

Study of D.C.Ionic Conductivity in BaCl₂:SiO₂ Composite Solid Electrolyte System

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ABSTRACT:

Study of d.c. ionic conductivity in pure BaCl₂ and BaCl₂ dispersed with the insulating material SiO₂ is presented in this work. Variation of dc ionic conductivity with temperature has shown a gradual enhancement of conductivity with m/o of dispersoid reaching to a maximum of nearly two orders of magnitude at 6.6m/o. The fall of enhancement was observed with further increase in m/o of dispersoid. The enhancement of conductivity in this system is interpreted due to increased concentration of charge carriers in the space charge region formed at the interface between the host BaCl₂ and insulating dispersoid particles SiO₂. XRD and FTIR studies have ruled out the formation of new compound or solid solution, between the host and the dispersoid, as there are no new peaks observed in all these systems.

Keywords: Composite solid electrolyte, dispersion, conductivity enhancement, space charge region.

INTRODUCTION:

Dispersion of second phase fine insulating particles in host materials is well known and they are called as dispersed solid electrolyte systems. These materials show high ionic conductivity, small activation energy for ion migration and low electronic conductivity and because of these reasons they play an important role in solid state ionics[1,2]. These materials are mainly used in rechargeable batteries, super capacitors, sensors, fuel cell etc.. Extensive studies have also been done on a number of dispersed solid electrolyte system where the ionic conductors having Na⁺,Li⁺,O²⁻,Ag⁺,No⁻³ as conducting species with the



enhancement of conductivity ranging from 1-3 orders of magnitude[3-10]. Barium Chloride is an ionic conductor with cubic structure, is an anti-frenkel type solid and mobile charge carriers are Cl^- ions. For the first time in 1978, C.C. Liang has shown the enhancement of conductivity in LiI by admixing the fine particles of an inert second phase SiO_2 [11]. Various models such as space charge layer model[12], average medium approximation[13], random resistor model[14] have supported the formation of space charge region at the interface between the host and dispersoid particles which is attributed to be responsible for the increased defect concentration. They inturn give rise the enhanced conduction in these systems. Hence in this paper we present the study of d.c. ionic conductivity in BaCl_2 and dispersed with SiO_2 in different mole percents with increasing temperature.

EXPERIMENTAL:

The host material BaCl_2 single crystals were grown by slow evaporation method, and these crystals crushed in to a fine powder using agate mortar and than sieved to have a uniform particle size. SiO_2 powder of microns size obtained from Sigma Aldrich used as dispersoid. Fine uniformly mixed powders were obtained by grinding for an hour using mortar and pestle after taking different stoichiometric ratios of host and dispersoid along with acetone which eventually evaporates. These powders were pressed in the form of pellets by applying suitable pressure and then sintered for about 24hrs. at 640°C . Silver paste was applied on either flat surfaces of the sample to enable good electrical contact and mounted between electrodes of the sample holder. After annealing for about 3hrs.current was recorded between room temperature and the melting point of the sample by maintaining uniform rate of heating.

RESULTS AND DISCUSSION:

XRD patterns of BaCl_2 and dispersed systems of SiO_2 are shown in fig.1. Distinct peaks in the XRD patterns of host and dispersed systems indicate that these materials are in crystalline nature. No additional peak is observed in dispersed systems as against to the constituent compounds show that there is no chemical reaction between host and dispersoid reveals that no indication of formation of any solid solution.

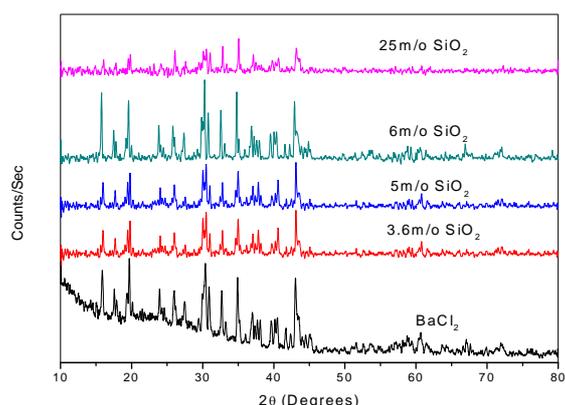


Figure1. X-ray patterns of BaCl_2 : SiO_2 Composite Solid Electrolyte System

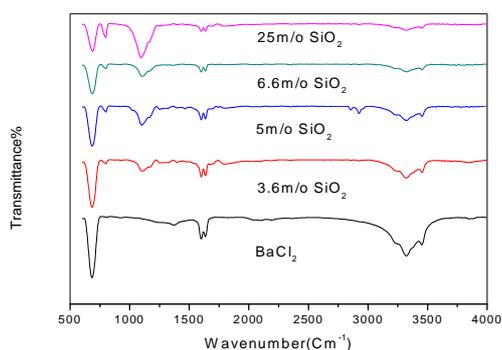


Figure 2. FTIR spectra of BaCl₂ and BaCl₂:SiO₂ at different mole percentages

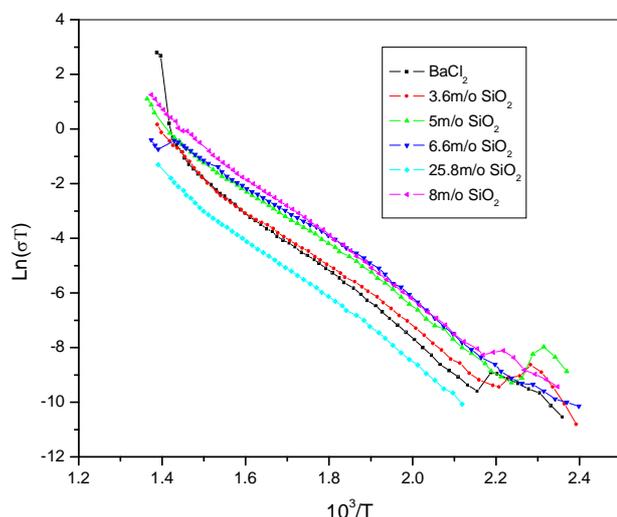


Figure 3. Ionic conductivity versus temperature of BaCl₂:SiO₂ (for different m/o)

FTIR spectra of host BaCl₂ and dispersed systems with different m/o silica in the wave number range from 600 cm⁻¹ to 4000 cm⁻¹ is shown in fig.2. Appearance of same bands in dispersed systems are found to be same with that of host and dispersoid materials confirms that there is no formation of solid solution.

Conductivity plots drawn between Ln(σT) versus 10³/T are shown in fig.3 for host and dispersed systems where in conductivity is found to increase with temperature. It can also be seen from the figure that the conductivity increases with m/o reaching to a maximum of nearly two orders of magnitude at the threshold value of 6.6m/o and with further increase in the m/o a decrement was observed which is known as negative Liang effect.

Enhancement of Conductivity in this system is interpreted in terms of formation of space charge region at the interface of the constituent materials [15-20]. In this region increasing the concentration of defects is due to attraction of anions on to the surface of the dispersoid or repulsion of anions in to interior of the host lattice. Between these two processes a former seems to be more appropriate than the later. A fall in conductivity enhancement was observed at higher m/o could be due to the fact that there is not enough host material to surround the dispersoid particles individually, leading to reduction in volume of the space charge region between two constituent materials.

Variation of mole percent and $\ln(\sigma T)$ is shown in fig.4. The decrease in the enhancement of ionic conductivity at higher m/o dispersoid could be due to the presence of excess silica in the host barium chloride leading to the reduction in the formation of space charge layer between two constituent materials[20].

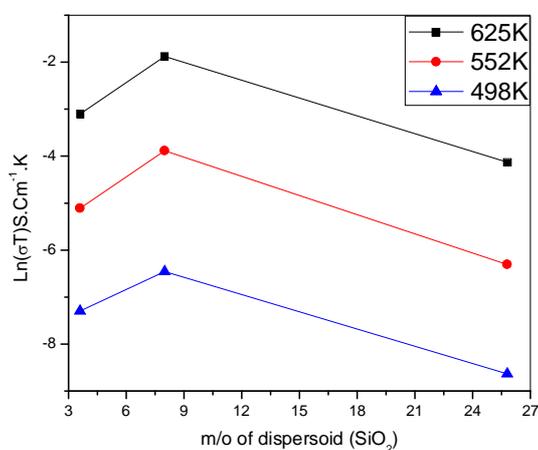


Figure 4. Ionic conductivity versus m/o of dispersoid at various temperatures

CONCLUSIONS:

BaCl₂:SiO₂ composite system has shown a maximum of nearly two order of magnitude of enhancement of conductivity. XRD and FTIR studies confirmed that no solid solution has been formed in BaCl₂:SiO₂ composite system. Conductivity studies reveal that the enhancement of ionic conductivity is found to increase with m/o. This is attributed to the increased number of charge carriers in the region at the interface. Decrease in the enhancement of ionic conductivity after threshold m/o could be due to the non-availability of enough host material to surround the dispersoid particles individually.

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