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Degrees of Freedom and Ionic Mobility in Silver Chalcogenide Glasses

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This work is a contribution to the understanding of ionic transport phenomenon in chalcogenide glasses. The dynamics of mobile species and the relaxational behavior of the glassy matrix near and below T_g are studied through mechanical spectrometry measurements. The intrinsic relaxation phenomena of the glassy matrix are studied against composition and the effect of thermal history is shown. The characteristic time for elementary jumps of silver ions is measured. © 1991 Academic Press, Inc.

1. Introduction

Investigation of ionic conductivity of vitreous materials is interesting from both practical and theoretical points of view. The practical aspect results from possible applications of ionic conducting glasses on one hand as solid state electrolytes in the field of microionics (*1, 2*) (RAM backup microgenerators, interdigited systems . . .) and on the other hand as high resolution photoresists for VLSI microlithography processes (*3–5*). The fundamental aspect is derived from the fact that mechanisms of ionic transport in glasses are not completely resolved. In particular, the evolution of parameters such as concentration, mobility of free carriers against composition, and temperature is not definitively established.

The aim of our work is to study the dynamics of mobile ions and the relaxational behavior of the glassy matrix where these ions move. As a matter of fact, any theory of ionic transport (weak or strong electrolyte) needs to be supported by experimental observations as complementary as possible. Generally, mobility (i.e., movement) of ions is investigated through measurements giving information about macroscopic quantities (electrical conductivity, diffusion constants . . .) or through spectroscopy techniques (NMR, IR . . .). In the first case, the micro–macro link is conditioned by models in which several parameters are involved. To achieve complementary information, we have used a method very sensi-

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tive to ionic or atomic degrees of freedom: the low frequency mechanical spectrometry. Such observations, in association with those given by more conventional methods, should lead to a better knowledge of microscopic mechanisms at the origin of ionic transport in glasses.

2. Very Low Frequency Mechanical Spectrometry

First, let us compare information given by mechanical and electrical spectrometry. For the sake of simplicity, we assume that only one kind of ion is mobile in a perfect medium. If we suppose that ions are not connected with electrical dipoles (nonpolarizing system), conduction takes place as a consequence of thermally activated jumps from site to site in energy profile a given in Fig. 1. Following this classical scheme, the complex permittivity $\varepsilon(i(\omega)$ of the material can be written

$$\varepsilon(i\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_0 - i\sigma_{dc}/\omega, \quad (1)$$

where

ε_0 = permittivity of the medium at infinite frequency

σ_{dc} = conductivity relative to mobile ions.

In this situation, the real component ε' exhibits no dispersion. The Cole–Cole representation of the complex impedance $z'(\omega) + iz''(\omega)$ is a semicircle and the $(-z'')$ component is maximum when $\omega\tau(T) = 1$, with

$$\tau(T) = \varepsilon_0(T)/\sigma_{dc}(T). \quad (2)$$

So, impedance spectrometry is related to the macroscopic quantity $\sigma_{dc}(T)$, representative of ionic transport, which can be written

$$\sigma_{dc} = C\mu Zq$$

with C, μ, Zq equal, respectively, to the concentration, the mobility, and the charge of free carriers.

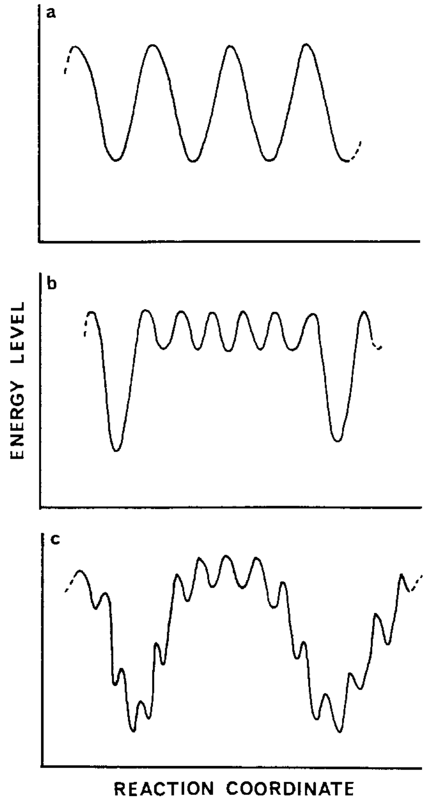

FIG. 1. Energy profile against configuration coordinate for the motion of mobile ions in the glassy matrix.

The mobility (i.e., mean velocity/electrical field ratio) is

$$\mu = \nu(\lambda^2 Zq/2\alpha kT)$$

with

$\nu = \nu_0 \exp(-E/kT)$

ν_0 = vibration or Debye frequency of the ion in the site

λ = mean distance of jump

α = numerical factor.

Let us now consider the response of the

same material to a shear stress field and suppose the temperature far below the glass transition. Under this applied shear stress, the glassy network exhibits naturally an elastic deformation. Moreover, some structural units, especially the mobile ions, can jump from one stable position to another as a consequence of thermally activated transitions. These transitions and the applied stress field can couple if both present components of the same tensorial nature. If some local symmetry exists (*6, 6a, 6b*), some sites are favored by the applied stress and populations reorganize among accessible sites, which leads to a relaxation process with a characteristic time,

$$\tau = N/\nu$$

with

N = numerical factor depending on the number of stable adjacent sites

$\nu = \nu_0 \exp(-E/kT)$.

However, contrary to an electrical field, the shear stress field does not induce a diffusional process of mobile ions over long distances. The mechanical relaxation process gives rise to energy loss and the imaginary component of the complex shear modulus $g(i\omega) = g'(\omega) + ig''(\omega)$ is maximum when $\omega\tau = 1$. The relaxation strength is proportional to $\delta C/kT$, δ being the shear strain increment for an event.

Thus, mechanical spectrometry measurements give two independent pieces of information: the concentration C of mobile particles (proportional to the relaxation strength) and the characteristic time of events from a microscopic point of view. The subset of ions moving in the rigid glassy network ($T < Tg$) can then be considered as subject to a secondary-like mechanical relaxation. On the other hand response to an electrical field, associated with long range transport, would resemble a primary relaxation. In fact, the mechanical equivalent of Eq. (2) is Eq. (3), describing the viscoelastic behavior of a glass near the glassy transition (*7*) and concerning all the structural units (i.e., primary or so-called α relaxation): at high temperature and if the observation time is long enough, ergodicity conditions (*8*) are fulfilled and the dynamical behavior of the glass becomes characterized by its viscosity $\eta(T)$. The macroscopic relaxation time can be written

$$\tau(T) = \eta(T)/G_0(T) \tag{3}$$

with

G_0 = elastic modulus at infinite frequency.

The actual situation can deviate from this simple and ideal case:

(i) some authors (*9*) consider glasses as weak electrolytes, i.e., all ions are not free to move at the same time. The concentration of free ions is then controlled by the equilibrium

$$-(X^+M^-) \rightleftarrows -(X^-) + (M^+)$$

with M = metallic atom (here: silver)

X = chalcogen atom (here: selenium).

The energy profile is rather that of the b-type in Fig. 1. Under these conditions, the activation energy of σ_{dc} is the sum of two components:

$$E = E_m + E_d/2$$

where

E_m = activation energy for migration

E_d = activation energy for the dissociation constant.

(ii) In addition, permittivity $\varepsilon(i\omega)$ (or $\sigma(i\omega) = i\omega\varepsilon(i\omega)$) generally presents a dispersion. To explain such a behavior associated with M^+ ions motion, a distribution of energy barrier is generally considered. Another hypothesis should be taken into account: the series-coupled mechanisms. Following this model, the creation of a mobile M^+ ion is the result of exploration of several energy levels (profile c in Fig. 1). Then, ergodicity conditions are broken at short times (high frequencies) and Eq. (1) becomes:

$$\begin{aligned}\varepsilon(i\omega) &= \varepsilon_0 + H'(i\omega)\\ &= \varepsilon_0 + H(i\omega) - i\sigma_{dc}/\omega \quad (4)\end{aligned}$$

The function $H'(i\omega)$, representative of the complex motions of ions, is generally expressed as a noninteger power-law of angular frequency, according to the assumption of series processes. The conduction term is the zero frequency limit of $H'(i\omega)$, while the term $H(i\omega)$ represents the contribution of ion motions in the sites. This mechanism is an alternative to the one proposed by Elliot (*10*) who considers that series process coupling in the site takes place at the arrival of another M^+ ion. We can remark that the expression for permittivity recalls a physical model used for describing the mechanical behavior of glassy materials near Tg. This model, developed elsewhere (*8*), is based on the concept of entropy fluctuations (domains of high entropy are called defective sites) and of correlated atomic motions. In this model the main mechanical relaxation α, concerning the whole disordered structure, is described by the following expression for the compliance:

$$\begin{aligned}j(i\omega) &= g^{-1}(i\omega)\\ &= G_0^{-1} + A \cdot H(i\omega) - i(A/\tau)/\omega \quad (5)\end{aligned}$$

where

A is a term proportional to the concentration of defective sites
τ is a characteristic mechanical relaxation time
$H(i\omega) = (i\omega\tau)^{-b}$

with

b the effectiveness of correlation ($b = 1$ no correlation; $b = 0$ correlation is maximum)

If the temperature is far below Tg, the glassy network is elastic and the only contribution to nonelastic deformation results from mobile units such as M^+ ions moving in a type c profile (Fig. 1). The situation is then more complex as different configuration modes (or transition) become possible. For example, a M^+ ion can move within the site bounded to X^- and explore the different energy levels (reorientation of the X^- M^+ dipole), then jump from one site to another (migration). In principle, mechanical spectrometry should give information about these different degrees of freedom if their characteristic times are distinct.

To sum up, if we consider the M^+ ion sublattice, the mechanical relaxation is secondary in nature, while the electrical response, associated to long range transport, can be compared to a primary relaxation.

From the experimental aspect, mechanical spectrometry consists of measuring the time-dependent strain of the sample γ under an applied stress ρ. The dynamic modulus is

$$\begin{aligned}g(i\omega) &= \rho(i\omega)/\gamma(i\omega)\\ &= g'(\omega) + ig''(\omega) = g(\omega)e^{i\varphi(\omega)}.\end{aligned}$$

Experiments were performed through temperature and/or frequency scanning with a low frequency torsional pendulum described elsewhere (*11*). This apparatus works in forced oscillations at very low relative strain level ($<10^{-5}$) in wide temperature and frequency ranges (77 to 550 K and 10^{-5} to 5 Hz).

3. The Material

Intensive research work on electrical properties of ion conducting glasses has been done during these last years (*12, 13*). However, few papers on mechanical properties of these materials and their comparison with electrical characteristics (*14, 15*) have been published.

Ge_ySe_{1-y} chalcogenide glasses in the composition range $0 < y < 0.25$ were chosen for this study. Indeed vitrification is possible over a wide composition domain and glasses can be obtained as bulk and thin-films. Moreover, measurements on glass $0.2Ag_2$–$0.8GeSe_3$ were performed to study the influence of silver on the glass network.

Bulk samples, typically 40 × 4 × 1 mm^3 are necessary to perform mechanical spectrometry experiments. For synthesis, appropriate amounts of pure products were mixed and introduced in a previously outgassed ampoule, which was then sealed under high vacuum (10^{-5} Torr). This ampoule had a volume of about 9 cm^3 and was half filled. The free volume was estimated to be nearly 5 cm^3. Under these conditions, 5×10^{-10} mole O_2 was present. Since synthesis was made with about 1/50 mole of glass, the rate of oxygen contamination did not exceed 10^{-9}. The melt was homogenized in a rocking furnace for several hours at 100 K above the liquidus. Bulk glassy material was obtained by air quenching. Internal stresses were released by annealing for several hours at a temperature a few degrees below Tg (*16*). The glass ingot was then cut into rectangular bars with a low speed diamond saw and the bar surfaces were polished with a diamond paste. This procedure did not induce significant internal stresses and no further annealing was carried out in addition to the first one that was necessary for cutting the ingot without breaking it.

4. Results

In order to characterize degrees of freedom associated with Ag^+ ions moving in the glassy chalcogenide matrix with no ambiguity, it is convenient to study the dynamical behavior of the pure glass first.

4-1. Effect of Composition (Ge_ySe_{1-y} Glass, $0 < y < 0.25$)

Addition of germanium increases its mean atomic coordination number $\langle c \rangle = 2y + 2$. As a consequence, some physical and thermodynamic properties (*17, 18*) such as elastic moduli (*19–21*) and glassy transition temperature (*22*) increase.

Ge_ySe_{1-y} glasses with increasing amounts of germanium were studied by low frequency mechanical spectrometry. Figures 2 and 3 present isochronal spectra (1 Hz) of modulus $g(T)$ and internal friction $\tan \varphi\ (T)$. All glasses exhibit subvitreous (or so-called β) relaxation, followed at higher temperatures by the main (or α) relaxation process resulting in an increasing of $\tan \varphi$ and a drastic decrease of modulus. β phenomenon, quasi-universally observed in disordered systems (*7, 23*), is attributed to localized motions of some structural units. The α relaxation process affects the whole glassy matrix and the corresponding behavior is described by Eq. (5).

The effect of measurement frequency is shown on Fig. 4, taking $y = 0.125$ as an example. An Arrhenius plot relative to the β process gives the corresponding activation energy, 0.76 ± 0.02 eV (nearly independent of composition), and the preexponential factor, 10^{15} Hz. This β peak is broader than expected for a single Debye relaxation process. This is generally observed in vitreous systems (*23*). The apparent activation energy of the α process is near by 2.6 eV in isostructural condition. This high value has been interpreted as a consequence of atomic correlated motions (*8*).

Isothermal curves shown in Fig. 5 are another illustration of the influence of frequency measurement. Experiments in isostructural conditions where carried out with a Se-rich glass ($y = 0.0505$), heated at 356

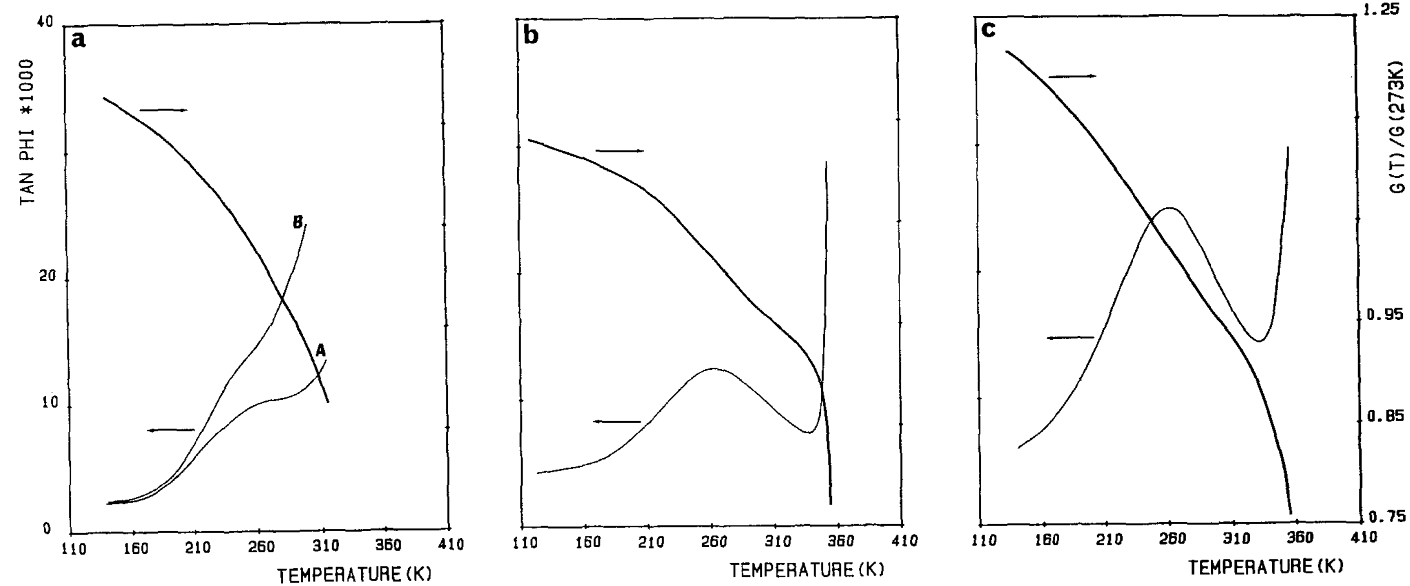

FIG. 2. Isochronal (1 Hz) tan φ (T) and modulus $g(T)$ spectra for chalcogenide glasses (low Ge content). (a) Se glass (curve A, glass stabilized at 283 K; curve B, glass stabilized at 293 K). (b) $GeSe_{18.8}$ glass. (c) $GeSe_9$ glass.

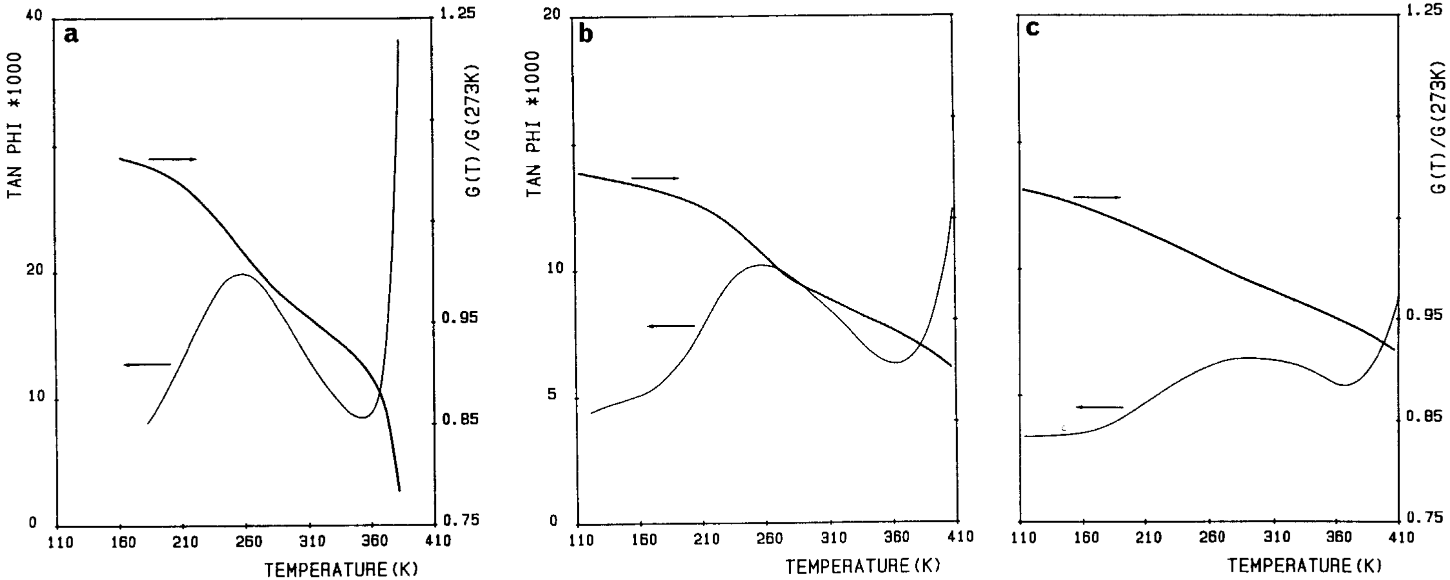

FIG. 3. Isochronal (1 Hz) tan φ (T) and modulus $g(T)$ spectra for chalcogenide glasses (high Ge content). (a) $GeSe_8$ glass. (b) $GeSe_4$ glass. (c) $GeSe_3$ glass.

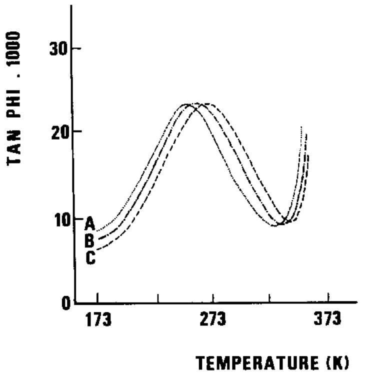

FIG. 4. Effect of frequency on the relaxation spectra of a GeSe$_7$ glass. Curve A, 0.1 Hz; curve B, 0.3 Hz; curve C, 1 Hz. Temperature shift in α and β regions gives the apparent activation energies.

K and aged 3 months at room temperature. When measurement temperature increases from 293 to 322 K, the shift from β to α regime in the frequency observation window (1 to 10^{-3} Hz) can be clearly observed. Analysis of the α process through this isothermal experiment can be performed by Eq. (5) where the quantity ω alone varies. This equation shows that the correlation coefficient b is given by:

$$\lim_{\omega\to 0}\frac{\partial g''(\omega)}{\partial g'(\omega)} = -\tan\left(b\frac{\pi}{2}\right).$$

A Cole–Cole plot in the low frequency range of the 322 K isotherm (relative to the α process) leads to $b = 0.2$. When structural units move independently (i.e., no correlation effect exists) b is equal to unity (*8*). This rather low value indicates a high correlation between atomic motions at the outset of the α process in this glass. It is noticeable that a frequency shift of the isotherms gives an apparent activation energy of about 2.6 eV, i.e., the same value calculated from isochronal curves in the same temperature range.

4-2. *Effect of Thermal History*

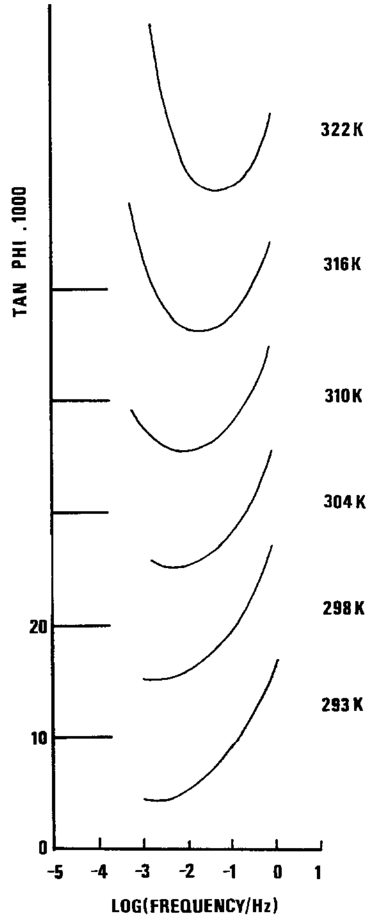

FIG. 5. Isothermal tan φ spectra measured in isostructural conditions. For convenience, isothermal curves are shifted 10×10^{-3} vertically at increasing temperatures (293 K isotherm is in the right position).

It is well known that physical and thermodynamic properties of a glass are dependent on its thermal history. A sample ($y = 0.0505$) was held at a temperature slightly higher than its Tg for several hours. Mechanical spectrometry measurements, carried out after this treatment, show that the α rising appears at a temperature much lower when compared to that observed on an as-prepared specimen (Fig. 6). This feature can be explained considering that: (i) thermal treatment at $T > Tg$ has increased fictive temperature of the glass and consequently induces an increase of coefficient A and a

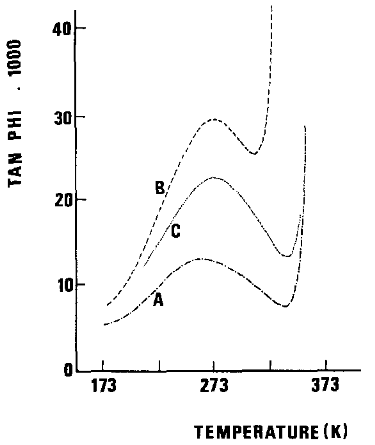

FIG. 6. Effect of thermal history on the relaxational behavior of a $GeSe_{18.8}$ glass. Curve A, as-prepared glass, obtained after slow cooling and annealing slightly below Tg. Curve B, after heating several hours at 356 K and cooled at room temperature. Curve C: same as B but subsequently aged at room temperature for 3 months.

decrease of characteristic time $\tau(T)$ in Eq. (3); and/or (ii) microphase separation leading to Se-rich microdomains presenting low glassy temperature transition has appeared (*16*). After ageing this sample for 3 months at room temperature, an increase in the α process temperature was observed: it is the manifestation of the well known physical ageing of glasses (*24*). Composition redistribution is far too slow below Tg and is to be ruled out. In addition, it can be observed that the β process strength increases upon heat treatment at $T > Tg$ and is depressed on ageing at room temperature, i.e. at $T < Tg$.

These observations demonstrate the importance of controlling the thermal history of a glassy specimen. As an example, the effect of fictive temperature on α relaxation of glassy selenium is clearly shown in Fig. 2a.

4-3. Effect of Silver Addition

The dynamic behavior of glass $0.2Ag_2Se$, $0.8GeSe_3$ has been studied and results have been compared to those of pure $GeSe_3$ glass. In the first case, an extra relaxation peak (of low strength but well resolved) was observed at low temperature. It can be attributed to degrees of freedom of Ag^+ ions. Activation energy (0.29 eV) and attempt frequency (10^{13} Hz) are deduced from shiftingfrequency measurement. Relaxation strength presents no significant variation in the temperature range 120–130 K. The peak is broader than a Debye peak and a distribution of energy barrier 0.023 eV around the mean value could explain this. Silver addition affects slightly the β peak, but decreases significantly the temperature of the α process (Figs. 3c and 7–9).

5. Discussion

The mechanical spectrometry method shows that chalcogenide Ge_ySe_{1-y} glasses exhibit degrees of freedom at $T < Tg$ which are manifested as β relaxation. This process

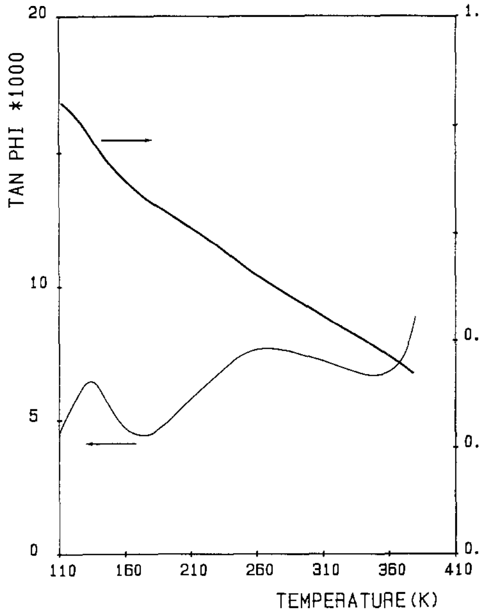

FIG. 7. Isochronal (1 Hz) Tan Phi (T) and modulus g(T) for a $0.2Ag_2Se$, $0.8GeSe_3$ glass.

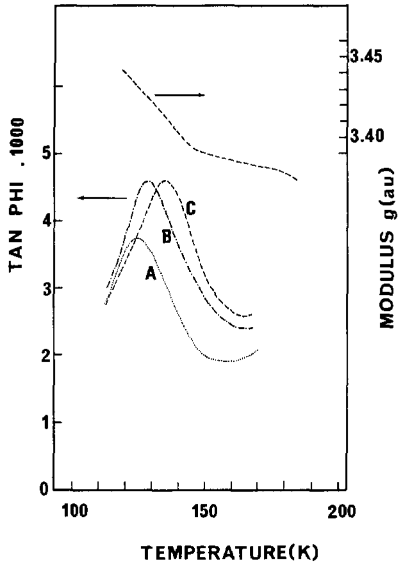

FIG. 8. Effect of measurement frequency on the low temperature peak of the silver chalcogenide glass. Curve A, 0.1 Hz; curve B, 0.3 Hz; curve C, 1 Hz.

is not resolved either through dielectric spectrometry as observed in the case of $As_x Se_{1-x}$ glasses (*25*) or through thermal analysis (*26*). This can be explained by the high sensitivity of mechanical spectrometry which allows observation of atomic motions which make very low contributions to specific heat.

It can be noticed that β relaxation strength (obtained after background substraction) goes through a maximum when y varies from 0 to 0.25 and that the peak temperature (which is 285 K for $y = 0.25$) is nearly constant and equals 264 K in the composition range $0 < y < 0.2$. Considering that this subvitreous relaxation process is linked to mechanical degrees of freedom of low-coordinated atoms (i.e., –Se–Se–), germanium addition would first increase the number of high mobility sites. This observation is consistent with the idea of close-packed microdomains (*27, 28*) (with composition close to $GeSe_2$), linked by Se-rich regions: as close-packed domains form more disorder is induced in the connective Se-rich regions, which may explain the increase of high mobility sites, i.e., the initial increase in β relaxation strength. For high values of y, the amount of Se-rich regions decreases and β relaxation strength logically vanishes. The sensitivity of β relaxation strength to thermal treatment suggests that quenching decreases the number of Van der Waals bonds and that the number of selenium atoms free to move increases, as previously discussed (*29*). In the case of pure selenium glass, β relaxation appears as a shoulder superimposed on the α process rising (Fig. 2). In this glass, local motions of –Se–Se– chains can combine with one another, leading to long range rearrangements since no crosslinking is present. So, in glassy selenium, the β mechanism is a precursor of main α relaxation.

Besides these intrinsic degrees of freedom of the Ge_ySe_{1-y} glassy matrix, silver addition leads to others: it has been seen (i) that the temperature of the α process is decreased and (ii) that an extra relaxation is observed at low temperature. Let us consider the schematic representation shown in Fig. 3. This situation gives electrical neutral-

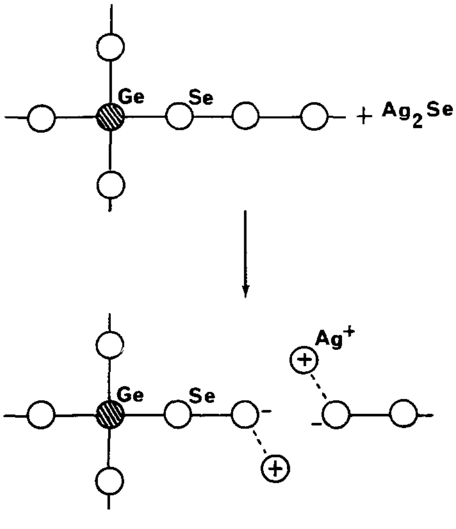

FIG. 9. Schematic representation of a silver ion site in a Ag–Ge–Se glass.

ity in a minimum volume and corresponds to a stable configuration. –Se–Se– bonds are broken, and from this classical representation, Ag_2Se behaves as a modifier of the Ge_ySe_{1-y} network. The formation of nonbridging selenium atoms would explain the decrease of glass transition temperature and, as a consequence, that of the α process.

Mechanisms responsible for the low temperature relaxation peak can be clearly attributed to thermally activated jumps of Ag^+ ions, but remain to be described from a microscopic point of view. *A priori,* mechanical spectrometry measurements alone cannot distinguish between dipole (Se^- Ag^+) reorientation or motion of Ag^+ ions over longer distances. However, it can be noticed that activation energy of this process (0.29 eV) is close to that measured for dc conductivity (0.33 eV) (*30*).

It is worth mentioning that the mean delay time between two consecutive jumps falls in the nanosecond range at room temperature as deduced from the Arrhenius law. That means that above room temperature, interaction with stress field and diffusive jumps is to be performed in the hypersonic regime through Brillouin scattering experiments (*31*).

Assuming (i) that Ge_ySe_{1-y} glasses present a microheterogeneous nature and (ii) that the Ag^+ path is not concerned with close-packed regions and recalling that photodoping is not efficient in pure selenium glass (*17*), it can be assumed that silver ions move in the highly disordered Se-rich regions, bording $GeSe_2$-rich microdomains. With this assumption, Ag^+ ions undergo interstitial-like jumps, leading to a relaxation process similar to that attributed to alkali ions in silicate glasses.

6. Conclusion

Low frequency mechanical spectrometry makes it possible to characterize different degrees of freedom in Ge_ySe_{1-y} glasses with or without mobile metallic ions.

Degrees of freedom intrinsic to the chalcogenide glassy matrix are responsible for a subvitreous, so-called β relaxation (attributed to local motions of low-coordinated selenium atoms) and for the main α relaxation (implying rearrangement of structural units over large distances).

Besides these intrinsic processes, a relaxation phenomenon attributed to thermally activated jumps of mobile metallic ions is observed at low temperature. From a microscopic point of view, this mechanism is identified with that of dc conductivity. It is then interesting to recall some experimental features obtained by means of the complex impedance method. Studies of dc conductivity, as a function of Ag_2Se content in the system $xAg_2Se - (1 - x)GeSe_3$ with $0.15 < x < 0.40$, show a drastic increase of conductivity for $0.15 < x < 0.25$ (*30*). For larger proportions of Ag_2Se, conductivity at room temperature becomes independent of composition. Activation energy remains nearly constant. Experiments on the systems $0.3Ag_2Se–0.7GeSe_2$, $0.3Ag_2Se–0.7GeSe_3$, $0.3Ag_2Se–0.7GeSe_4$ show that dc conductivity measured at room temperature drastically increases between $GeSe_3$ and $GeSe_4$, while its activation energy remains nearly constant.

Mechanical spectrometry studies are now being performed on glasses with different silver contents to test the effects of composition on the dynamics of metallic ions and to try to correlate the results with those observed through σ_{ac} and σ_{dc} measurements.

References

1. Y. Ito, K. Miyauchi, and T. Kirino, *Nippon Kagaku Kaishi* **86**(3), 445.
2. V. Delord, Thesis Montpellier (1986).
3. A. Tissier, J. Galvier, C. Masurel, and M. Pons, *Vide Couches Minces Suppl.* **128,** 203 (1983).
4. Y. Utsugi, A. Yoshikawa, and T. Kitayama, *Microelectron. Eng.* **2,** 281 (1984).
5. K. L. Tai, E. Ong, and R. G. Vadimsky, *Proc. Symp. Inorg. Resist. Syst.* (ECS-82-9) 37 (1982).
6. A. S. Nowick, *J. Phys. Colloq. C* **10** (Suppl. 12), 507 (1985).

6a. B. S. Berry, and A. S. Nowick *in* "Physical Acoustics" (W. P. Mason, Ed.), Vol. III, Part A, pp. 1–42, Academic Press, New York (1966).

6b. C. Wert, *in* "Physical Acoustics" (W. P. Mason, Ed.), Vol. III, Part A, pp. 43–75, Academic Press, New York (1966).

7. J. Perez, J. Y. Cavaillé, S. Etienne, and F. Fouquet, *Annal. Phys.* **8,** 417 (1983).

8. J. Perez, J. Y. Cavaillé, S. Etienne, and C. Jourdan, *Rev. Phys. Appl.* **23,** 125 (1988).

9. D. Ravaine and J. L. Souquet, *Phys. Chem. Glasses* **18,** 27 (1977).

10. S. R. Elliot, *Solid State Ionics* **27,** 131 (1988).

11. S. Etienne, J. Y. Cavaillé, J. Perez, R. Point, and M. Salvia, *Rev. Sci. Inst.* **53,** 1261 (1982).

12. H. Tuller and D. Button, 6th RISO International Symposium. "Transport Structure Relation in Fast Ion and Mixed Conductors" (F. Poulsen, N. Anderson, K. Clausen, S. Skaarup, and O. Sorensen, Eds.), p. 119 (1985).

13. A. Pradel and M. Ribes, *Mater. Chem. Phys.* **23,** 121 (1989).

14. T. J. Higgins, P. B. Macedo, and V. Volterra, *J. Am. Ceram. Soc.* **55,** 488 (1972).

15. C. A. Angell, *Mater. Chem. Phys.* **23,** 132 (1989).

16. C. Peyroutou, S. Peytavin, M. Ribes, and H. Dexpert, *Solid State Chem.* Part I 82, 70 (1989) and Part II 82, 78 (1989).

17. J. C. Phillips, *J. Noncryst. Solids* **34,** 153 (1979); **43,** 37 (1981).

18. S. Asokan, G. Parthasarathy, and E. S. R. Gopal, *Phys. Rev. B* **35,** 8269 (1987).

19. H. He and M. F. Thorpe, *Phys. Rev. Lett.* **54,** 2107 (1985).

20. J. Y. Duquesne, Thesis Paris (1985).

21. S. S. Yun, Hui Li, R. L. Cappelletti, R. N. Enzweiler, and P. Boolchand, *Phys. Rev. B* **39,** 8702 (1989).

22. S. Asokan, G. Parthasarathy, and E. S. R. Gopal, *J. Noncryst. Solids* **86,** 48 (1986).

23. G. P. Johari, *Ann. NY Acad. Sci.* **279,** 101 (1976).

24. J. Y. Cavaillé, S. Etienne, J. Perez, L. Monnerie, and G. P. Johari, *Polymer* **7,** 686 (1986).

25. R. Mohan, Suda Maladevan, and K. J. Rao, *Mater. Res. Bull.* **15,** 917 (1980).

26. M. T. Clavaguera-Mora, M. D. Baro, S. Surinach, J. Saurina, and N. Clavaguera *in* "Basic Features of the Glassy State" (J. Colmenero and A. Alegria, Eds.), p. 360, World Scientific Publishing Co. (1990).

27. W. Bresser, P. Boolchand, and P. Suranyi, *Phys. Rev. Lett.* **56,** 2493 (1986).

28. P. Boolchand, R. N. Enzweiler, R. L. Cappelletti, W. A. Kamitakahara, Y. Cai, and M. F. Thorpe, *Solid State Ionics* **39,** 81 (1990).

29. S. Etienne, J. Y. Cavaillé, J. Perez, and G. P. Johari, *Phil. Mag. A* **51,** L35 (1985).

30. S. Tranchant, S. Peytavin, M. Ribes, A. M. Flank, H. Dexpert, and J. P. Lagarde, 6th RISO International Symposium. "Transport Structure Relation in Fast Ion and Mixed Conductors." (F. Poulsen, N. Anderson, K. Clausen, S. Skaarup, and O. Sorensen, Eds.) p. 425 (1985).

31. L. M. Torell and L. Börjesson, Collected Papers, XIV International Congress on Glass, p. 153 (1986).