Materials Science and Engineering B 178 (2013) 775–784

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Relaxation process in PbI_2–Ag_2O–V_2O_5–B_2O_3 system: Dielectric, AC conductivity and modulus studies

Manish S. Jayswal [a], D.K. Kanchan [a,*], Poonam Sharma [a], Nirali Gondaliya [a,b]

[a] Solid State Ionics and Glass Research Laboratory, Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat 390002, India
[b] Department of Engineering Physics, Sadvidya Mandal Institute of Technology, Bharuch, Gujarat, India

ARTICLE INFO

Article history:
Received 12 September 2012
Received in revised form 12 March 2013
Accepted 14 March 2013
Available online 29 March 2013

Keywords:
AgI
Glass
AC conductivity
Dielectric relaxation
Scaling

ABSTRACT

Silver ion conducting super-ionic glass system $xPbI_2$–$(100-x)$ [Ag_2O–$2(V_2O_5$–$B_2O_3)$], where, $5 \le x \le 25$, were prepared via melt quenching route and -characterized by XRD and DSC. Their electrical properties were measured by impedance spectroscopy in the frequency range of 2 MHz to 20 Hz from 30 to 120 °C. The electrical relaxation mechanism has been studied using AC conductivity, dielectric modulus function and frequency dependent dielectric permittivity over a wide range of frequency and temperature. Two different scaling approaches for AC conductivity as well as dielectric permittivity spectra were used to understand the nature of relaxation processes.

1. Introduction

Ion conducting glasses are a class of materials that exhibit electrical conductivity by means of motion of ions (anions or cations) in amorphous phase and generally exhibit much higher ionic conductivity than their crystalline counter-parts [1]. In addition to high ionic conductivity, these materials possess excellent chemical durability and tuning of their desired physical properties by varying their chemical composition is possible. These properties make them useful as solid electrolytes in "all solid state batteries", electro-chromic devices, gas sensors, and many more electrochemical applications [2–4]. Electrical conduction in ion conducting glasses is known to take place via hopping of mobile ions between available equivalent sites. The charge dynamics in these materials can be understood using various formalisms of impedance spectroscopy, namely complex impedance $Z^* = Z'(\omega) - iZ''(\omega)$, complex conductivity $\sigma^* = \sigma'(\omega) + i\sigma''(\omega)$, complex dielectric permittivity $\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$, complex modulus formalism $M^* = M'(\omega) + iM''(\omega)$, where, $\omega = 2\pi f$. Although all of these formalisms are interchangeable and represent the same microscopic data, each of them uniquely identifies various contributions toward charge conduction mechanism [5]. A thorough description of these formalisms can be found in Ref. [6]. In the present work, authors have used the complex conductivity, σ^*, complex dielectric permittivity, ε^* and complex modulus formalism M^* to understand the ion relaxation process in Ag^+ ion conducting superionic glass system. The real parts of σ^* and ε^* are called AC conductivity, σ' and dielectric constant, ε' respectively and the data are analyzed in terms of conductivity relaxations and dielectric relaxations. Universality of conductivity and dielectric relaxation processes in an ion conducting glass system can be established using scaling of respective spectra to show whether the processes are independent of charge concentration and/or are thermally activated. The conductivity and dielectric spectra could not be scaled using the same scaling laws, and the authors had to apply different scaling laws for AC conductivity and dielectric spectra. The details have been given in forthcoming sections separately.

The high ionic conductivity of AgI doped glass materials has led to a systematic investigation of their various physical and chemical properties. These glasses possess high ionic conductivity and good chemical durability which makes them useful as solid electrolytes. It is also a well-established fact that AgI has a characteristic disordered structure in α-phase with an increase in conductivity by more than three orders of magnitude at 147 °C. We froze α-phase of AgI, which exists above 147 °C, in the glass structure, a prototype super ionic conductor which facilitates in conduction process. It has low activation barrier for migration and high conductivity. Therefore, glasses are found to be a suitable to house the highly conducting α-AgI phase at room temperature.

Instead of directly doping AgI in the host glass matrix, many workers have adopted other routes to stabilize highly conducting

* Corresponding author. Tel.: +91 265 2795339x24.
E-mail addresses: d_k_kanchan@yahoo.com, dkkanchan.ssi@gmail.com (D.K. Kanchan).

0921-5107/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mseb.2013.03.013

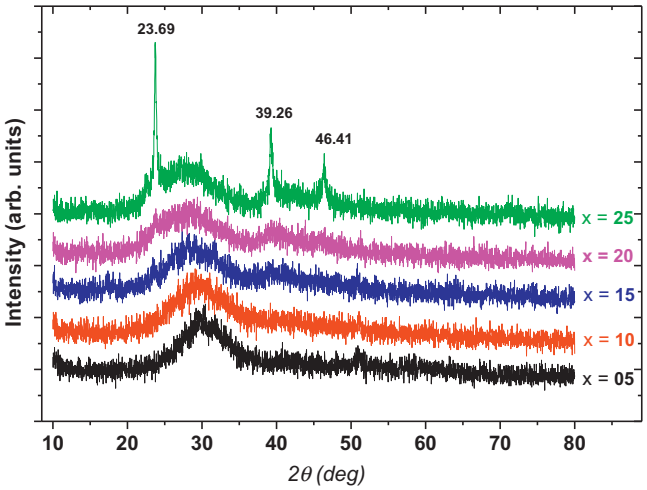

Fig. 1. XRD spectra for all compositions (*Y*-axis data is in arbitrary units).

AgI phase in glasses by doping with a suitable MI_n (M = Pb, Cu, Cd, etc.) type salt in an Ag_2O as a result of exchange reaction between the two, based on Lewis HSAB (Hard and Soft Acids and Bases) principle [7]. Incorporation of metal halides in the mixed glass formers plays the role of enhancing the conductivity of conventional glasses to achieve the values of super ionic conductors.

Keeping in view of all these points, the present study aims to study the effect due to varying concentrations of a new dopant salt, PbI_2, in the case a glass system of composition $xPbI_2$–$(100-x)$ [Ag_2O–$2(0.7V_2O5$–$0.3B_2O_3)$], where, $5 \leq x \leq 25$, is prepared in order to understand the electrical relaxation properties using AC conductivity, modulus formalism and frequency dependent dielectric permittivity. Here V_2O_5–B_2O_3 acts as the host glass system. PbI_2 is the dopant salt and may react with Ag_2O to form two AgI and one PbO molecule in the end product.

2. Experimental

Analytical Reagent grade starting chemicals: PbI_2 (National Chemicals, India, ≥99%), Ag_2O (Qualigens, ≥99.9%), V_2O_5 (Loba Chemie, India, ≥99%), and H_3BO_3 (S.D. Fine Chemicals, India, ≥99.5%) were taken in their appropriate mole% concentrations, crushed and then mixed thoroughly using an agate mortar pestle for 2 h. The mixture, kept in a porcelain crucible, was maintained at

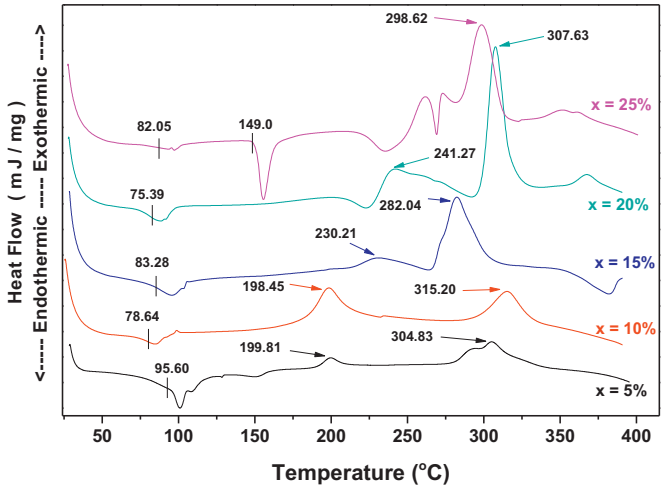

Fig. 2. DSC scans for all glass compositions (*Y*-axis data is in arbitrary units; all values with arrow marks are in °C units).

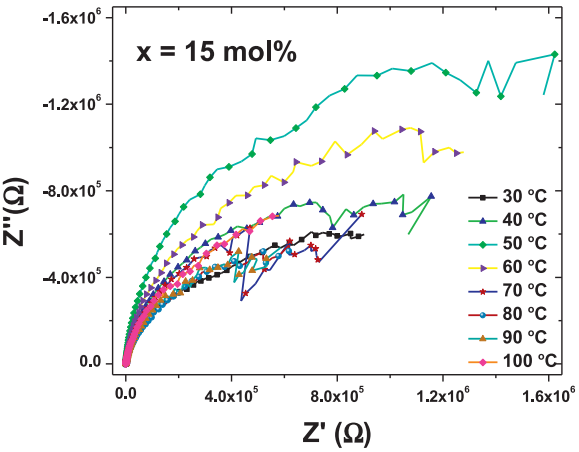

Fig. 3. $Z'' \rightarrow Z'$ spectra for $x = 15$ mol% sample at various temperatures.

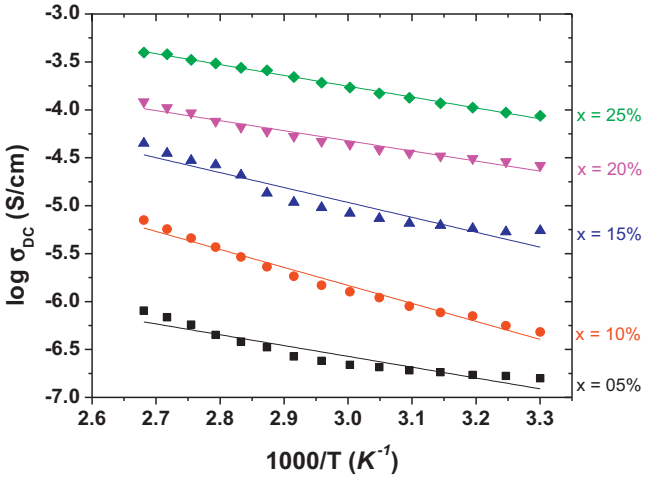

Fig. 4. Arrhenius plots of DC conductivity for different compositions.

400 °C for half an hour to completely convert H_3BO_3 into B_2O_3. After that, the samples were melted at 700–800 °C in a muffle furnace for 3–4 h. The melt was poured on a thick metallic copper block and quenched with other similar copper block at room temperature. Thin glass sheets of approximately 0.3–0.5 mm thickness were obtained. The as quenched samples of 0.5 cm^2 area were used for electrical measurements. Fine pulverized powdered samples were

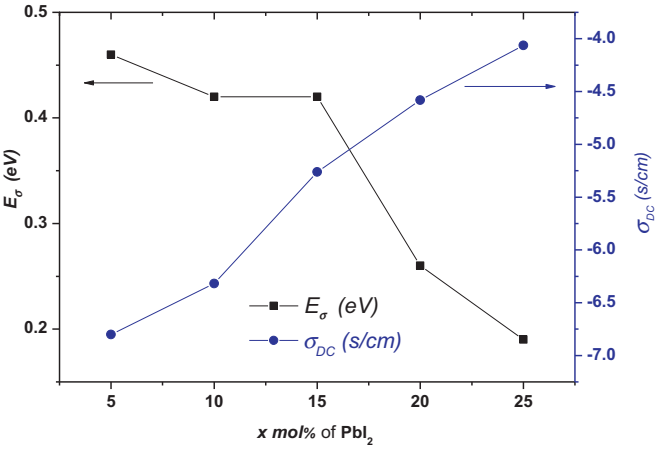

Fig. 5. Variation of activation energy and DC conductivity (at 30 °C) as a function of PbI_2 concentration.