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# DC ionic conductivity studies on NaNO<sub>3</sub>: SiO<sub>2</sub> composite solid electrolyte system

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# ABSTRACT

The study of charge transport in pure NaNO<sub>3</sub> and NaNO<sub>3</sub>: SiO<sub>2</sub> dispersed solid electrolyte system with 6.59, 12.42, 17.53 and 22.06 mole percentages of SiO<sub>2</sub>(10nm), has shown that there is an increase in conductivity as the temperature rises from room temperature up to near the melting point of pure system. The enhancement of dc ionic conductivity is observed to increase with m/o and reaches to maximum at 12.42 mole percent, followed by a fall of conductivity with further increase of dispersion. X-ray diffraction patterns of pure Sodium Nitrate, Silica and 12.42, 17.53 m/o dispersed systems have shown that pure phases of host and dispersoid materials coexist in the dispersed system was explained due the increased concentration of defects in space charge region formed between the host and nano particles of dispersoid.

Keywords: Composite solid electrolyte, conductivity enhancement, Dispersion, Space charge region.

# INTRODUCTION

The materials, which exhibit electric conduction through the migration of ions, are called solid electrolytes. The ionic conductivity of these solids is exceptionally high and comparable to that of aqueous electrolytes. Therefore, they can be potentially utilized as an excellent replacement with liquid/aqueous electrolytes to fabricate solid state electrochemical devices. These solid materials, which exhibit high ionic conductivity ( $10^{-2}$  to $10^{-6}$  S/cm), negligible electronic conductivity (10<sup>-8</sup> S/cm) and low value of activation energy (<1 eV) for ion migration, are broadly referred to as 'superionic solids' or 'solid electrolytes' or 'fast ion conductors [1]. A large number of solids exhibiting fast ion transport involving variety of conducting species such as H<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, O<sup>2-</sup>, F etc. Among these Li<sup>+</sup> and Na<sup>+</sup> ion conducting solid electrolytes have been developed recently and used them in the fabrication of high energy storage batteries because of their light weight and high electrochemical potential [2,3]. Sodium nitrate exhibits ionic conductivity in the order of 10<sup>-4</sup> S/cm and the ion transport is mainly due to cation Frenkel defects [4]. The crystal of structure of NaNO<sub>3</sub> is rhombohedral calcite structure with a space group R3c, with two molecules in the unit cell and has an orientational disorder of nitrate ion at 548K [5]. Several approaches have been employed to enhance the conductivity in solid electrolytes at ambient temperatures [6]. A large enhancement in conductivity (nearly 2-3 orders) is achieved by the addition of dispersed second phase particles to normal ionic conductors. The ionic conductors containing dispersed second phase particles are called composite solid electrolytes or dispersed solid electrolytes. Composite solid electrolytes, a novel class of materials attracting tremendous technological interest in the recent years, are high ion conducting multiphase solid systems created a center of attraction after Liang at al [7]. They are mostly two-phase mixture, in which both phases (ionic salt and

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dispersoid) coexist together separately in the composite system. The size of particles of second phase dispersoid play significant role in improving the conductivity of the host material. The reported research shows that the dispersal of nanosize particles would result into a significant enhancement in the conductivity [8]. The study of ionic transport in NaNO<sub>3</sub> dispersed with Al<sub>2</sub>O<sub>3</sub> showed enhancement in conductivity [9]. Hence in the present study, NaNO<sub>3</sub> was dispersed with nano SiO<sub>2</sub> to improve the ionic conductivity in the system.

#### **MATERIALS AND METHODS**

The starting host material, NaNO<sub>3</sub>, was from Analar Grade with 99.8% purity. The powder was dissolved in distilled water and grown as single crystals from solution growth techniques. These crystals were ground into fine powders and used as host material. The dispersoid SiO<sub>2</sub> (10-20 nm) of 99.8% was taken as received from Aldrich chemicals. Both these (host and dispersoid) powders were mixed in a particular composition in the presence of acetone and ground in an agate mortar for about 30 - 40 minutes and allowed to evaporate at about 100°C. Pellets of 10 -12mm diameter and 2mm thickness were prepared by using a die at a pressure of about 5tonnes/sq.m. The pellets so obtained were sintered at 250°C for 20 h. After polishing the surfaces, a quickly drying silver paste was applied for electrical contact. The pellet was mounted in a spring-loaded crystal holder and annealed at 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 1V was applied across the sample and the current was measured by using HP34401A digital multimeter.

# **RESULTS AND DISCUSSION**

X-ray diffraction patterns, of the pure NaNO<sub>3</sub>, SiO<sub>2</sub>, and dispersed with SiO<sub>2</sub> (17.53 m/o and 31.50 m/o) solid electrolytes, recorded at room temperature by Regaku miniflex diffractometer, are shown in Fig.1. It is observed that the pure NaNO<sub>3</sub> has distinct peaks indicating that it has a crystalline structure and XRD of pure SiO<sub>2</sub> shows that widening of the prominent peak along with high intense background pattern indicates that size of SiO<sub>2</sub> particles is in the order of nanometers. It is noticed from the Fig.1 that the peaks are sharp for SiO<sub>2</sub>-containing composites as compare to the pure NaNO<sub>3</sub> peaks, indicating increased crystallanity. No additional peaks were observed in the dispersed composite systems. Dispersion of SiO<sub>2</sub> does not affect the XRD patterns, which signifies that no chemical reaction or formation of solid solution takes place between NaNO<sub>3</sub> and SiO<sub>2</sub>. XRD reveals that the two parent phases exists separately i.e. the samples remain in biphasic mixture of NaNO<sub>3</sub> and SiO<sub>2</sub> [10-11]. Similar observations were made in NaNO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, NaCl–Al<sub>2</sub>O<sub>3</sub>, KCl–Al<sub>2</sub>O<sub>3</sub> and CsCl–Al<sub>2</sub>O<sub>3</sub> solid electrolyte systems [9, 12-14].

Fig. 2 shows the variation of DC ionic conductivity obtained from two-probe DC technique, with reciprocal temperature in the dispersed NaNO<sub>3</sub> system between 160°C and nearly the melting point of the host material (NaNO<sub>3</sub>) with different mole percentages of the SiO<sub>2</sub> (10-20 nm) dispersoid namely,0, 6.59, 12.42, 17.53, and 22.06. The conductivity of each sample is noticed to increase with temperature. Conductivity of pure NaNO<sub>3</sub> can be seen to increase linearly up to its transition temperature,  $275^{0}$  C (1.82 on X-axis) followed by deviation from its linearity. In SiO<sub>2</sub> dispersed composite solid electrolyte systems, the enhancement of conductivity is observed to increase with mole percent (m/o) and attains maximum at12.42 m/o, followed by a decrease in the conductivity. The maximum enhancement in conductivity for 12.42 m/o dispersed system is noticed to be 1-2 orders of magnitude with respect to pure NaNO<sub>3</sub> at high temperatures in the extrinsic region of conductivity. However in the low temperature region (above 2.05 on X-axis) the conductivity of 12.42 m/o is seen to decrease with respect to 17.53 m/o of SiO<sub>2</sub>. The enhancement in the 12.42m/o with respect to pure NaNO<sub>3</sub> is found to be smaller at low temperatures and gradually increases with increasing temperature .The Variation of conductivity as a function of mole percent of SiO<sub>2</sub> in the dispersed NaNO<sub>3</sub> system at 200<sup>0</sup>C and 250<sup>0</sup>C are shown in Fig.3.



Fig.1: X-ray diffraction patterns of the pure NaNO<sub>3</sub> and pure SiO<sub>2</sub>, NaNO<sub>3</sub> dispersed with SiO<sub>2</sub> (17.53 m/o and 31.50 m/o) solid electrolytes



Fig. 2: Variation of conductivity with reciprocal temperature in the pure NaNO3 and dispersed with different m/o of SiO2 systems

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Fig. 2: Variation of conductivity with m/o of SiO\_2 at 200°C and 250°C

The activation energies obtained from the slopes of the log  $\sigma$  vs. 1000/T plots vary between the 0.8-1.18eV. The activation energies for composites are slightly lesser than that of pure system. This could be due to increased number of cation vacancies in the space charge region resulting in the lesser energy required for Na<sup>+</sup> ion mobility [15].

In the transport properties of polycrystalline and polyphase (composite) materials, interfaces play an important role. Enhanced ionic conduction along interfaces can be observed for two reasons. Firstly, the interface core itself is a disordered region, where defect formation and migration energies are generally notably reduced. This leads to enhanced ionic transport within the interface core (grain boundary diffusion). The conductivities studies on polycrystalline oxides like NiO and MgO were explained on the basis of grain boundary diffusion [16], but there seems to be no similar study in composite materials. It may be due to small core effects. Secondly, due to the increased concentration of point defect at the interfaces where the space charge layer is formed because of the interaction between the phases [17, 18].

Many other experimental observations are in agreement with the space charge layer model such as  $AgCl-Al_2O_3$ ,  $NaNO_3$ -  $Al_2O_3$ . The enhancement of conductivity in the present system is explained using Maier's space–charge model [18]. Enhanced defect concentration in the space charge layer formed between the  $NaNO_3$  and  $SiO_2$  can be the main reason for the enhancement of conductivity [19, 20] .According to the Maier's space–charge model, the composite solid electrolyte is enriched with defects in the space–charge region at interface, especially if the surface interaction between the phases of a composite takes place. Strong ion-ion interactions may be represented as a process of the chemical adsorption of ions to the oxide surface [21, 22]. In ionic salts, there is the lattice distortion associated with the asymmetric field at the surface. As a result, all the characteristics of point defects and impurity ions located on the surface differ from those in the bulk. Their difference is the reason for the specific adsorption of defects at the crystal surface [23]. The insulating oxide particles can be associated with different hydroxyl groups called nucleophilic groups on their surfaces. The positive ions in the surface of MX are attracted by the hydroxyl groups i.e.,  $M^+$  ions shift from the MX to the MX–A interface. As a result, a positively charged layer enriched with cations is formed between the surface layers of the phases (MX and A) and a layer of cationic vacancies, which describe the surface disordering i.e. enhanced defect concentration at the MX and A interface [24].

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The fall of the enhancement of conductivity after reaching the maximum value can be understood as explained as follows. Initially, for low m/o of the dispersoid, the total surface area of contact between the host matrix and the dispersoid particles is small. As the m/o increases, the total surface area in contact increases leading to an increase in the enhancement of conductivity. Further increase of m/o of SiO<sub>2</sub>, host material is not enough to surround the dispersoid particles individually. This leads to an agglomeration of the particles of the dispersoid leading to a fall of total effective surface area of contact [25].

# CONCLUSION

Enhancement of dc ionic conductivity is observed in pure NaNO<sub>3</sub> when dispersed with insulating nano particles of dispersoid,  $SiO_2$ . This enhancement is noticed to increase with mole percent of the dispersoid up to 12.42 where it reaches to a maximum then after the fall of enhancement was observed with further increase of m/o of  $SiO_2$ . XRD patterns reveal that both host and dispersoid phases exist separately indicates that neither chemical reaction nor formation of solid solution had taken place between them. These results have been interpreted basing on the theory given by Maier's approach and space-charge layer model given by Wagner et al where in enrichment of point defects in the space charge layer formed between the host ionic material and insulating dispersoid has been proposed.

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