

Studies on DC Ionic conductivity of (1-x) NaNO₃: X ZrO₂ Solid Electrolyte System

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Abstract

In the present study, ZrO₂ (<100nm in size) was dispersed into NaNO₃ (host) using mechanical milling for an hour in the presence of acetone and it is done for different m/o of ZrO₂. The so obtained powder was pressed as pellet with applying 5 tones/cm² pressure and sintered 2at 250°C for 20 hours. On these pellets the dc ionic conductivity was carried out with varying temperature from room temperature up to the melting point. Enhancement in conductivity with m/o ZrO₂ was observed with a threshold at 15 m/o ZrO₂. The maximum enhancement is observed to be 1- 2 orders of magnitude with respect to the host in the extrinsic conduction region. XRD, DSC and SEM Characterizations on these dispersed systems were also done. XRD and DSC ruled out the formation of solid solution between the host and dispersoid. The formation of Space charge layer and enhanced grain boundaries which causes to the increased defect concentration profiles in the host and that is thought to be the possible reason for the conductivity enhancement .Accordingly, activation energy is found to decrease up to threshold, beyond that it was observed to increase with m/o. in the extrinsic conduction region. The fall of enhancement of conductivity at higher/o is due to the Blocking Effect of ZrO₂ particles between the interfaces of host and dispersoid.

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Introduction

For the last four decades, researchers working in the field of Solid State Ionics were attracted towards the Dispersed Composite Electrolyte Systems (DSES) after Liang[1] reported that the conductivity of composite solid electrolytes increases due to the influence of heterogeneous doping of insulating particle. Such dispersed composite systems are mostly two-phase solid mixers [2],in which first phase is a normal ionic conductor /moderate ionic conductor (such as alkali/alkaline earth- halides,sulphates ,bisulphate's, sulfides,carbonates,nitratesetc etc.)and second phase is either another

ionic solid or a chemically inert, insulating oxides (Al_2O_3 , SiO_2 , Flyash, CeO_2 , ZrO_2) or ferroelectric oxides such as Fe_2O_3 , BaTiO_3 , SrTiO_3 etc. It was widely accepted that DSES are higher ionic conductive than that of their constituent phases [3-12]. In addition to the substantial change in ionic conductivity, the changes occur in thermo dynamical parameters and mechanical properties of ionic conductors. Hence they are found to be promising materials for solid state high energy batteries, solar cells, fuel cells, super capacitors, gas sensors and many more electrochemical devices to meet the needs of modern civilized society [13]. The conductivity enhancement of such composites were explained by many theoretical models such as Jow and Wagner's model [14,15], Maier's adsorption- desorption model [16-19] and percolation mode [20,21,36]. It is commonly accepted that the mechanism of enhancement is due to the increased defect concentration at the interfaces of host and dispersoid phases [22]. The observations reported by various researchers on composite solid electrolytes state that the affecting factors of conductivity enhancement are the formation of space charge layers [19,23], formation of more number of grain boundaries [24,25], effective surface area of the second phase with the first phase [26], particle size of the dispersoid [27], volume fraction of the dispersoid [14,15], ionic radius of mobile ion in the host [13]. Keeping these observations in view, we have chosen a Frenkel Type cationic conductor NaNO_3 as a host and inert insulating oxide ZrO_2 (<100nm) as a dispersoid. The data presented in this paper includes characterization and ionic conductivity measurement.

Experimental

The host material NaNO_3 with $\geq 99.5\%$ purity was received from Sigma –Aldrich Chemicals dissolved in double distilled water and obtained fine single crystals by slow evaporation method. This was done to improve the purity of the host further. The dispersoid ZrO_2 (<100nm) with 99.9% purity was also received from Aldrich Chemicals. Both the powders of host and dispersoid taken in required compositions (0,5,10,15,20,25 m/o) were mixed in an agate mortar and ground in the presence of acetone about an hour until acetone completely evaporated. This was done to obtain uniform composition to increase the contact surface area of the dispersoid with the host [26]. By using steel die, pellets of 8mm diameter, 3-4mm thickness at a pressure of 5 tones/ cm^2 were prepared and sintered them at 250°C for 20 hours in a muffle furnace. After cleaning the surfaces, silver paint was applied on the flat surfaces of the pellet for good electrical contact. Then pellet was mounted between the electrodes of spring loaded sample holder. Annealing was done at 150°C for 4hr before the beginning of conductivity experiment. A small dc voltage of 1.5 V was applied across the sample and a constant rate of heating about $2^\circ\text{C}/\text{minute}$ was maintained throughout the experiment. The current readings were noted from room temperature to nearly the melting point of the host material by using nano ammeter. The same procedure was followed for pellets of various compositions of present system.

Results and Discussions

A. XRD (X-ray Diffractometry):

Figure 1 shows the XRD patterns of pure NaNO_3 and other dispersed systems with different mole percentages of ZrO_2 . As there are no other peaks other than those of host and dispersoid materials one can conclude that there is no

Formation of solid solution between the host and dispersoid. Similar observations were noticed in the case of $\text{NaCl-Al}_2\text{O}_3$, $\text{KCl-Al}_2\text{O}_3$, $\text{CsCl-Al}_2\text{O}_3$, $\text{NaNO}_3\text{-Al}_2\text{O}_3$, $\text{CsNO}_3\text{-Al}_2\text{O}_3$ etc [28,29,30,31,32].

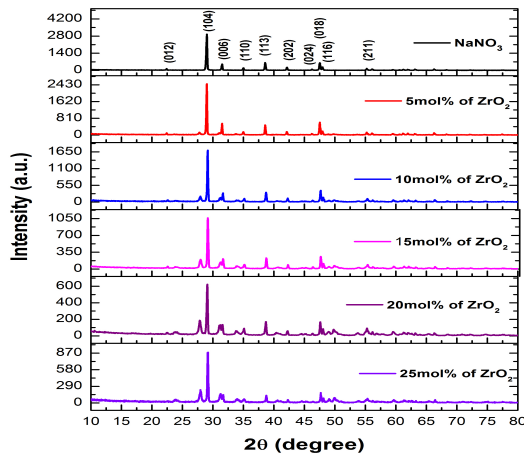


Figure 1: X-ray diffractograms of pure and dispersed systems

B. DSC (Differential Scanning Calorimetry)

Figure 2 shows the DSC curves of pure NaNO_3 and different compositions of dispersed systems. Trace for pure NaNO_3 consists of two peaks, a small peak at about 275°C corresponds to its phase transition and sharp peak (endothermic) occurring at about 308°C shows its melting point. [32,33]. All the remaining dispersed systems show no significant changes indicating that there was no solid state reaction between the Host and dispersoid. ZrO_2 content in the composite systems does not seem to alter the phase transition temperature. Dispersed systems of 5, 10, 20 and 25 mol% showed little distortion at the melting point peaks. This may be due to the formation of amorphous phase at the interfaces between the host and dispersoid. [25,34]

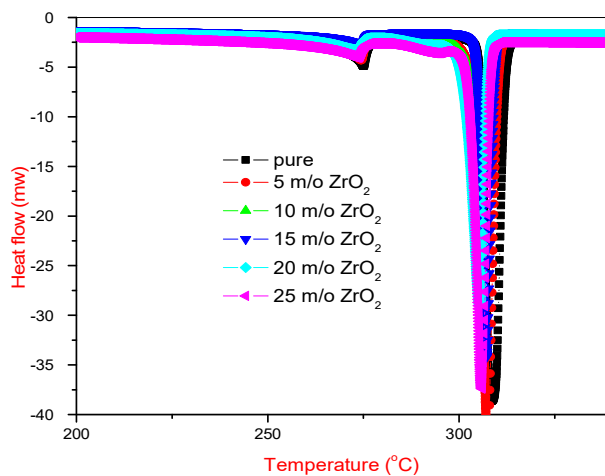
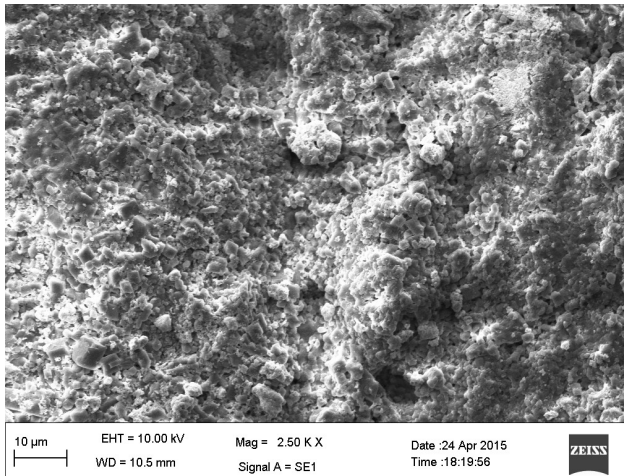


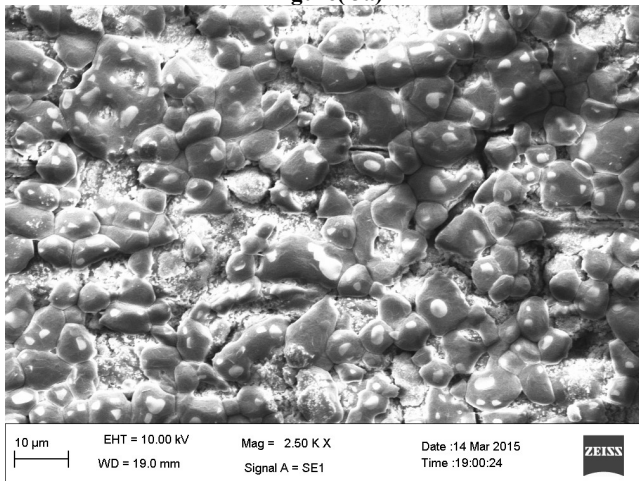
Figure 2: Dsc curves of pure and dispersed systems.

C.SEM Analysis

Figures 3a, 3b, 3c,3d,3e show the SEM images of dispersed systems of different mol percentages 5,10,15,20,25 respectively. It can be seen from the figures that threshold dispersed system (15 mol%) has more number of grain boundaries compared to the rest of the systems. This could increase the defect concentration at grain boundaries due to greater number of interfaces, hence, greater number of space charge layers between host and dispersoid [24]. In the case of compositions with higher m/o the dispersoid particles were seen to be agglomerated which result in blocking effect. This could be the reason for fall of conductivity beyond the threshold composition



Figure(3a)



Figure(3b)

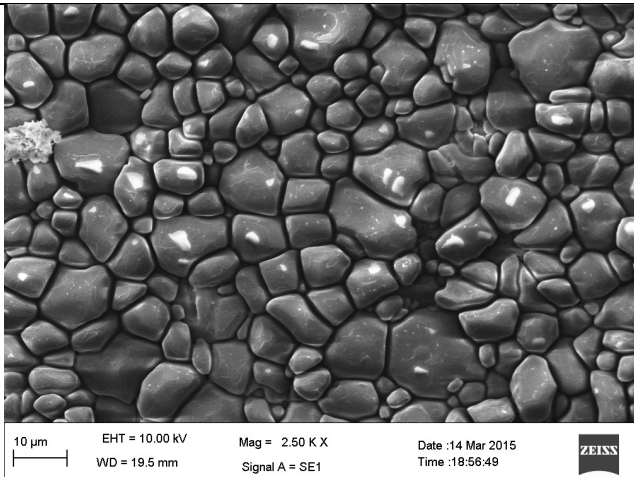
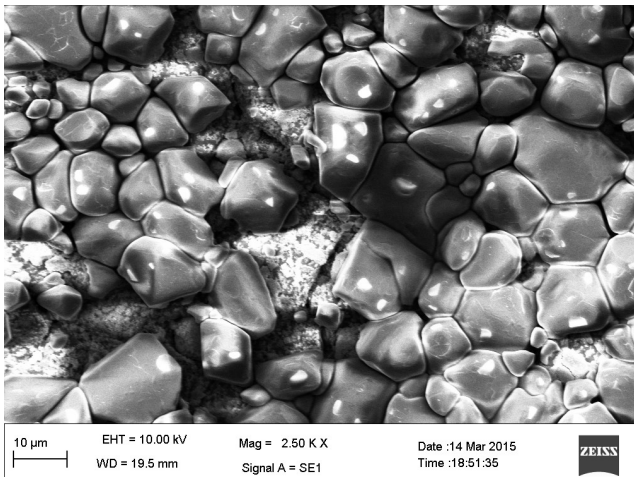


Figure (3c)



Figure(3d)

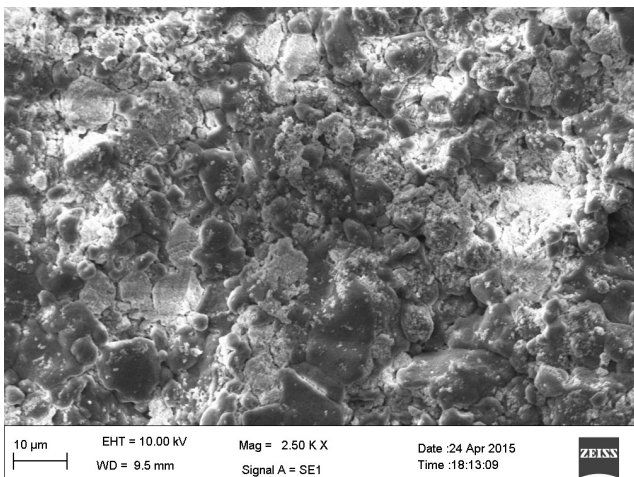


Figure (3e)

D.DC Ionic Conductivity

Figure 4 shows the variation of $\text{Log}(\sigma T)$ versus reciprocal temperature for pure host and various compositions of present system in the temperature range from 150°C to nearly melting point of the host material.

The plots reveal that conductivity in all the above systems is found to increase with the reciprocal of temperature almost linearly as per Arrhenius equation. In the dispersed compositions the enhancement of conductivity is found to increase with increase of mol percentage and attained a maximum for 15 m/o and decreased for further increase of m/o of ZrO_2 . The maximum enhancement observed is to be 1 to 2 orders of magnitude with respect to the host in the extrinsic conduction region for peaking m/o.

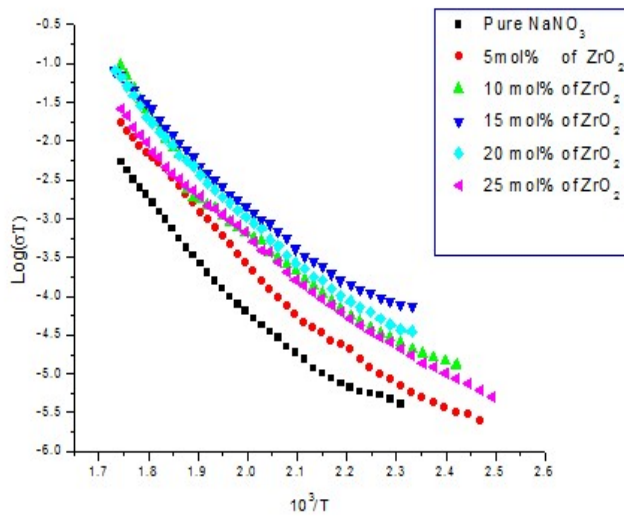


Figure 4: $\text{Log}(\sigma T)$ S/cm versus $(10^3/T)\text{K}^{-1}$

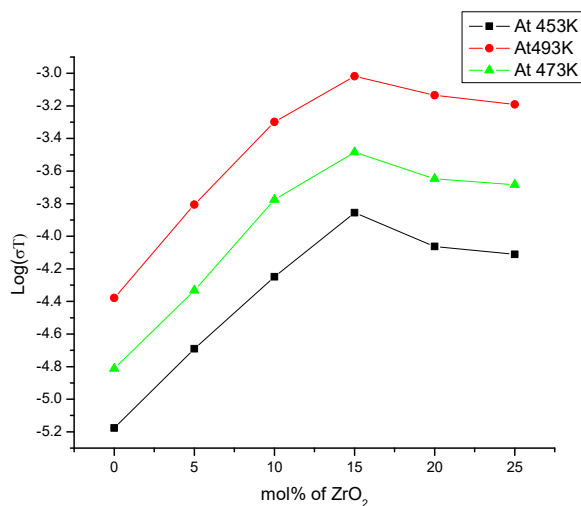


Figure 5: Conductivity versus m/o of ZrO_2

Figure 5 shows the variation of $\text{Log}(\sigma T)$ versus mol percentages of ZrO_2 of composite systems. From the figure it can be noticed that enhancement of conductivity is found to exist in the extrinsic conduction region and maximum at 15 mol% composition. The activation energies calculated from slopes of the plots in the temperature range 160-220 $^{\circ}\text{C}$.

Table 1, reflects that the activation energies obtained for various compositions vary between 0.7973 eV-1.0061 eV. It is clear that the activation energy was found to be the least i.e 0.7973 eV for threshold m/o of dispersion.

Table 1: Activation energies of composite system (1-x)NaNO₃:xZrO₂

Mole percentage	Temperature range in $^{\circ}\text{C}$	Activation energy in e.V.
0	160-220	1.0080
5	160-220	0.9302
10	160-220	0.9264
15	160-220	0.7973 *
20	160-220	0.8893
25	160-220	1.0061

This could be explained by means of Maier's Adsorption –Desorption model. The attraction of Na^+ cations from the host by the hydroxyl/nucleophilic groups existing on the surfaces of dispersoid particles at the interfaces of host and dispersoid with the consequence of local deviation from electroneutrality. It results the space charge layer formation at the interfaces, thereby increasing the defect concentration and leading to major conductivity enhancement [16, 17, 18, 19, 31].

Percolation model explains the present system in such a way that in the composites with dispersed insulating particles, the smaller size of the dispersoid particle with respect to the ionic conductor(host) grains contributes to formation of continuous particle monolayers, hence there by continuous conducting paths(percolation paths) enhance the ionic conductivity[20,21].

The formation of greater number of grain boundaries, which can be seen in SEM images, for the threshold m/o composition also another factor caused to enhance the conductivity. Enhanced charge transportation along grain boundaries may also influence the conductivity enhancement.

The fall of conductivity observed at higher m/o compositions was attributed to the agglomeration of dispersoid particles among the grains of the host which is observed in SEM images. It reduces the effective surface area of dispersoid phase with the host phase and also blocks the conducting paths. Hence, conductivity is decreasing at the m/o beyond the threshold percentage [24,31-35].

Conclusions

In the present solid electrolyte system (1-x) NaNO₃:xZrO₂, nano sized dispersoid ZrO₂(<100nm) particles and formation of large number of grain boundaries play an important role in enhancing the ionic conductivity by forming the space charge regions in the adjacent layers at its interfaces with the host and increased charge transportation along the grain boundaries. The maximum enhancement obtained for 15m/o of ZrO₂ dispersion in the extrinsic

conduction region with the least activation energy 0.7973eV. XRD, DSC ruled out the formation of solid state reaction between the host and dispersoid which is generally expected in the heterogeneous doping composites. SEM explained the grain boundary diffusion and blocking effect.

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