Ionic conductivity studies in $Ba(NO_3)_2$-KNO_3 mixed crystals

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ABSTRACT

D.C. Ionic conductivity, DSC, DTA and XRD measurements were made in pellets of pure $Ba(NO_3)_2$,KNO_3 and in different compositions of $Ba(NO_3)_2$-KNO_3 mixed crystals in the temperature range from room temperature to melting points of their respective systems. The results indicate that the conductivity in the extrinsic region of $Ba(NO_3)_2$ increased as the m/o of KNO_3 increased up to 91 m/o and then for 95 m/o conductivity falls. The activation energies are calculated for all the compositions and it is found minimum for 91 m/o. XRD, DSC and DTA studies reveal that new phases are formed in mixed systems.

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INTRODUCTION

Physical properties of $Ba(NO_3)_2$ and KNO_3 have been studied by various researchers previously. Studies on KNO_3 include ac conductivity near the phase transition points[1], enhancement of dc Ionic conductivity in KNO_3-Al_2O_3 composite solid electrolyte system[2], phase transition in KNO_3[3] etc. Similarly, Investigations in $Ba(NO_3)_2$ include elastic constants[4] , temperature variation of lattice parameter[5], dielectric constant[6], temperature dependence of piezo optic behavior[7], temperature variation of photo elasticity[8], photo elastic constants[9],micro hardness[10], photo elastic dispersion[11] and Ionic conductivity in single crystals of $Ba(NO_3)_2$[12]. Some of these composite solid electrolytes exhibit high ionic conductivity and good mechanical properties and are found to be promising materials for solid state batteries, fuel cells, electrodes etc[13-14]. Measurement of Ionic conductivity is a very sensitive and useful experimental tool in understanding the defect properties of crystals. As well they are useful in a number of possible technical devices. To understand these defect properties we have undertaken the study of ionic conductivity in pure and mixed pellets of alkali and alkaline earth nitrates.

Survey of literature indicates that there is no work on dc ionic conductivity of mixed crystals comprising of alkaline earth nitrates as against alkali nitrates in general and no such conductivity work on $Ba(NO_3)_2$ and KNO_3 mixed crystals in particular. Hence, in this paper we report our studies of dc ionic conductivity of pure and mixed crystals of barium nitrate and potassium nitrate.

MATERIALS AND METHODS

Experimental details:
The starting materials were from Qualigens fine chemicals (SQ) of 99.5% purity. $Ba(NO_3)_2$ and KNO_3 were obtained by crushing single crystals grown by slow evaporation method. The powders of the samples were mixed in the presence of acetone and were ground in an agate mortar for about an hour. The pellets of 8mm diameter and 3 mm thickness were prepared at a Pressure of 0.89GPa by using hydraulic press. These pellets were sintered at $^2/_3$ of

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their melting point for about 24 hrs. After cleaning the surfaces an electrode material (silver) was applied for good electrical contact.

Pellet was then mounted in a spring loaded sample holder and annealed at about 150°C for 4 hrs before the data was recorded. A constant rate of heating of 2° C/min was maintained through the experiment. The temperature was recorded by Cr-Al thermocouple. A small dc voltage of 1.5V was applied across the sample and the current was measured on a digital dc nano ammeter. Data was recorded on at least three to four samples each of pure and mixed pellets, running a minimum of three cycles on each sample. Similar experimental conditions were maintained for all the samples and the data showed a reasonably good reproducibility.

RESULTS AND DISCUSSION

DTA and DSC traces of pure $Ba(NO_3)_2$,KNO_3 and their mixed systems with 48m/o,63m/o, 79m/o,91m/o and 95m/o are shown in figure 1 and 2 respectively. From both the figures it can be seen that in $Ba(NO_3)_2$ there are two transitions at 186°C and 315°C and its melting point at 590°C which appear in the form of three endotherms[15] and in KNO_3 we have two endotherms corresponding to one transition[2] at 133°C and its melting point at 336°C. The melting point of mixed crystals is usually lower than either of the pure components and in this case it is found to be at about 290°. In 48m/o,63m/o,79m/o the transition temperature is found near 210°C and in 91m/o the transition temperatures found near 133°C and 210°C, in 95m/o it is found near 133°C. This shows that the DTA and DSC curves for 91m/o are very distinct compare to other mole percentages which showed two transition temperatures.

X-ray diffraction data, collected from powder samples using an automated X-ray powder diffractometer for pure $Ba(NO_3)_2$,48m/o,63m/o,79m/o,91m/o,95m/o and pure KNO_3, are shown in figure 3. Highly intencified peaks are observed in 91m/o and new peaks are indicated with miller indices. The existence of new peaks in the patterns of the mixed systems indicates the formation of solid solutions. Ionic radii of K^+(1.33A°) and Ba^{2+}(1.35A°) are closely matched[16]. This imply that the formation of aliovalent substitutional solid solution in the present mixed system. Presence of new peaks indicates that lattice constants typically vary linearly with solid solution composition (vegards law).
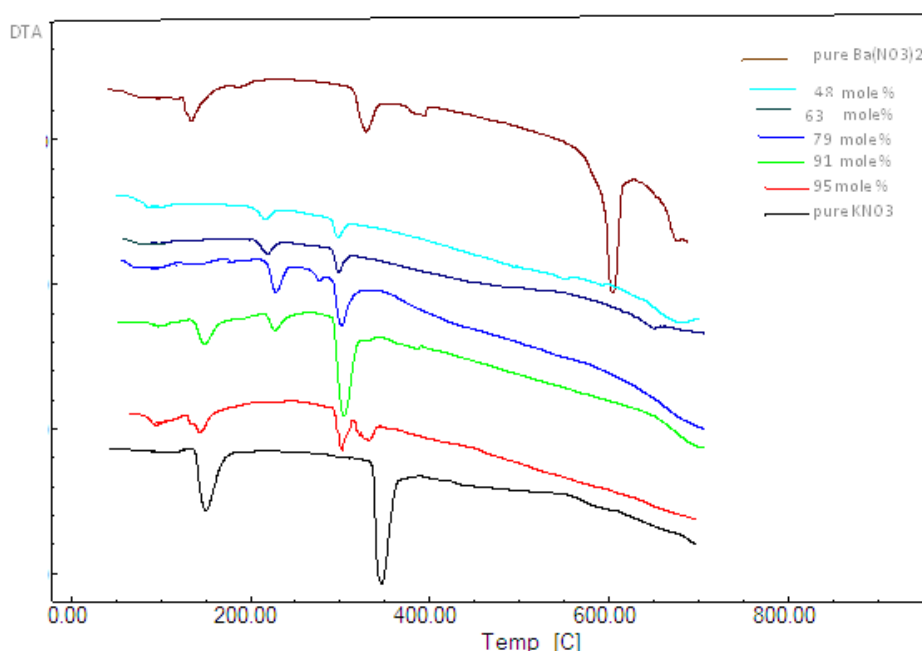

Fig 1 : DTA Curves

The temperature dependence of dc ionic conductivity with reciprocal temperature for pure and mixed systems with 48,63,79,91 and 95 mole percentages are shown in figure 4. In order to increase the clarity of the figure, the data for pure $Ba(NO_3)_2$ and KNO_3 are shown only up to 290°C(1.77 on X-axis) because the melting point of mixed systems is found nearly at 290°C. It is found that the melting point of composite systems is lower than the melting points of individual components.

All the mixed systems including pure KNO_3 and $Ba(NO_3)_2$ showed four regions[12]. However, fourth region in case of $Ba(NO_3)_2$ is not shown as its melting point is very high. Based on the observations cited above, starting from high

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temperature we are lead to believe that these regions correspond to extrinsic, extrinsic unassociated, extrinsic associated, extrinsic precipitated regions respectively. Conductivity is seen to increase linearly with temperature followed by a discontinuity . In case of pure $Ba(NO_3)_2$ the sharp increase in conductivity is observed near 295^oC(not shown) and in pure KNO_3 the sharp increase in conductivity is observed near 145^oC(2.39 on X-axis). In the compositions of 48m/o, 63 m/o and 79m/o the sharp increase in conductivity is found to be around 215^oC(2.05 on X-axis) where as in case of 91 m/o, 95 m/o the sharp increase in conductivity is observed at around 140^oC(2.42 on X-axis).
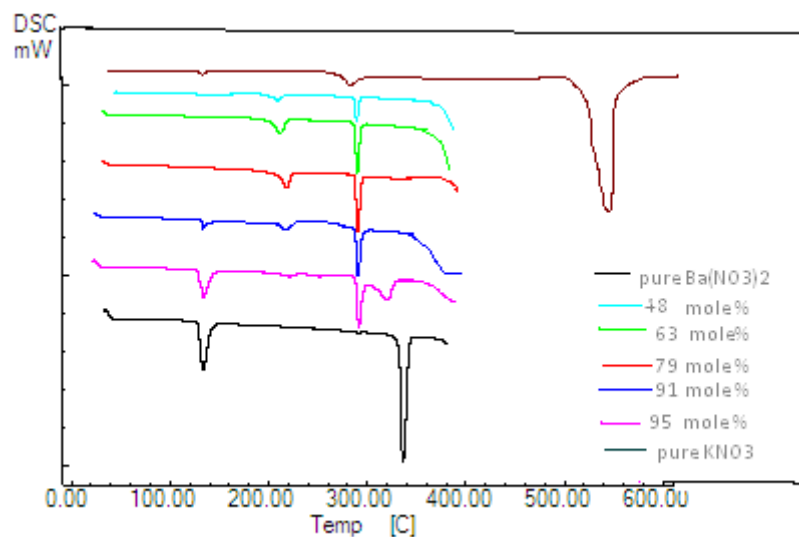

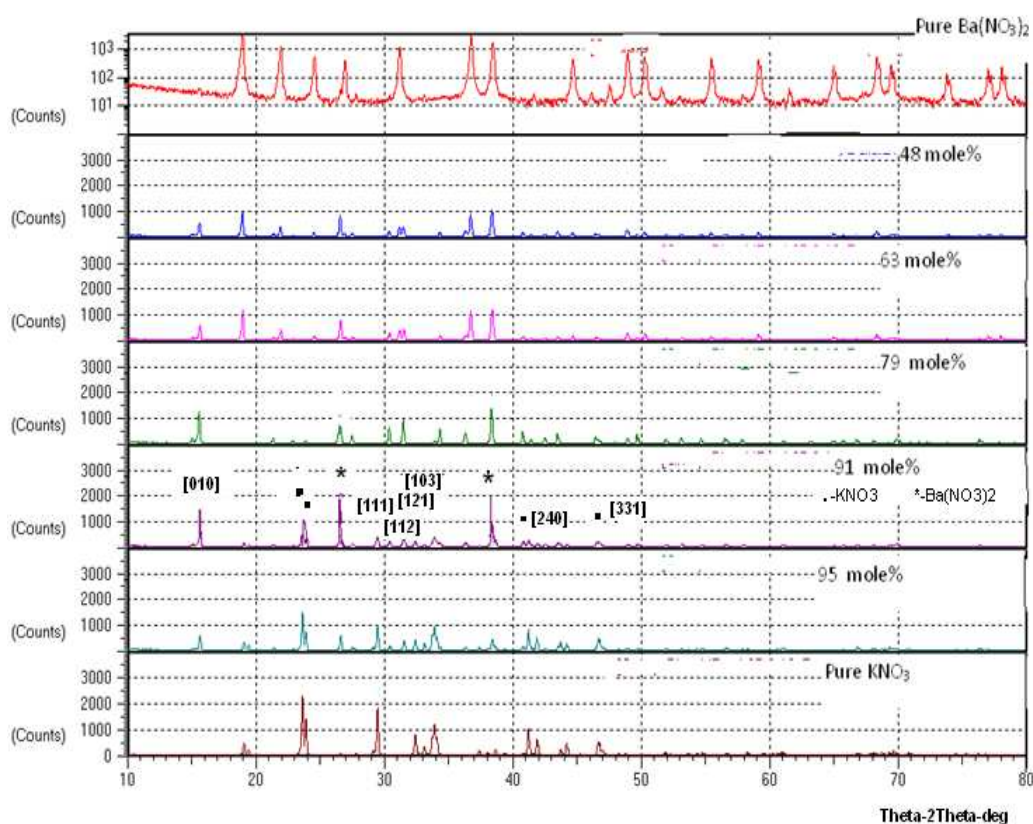**Fig 2: DSC Curves**

Fig 3: X-ray powder diffraction

The conductivity is found to increase only a little for mole percentages below 48 m/o. Increase became rapid from 48m/o with further increase in KNO_3 content. This type of enhancement in conductivity is also observed in AgBr-

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AgCl mixed crystals[17]. Enhancement in conductivity is observed to increase with m/o with a threshold at 91 mole percent where from enhancement starts falling with further increase in mole percent i.e. for 95 m/o. The maximum enhancement at 91 m/o is observed to be about 5 orders of magnitude with respect to pure $Ba(NO_3)_2$ in the extrinsic conducting region.

Variation of $\ln(\sigma T)$ with mole percent of KNO_3, at different temperatures, is shown in figure 5. Conductivity attained a maximum value at 91 m/o and from then it is found to be decreasing. It may be noticed from the plot that the conductivity values for pure $Ba(NO_3)_2$ at about 200^oC and 270^oC are -11.5 and -6.79 $\Omega^{-1}cm^{-1}$ k where as these are -6.26 and 3.81$\Omega^{-}cm^{-1}$ k for 91 m/o respectively[18]. This is in agreement with the results obtained from figure 4.

The enhancement in conductivity is explained as follows. In fluorite type materials like $Sr(NO_3)_2, Ba(NO_3)_2$ etc.,[12] anti frenkel defect is thought to be predominant, where as in case of KNO_3 Frenkel is predominant defect[19]. These defects are point defects whose presence in a crystal introduces distortions. If the imperfection is a vacancy, the bond that the missing ion would have formed with its neighbour will be absent, this gives rise to elastic strain and this factor tends to increase the energy of the crystal. Vacancies are always present at any temperature between 0^oK and melting point of the crystal. As the temperature is increased, the number of vacancies also increases. If the cation and anion are of different sizes we expect the energies to put either of them into interstitial positions to differ considerably. Consequently electrical conductivity in mixed crystal depends predominantly on Frenkel or anti-Frenkel defects. Anti-frenkel disorder consists of anion interstitials and their vacancies where as Frenkel disorder involves equal number of cation interstitials and their vacancies. It appeared reasonable to extend this mechanism in $Ba(NO_3)_2$ that the conductivity is mainly due to the transport of anion defects[20] and in case of KNO_3 it is the cation defects.
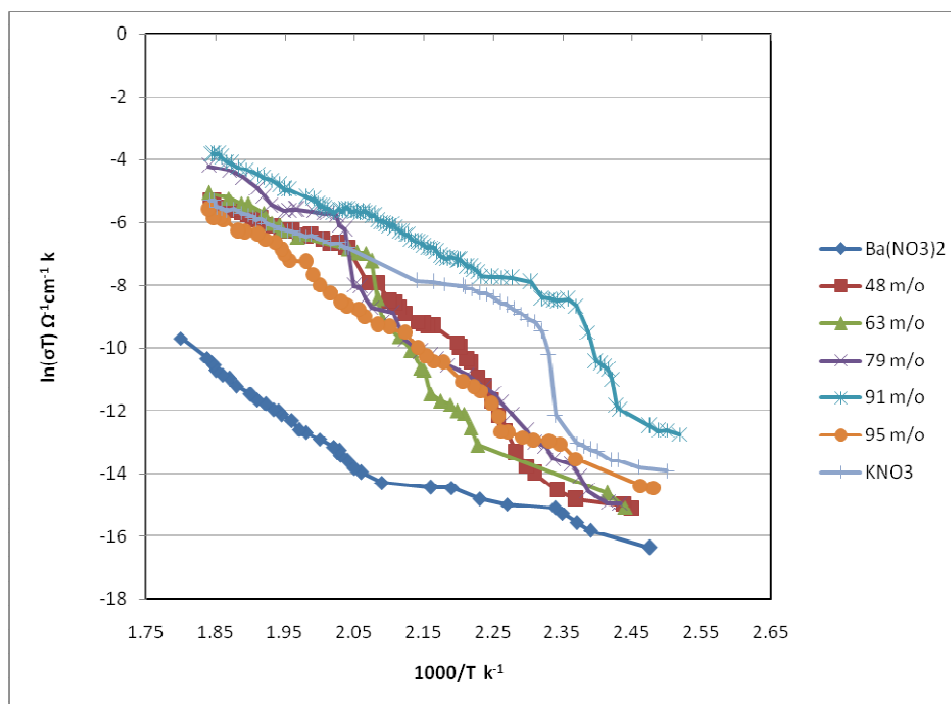

Fig 4. Ln(σT) versus 1000/T for Pure Ba(NO₃)₂,KNO₃ and   Ba(NO₃)₂:KNO₃ at different mole percentages.

The enhancement of conductivity at 91 m\o could be due to the creation of a cation vacancy or an interstitial anion. The second case is ruled out because for an interstitial anion more energy and more space is needed but activation energy is less (refer Table-I). Supporting the first case i.e at 91 m\o the number of K^+ ion vacancies formed could be maximum . Since the conductivity due to K^+ ion motion in KNO3 the maximum enhancement is observed. The activation energy is also found minimum at this m\o. The energy required for motion of K^+ ion could be minimum. According to wagner effect, the increase in number of cation vacancies greatly out-weighs any change of migration parameters due to lattice shrinkage, and large increases are observed in ion conductance. The greater electrostatic forces associated with the higher charges appear to cause a shrinkage which hinders ion migration. A marked increase in conductivity is found on introducing Ba ions in solid solution in crystalline KNO_3 [16]. As well presence of solid solution, if called a third phase will be associated with greater disorderliness leading to increase in entropy and subsequently increasing the concentration of more defects contributing to the

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enhancement of ionic conductivity. The conductivity studies on mixed crystals[20] also confirmed that the concentration of vacancies in mixed crystals exceeds that in pure components. This process can be considered responsible for the observed increase in the conductivity in 91 m\o. At 95m\o the content of $Ba(NO_3)_2$ is less and the number of vacancies formed will also be less. Therefore there is a decrease in conductivity and also decrease in activation energy. Activation energies calculated for pure and mixed systems also reveal the same.
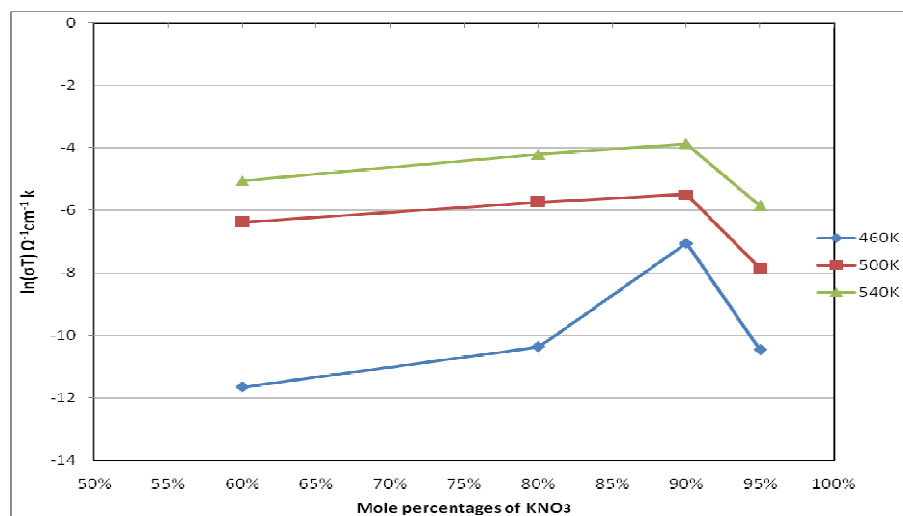

Fig 5. Ln(σT) versus different mole percentages of KNO₃.

Table-I : Activation energies for Ba(No₃)₂-KNO₃ composites.

Mole Percentages	Temperature range(°C)	Activation Energies(eV)
$Ba(NO_3)_2$	200-270	1.5
48%	200-270	1.08
63%	200-270	1.45
79%	200-270	1.48
91%	200-270	0.78
95%	200-270	1.25

Table-I shows the activation energies, obtained from DC Ionic conductivity, for $Ba(NO_3)_2$-KNO₃ system in the temperature range of 200°C-270°C for different mole percentages. These results are in good agreement with those reported in literature.The activation energy is found to be maximum for pure $Ba(NO_3)_2$ and as the mole percentage of KNO₃ in $Ba(NO_3)_2$ increases it is found to be decreasing. In case of 91m/o it is found to be minimum where the enhancement in conductivity is maximum. With further increase of mole percent activation energy is found to increase. The enhancement of conductivity in this region could be attributed to the increased concentration of cation defects. This could be seen in the form of higher values of intercepts on the ordinate revealing that pre exponential factors are more. The lowering of activation energy can be interpreted in terms of the decreased number of vacancies.

CONCLUSION

The mixed systems of $Ba(NO_3)_2$–KNO₃ have been investigated through DTA, DSC, XRD and dc ionic conductivity techniques. These results lead to the conclusion that the enhanced conductivity in $Ba(NO_3)_2$–KNO₃ composites is due to the increase in number of K^+ ion vacancies. The increase in number of cation vacancies greatly out- weighs any change of migration parameters due to lattice shrinkage, and large increases are observed in ion conductance. As well formation of solid solution in the mixed system $Ba(NO_3)_2$–KNO₃ enhances ionic conductivity. Again at higher m\o the decrement in conductivity could be due to the formation of less number of cation vacancies as the content of $Ba(NO_3)_2$ is less.

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