographs are the ones to connect in the silver-rich glass. Similar results were obtained for the $(Ag_2S)_x(As_2S_3)_{100-x}$ glasses and as a matter of fact, the FE-SEM micrographs clearly indicate that the change in conductivity regime occurs when the regions of the Ag-rich phase start to connect in either $(Ag_2S)_x(GeS_2)_{100-x}$ or $(Ag_2S)_x(As_2S_3)_{100-x}$ glasses. This behaviour is characteristic of a percolation threshold, the Ag-poor phase (Ag-rich phase) being responsible for the conductivity at low silver (high silver) content. Previous radioactive tracer measurements have shown that the conductivity was mainly ionic even for glasses with low silver contents [17]. The existence of the percolation threshold therefore explains the jump in conductivity observed.

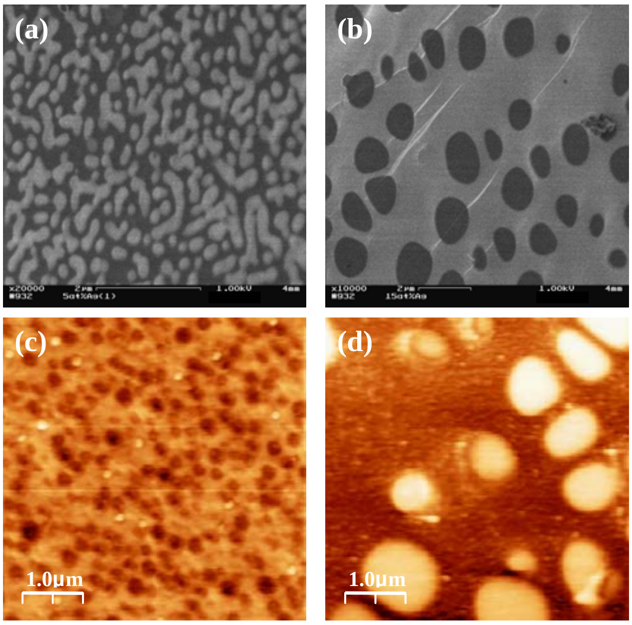

Fig. 2. FE-SEM micrographs of the $(Ag_2S)_x(GeS_2)_{100-x}$ glasses containing 5 at % Ag (a) and 15 at % Ag (b) [11]; EFM micrographs of the same glasses, i.e. $(Ag_2S)_x(GeS_2)_{100-x}$ with 5 at % Ag (c) and 15at % Ag (d) (applied voltage = - 3V).

At the opposite the conductivity of the $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ with different content in silver does not show any jump in the conductivity when the amount of silver is changed. All the more does one observe a change in conductivity regime at about 8 at. % in silver as shown in Fig. 1. The FE-SEM investigation revealed that these glasses are homogeneous whatever the amount of incorporated silver. Examples are given in Figs. 3a and 3b where the FE-SEM images of two glasses containing 5.8 and 16.7 at.% in silver respectively are shown.

The EFM technique was used to characterise the glasses from the three previously studied systems. Typical EFM images are given in Figs. 2c, 2d, and 3c, 3d for the $(Ag_2S)_x(GeS_2)_{100-x}$ and $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses respectively. The obtained images contain only the electrical signature of the sample surface since any topographical signature had been identified during a first sweeping of the cantilever over the sample and discarded during the second sweeping when the cantilever is polarised at -3V. While the images of the $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses containing 5.8 and 16.7 at.% in silver, shown in Fig. 3c and 3d respectively, are smooth and therefore indicate electrically homogeneous samples, the images of the $(Ag_2S)_x(GeS_2)_{100-x}$ glasses containing 5 and 15 at.% in silver and shown in figures 2c and 2d respectively contain dark and clear areas which are the signatures of an electrically heterogeneous sample with regions of high and low dielectric constants respectively.

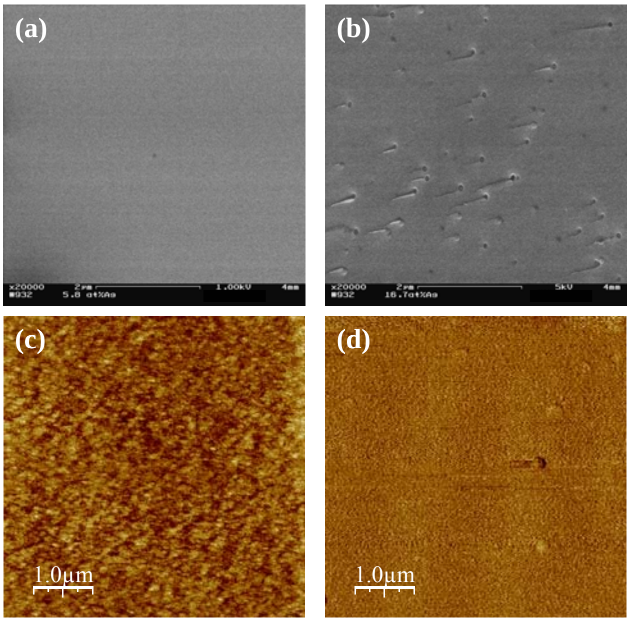

Fig. 3. FE-SEM micrographs of the $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses containing 5 at % Ag (a) and 15 at % Ag (b); EFM micrographs of the same glasses, i.e. $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ with 5.8 at. % Ag (c) and 16.7 at. % Ag (d) (applied voltage = - 3V).

In the case of $(Ag_2S)_x(GeS_2)_{100-x}$ glasses with 5 at. % in silver, the dark zones (where the cantilever is strongly attracted) are dispersed in a clearest matrix (where the cantilever is less strongly attracted). The situation changes for the 15 at % Ag glass with the clear areas being then embedded in the dark matrix. From a general point of view, the dielectric constant of an ion conducting glass is all the higher that the content in modifier cations is large. It is a consequence of the polarizing character of these species. Therefore the dark zones correspond to the regions of high Ag content while the clear ones are the Ag-poor zones (a situation reversed from the FE-SEM images where the clear/dark zones are the Ag-rich/Ag-poor ones respectively!).

All the EFM images which show the electrical heterogeneousness existing in the samples correlate very well with the FE-SEM images which are the signature of chemical heterogeneousness of the samples. As a matter of fact, the distribution and size of the dark/clear spots in EFM images of $(Ag_2S)_x(GeS_2)_{100-x}$ glasses are similar to the distribution and size of the silver rich/silver poor phases in the corresponding FE-SEM images (Fig. 2). Moreover all the images of the $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses, either obtained by FE-SEM or EFM, shown in Fig. 3, indicate that the samples are homogeneous, both chemically and electrically.

This study validates the EFM technique as a convenient tool to investigate electrical heterogeneousness in inorganic glasses. It helped us in visualising a phase separation in ionic conductive glasses from an electrical point of view for the first time.

Ag – Ge – Se system

Owing the encouraging results obtained in the sulphide systems, a similar investigation was performed in a selenide system, *i.e.* Ag-Ge-Se. Among the previous studies on bulk $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with different content in silver, two are related to the homogeneity in the glasses and are therefore of particular importance for our investigation. The first one is an early study by Gutenev and coworkers who indicated a phase separation probed by optical microscopy [18]. The second was performed by Wang and coworkers [19]. On the basis of a temperature modulated differential scanning calorimetry investigation, the authors conclude to a macroscopic phase separation in $Ag_x(Ge_ySe_{1-y})_{100-x}$ bulk glasses ($y = 0.20, 0.25, x \neq 0$). While a bimodal glass transition temperature was clearly evidenced when $y = 0.20$, a huge crystallisation peak corresponding to the appearance of the Ag_8GeSe_6 argyrodite, made a straightforward observation of two endotherms very difficult in the case of glasses with $y = 0.25$ (the one of interest in our investigation). However, careful measurements and a controlled crystallisation process helped the authors in identifying a second weak endothermal accident which would be the signature of a second glass transition temperature for glasses with $y = 0.25$ and $x > 10$. The EFM investigation could clearly help in getting additional information on the homogeneity of the glasses.

But let us first indicate the previous investigation on the electrical properties of these glasses. An early work was carried out in our team many years ago [20]. More recently the evolution of conductivity at room temperature with the silver content for the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with different content in silver was studied by Kawasaki and coworkers [21] and by Ureña and coworkers [22]. The results are given in Fig. 4. A similar trend as that reported for the $(Ag_2S)_x(GeS_2)_{100-x}$ glasses is observed, *i.e.* a sudden jump in conductivity of 7 orders of magnitude from 10^{-12} to 10^{-5} Scm^{-1} for a composition corresponding to $x \sim 8$-10 at. % Ag.

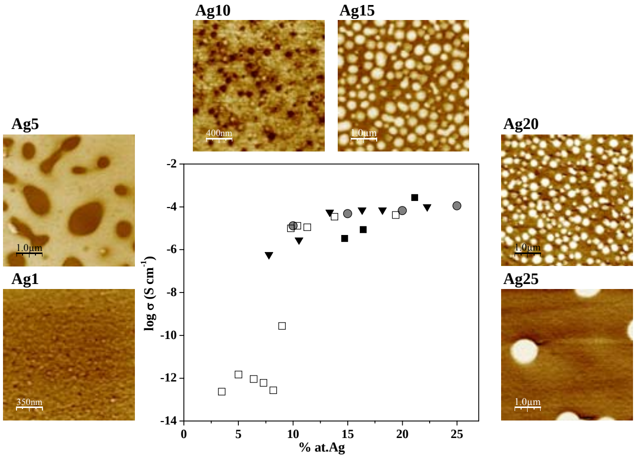

Fig. 4. Variation of the conductivity at room temperature with silver content (in at.%) for glasses $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ (data from ref :■ ▼ Tranchant et al. [20]; □ Kawasaki et al. [21]; ● Ureña et al. [22]) and EFM micrographs (applied voltage = - 3V) of the glasses with x = 1, 5, 10, 15, 20 and 25 at. % Ag (named in the figures Ag1, Ag5, Ag10, Ag15, Ag20 and Ag25 respectively).

The EFM images obtained when a voltage of -3V was applied to the tip of the cantilever are shown in Fig. 4 for six glasses belonging either to the zone of low conductivity or else to that with high conductivity. Clearly electrical heterogeneousness can be seen in most images with a distribution of clear/dark zones of various sizes depending upon the composition. On the whole several pieces of information can be deduced from the images:

1- A phase separation is observed in the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses as shown in Fig. 4. For the glasses containing less silver than 8 at. % Ag, *i.e.* for the low conducting glasses, the clear areas on the micrographs, *i.e.* those corresponding to the lowest silver content, are the interconnecting ones. At the opposite for glasses having a silver content larger than about 10 at. % Ag, it is the dark areas, *i.e.* those with high silver content which connect. The microstructure of the glass with 10 at. % in silver shows the smallest features of about 30-50 nm in size compared to the 10 times larger features observed in most of the other glasses. Therefore, as shown in Fig. 4, the phase separation and the subsequent percolation threshold help us in explaining – as in the homologous sulphide glasses - the important jump observed in the conductivity at about 8-10 at. % in silver.

2- Note that the glass with the lowest silver content, *i.e.* 1 at. %, appears to be homogeneous at least in the resolution limit of the apparatus.

3- At the opposite the phase separation still exists even at the highest silver content, *i.e.* for the glass with 25 at. % in silver, with spherical clear features of low dielectric constant and size of about 0.8-0.9 µm. Such a result contrasts with that obtained for the $(Ag_2S)_x(GeS_2)_{100-x}$ glasses which were shown to become homogeneous at high silver content [11].

4. Conclusion

The combined investigation of electrical conductivity by CIS and microstructure by FE-SEM and/or EFM helped us in identifying a phase separation as being responsible for the big jump of several orders of magnitude observed in the "conductivity versus silver content" curve in both sulphide Ag_2S-$Ge(As)S_2$ and selenide $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses. At the opposite the glasses $(Ag_2S)_x(GeS)_{60}(GeS_2)_{40-x}$ glasses were shown to be homogeneous. It was the first time that the electrical field microscopy was used to characterise inorganic glasses and it is the first time that a phase separation in ionic conductive glasses is visualise from an electrical point of view. The study validates the EFM- Electric Force Microscopy - as a very convenient method to investigate ionic conductive glasses. This new technique is very complementary from FE-SEM which gives a chemical signature of the material as compared to the electrical one for EFM.

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