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Physica B 362 (2005) 193–198
PHYSICA B
www.elsevier.com/locate/physb

DC ionic conductivity of $NaNO_3$: γ-Al_2O_3 composite solid electrolyte system

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Received 3 November 2004; received in revised form 5 February 2005; accepted 7 February 2005

Abstract

We present DC ionic conductivity measurements on composites formed between Na^+ ion conductor ($NaNO_3$) and dispersed insulating oxide (alumina). Enhancement of conductivity is noticed to increase with mole percent (m/o) of the dispersoid. The maximum enhancement observed is more than two orders of magnitude with respect to the host material. X-ray diffraction and differential scanning calorimetry studies ruled out the formation of solid solutions between the host material and the dispersoid. The experimental data indicating higher conductivity in dispersed system is interpreted in terms of the formation of space charge layer between the host material and the dispersoid in which defect concentration increases and that is thought to be the possible mechanism of conductivity enhancement. Activation energies obtained from the conductivity data in the extrinsic conduction region indicated least value for the systems at threshold mole percentage.

Keywords: Composites; Space charge layer; Solid electrolyte; Ionic conductivity; Dispersoid

1. Introduction

In the recent times, heterogeneous doping has been employed to enhance the conductivity of solid electrolytes. It involves the dispersion of submicron insulating particles in the host matrix, thereby forming a composite. In general, it is believed that no chemical reaction is found to occur between the host matrix and the dispersoid in the composite solid electrolyte systems [1].

The ionic conductivity of several solid electrolytes has been found to increase significantly with dispersion of insulating second phase particles. The degree of enhancement depends largely on concentration, size and type of dispersoid particles. Such type of behavior was noticed in many

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0921-4526/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.physb.2005.02.011

systems in the recent past, namely, LiI–Al_2O_3 [1], CuCl–Al_2O_3 [2], AgI–Al_2O_3 [3], $Sr(NO_3)_2$–Al_2O_3 [4], CsCl–Al_2O_3 [5], Li_2SO_4–Al_2O_3 [6], Na_2SO_4–Al_2O_3 [7], Rb/$CsNO_3$–SiO_2 [8], $CsHSO_4$–SiO_2 [9], etc. Several theoretical models, such as space charge layer model [10], random resistor model [11] have explained this phenomenon. It is widely accepted that the mechanism of enhancement is through the generation of excess defects in the host matrix phase in the vicinity of the dispersoid [12]. As far as the host material is concerned, the focus has now been changed from halides of alkali/silver metals to predominantly nitrates, sulphates, carbonates, and other salts of alkali metals in the recent investigations [11]. Among the alkali nitrates we have chosen sodium nitrate not only because of its low melting point but also of its smaller cationic radius.

It has been reported [13,14] that there is 2–3 orders of magnitude of enhancement of conductivity due to the formation of disordered phases in the case of $RbNO_3$ dispersed with Al_2O_3. The thermal stability and mechanical properties of these systems were found to have been improved. All these characteristics exhibited by these composites make them very attractive for various electrochemical devices, such as solid state batteries, sensors, intermediate temperature fuel cells, etc. In this study we present the DC ionic conductivity of composites of $NaNO_3$–Al_2O_3 with varying mole percentages and their characterization by using the techniques like differential scanning calorimetry (DSC) and X-ray diffractometry (XRD) so as to understand better the transport properties of nitrate-based materials. An attempt is made, with the help of various existing theoretical models, to explain our results on DC ionic conductivity and to identify the possible mechanism of enhancement of conduction in these systems.

2. Experimental

The starting host material, $NaNO_3$, was from Analar Grade BDH (British Drug House). The powder was dissolved in double distilled water and single crystals obtained by the method of slow evaporation were crushed. And the dispersoid (Al_2O_3 of size 60 nm) of 99.8% was used as received from Adolf Meller Co. Both the (host and dispersoid) powders taken in particular composition were mixed in the presence of acetone and ground in an agate mortar. This process of grinding was continued for about an hour, until the acetone got evaporated completely. Pellets of 10–12 mm diameter and 3.4 mm thickness were prepared by using a steel die at a pressure of about 0.46 GPa. The pellets so obtained were sintered at 250 °C for 24 h. After polishing the surfaces, a quickly drying carbon dag was applied for electrical contact. The pellet was mounted in a spring-loaded crystal holder and annealed at about 150 °C for 12 h before the start of an actual experiment. A constant rate of heating of about 2 °C per minute was maintained. The temperature recorded was by a Cr–Al thermocouple. A small DC voltage of 1 V was applied across the sample and the current was measured by using HP34401A digital multimeter.

3. Results and discussion

Fig. 1 shows the variation of $\log\sigma$ with reciprocal temperature covering from room temperature to nearly the melting point of the host material for pure $NaNO_3$ and dispersed with 5, 10, 15, 20 and 25 mole percentages of alumina. Conductivity of pure $NaNO_3$ can be seen to increase linearly up to its transition temperature, 275 °C (1.824 on X-axis) followed by deviation from its linearity. In the dispersed system the enhancement in conductivity is observed to increase with mole percent (m/o) with a threshold at 15 m/o where from enhancement starts falling with further increase in m/o, i.e. for 20 and 25 mole percentages. The maximum enhancement at 15 m/o is observed to be above two orders of magnitude with respect to pure $NaNO_3$ in the extrinsic conduction region. It may be noticed from the plot that conductivity for pure at about 200 °C (2.11 on X-axis) is between 10^{-8} and 10^{-7} S/cm whereas it is about 10^{-5} S/cm for $NaNO_3$:γ-Al_2O_3 for 15 m/o. Dependence of conductivity on mole percentage of alumina, temperature as a