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Ionic conductivities in crystalline, glassy, and liquid $AgAsS_2$

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ABSTRACT

Ionic conductivity in $AgAsS_2$ has been measured at 20–600 °C for crystalline, glassy, supercooled, and liquid states. The liquids possess substantially smaller activation energies (~0.2 eV) and conductivity prefactors (~3 S/cm) than those in the solids. Other electrical characteristics are discussed, taking calorimetric and dilatometric results into account.

1. Introduction

The ionic conduction in condensed matters has been a subject of continuous studies stemming from fundamental interests in ion-transport mechanisms and wide applications to batteries, photographic films, ion sensors, and so forth. Mobile ions are H^+, Li^+, Ag^+, etc., and matrices may be oxides, chalcogenides, and halides of crystalline, glassy, powdered, and ceramic forms, in which an ion-conducting glass remains to be a focus, due to its good conductivity and compositional variability [1]. However, the conduction mechanisms remain vague, with a primary reason that the atomic structure in non-crystalline materials, which may be heterogeneous, cannot be explicitly identified.

Among the ion-conducting glasses, the Ag-chalcogenide system attracts substantial interest since it is relatively stable [2–4] and a heavy atom Ag is, in comparison with Li etc., easily detected by x-rays. In addition, the material behaves as an “ion-conducting amorphous semiconductor” [5], which exhibits promising photo-electro-ionic phenomena [6]. Accordingly, a lot of electrical studies have been performed so far, most of which concern with compositional [2,7–11] and/or spectral [12–16] variations. We may refer also to recent computer-aided structural analyses [17,18]. However, temperature dependence is less explored, or varied temperature ranges have been limited to solid phases [7,13,15,16,19], and the ionic conductivity in (supercooled) liquid states has hardly been studied [12].

Extending previous studies [5,20–22], we here investigate the ionic conductivity in $AgAsS_2$ of crystalline, glassy, and liquid forms using a special sampling technique. Thermal properties have also been inspected, and these results are discussed in a unified way for obtaining insights into the ionic conduction in condensed matters. Specifically, we will consider the ionic conductivity in a supercooled phase in light of the free-volume model.

2. Experiments

$AgAsS_2$ glass (g-$AgAsS_2$) was prepared through the conventional melt-quenching method, the detail being described previously [21]. The glass was crushed into powders, and those of about 5 mg were inserted into quartz-glass pipes with a length of ~2 cm and an inner diameter of 1 mm and then packed in to the central part using two Au rods with a diameter of 1 mm and a length of ~2 mm, which were compressed with Cu rods with the same diameter, which were connected to Cu wires. As exemplified in Fig. 1, the powder became to ~2 mm in length upon compression. (We tried also Ag rods instead of Au, but the conductivity of $AgAsS_2$ could not be evaluated owing to a resistance drop at temperatures above ~200 °C, which was probably caused by formation of conducting crystalline Ag_2S paths.) This encapsulated Cu:Au:$AgAsS_2$:Au:Cu sample was set in an Ar-flowing small furnace and heated. Sample temperature was monitored, with an accuracy of about ±10 °C, using a thermocouple in a quartz-glass pipe, which was bundled with the sample pipe. Such a sample assembly having small thermal capacity is required for obtaining rapid quenching rates.

Ac conductivity of the sample was evaluated from currents, which were measured using a lock-in amplifier (NF, 5610B) under applied voltages of 1 − 100 mV, at sample temperatures of 20–600 °C. However, upon temperature variations, the packed $AgAsS_2$ could not retain the columnar shape, due to material leakage during melting and thermal volume changes. Accordingly, the accuracy of the conductivity value may be ±50%, or the absolute value may be twice of the calculated ones, owing to the leakage. In addition, subsidiary thermal analyses

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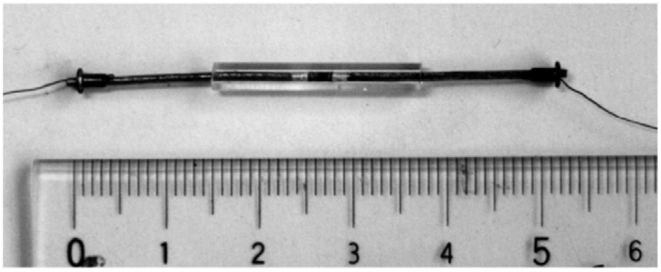

Fig. 1. A photograph of an encapsulated Cu:Au:$AgAsS_2$:Au:Cu sample.

were performed using a conventional calorimeter (DTA) and a dilatometer. (The actual composition in these thermal measurements was found to be $Ag_{30}As_{20}S_{50}$ by x-ray microprobe analyses, while its thermal property could be regarded to be nearly the same to that in $AgAsS_2$).

3. Results

Fig. 2 exemplifies frequency dependence of ac currents at room and high temperatures. We see in both cases that the currents are nearly constant at a frequency range of 10^2–10^4 Hz, which suggests that the value is governed by bulk dc ionic components without electrode and capacitance effects [16]. Accordingly, we select 1.2 kHz for investigating temperature variations.

Fig. 3(a) shows a DTA curve of g-$AgAsS_2$ obtained under a heating process at a rate of 10 °C/min. We see a glass-transition step at ~150 °C, in consistent with previous results [2,23,24]. Then two exothermic peaks appear at around 250 °C, which can be ascribed to crystallization to proustite (Ag_3AsS_3 crystal with a crystallization temperature of ~210 °C) and smithite ($AgAsS_2$ crystal, ~260 °C) [23]. At ~430 °C, we see a prominent endothermic dip, a signature of the melting of smithite [2,23]. The melting of proustite at 490 °C [2] is located out of the measurement range ($\leq$ 450 °C), and it cannot be seen.

We have examined also a dilatometric characteristic (not shown) using a polished glass rod with a diameter of ~5 mm and a length of ~15 mm. Around room temperature, the sample expanded with a linear coefficient α of 1.7×10^{-5}/K, in consistent with a previous datum [24], and then it increased to 2.4×10^{-5}/K above ~145 °C ($\approx T_g$). At ~160 °C, the sample became fluid, which hindered further measurements. Trials measuring thermal expansion coefficients in the liquid state were unsuccessful due to material bubbling.

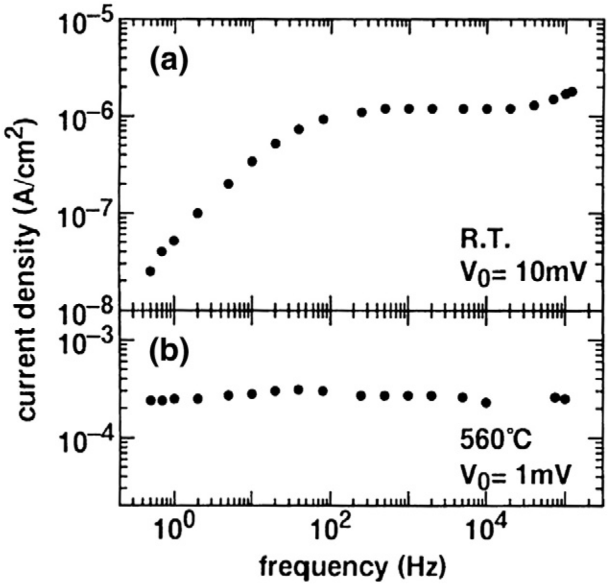

Fig. 2. Frequency spectra of current densities in an Au:$AgAsS_2$:Au sample in glassy (a) and liquid (b) states under the applied voltages (V_0) specified.

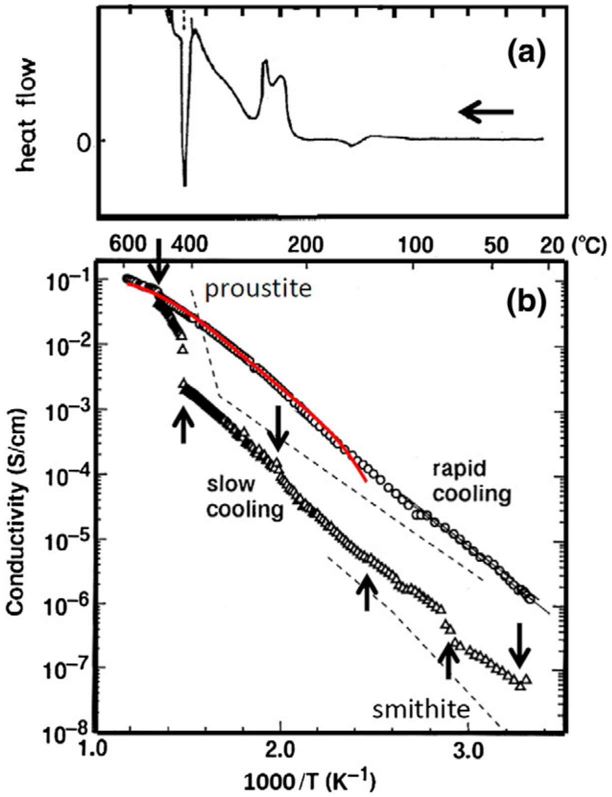

Fig. 3. Heat flow (a) and electrical conductivity (b), upon rapid (○), and slow (Δ) coolings, in $AgAsS_2$ as a function of temperature T. Electrical conductivities of single-crystalline $AgAsS_2$ [19] and Ag_3AsS_3 [27] are also plotted by dashed lines for comparison. Upper and lower-directing arrows in (b) indicate phase transition points in $AgAsS_2$ [19] and Ag_3AsS_3 [28,29], and the red solid line delineates a VFT curve (see, the text).

Fig. 3(b) shows a series of results of the electrical conductivity σ upon temperature changes. At the outset, the sample was heated to a liquid phase, ~580 °C, compacted there, and cooled down. In the liquid phase, $\sigma \approx 10^{-1}$ S/cm, the value being at a superionic level. In addition, it seems that the liquid undergoes an Arrhenius-type temperature variation, $\sigma \approx \sigma_0 \exp(-E_a/k_BT)$, in consistent with results reported for Ag-S(Se) [25,26]. (However, the limited measurable range of ~100 °C in the liquid phase makes this assertion tentative.) The parameters σ_0 and E_a are listed in Table 1. Behaviors after solidification depended upon cooling rates.

Table 1
Summary of the activation parameters obtained in the present study, in comparison with those previously reported. The parameters are calculated at room temperature, except for the values in the liquid and supercooled phases and the parenthesized ones, which are averaged over the crystalline phases from room temperature to 420 °C. Note that σ_0 is evaluated through extrapolation so that the accuracy is worse.

Material	σ_0 [S/cm]	E_a [eV]	Reference
Liquid	4	0.25	Present
Supercooled	2	0.17	Present
Glassy	50 ± 20	0.45 ± 0.05	Present
	50	0.45	7
	30	0.38	19
	7	0.37	16
	100	0.48	15
Crystalline	0.02 (~20)	0.32 (~0.5)	Present
Smithite	100	0.62	19
Proustite	3	0.42	27
	20	0.17	28
	0.1	0.39	29