Journal of Alloys and Compounds, 211/212 (1994) 333–336
JALCOM 054

Anelasticity and viscosity of superionic conducting glasses

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Abstract

The anelasticity and viscosity of AgI–$AgPO_3$ glasses have been measured from room temperature up to near the glass transition temperature by shearing a cubic specimen under a constant load and observing the time-dependence of the shear strain by an optical method. The data were analyzed by adopting a mechanical model of the standard linear solid + a viscous solid, and the viscosity, the anelastic modulus and the anelastic relaxation time have been determined. The viscosity and the anelastic modulus decreased with temperature, while the relaxation time had no apparent temperature dependence. The results for two glasses, $AgPO_3$ and $(AgI)_{0.5}(AgPO_3)_{0.5}$, are presented and some qualitative discussions are given on the basis of the microscopic structures of materials.

1. Introduction

The interest of studying superionic conducting glasses is dual: first, there are many unresolved problems concerning glassy state of materials; second, superionic conduction in solids is very special and is like the conduction in electrolytes. Superionic conductors are sometimes called solid-state electrolytes, while glasses are regarded as supercooled high-viscosity liquids, that is, glasses are mechanically liquid-like and superionic conductors are electrically liquid-like. Moreover, superionic conduction is considered to be closely related to the structure of the material and, of course, the mechanical properties fully reflect the material structure. The purpose of our present study is to investigate superionic conduction by using the mechanical, especially viscoelastic, properties of materials as useful probes; and to approach an understanding of the glassy state in general, especially of the superionic conducting glasses.

The typical superionic conducting material AgI–$AgPO_3$ glass system was used for our investigation, and the anelasticity and viscosity of the material were studied. A preliminary report of the study has been published elsewhere [1]. On the other hand, there have been a number of internal friction or sound attenuation experiments on the same glasses [2–4]. These studies are effective for observing fast mechanical relaxation related to the movement of structural units of small size. Our study is intended to observe the slow movement of larger structural units.

2. Experimental method

The specimens used were glassy $(AgI)_x(AgPO_3)_{1-x}$ ($x = 0$–0.5). They were prepared as follows. A mixture of appropriate amounts of powdered $AgNO_3$, $NH_4H_2PO_4$ and AgI was melted and kept at 500 °C for 2 h, and the melt cast into a suitable form. Cubes of 1 cm^3 were prepared through cutting and lapping processes. The parallelism of the coupled faces was better than 30 min. The specimens were protected from exposure to strong light, and from contact with chemically active materials. After mechanical measurement, the glass transition temperature of the measured specimen was determined by conventional differential thermal analysis (DTA).

The principle of mechanical measurement adopted in the present study is as follows. The lower and upper faces of the specimen are bonded to fixed and movable stainless steel testing plates, respectively. The most favorable bonding material was found to be Sauereisen No. P-1, which usually offered a strong, rigid bonding even at elevated temperatures. A constant shearing load is applied to the movable plate by a weight-and-pulley system. Lateral displacement of the movable plate is measured and recorded as a function of time by using the HP-5528A laser measurement system, which utilizes an optical heterodyne interferometric method. Sensitivity of the displacement measurement is 10 nm. The temperature of the specimen is controlled by a small furnace installed around the specimen with an accuracy of 0.1 °C during a run of the experiment.

One of the characteristics of the present method is that viscoelastic deformation of the specimen occurs

SSDI 0925-8388(93)00054-3

under almost pure shear stress, which makes the experimental situation very simple. A detailed description of the experimental method will appear in a separate publication.

3. Results and analysis

Examples of raw data obtained by the present experimental method will first be shown in the form of a recorded chart: the displacement D of the upper face of specimen *vs.* time t after load W is applied to the specimen. The results in Fig. 1 are for a polycrystalline lead (a) and for a glassy $(AgI)_{0.5}(AgPO_3)_{0.5}$ (b). In both data, the displacement as a function of time can be divided into four stages: an instantaneous increase (I) followed by a gradual increase (II) when the load was applied; and an instantaneous decrease (III) followed by a gradual decrease (IV) after the load was removed.

In stages I and III, the displacement is generally due to elastic shear deformation plus rotational deformation of the specimen, to elastic deformation of instrumental origin such as shear deformation of the bonding material and so on. These deformations are considered to be reversible. Really in the case of the glass (b), the amounts of displacement D_1 and D_2 shown in the figure are almost the same. However, in the case of the crystal (a), D_2 is apparently smaller than D_1. That is, there occurs an irreversible deformation. The origin of that may be fast plastic deformation of the material due to rapid irreversible movement of crystal dislocations. These results are very reasonable, showing the sensitivity of the present measuring method.

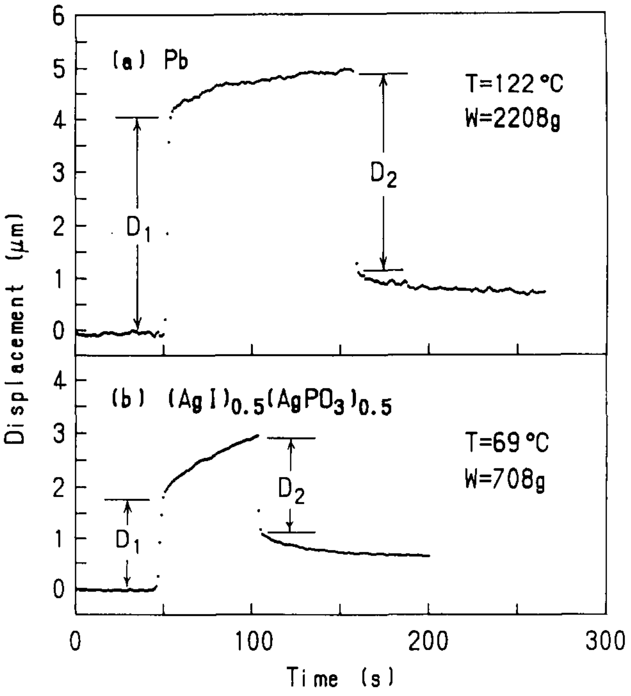

Fig. 1. Recorded charts of the displacement of the upper face of the specimen *vs.* time when shearing load W is applied and removed, for Pb polycrystal (a) and $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass (b). D_1 and D_2 are the instantaneous increase and decrease of the displacement.

In stage IV, the displacement decreases exponentially and reaches a definite value, which is a typical anelastic or mechanical relaxation behavior. The origin of the relaxation in the crystal may be slow movements of lattice defects, details of which are, however, not discussed here. On the other hand, the anelastic behavior observed in the glasses is the real object of the present study.

In stage II, the displacement first increases as the usual mechanical relaxation, and then the increase becomes linear with time. In the case of crystals, such a linear time-dependent behavior is frequently observed as stationary (secondary) creep, which is considered to be due to a balance of the creation and annihilation of dislocations. In stationary creep deformation, the displacement rate (dD/dt) is constant with time, but is in general strongly dependent on applied load [$(dD/dt) \propto W^n$; $n = 3$–4.5]. However, in the case of the present glasses, it can be shown experimentally that the displacement rate is proportional to the applied load [$(dD/dt) \propto W$]. Thus, the linearly time-dependent behavior is of the (Newtonian) viscous type in the glasses. The viscosity of the glasses is also another object of the present study.

After considering the above characteristics of the glasses, the following mechanical model is adopted to analyze their viscoelasticity. The model is composed of a standard linear solid [5] and a viscous dashpot connected in series with it. The behavior of the mechanical model is as follows. When a constant stress σ is applied to the model at time $t=0$, and then removed at $t=t_0$, the produced time-dependent strains ϵ (t) and ϵ' ($t'=t-t_0$) can be represented as

$t<t_0$, $\sigma \neq 0$:

$$\epsilon(t)=a+b[1-\exp(-t/\tau)]+ct \tag{1}$$

$t>t_0$, $\sigma=0$:

$$\epsilon'(t')=d+b\exp(-t'/\tau) \tag{2}$$

where a, b, c and d are parameters, and τ is the anelastic relaxation time. The stress and strain can be related to the experimentally determined quantities in the present case as $\sigma=W/S$ and $\epsilon=D/H$, where W is the load, S is the area of upper specimen surface, D is the displacement and H is the specimen height. By using experimental ϵ' (t') curve and eqn. (2), parameters d, b and τ can be determined. Then, by using the ϵ (t) curve and eqn. (1), parameters a and c can be obtained.

Concerning the anelasticity, the relaxation time and also strength of relaxation are the most important quantities. Here, the anelastic modulus M_a, which is defined as the ratio between the applied stress and the anelastic strain, is used. Therefore, a small anelastic modulus corresponds to a strong anelasticity. The anelastic modulus can be calculated from the applied stress σ and the anelastic strain $\epsilon_a = \epsilon'(0) - \epsilon'(\infty) = b$, namely, $M_a = \sigma/b$.

The viscosity is as usual, simply determined by the definition as $\eta = \sigma/(\mathrm{d}\epsilon/\mathrm{d}t) = \sigma/c$. The viscosity can also be determined by another method in the present case of glasses. The strain $\epsilon'(t')$ approaches the remaining strain produced by viscous flow during the stressed state, namely, $\epsilon'(\infty) = d = ct_0$. Therefore, the viscosity is also given as $\eta = \sigma/(d/t_0)$. Comparison of the two viscosity values derived from the two independent methods is useful in checking the reliability of the experiment. Usually the first method gives more accurate results.

In Fig. 2, the displacement *vs.* time data for glassy $AgPO_3$ (a) and $(AgI)_{0.5}(AgPO_3)_{0.5}$ (b) at the same temperature are given. The continuous lines in the figures are the parameter-fitted curves, and the fittings seem to be acceptable. An explanation must be given here. The deformations in stage I (D_1) and in stage III (D_2) are not equal in the case of $AgPO_3$ glass (a). This is due to a technical reason as the bonding between the specimen and the testing plate is not so tight for this material, and an irreversible transient deformation occurs due to a slip of the bonding at loading. However, measurement in the later stages is not disturbed by this problem.

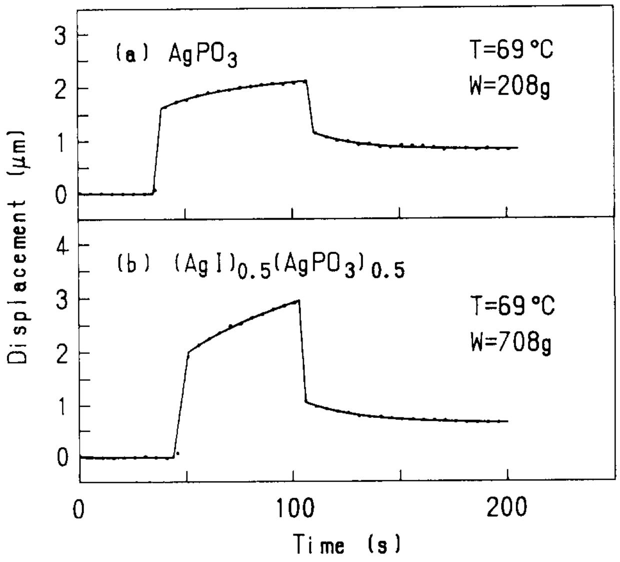

Fig. 2. Displacement *vs.* time data for two kinds of glasses. The small dots are data points, and the lines are parameter-fitted curves using the viscosity + anelasticity expressions, eqns. (1) and (2).

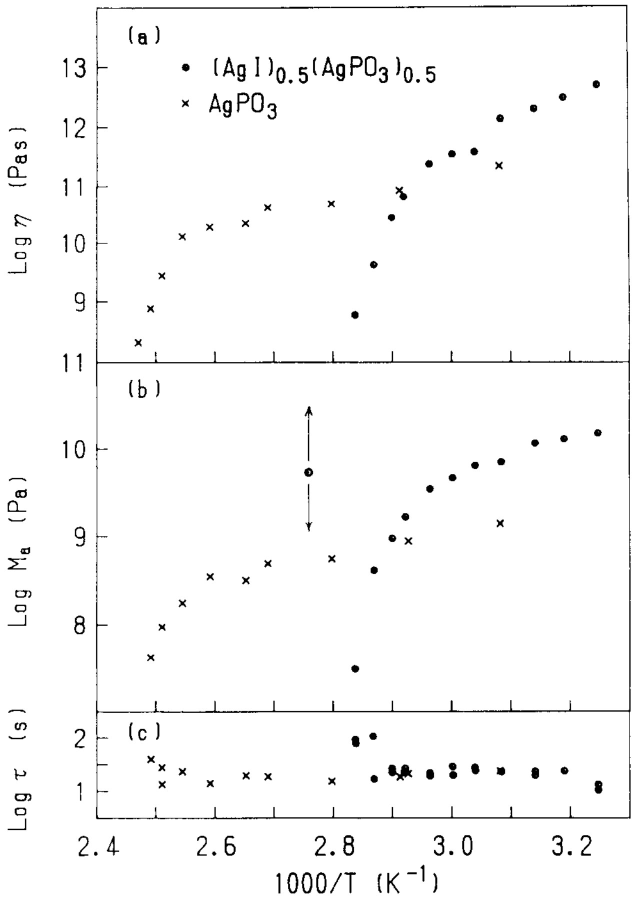

Fig. 3. Logarithms of viscosity η, anelastic modulus M_a, and anelastic relaxation time τ *vs.* inverse temperature T^{-1} for two kinds of glasses. The arrows in (b) indicate the glass transition temperature of the $(AgI)_{0.5}(AgPO_3)_{0.5}$ glass.

The displacement *vs.* time measurements have been made at various temperatures, and the temperature dependences of the viscosity η, the anelastic modulus M_a, and the relaxation time τ were obtained. It is especially noted here that $(AgI)_{0.5}(AgPO_3)_{0.5}$ is a typical superionic conductor, and its electrical conductivity is several orders of magnitude higher than that of $AgPO_3$. In the present article, comparison of the viscoelastic properties of the two materials is solely described. The results are compiled in Fig. 3 for the two glasses, where the conventional log *vs.* inverse temperature plots are used.

4. Discussion

The characteristics of the experimental results obtained for two glassy materials, $AgPO_3$ (glass I) and $(AgI)_{0.5}(AgPO_3)_{0.5}$ (glass II) can be summarized as follows.

1. As a whole, the viscosity η is larger in glass II than in glass I. In both glasses, the viscosity gradually de-

creases with temperature. The decrease becomes more rapid at higher temperatures, where log η seems to be proportional to $1/T$. The slope of the log η *vs.* $1/T$ line is almost equal in the two glasses. The rapid decrease of viscosity starts below the glass transition. The glass transition temperature T_g for glass II is shown by the arrows in (b), and T_g for glass I is situated to the left, and is outside of the figure.

2. The anelastic modulus M_a is larger in glass II than in glass I. In both glasses, the modulus gradually decreases with temperature, and the decrease is smooth all over the temperature range.

3. The anelastic relaxation time τ has no apparent temperature dependence in both glasses. The values of relaxation time scatter in a wide range of 10–100 s.

Now, the usually accepted structural model of the AgI–$AgPO_3$ glasses will be described here [6–8]. Both in glass I and glass II, the glass-forming network is composed of chains of PO_4 tetrahedral units which shear two O atoms. In glass II, microdomains composed of AgI, which are important for ionic conduction, are considered to exist between the chains. It is assumed that the microdomains have a plasticizing effect on the vibrational motion of $AgPO_3$ chains, which can be presumed from the fact that the addition of AgI lowers the glass transition temperature of the material. The idea is also useful to explain the thermal transport properties of the glasses [9]. However, the viscoelasticity we are now concerned with is a quasi-static or a relatively slow phenomenon. In this case, it must be considered that the addition of AgI has a reinforcing effect for the viscoelasticity of glass.

The interpretation of the experimental results 1–3 through the above microscopic picture will be given successively.

1. At lower temperatures, the viscous motion of the glasses is due to an irreversible rearrangement of $AgPO_3$ chains caused by an external force. Remember that the chains are first irregularly arranged because of the glassy state of the material. The process is a kind of thermally activated one, but the activation energies are widely distributed. Then, the viscosity smoothly decreases at low temperatures. The viscous motion is somewhat suppressed in glass II due to the existing AgI domains, and the overall viscosity is larger in the material. Finally, at higher temperatures, the bonds between P and O became broken. The process has a definite activation energy, and there must be a linear relation between log η and $1/T$. The activation energy should be the same in glass I and glass II. The observed activation energy is very close to the theoretical P–O binding energy, 340 kJ mol^{-1} [10].

2. The anelasticity arises from reversible rotation and deformation of PO_4 tetrahedral units. The activation energies for the processes are widely distributed, and the anelastic modulus smoothly decreases with temperature. The above motions are suppressed by added AgI, and therefore anelasticity is weaker and the anelastic modulus is larger in glass II.

3. The activation energies for anelastic relaxation, and thus the relaxation time are widely distributed. The relaxation time itself is not definitely different in glass I and glass II, since the activation process is the same in the two materials.

Finally, it is noted that large changes of viscoelasticity can occur at temperatures different from the glass transition, since mechanisms of the two phenomena may be different as suggested above.

In conclusion, the present experimental results can be explained at least qualitatively on the basis of the microscopic structure of the materials. We are continuing the experiments for AgI–$AgPO_3$ glasses with different AgI contents, and an extensive report of the study will appear in the near future.

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