DC IONIC CONDUCTIVITY STUDIES ON Ba(NO$_3$)$_2$ Dispersed With SiO$_2$

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ABSTRACT

Ionic conductivity of alkaline earth nitrates show an increase when dispersed with the insulating materials such as SiO$_2$,CeO$_2$,Al$_2$O$_3$ etc of various particle sizes and mole percentages. The experiments were carried out on Ba(NO$_3$)$_2$ to study the DC ionic conductivity in its pure form and dispersed with SiO$_2$. No enhancement in conductivity was observed when Ba(NO$_3$)$_2$ is dispersed with SiO$_2$ of mole percentages 3,6,10,15,20,25,30,35 and even at higher mole % such as 40, 60,70,80. But when the host material is dispersed with 0.5mole % of SiO$_2$ an increase is found. The enhancement is found to be of the order of two to three magnitudes in extrinsic region. The increased conductivity in extrinsic region could be explained based on space charge model. Characterization of pure and dispersed systems is done through XRD, SEM and FTIR. Further, activation energies were calculated in intrinsic, extrinsic motion and extrinsic unassociated regions of conductivity starting from high temperature end.

Keywords— Dispersoid, host material, space charge , DC conductivity, activation energy, heterogeneous doping.

INTRODUCTION

Ionic conduction in solid electrolytes is found to be due to mobility of cation /anion. In most of these materials, crystal defects provide the pathway for conduction of the ions. These solid electrolytes show enhancement in conductivity by heterogeneous doping as is evident from the present study. Thermal, optical and mechanical properties of Ba(NO$_3$)$_2$ were studied in the past by Sir Deshmukh(1966,1975), Krishna Rao and Krishna Murthy (1964,1973) et al. Ionic conductivity observations of alkali, alkaline earth nitrates show the enhancement of the order of one to three magnitudes by heterogeneous doping with dispersoids such as SiO$_2$,CeO$_2$,Al$_2$O$_3$, fly ash etc[1]-[4]. The reason for increase in conductivity was explained on defect concentration mechanism [5],[6] produced due to dispersion of these nano sized compounds. The characterization of the prepared samples was done through XRD, FT-IR, and SEM.

Experimental

Ba(NO$_3$)$_2$ powder is obtained from universal laboratories. Crystals of this salt were prepared by slow evaporation method at room temperature. These crystals were crushed and ground in an agate mortar and sieved through a 63µm sieve to obtain powder of uniform crystal size. SiO$_2$ of 99.9% purity and 10-25nm particle size was obtained from Sigma Aldrich Company. SiO$_2$ is mixed with Ba(NO$_3$)$_2$ in the mole percentage 1, 0.2, 0.5 in the presence of acetone. The pellets of these samples were prepared by applying a pressure of about 3KN. These pellets were sintered at 300^{0}C for about 24 hours. The pellets were coated with silver paste for good electrical contact before keeping them for conductivity measurements in a sample holder. A constant rate of increase in temperature 2^{0}C/min was maintained throughout the experiment which was recorded by

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Cr-Al thermocouple. Data were recorded from room temperature to the melting point by applying constant DC voltage of 1.6 volts. However stable values of current could be obtained from about 150^0C. The characterization of the samples was done through XRD, SEM, and FT-IR.

results and discussions

Ln(σT) versus 1000/T graphs were plotted to study the variation of conductivity of Ba(NO$_3$)$_2$ when dispersed with SiO$_2$ of mole percentages 1, 0.2, 0.5 at temperatures starting from 150^0C to 520^0C. Current values were recorded by using a digital nano ammeter. In fig.1 the graphs of pure Ba(NO$_3$)$_2$ and dispersed with 1, 0.2, 0.5 mole % of SiO$_2$ were shown. At high temperature the plots of three samples were observed to be merged where as a marked increase in the conductivity is found in extrinsic region when the host material is dispersed with 0.5 mole % of SiO$_2$. The enhancement is found to be of the order of two to three magnitudes. The enhancement in conductivity is explained based on space charge model [7], [8]. According to Maier's space charge model the solid electrolyte is enriched with defects in the interface space charge region. The space charge model is applicable where structural changes and thermodynamic properties do not change with heterogeneous doping [9]. Ba(NO$_3$)$_2$ is anti Frankel type solid in which the conductivity is thought to be due to anion migration through crystal defects[10]. The increase in conductivity in the extrinsic region could be due to increase in the concentration of defects at grain boundaries. Further, the dispersed solid electrolyte system is considered as two phase system[8] and the conductivity is explained on the basis of a) Structural defects of the host material b) Interfaces formed between the boundaries of host and dispersoid particles[11]-[13]. Activation energies calculated in all the three regions were shown in table. The low values of activation energies in extrinsic region as against those in intrinsic region could be due to increased concentration of defects in the interfacial layer [9]. X-ray diffraction patterns obtained using powder X-ray diffractometer are shown in figure 5. No new peaks were observed in the XRD patterns of all the three samples when compared with that of pure Ba(NO$_3$)$_2$, indicating that there is no formation of new phase. So the enhancement conductivity cannot be attributed to the phase changes. FT-IR spectra of the four samples were shown in fig 6. These spectra indicate the coincidence of absorption peaks which ruled out the presence of new compounds formed as a result of dispersion. SEM pictures of all samples were shown in figures 7 to10 . These studies show the agglomeration of particles and the surface structure of all samples. Prior to the above said results, conductivity experiments were performed for the composites of Ba(NO$_3$)$_2$ dispersed with 3,6,10,15,20,25,30,35 and 40,60,70,80 mole % of SiO$_2$ and graphs were shown in figs 2, 3 & 4 respectively in which no enhancement was noticed.

Conclusion

The DC ionic conductivity of Ba(NO$_3$)$_2$ dispersed with SiO$_2$ shows enhancement of the order of two to three magnitudes in extrinsic region when the host material is dispersed with 0.5 mole %. The reason for enhancement was explained on the basis of formation of interfaces at the grain boundaries as suggested in the space charge model. And it is interpreted in terms of increased defect concentration at phase boundaries and decrease in conductivity is explained in terms of reduction of phase boundaries. The activation energy in the extrinsic region is found to be minimum (0.4723eV) at the threshold concentration of 0.5m%.
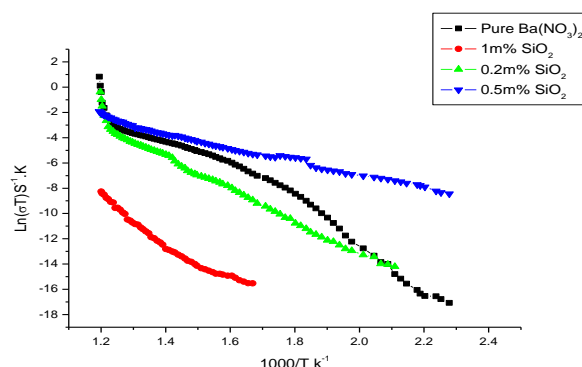

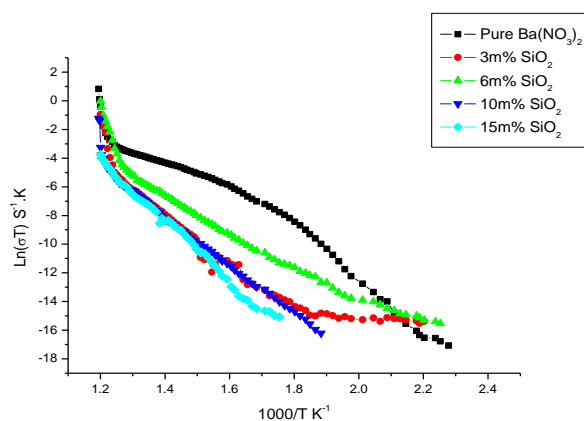Fig. 1: Ln (σT) versus 1000/T for Ba(NO$_3$)$_2$ and dispersed with 1, 0.2, 05 mole % of SiO$_2$

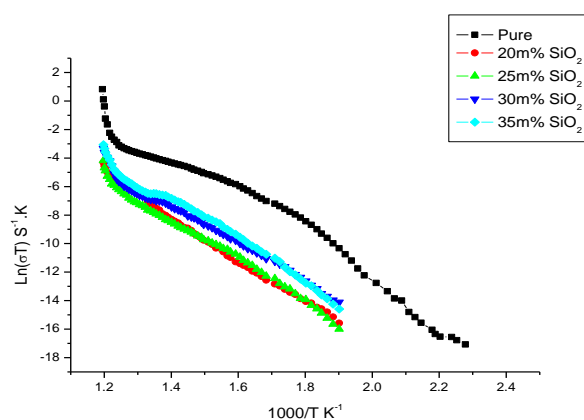Fig.2: Ln (σT) versus 1000/T for Ba(NO$_3$)$_2$ and dispersed with 3, 6, 10, 15 mole % of SiO$_2$

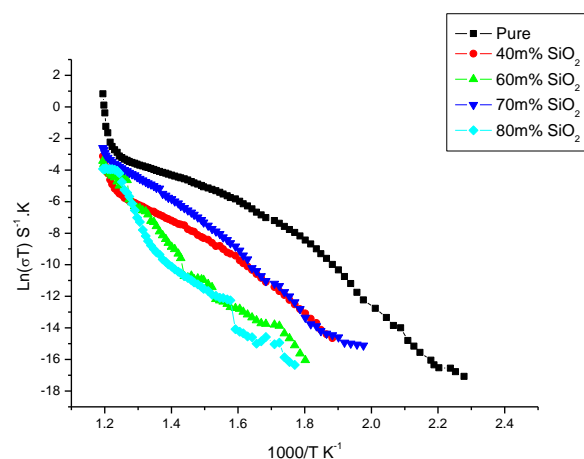Fig.3: Ln (σT) versus 1000/T for Ba(NO$_3$)$_2$ and dispersed with 20,25,30,35 mole % of SiO$_2$

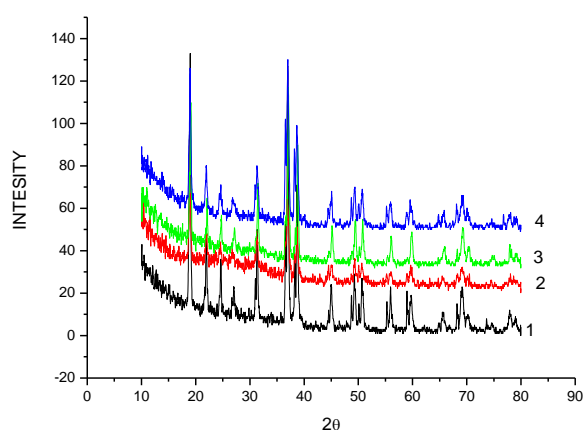Fig.4: Ln (σT) versus 1000/T for Ba(NO$_3$)$_2$ and dispersed with 40,60,70,80 mole % of SiO$_2$

Fig. 5: X-ray powder diffractograms of 1.$Ba(NO_3)_2$,

2. $Ba(NO_3)_2$ dispersed with 1 mole % of SiO_2

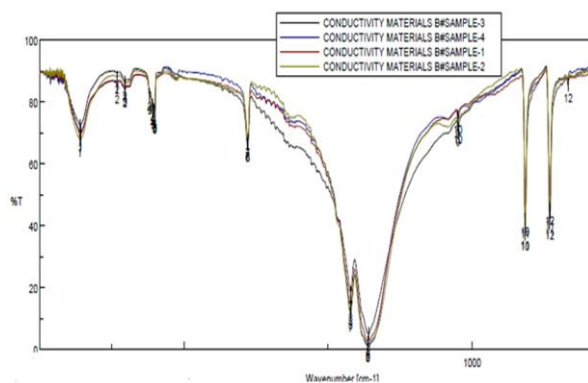3. $Ba(NO_3)_2$ dispersed with 0.2 mole % of SiO_2

4. $Ba(NO_3)_2$ dispersed with 0.5 mole % of SiO_2

Fig.6: FT-IR spectra of $Ba(NO_3)_2$ and $Ba(NO_3)_2$ dispersed with 1, 0.2, 0.5 mole % of SiO_2
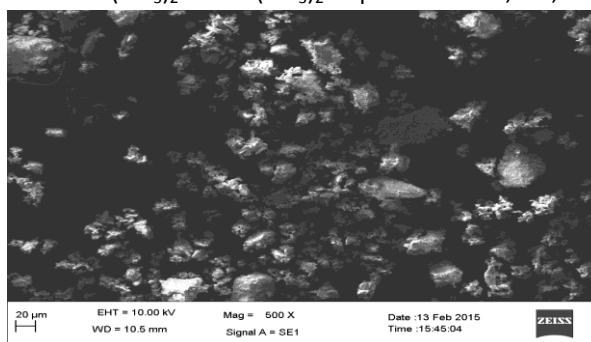
Fig.7: SEM of $Ba(NO_3)_2$

Fig.8: SEM of $Ba(NO_3)_2$ dispersed with 1mole % of SiO_2

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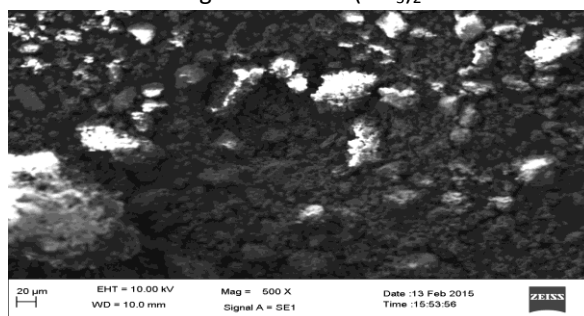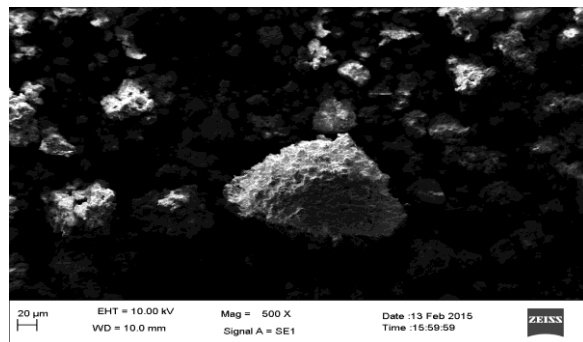
Fig.9: SEM of $Ba(NO_3)_2$ dispersed with 0.2 mole % of SiO_2
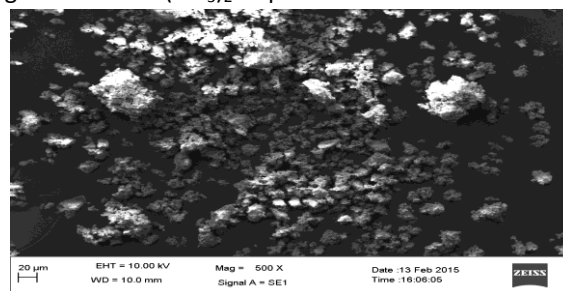
Fig.10: SEM of $Ba(NO_3)_2$ dispersed with 0.5 mole % of SiO_2

TABLE: Activation Energies

Sample	200^0C-300^0C	300^0C-400^0C	400^0C-520^0C
$Ba(NO_3)_2$	1.3354 eV	0.6948 e V	0.1792 eV
$Ba(NO_3)_2$ with 1m%SiO_2	-	0.8640 e V	1.8060 eV
$Ba(NO_3)_2$ with 0.2m%SiO_2	1.1199 e V	0.9852 e V	1.4391 eV
$Ba(NO_3)_2$ with0.5m%SiO_2	0.4170 eV	0.4723 e V	0.6572 eV

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