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Impedance spectroscopic characterization of Sm_2O_3 containing lithium borate glasses

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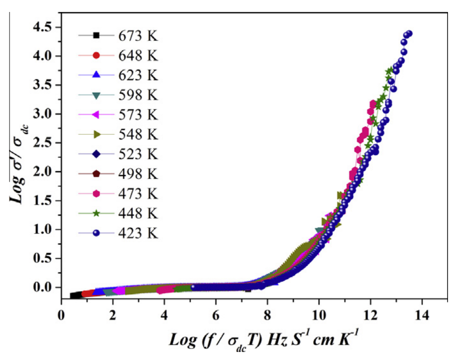
HIGHLIGHTS

- Lithium borate glasses containing Sm_2O_3 were prepared by conventional melt quench technique.
- Conductivity of glasses decreases due to decrease in mobility of lithium ions.
- Scaling indicates that the conduction mechanism is independent of temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

27.5 Li_2O–(72.5–X) B_2O_3–X Sm_2O_3 (X = 0.5, 1, 1.5 and 2) were prepared by conventional melt quench technique. Impedance spectroscopy (IS) is used to study the electrical properties of these prepared glasses. Modulus formalism is introduced to study relaxation behaviour of these glasses. Scaling model shows the good overlap of data on single master curve which suggests that conduction mechanism in these glasses is compositional dependent. Variation of dielectric constant and dielectric loss with the addition of Sm_2O_3 and frequency are discussed here.

Introduction

The importance of impedance spectroscopy (IS) is justified because of its importance in material characterization [1]. It is the basic tool to characterize electrical properties of materials in which the overall material behaviour is governed by the number of strongly coupled processes. IS can be used to investigate dynamic of charge in any kind of solid liquid or amorphous materials {e.g. ionic, semiconducting, mixed electronic–ionic and dielectrics (insulators)} [1].

Glass is most fascinating materials and attracted much interest both scientifically and technologically since it is transparent, chemically inert and ecofriendly [2–4]. Among the other glasses, lithium borate glasses have many advantages as a solid electrolyte because simplicity in manufacturing, isotropic properties and wide variety of possible compositions [4,5]. Li^+ ion conducting solid electrolytes offer good prospects in high energy density batteries and other electrochemical applications due to their light weight and most electropositive nature [5]. Borate glasses are interesting to study as compared to other glasses (e.g. silicate or phosphate)

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due to their coordination geometry, higher bond strength, high transparency, low melting point, high thermal stability and good rare earth ions solubility [4–7].

Use of rare earths (REs) elements or lanthanide in glasses makes them feasible to design various electro-optic and optical devices like lasers, color displays, amplifiers and solid state lighting devices [7–11]. Even if rare earth glasses offer great optical applications, it has been reported that they not contribute much to conductivity. It is reported that conductivity of glasses decreases with the addition of rare earth ion which is due to higher atomic weight and large ionic radius of rare earth ionic as compared to other component in glass system [12–14].

This paper intend to provide impedance spectroscopies studies for lithium borate glasses containing Sm_2O_3 with special emphasis on modulus formalism, conductivity formalism and conduction mechanism. By keeping in mind the importance of lithium borate glasses as glassy or vitreous solid electrolyte we have prepared the lithium borate glasses containing Sm_2O_3 by conventional melt quench technique. In this paper we have reported DC conductivity analysis of these glasses. Ion conduction mechanism is discussed by studying the modulus formalism and conductivity formalism. Dielectric behaviour is also reported in the present manuscript.

Material and methods

Glasses with the general formula 27.5 Li_2O–(72.5–X) B_2O_3–X Sm_2O_3 (X = 0.5, 1, 1.5 and 2) were prepared by conventional melt quench technique. Starting materials used for preparing glasses are Li_2CO_3, B_2O_3 and Sm_2O_3 (Merck Germany purity 99.99%). Appropriate quantity of chemicals mixed and melted in furnace at 1250–1300 K depending on composition in alumina crucible. After melting the melt was stir for 3–4 times to assure the homogeneity. Glasses were obtain by air quenching the melt in aluminium moulds. Obtained glasses were annealed for 573 K for 2 h in preheated furnace and then allowed for cooling to room temperature in an annealing furnace. Prepared glass samples were polished to get parallel faces of desired dimensions. Parallel faces of glass samples were coated with silver paint and these glass samples were arranged between two silver electrodes of sample holder. Before measurement all contacts and continuity of samples were confirmed. Impedance measurements were carried out for polished glass samples as a function of temperature using high resolution dielectric analyser (Novocontrol Make) in the frequency range 2 mHz to 20 MHz. The conductivity was determined from the impedance plots considering geometrical dimensions of the sample. DTA for all glass samples were recorded using Perkin–Elmer Diamond Thermal Analyser with heating rate of 10 °C/min for determining glass transition temperature (T_g).

Results and discussion

Electrical properties

Fig. 1 shows the variation of conductivity with temperature. From this figure it is observed that conductivity of glasses increases with increase in temperature according to Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \quad (1)$$

where E_a is the activation energy, σ_0 is pre-exponential factor, k_B is the Boltzmann constant and T is temperature.

Fig. 2 shows the variation of conductivity and activation energy at 548 K with the addition of Sm_2O_3. It is observed from this figure that the electrical conductivity decreases and activation energy increases with Sm_2O_3. These results are in good agreement with those reported earlier where conductivity decreases with the addition of rare earth oxide [12–19]. Since lithium content is kept constant in the present study and Sm_2O_3 is added at the expense of B_2O_3, decrease in conductivity and increase in activation energy attributed to decrease in mobility of lithium ions due to increase in rigidity of glass structure. Higher atomic weight and large ionic radius of Sm^{3+} ions also causes hindrance to mobile Li^+ ions [14].

Fig. 3 shows the variation of glass transition temperature (T_g) with Sm_2O_3. From this figure it is observed that glass transition temperature increases with the addition of Sm_2O_3. The increase

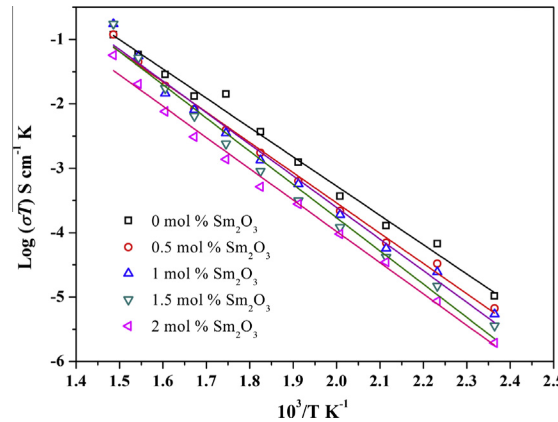

Fig. 1. Variation of conductivity with temperature.

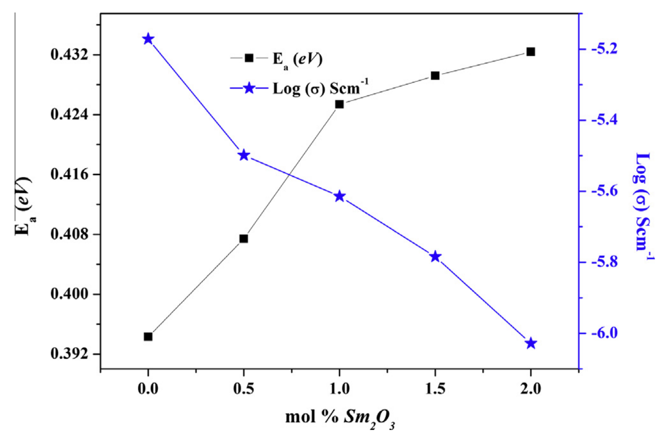

Fig. 2. Variation of conductivity and activation energy with mol% Sm_2O_3.

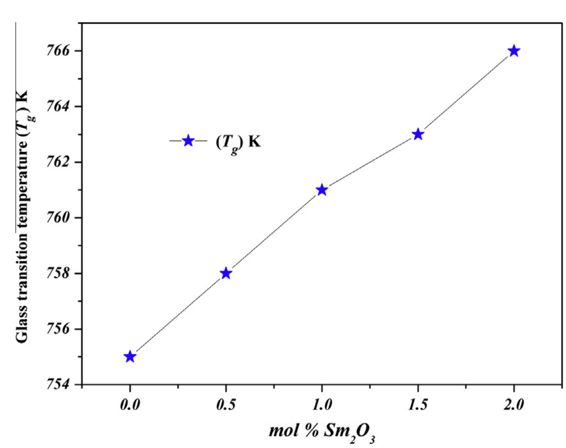

Fig. 3. Variation of glass transition temperature (T_g) with Sm_2O_3.