Ion dynamics in organic-inorganic composite superionic conductor glasses

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Ionic transport in glass and supercooled liquid is an interesting topic relating to the glass transition phenomena, which is also of importance in some energy devices application.

Generally, ions and molecules in a liquid will freeze in to a solid state below the glass transition temperature Tg. However, in case of so called "superionic conductor glasses (SIG)", the mobile ions are decoupled from the dynamics of the matrix ions or molecules and are still mobile even in the glassy state. The mobile ions in SIG can be regarded as a liquid confined in nano-spaces. Thus, the localization of the mobile ions in the SIG is considered as a second glass transition, although whose detailed mechanism is still unclear.

Authors discovered new types of SIG composed of organic alkalliammoniumiodide and silver iodide, which exhibited clear transition from insulator to superionic state by varying the glass composition as shown in figure 1[1,2], However, the detailed results of the frequency and temperature dependence of the ionic conductivity have not been reported.

So, in this paper we will give some dynamic information from the ac conductivity of the organic-inorganic composite superionic conductor glasses as a function of temperature.

EXPERIMENTS

Sample glasses were prepared from the melt of silver iodide(AgI) and various tetraalkylammonium-iodides by rapid quenching method. The glass transition temperatures were determined by DSC analysis. Ionic conductivity was measured from 1 Hz to 1MHz by Solartron impedance analyzer.

RESULTS and DISCUSSIONS

An example of the frequency and temperature dependence of the ionic conductivity is shown in Fig. 2, where a theoretical fitting by a power-law dependence as,

$$\sigma[\omega] = \sigma[0][1 + (i\omega\tau)^n] + i\omega\varepsilon_\infty \qquad (1)$$

is shown by solid curves, where $\sigma[0]$ is the dc conductivity, t is the relaxation time, ε_∞ is the high frequency permittivity and n is the frequency exponent. The deviation of the experimental data from the theoretical one at low frequency is due to the interfacial polarization between the sample and electrodes.

DC conductivity $\sigma[0]$ of the different glasses are shown in Fig. 1 as a function of the volume fraction f of the AgI in the glasses. A clear transition from insulator to superionic state is seen in the vicinity of the ϕ=0.35, which is attributed to a percolation transition of AgI clusters in the alkylammonium matrix. The volume dependence is expressed by

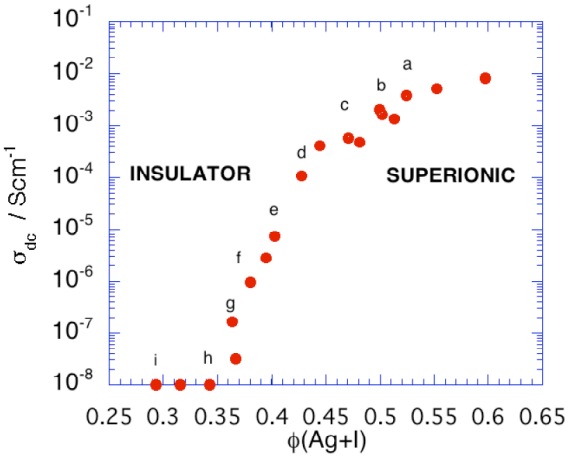

Fig.1 Ionic conductivity of organic-inorganic composite superionic conductor glasses as a function of the volume fraction of Ag and I.

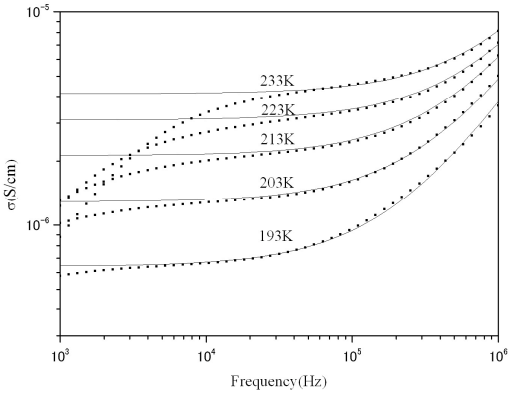

Fig. 2 Frequency dependence of the conductivity of AgI-TMAI-TEAI-TPAI(80-2-10-8) glass.

$$\sigma[\phi] \approx (\phi - \phi_0)^\mu \qquad (2),$$

where ϕ_c=0.3 and μ~4.5.

Percolation theories predict a large frequency dependence in the conductivity near the threshold, which is in good agreement with those observed in the present experiments as shown in Fig. 1.

Ionic transport in organic-inorganic composite glasses can be explained by a percolation model.

References

[1] J. Kawamura, N. Kuwata, and Y. Nakamura, Solid State Ionics 113-115 (1998) 703.
[2] N. Kuwata, J. Kawamura, and Y. Nakamura , Solid State Commun. 124 (2002) 221.