Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Ionics 176 (2005) 1271–1280
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Ion dynamics in mechanochemically synthesized amorphous fast ionic conductor Ag_2S–Sb_2S_3

J.P. Tiwari, K. Shahi*

Materials Science Programme, Indian Institute of Technology Kanpur-208016, India

Received 21 October 2004; received in revised form 23 December 2004; accepted 18 January 2005

Abstract

Frequency dependent electrical conductivity (σ') of mechanochemically synthesized amorphous fast ion conductors (FICs) xAg$_2$S–Sb$_2$S$_3$ (x=70, 80, 85) is investigated in the frequency range 5 Hz–13 MHz and temperature range 95–385 K. While the universal dynamic response (UDR) model, $\sigma(\omega)=\sigma_{dc}(T)+A(T)\omega^n$, does reproduce the shape of $\sigma(\omega)$ spectra, the $\sigma_{dc}(T)$ and $A(T)$ show anomalous characteristics. Both exhibit two distinct Arrhenius regions, a low temperature region with a lower value of activation energy (E) and a high temperature region with higher value of activation energy. Further the frequency exponent n is a (decreasing) function of temperature, decreasing slowly at lower temperatures but more rapidly at higher temperatures. The correlation $E_{ac}=(1-n)E_{dc}$ appears satisfactory in the low temperature region but unsatisfactory at higher temperatures. The isochronal representation of ac conductivity, σ' vs. 1000/T at different frequencies, reveals the existence of a third regime, which is currently under active discussion and is known as superlinear power law (SLPL).

Keywords: Mechanochemistry; Ball-milling; Frequency dependent conductivity; Amorphous electrolytes; Power law behaviour of the ac conductivity

1. Introduction

α-AgI is the earliest known and yet the best known superionic conductor above T_c=148.5 °C [1]. α-Ag$_2$S is very similar to α-AgI except that it has a higher T_c=177 °C [2]. Their exceptionally high ionic conductivity (~1 Ω^{-1} cm^{-1}above T_c) is attributed to their unique crystal structure which is variously described as liquid-like or molten-sublattice type in which the mobile cations are in a highly disordered (amorphous) state. During the last three decades, a great deal of effort has been made, with considerable success [3–7] to essentially stabilize this highly disordered, liquid-like and yet crystalline structure [8,9] at room temperature.

Subsequently, various rapid quenching techniques were employed to synthesize noncrystalline or glassy [10–12] fast ion conductors (FICs). Even though α-AgI (or Ag$_2$S) structure could not be frozen at room temperature all by itself, many FIC glasses have been synthesized in a variety of binary and ternary systems involving AgI [13–21] or Ag$_2$S [22–30] as one of the components. These melt-quenched (MQ) glassy FICs are extensively studied but the issues related to the ion dynamics and various relaxation processes are far from settled [10,31–38].

More recently, high energy ball-milling at room temperature has been successfully used to form amorphous FICs [39–52] which are, by and large, similar to the MQ glasses. However, there are subtle but significant differences between the mechanically-milled (MM) and the MQ amorphous FICs. For instance, the MM glasses generally have a higher conductivity, lower glass transition (T_g) and crystallization (T_c) temperatures and higher enthalpy (ΔH) and entropy (ΔS) changes at T_c as compared to MQ glasses. Even more striking is the fact

* Corresponding author. Also with the Department of Physics, Indian Institute of Technology Kanpur-208016, India. Tel.: +91 512 259 7809; fax: +91 512 259 0914/259 0260.
E-mail address: kshahi@iitk.ac.in (K. Shahi).

0167-2738/$ - see front matter
doi:10.1016/j.ssi.2005.01.005

that the crystallization in MM glasses generally occurs in two stages [53] while the MQ glasses generally show a single crystallization temperature. Interestingly, the dc conductivity (σ_{dc}) vs. inverse temperature behaviour of MM glasses is found to exhibit two distinct Arrhenius regions, a low temperature region with a lower activation energy and a high temperature region with a higher activation energy. The existence of two crystallization temperatures in the DSC results and two distinct Arrhenius regions in σ_{dc} vs. $1/T$ behaviour has given rise to a strong conjecture that there are two distinct bonding states for the Ag^{+} ions. Of course, further investigations are desirable to establish these observations.

The frequency dependence of the real part of the complex conductivity

$$\sigma^{*} = \sigma'(\omega) + j\sigma''(\omega) \tag{1}$$

is extremely useful in understanding the microscopic mechanisms of ion dynamics and various relaxation processes in glassy electrolytes. A large number of FIC glasses have been investigated during the last two decades [54–62]. The ac conductivity (σ') comprises three different contributions. First, a frequency-independent or dc conductivity (σ_{dc}), arising from the long-range hopping of the mobile ions, given by

$$\sigma_{dc}(T) = \sigma_0 \exp\left(-\frac{E_{dc}}{kT}\right) \tag{2}$$

where σ_0 is the preexponential factor, the thermal activation energy for E_{dc} conduction and kT the thermal energy. This dc contribution is invariably present in all glassy FICs and is well understood. Second, a frequency dependent conductivity which obeys a power law is of the type

$$\sigma(\omega, T) = A(T)\omega^{n} \tag{3}$$

where $A(T)$ is independent of frequency and has Arrhenius temperature dependence

$$A(T) = A_0 \exp\left(-\frac{E_{ac}}{kT}\right) \tag{4}$$

where A_0 is a constant for a material and E_{ac} is called ac activation energy. The frequency exponent n is supposedly a constant ($0<n<1$).

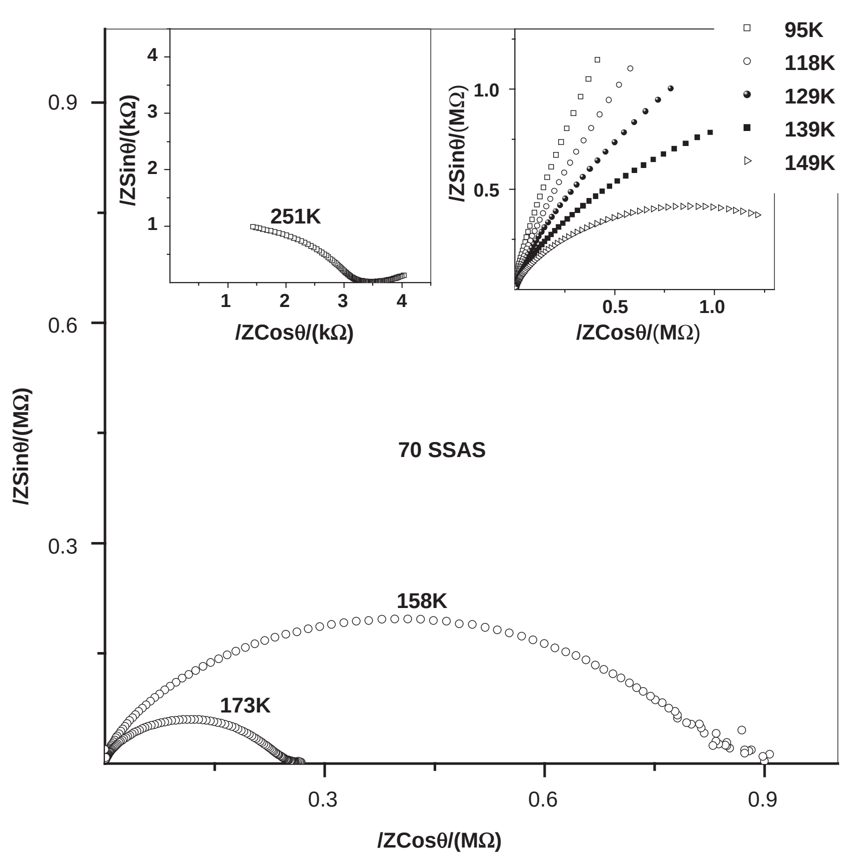

Fig. 1. Impedance plots for the mechanochemically synthesized $70Ag_2S–Sb_2S_3$ (70 SSAS) amorphous fast ion conductor at different temperatures. Insets of the plots show the temperatures for which complete spectra are not accessible.