JOURNAL DE PHYSIQUE IV
Colloque C8, supplément au Journal de Physique III, Volume 6, décembre 1996

New Insights of the Solid State Transformations in the Ag-Se-Ge System: a Mechanical Spectroscopy Study

S. Etienne, G. Taillades*, A. Pradel* and M. Ribes*

LMPSM, UA 155 du CNRS, Ecole des Mines, Parc de Saurupt, 54042 Nancy cedex, France
** LPMC, UMR 5617 du CNRS, Université Montpellier II, Place E. Bataillon, 34000 Montpellier cedex, France*

Summary: a study of degrees of freedom exhibited by partially crystallised material of the system Ag-Se-Ge is reported. Mechanical spectroscopy reveals 3 processes in the temperature range 250K to 330K. Two processes at 298K and 315K are assigned to solid state transformations in Ag_8GeSe_6 crystallites. A broad relaxation process exhibiting a high activation energy is connected to cooperative events assumed to occur in the glassy matrix. The two first processes also manifest in DSC experiments. The high temperature one is definitively attributed to allotropic transformation of Ag_8GeSe_6 crystalline phase. The low temperature one is reported for the first time in this paper and is attributed to the transformation of a crystalline metastable phase induced by constraints imposed by the surrounding glassy matrix.

1 INTRODUCTION

A study of glassy chalcogenide material of composition $0.2Ag_2Se,0.8GeSe_3$ has been previously reported [1,2]. It was shown that this material exhibits two relaxation processes: a so called β or sub Tg relaxation attributed to localised atomic motions and a main relaxation presenting cooperative features connected to the glass transition. In addition, a low temperature relaxation process was observed near 125K (frequency 1Hz) induced by the thermomechanically activated jumps of Ag^+ ions, in agreement with electrical conductivity measurements. A glass containing a slightly higher amount of Ag_2Se ($0.25Ag_2Se,0.75GeSe_3$) and presenting partial crystallisation is studied in this paper. The effect of this crystallisation on the different degrees of freedom as sudied by means of mechanical spectroscopy is reported. Additional data are provided by calorimetry and electrical measurements.

2 EXPERIMENTAL PROCEDURE

2.1 Material and specimen preparation

The appropriate amount of reacting materials were introduced in a silica ampoule which was evacuated up to 10^{-4} torr, sealed and placed in a rocking furnace. The product was heated at 900°C to obtain a homogeneous liquid and then allowed to cool down to room temperature. The ingot was cut in platelets of dimensions $40x6x0.7mm^3$ and $6x6x0.7mm^3$ for mechanical spectroscopy and electrical conductivity measurements respectively and polished.
In addition, a batch of pure Ag_8GeSe_6 was prepared according to ref [3]. Electrical conductivity measurements were carried out on a pellet of 10mm in diameter and 1mm thick.

2.2 Experimental Techniques

WAXS patterns were taken at room temperature with a Rigaku diffractometer (Cu Kα radiation) equipped with a $\theta/2\theta$ goniometer.
Calorimetry characterisation were carried out with a DSC 200 Netzsch. The heating rate was 10K/min.

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jp4:19968141

Electrical conductivity σ_{DC} was assessed *via* impedance spectroscopy by extrapolation down to zero frequency. The setup consisted of a General Radio model 1693 impedance meter and a cell allowing measurements in the range 220K-400K under vacuum. The electrical contacts were platinum deposited electrodes.
The dynamic mechanical modulus $G^*(j\omega)=G'(\omega)+jG''(\omega)=G(\omega)\exp j\varphi(\omega)$ was measured by means of a low frequency spectrometer previously described [4] working in the temperature/frequency range 90K-500K/10^{-4}-10Hz. The strain amplitude did not exceed 10^{-5}.

3 RESULTS

3.1 Characterisation by WAXS

WAXS pattern shows diffraction lines characteristic of the crystalline Ag_8GeSe_6 phase. These sharp lines are superimposed on the broad diffraction halo of the glassy $GeSe_3$ rich matrix.

3.2 Mechanical Spectroscopy Results

Figure 1 shows results of low frequency mechanical spectroscopy. The isochronal curves (figure 1a) clearly displays 3 relaxation processes in the temperature range 250K-350K. The two processes occuring at 298K and 315K manifest as sharp peaks associated with a modulus anomaly. The shoulder near 200K is identified as the β relaxation[1]. The temperature and intensity of the broad peak that develops in the range 250K-330K are sensitive to the measurement frequency, in contrast with the previous ones. The evolution of the broad peak is presented in more details in isothermal regime (figure 1b).

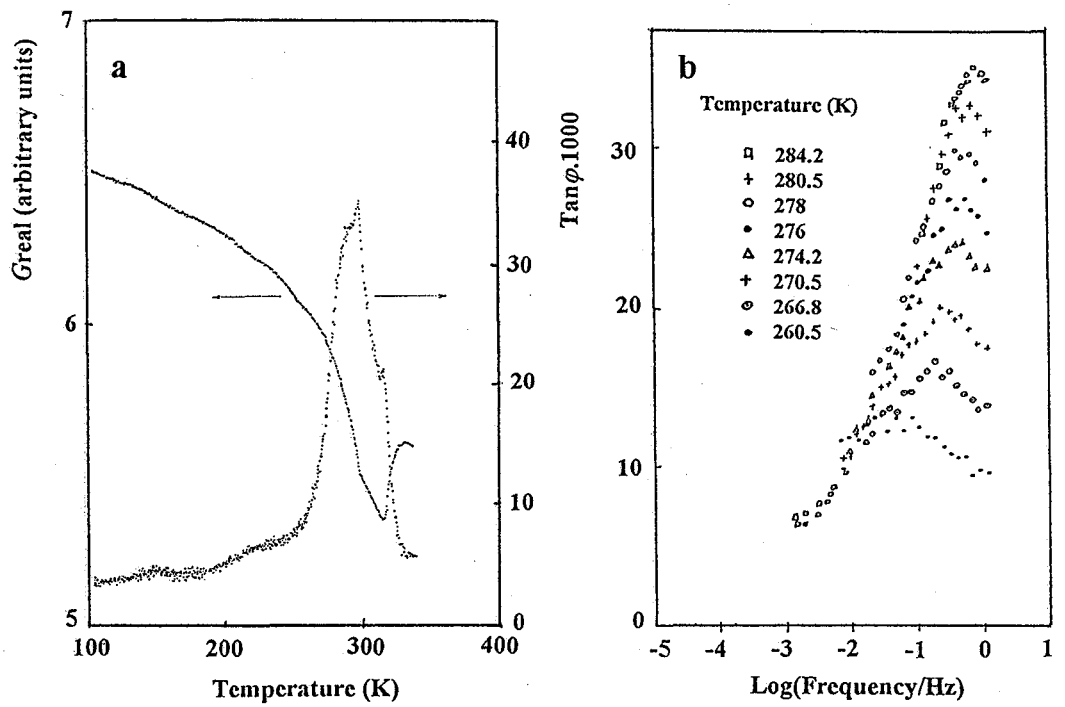


Figure 1: Dynamic behavior measured by low frequency mechanical spectroscopy:
a) isochronal mode and b) isothermal mode (only tanφ is represented)

It is to be underlined that the low temperature relaxation peak attributed to the jumps of Ag^+ ions in the glassy matrix has almost vanished.

3.3 Calorimetry study

Calorimetry experiments are carried out in the temperature range 250K-573K. The glass transition of the glassy matrix is thus determined equal 470K according to the onset of the endotherm. As shown in figure 2, several thermal effects are observed in the range 250K-350K: four endothermic peaks develop at 278K, 299K, 320K and 345K. A shoulder is also present on the low temperature tail of the 320K peak.

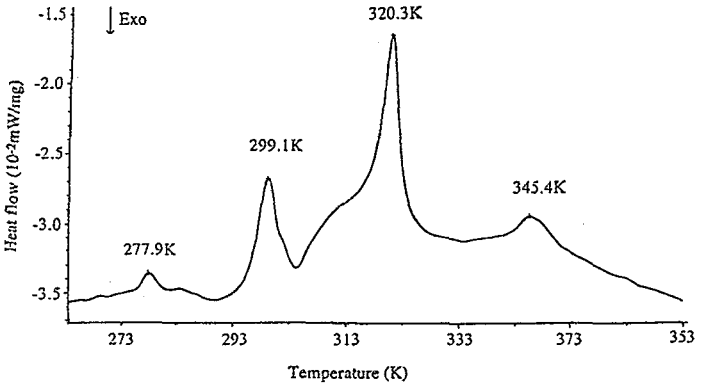


Figure 2: Calorimetry scan (10K/min). Only the part under interest 250K-350K is represented.

3.4 Electrical Conductivity

The complex impedance plots clearly show two semicircles indicating an electrical inhomogeneity of the

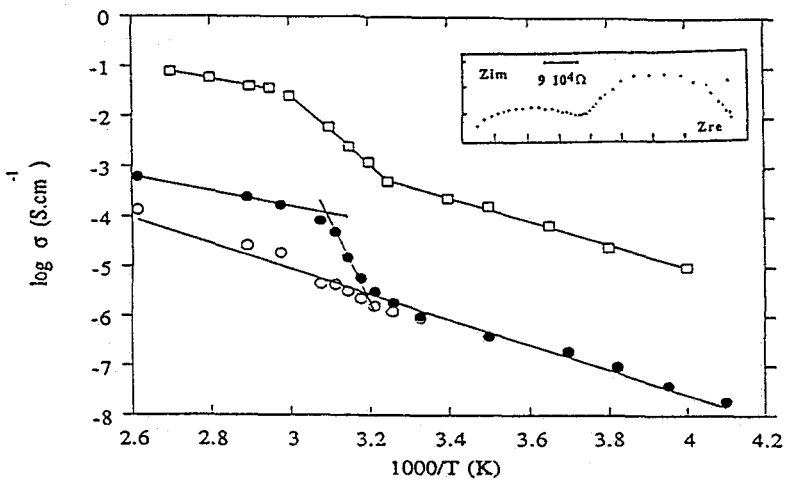


Figure 3: Arrhenius plot of pure Ag_8GeSe_6 (□) and of the phases present in $0.25Ag_2Se,0.75GeSe_3$ (low frequency (○) and high frequency (●) semicircles). The Cole Cole plot at 303K is shown in the inset.

material and therefore the presence of at least two phases (inset in figure 3). The two semicircles can be independently analysed. Their temperature dependence is reported in figure 3 together with that of the pure Ag_8GeSe_6 crystalline compound. The dc conductivity deduced from the high semicircle shows a jump of about two orders of magnitude at a temperature of about 320K close to that observed on the pure Ag_8GeSe_6 conductivity curve. Moreover the activation energies of the low and high temperature conductivities are similar for both materials *i.e.* 0.51 and 0.3eV for the partially crystallised material respectively and 0.45 and 0.33eV for Ag_8GeSe_6. On the other hand the dc conductivity deduced from the low frequency semicircle obeys an Arrhenius law with an activation energy of 0.51eV in the whole investigated temperature range. The conductivities of the phases present in the examined material are similar at low temperature.

4 DISCUSSION AND CONCLUSION

Mechanical spectroscopy, electrical conductivity and DSC measurements show that the partial crystallisation of $0.25Ag_2Se,0.75GeSe_3$ proceeds in a complex way. The presence of the crystalline phase is obvious (lines in the Xray diffraction pattern, endothemic peaks at 278K and 321K on the DSC curve corresponding to the successive allotropic transformations $\alpha' \rightarrow \beta' \rightarrow \gamma$ of Ag_8GeSe_6 phase [3], jump in the conductivity curve at about 320K very similar to that observed for the pure Ag_8GeSe_6 conductivity ($\beta' \rightarrow \gamma$), sharp peak indicating a phase transition at the same temperature on the isochronal $\tan\varphi$ curve). Other features show that one or more additional phases are present. For example, if the high temperature endotherm at 345 K has already been reported by Gorochov in the DTA curve of pure Ag_8GeSe_6 even though it was not identified, the additional peak at 299K on the DSC curve has never been reported. It is assigned to a second crystalline phase which undergoes a transition at this temperature. This fact is supported by the sharp $\tan\varphi$ maximum with the temperature peak unsensitive to frequency which is observed at the same temperature by mechanical spectroscopy. The presence of the low frequency semicircle on Cole Cole impedance plots and the high values of the conductivity deduced from this semicircle indicate that a second conductive phase is present.

As a result a non negligeable amount of silver is not incorporated in the Ag_8GeSe_6 crystallites.Whether it is present in the glassy matrix or in the second crystalline phase cannot be deduced from conductivity measurements. The mechanism responsible for the broad $\tan\varphi$ peak observed on isochronals (figure 1a) is more difficult to identify. Frequency scans (figure 1b) show that it is a relaxation process, but with a strong departure from Arrhenius behaviour (high apparent activation energy and strength sensitive to temperature). It could be assigned to the nanocomposite structure *i.e.* constraints of amorphous matrix on crystallites of different chemical compositions with misfit of thermal expansion. These observations reveal the behavior complexity of the material resulting from $0.25Ag_2Se,0.75GeSe_3$ partial crystallisation and illustrate the interest of complementary techniques. Further experiments are in progress in order to better clarify this behavior.

References

[1] Etienne S., Perez J., Peytavin S. and Ribes M., J. Solid State Chem., **92** (1991) 27-38

[2] Etienne S., Pradel A. and Ribes M., J. Non-Cryst. Solids, **131-133** (1991) 1072-1075

[3] Gorochov O., Bull. Soc. Chim. France, **6** (1968) 2263-2275

[4] Etienne S., "*Low frequency: Special Techniques*", in *Mechanical Spectroscopy in Materials Science*, Magalas L.B. Ed., (Chapman and Hall, London, in press).