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Ionic transport study in $[NaNO_3]_{100-x}$:$[Sr(NO_3)_2]_x$ mixed solid electrolyte system

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Na^+ ion-conducting solid electrolyte of sodium nitrate ($NaNO_3$) and $Sr(NO_3)_2$ mixed crystals were grown by slow evaporation technique. XRD, FTIR, SEM characterizations and AC, DC conductivities were carried out on the pellets. Conductivity in these mixed solid electrolytes was noticed to increase with increase in m/o $Sr(NO_3)_2$ upto 14.68 followed by decrease. The conductivity in 14.68 m/o $Sr(NO_3)_2$ is more than one order of magnitude as compared to $NaNO_3$ in the extrinsic region. Ionic transport in these mixed systems is explained.

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1. Introduction

Rapid growth in technology demands high energy density power sources. The researchers in the field of Solid-State Ionics search for new and improved conductivity of solid materials at ambient temperatures with enhanced efficiencies. Such solid electrolytes having high ionic conductivity, low electronic conductivity and minimum activation energy for ion hoping at ambient temperatures are known as Super or Fast Ionic Conductors [1-2]. A significant attention is drawn to develop high energy storage sources and hence on new superionic materials because of their unique transport properties and using in many electrochemical devices like primary and secondary batteries, electro-chromic displays, solid state sensors, super capacitors thermoelectric devices, fuel cells, solar cells, memory devices and high energy storage batteries etc [1-3].

Solid electrolytes containing dispersed second phase insulating and chemically inert particles are called dispersed solid electrolytes. They are mostly two-phase mixtures, containing a moderately conducting ionic solid such as $NaNO_3$, AgI, CuI etc. as first phase host salt and second phase materials such as, Al_2O_3, SiO_2, ZrO_2, CeO_2, and Fe_2O_3 etc or another low ionic conducting solids such as, AgBr, AgCl and KCl etc[4-5].

The classification of solid electrolytes is also based on the ion mainly responsible for the conductivity. Different mobile ion conducting species have been observed in the various types of solid electrolytes. They are cationic conductors and anionic conductors. The cationic conductors are Na^+, Li^+, Cu^+, Ag^+, K^+, Cs^+, Rb^+, Ti^+, H^+ and the anionic conductors are O_2^{--}, F^-, NO_3^-. Recently, Na^+ ion-based Na-S, ZEBRA (Zero-Emission Battery Research Activities) and sodium-air (Na-O_2) batteries have been fabricated by using Sodium β"-alumina [6-8]. Other Na^+ ion based fast ion conductors are also under development. In the development of batteries, instead of lithium-ion conductors, sodium ion conducting solid electrolyte systems have been attracting the material scientists for the last few years, because of high energy density, light weight, high electrochemical potential, rich availability, eco- friendly and economy of sodium salts. The discovery of enhanced sodium ion transport in these systems has motivated us to undertake the present work in other fast Na^+ conductors. Hence, the present work is directed towards investigation of Na^+ ion conductor systems.

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In the present study, $NaNO_3$ was mixed with different mole percent (m/o) of $Sr(NO_3)_2$ to enhance the ionic conductivity. In order to obtain further enhancement of conductivity, a new host material (mixed system) namely, $[NaNO_3]_{85.32} - [Sr(NO_3)_2]_{14.68}$, was chosen among various compositions

2. Experimental

In this study, slow evaporation technique was used to grow the mixed single crystals of $NaNO_3$ and $Sr(NO_3)_2$ (99.9% purity) with different mole percent. These single crystals are ground in agate mortar for several hours and XRD and FTIR were recorded. This so obtained powder pressed as pellets at a pressure of about 4 tones/sq.m by using hydraulic press. Sintering was done for these pellets at 250°C for 24 hours. SEM, EDAX and AC impedance measurements (1 Hz to 10 MHz) were taken on these pellets.

3. Results and discussion

3.1. X-ray Diffraction (XRD):

Xrd patterns of $[NaNO_3]_{100-x}$:$[Sr(NO_3)_2]_x$ mixed systems have been plotted and shown in Fig.1. It can be seen from the figure that there is a decrease in intensity of peaks of mixed systems with respect to their pure nitrate systems. Also, the peak positions were observed to shift slightly towards higher angles indicating a slight change in the lattice parameter [4]. The structural parameters of cubic structure of $Sr(NO_3)_2$ such as Miller indices (h k l), interplanar spacing and lattice parameter obtained from diffraction angles and these are similar to the results of JCPDS file No.76-1375. Careful examination of X-ray diffraction peaks of mixed systems (Fig.1) confirms the presence of same peaks belongs to constituent nitrate systems only, which rules out the formation of new structure in the mixed systems [9]. It can also be observed from XRD pattern of 4.27 m/o $Sr(NO_3)_2$ that all the peaks are due to sodium nitrate only and there are no peaks of strontium nitrate. From patterns of higher m/o $Sr(NO_3)_2$ the peaks corresponding to both the nitrates are seen without any additional peak, which indicates that the coexistence of two phases, i.e. the rhombohedral phase of $NaNO_3$ and the cubic phase of $Sr(NO_3)_2$ [9-10].

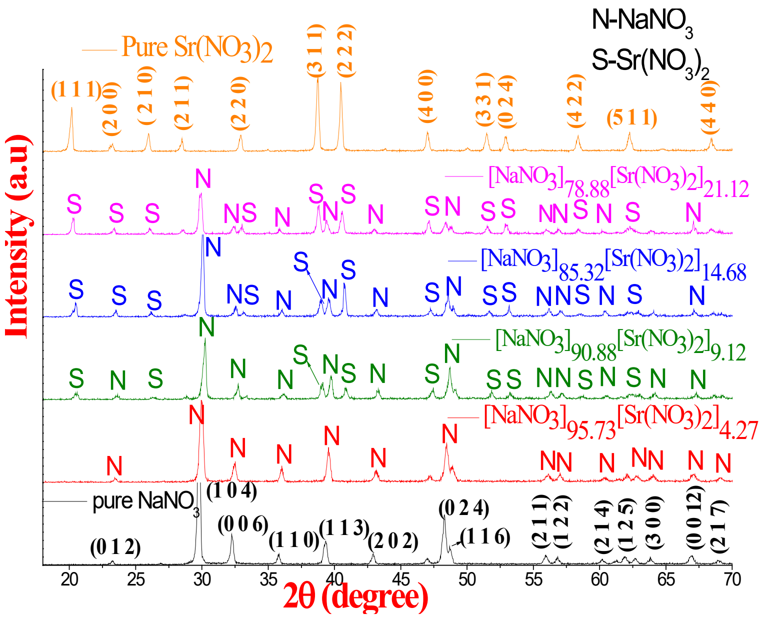


Fig. 1. XRD patterns of $[NaNO_3]_{100-x}$: $[Sr(NO_3)_2]_x$ mixed systems.

3.2. Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR spectra of $[NaNO_3]_{100-x}$:$[Sr(NO_3)_2]_x$ mixed systems are shown in Fig.2. The bands at 725, 835, 1385, 1626, 1792, 2093, 2426, 2764 cm^{-1} in pure $NaNO_3$ and 735, 814, 835, 1385, 1792, 2104, 2449, 2768 cm^{-1} in the case of $Sr(NO_3)_2$ are observed. These band frequency modes are assigned as υ_2 = 835 cm^{-1}, υ_3 = 1385 cm^{-1} and υ_4 = 725 cm^{-1} or 735 cm^{-1}. These bands are similar with respect to earlier reported bands on the same systems [11]. The vibration bands υ_2 and υ_3 are observed in both the patterns of pure nitrate systems, which are pertaining to vibration modes of nitrate ion. The band width of asymmetric stretching peak (υ_3) is broader in strontium nitrate than in sodium nitrate. It is seen from Fig.2 that the 4.27 m/o $Sr(NO_3)_2$ contains the same bands as in the pure $NaNO_3$ and no change in the band positions of 725, 835 and 1385 cm^{-1}. All the vibration modes, which are seen in pure $Sr(NO_3)_2$ and $NaNO_3$, appear from 9.12 m/o onwards, which indicates the co-existence of two phases in the same sample.

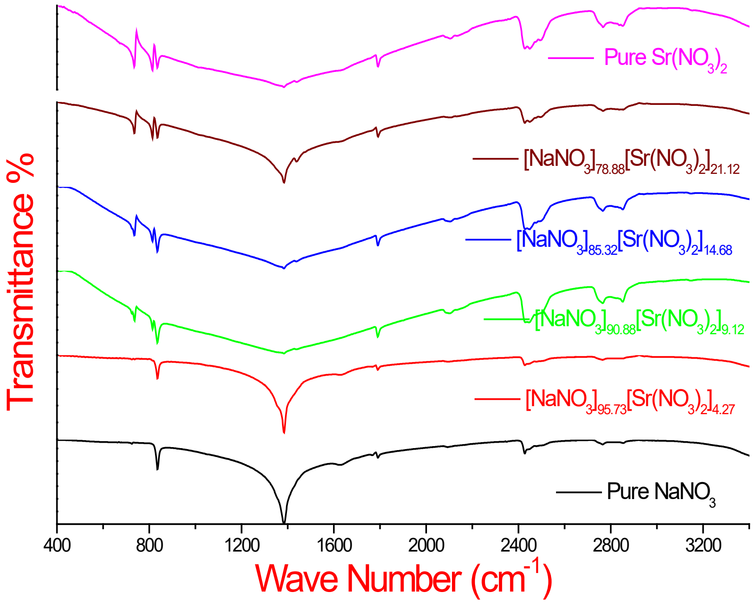


Fig. 2. FTIR spectra of $[NaNO_3]_{100-x}$: $[Sr(NO_3)_2]_x$ mixed systems.

3.3. Scanning Electron Microscope (SEM)

Scanning Electron Micrographs of $[NaNO_3]_{100-x}$: $[Sr(NO_3)_2]_x$ (sintered pellets) are shown in Fig.3. SEM images of pure and mixed systems show that the existence of not only grains of sodium nitrate but also the regions of small grains corresponding to strontium nitrate also reveals the coexistence of two phases in the mixed system[12].

It is clear from XRD, FTIR and SEM studies on pure and mixed systems that upto 4.27 m/o $Sr(NO_3)_2$ appears with only $NaNO_3$ structure contains with Sr^{+2} ions and for higher m/o it is a coexistence of two phases with $NaNO_3$ containing dissolved Sr^{+2} ions and $Sr(NO_3)_2$ containing dissolved Na^+ ions.

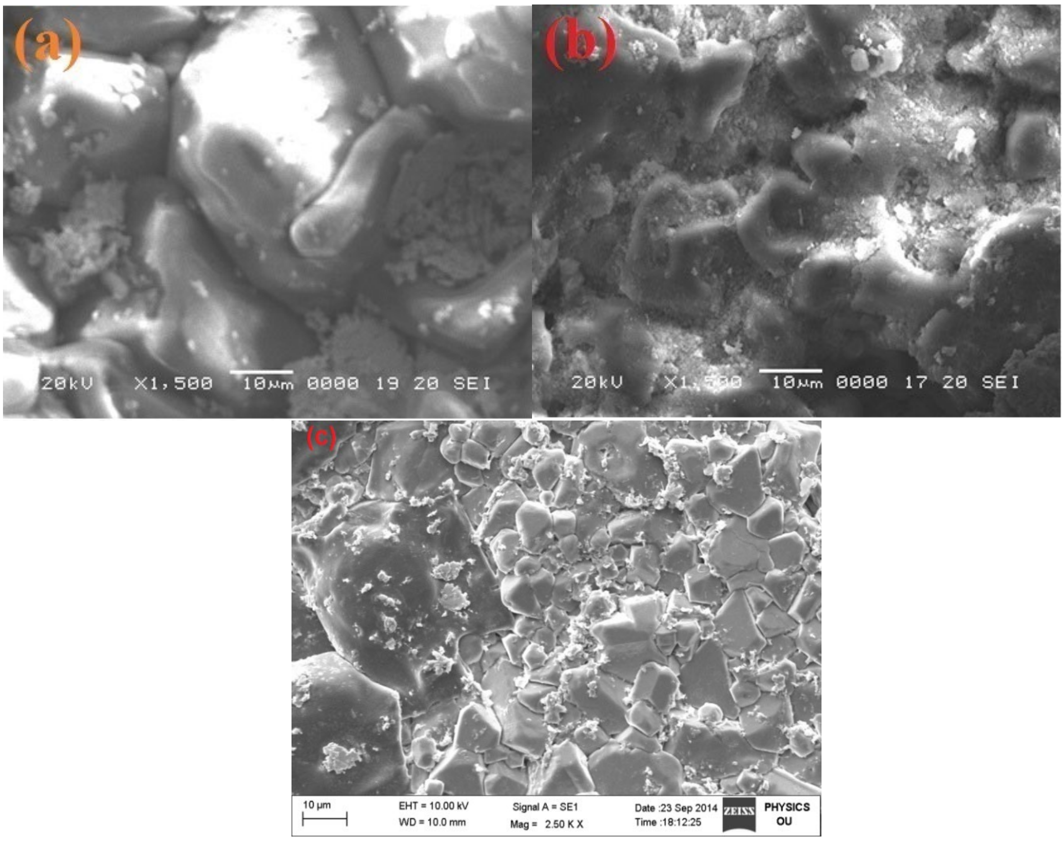
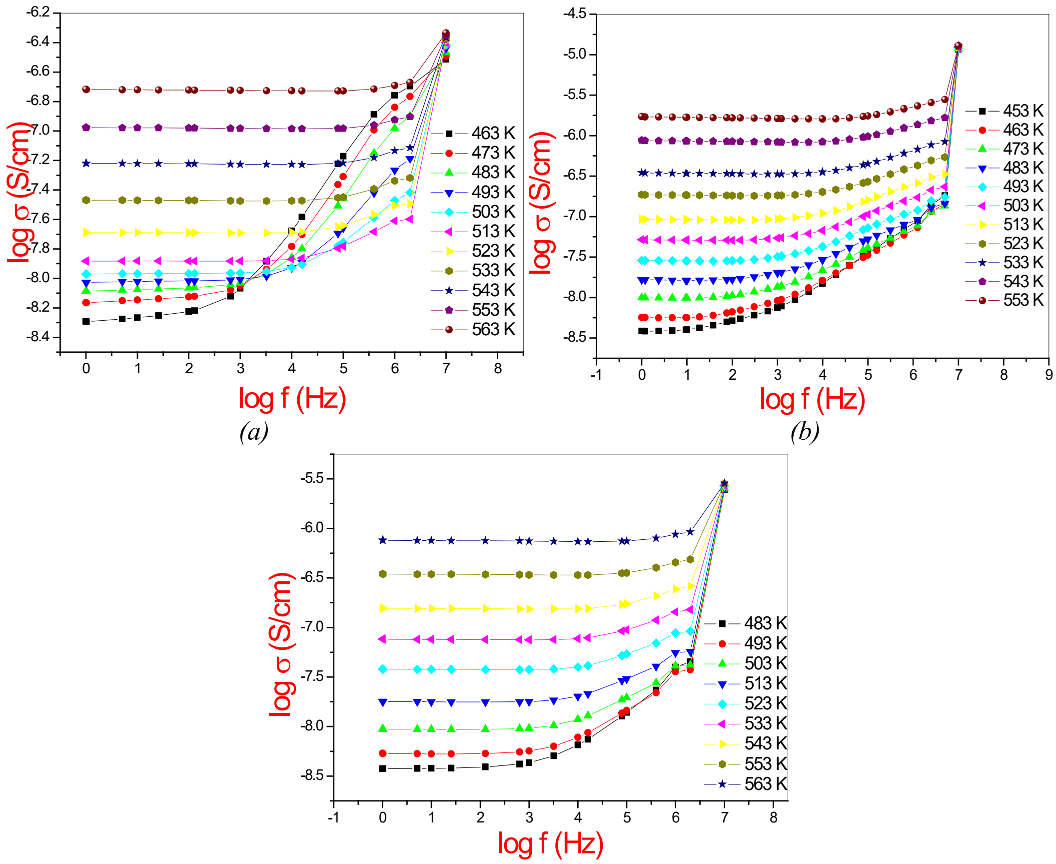


Fig. 3. SEM pictures of $[NaNO_3]_{100-x}$*:* $[Sr(NO_3)_2]_x$ *mixed systems (a) x = 0 (b) x = 100 and (c) x = 14.68.*

3.4. Conductivity study

Variation of ac conductivity with frequency of $[NaNO_3]_{(100-x)}$:$[Sr(NO_3)_2]_x$ mixed systems for x = 0, 14.68 and 21.12 at various temperatures are shown in Fig.4 (a, b & c). AC conductivity with frequency is constant at low frequencies and a dispersion of the conductivity is observed at higher frequencies. As the temperature rises, the constant region increases, and conductivity dependent region decreases. The hoping frequency (f_h) is the frequency at which the constant region switches over to dependent region at higher frequencies. This dispersion represents conductivity relaxation [13]. The conductivity relaxation could be understood from the forward-backward hoping of charges or ions at dispersion point. As the temperature increases, hoping frequency shifts towards the higher frequencies.



(a) *(b)*

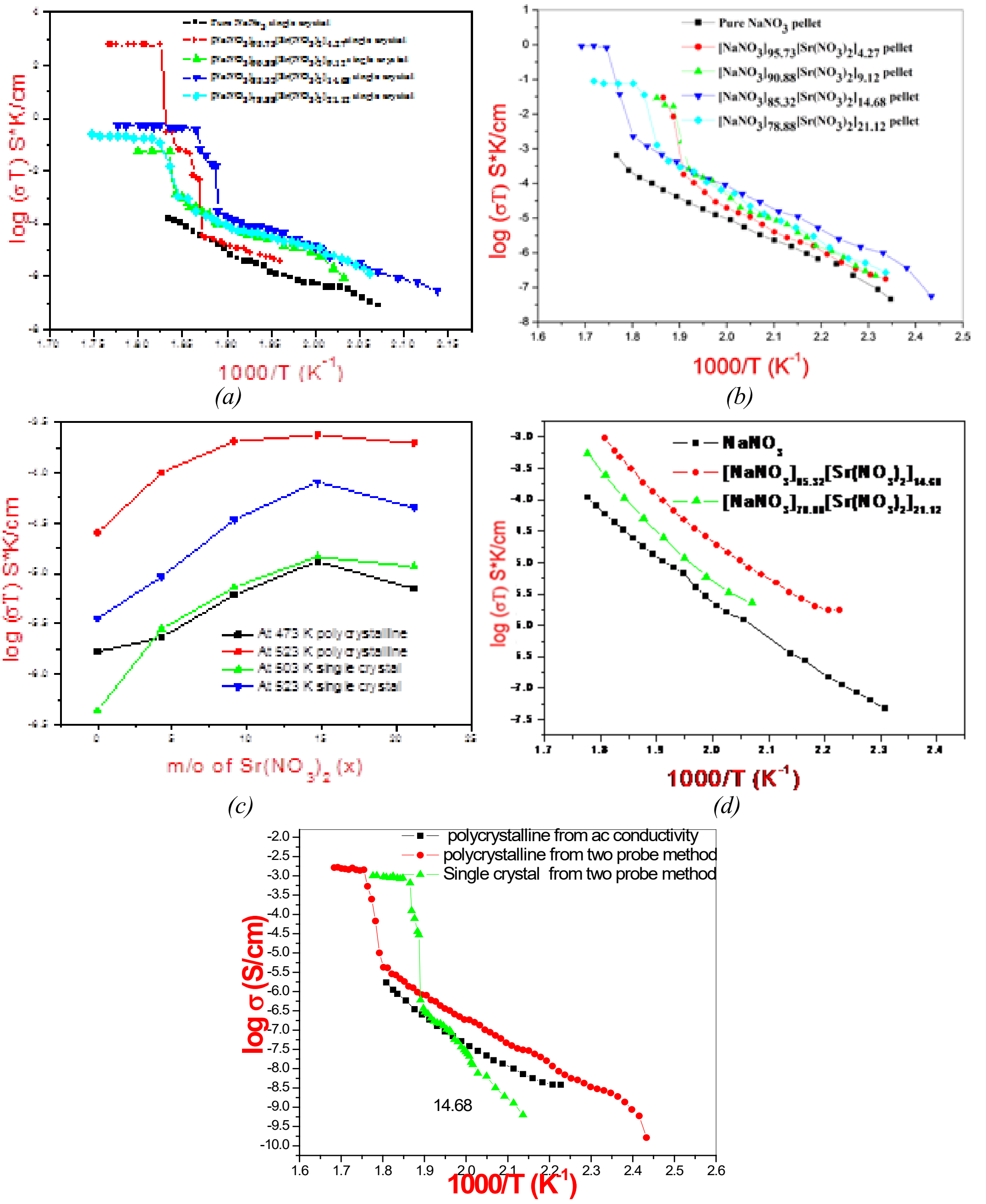
(c)

Fig. 4. (a) Variation of ac conductivity with frequency of pure $NaNO_3$ at different temperatures; (b) Variation of ac conductivity with frequency for 14.68 m/o $Sr(NO_3)_2$ at different temperatures; (c) Variation of ac conductivity with frequency for 21.12 m/o $Sr(NO_3)_2$ at different temperatures.

Variation of ac conductivity with frequency in each system is given by using jump relaxation model. According to this model, ions jump from one vacant site to another site in the constant region of conductivity at low frequencies. This jumping mechanism of ions among vacant sites is known as hopping, which contributes dc conductivity whereas dispersion region is at high frequencies is due to the forward–backward hopping together with relaxation of the ions. If a mobile ion hops from its original site to neighboring vacant site, the potential among the surrounding ions may be changed. The system then tends to minimize the potential either by correlated backward hop (back-hop) of the ion itself or by rearrangement of its neighboring ions. In the former case, the back-hop of the ion cancels the previous forward jump, which turns out to be an unsuccessful jump of an ion whereas in latter case the ion successfully moves to a new state. The successful forward jumps of the ions contribute to the long-range ion transport (dc conductivity) at the low frequencies whereas unsuccessful jumps i.e. both forward and backward hops increases the conductivity at high frequencies [14-15].

Fig.5(a) and Fig.5(b) show the variation of log(σT) versus 1000/T of $[NaNO_3]_{(100-x)}$:$[Sr(NO_3)_2]_x$ mixed systems for single crystals and pellets, from 400 K to 563 K. Dc conductivity is noticed to increase with rise in temperature in all m/o. Fig.5 (c) shows that the dc conductivity enhances with m/o and a peak at 14.68, followed by decrease.

Maximum enhancement at 14.68 m/o is ≈ ten times as compared to $NaNO_3$. It is observed, from Fig.5 (c) that the values of log(σT) in pellet form is comparatively larger than that in single crystals for all m/o . Activation energies (E_g) and pre- exponential factors(A) of pure and mixed systems of both pellets and single crystals are shown in Table 1.



(a) *(b)*

(c) *(d)*

(e)

Fig. 5. (a) Variation of log (σT) versus 1000/T of $[NaNO_3]_{(100-x)}:[Sr(NO_3)_2]_x$ mixed single crystals; (b) Variation of log (σT) versus 1000/T of $[NaNO_3]_{(100-x)}:[Sr(NO_3)_2]_x$ mixed systems (pellets) for x =0, 4.27, 9.12, 14.68 and 21.12; (c) Variation of log (σT) with m/o (x) Sr $(NO_3)_2$ for both single crystals and pellets; (d) Variation of dc conductivity (extracted from ac data) with reciprocal of temperature; (e) Log σ versus reciprocal temperature for 14.68 m/o $Sr(NO_3)_2$ [extracted from ac data and dc two probe.

The values of dc conductivity are obtained by extrapolating the ac conductivity data to zero frequency for all temperatures and is shown in Fig.5 (d). This is like data obtained from dc two probe method data. Activation energies are calculated using Arrhenius conductivity relation

These are shown in Table.1. For comparison, the variation of dc conductivity with temperature on pellets is taken in different methods such as dc two probe, extracted from ac conductivity data and hoping frequency data and is shown in 5(e). It is observed from fig.5 (e) that dc conductivity behavior is similar in all methods. Activation energies of mixed systems were also calculated from ac hoping frequency data and shown in [16] Table 1

The conductivity enhancement in the mixed systems increases initially with m/o $Sr(NO_3)_2$ giving rise to a peak at 14.68 and decreases further. It is confirmed from the XRD, DSC, FTIR and SEM studies that the present mixed system is in rhombohedral phase of $NaNO_3$ saturated with Sr^{+2} ions at 4.27 m/o $Sr(NO_3)_2$ (small m/o) and for larger m/o $Sr(NO_3)_2$, coexistence of rhombohedral phase of $NaNO_3$ saturated with Sr^{+2} ions and cubic phase of $Sr(NO_3)_2$ saturated with Na^+ ions. The enhancement in conductivity could be due mainly to two factors. The first one is by the substitution of aliovalent ion i.e. Sr^{+2} ions in $NaNO_3$ phase and Na^+ ions in $Sr(NO_3)_2$ phase. The substitution of Sr^{+2} ions in $NaNO_3$ phase might be predominant in the present mixed systems because the rich content is $NaNO_3$. The second one is due to interface boundaries between the two phases (multi phase effect). Now the question arises whether the enhanced conduction is due to aliovalent substitution or multi phase effect. The meager increase for enhanced conduction upto 4.27 m/o $Sr(NO_3)_2$ seems to be substitution effect and for further m/o $Sr(NO_3)_2$ combined multi-phase and substitution effect. Because, it is observed from Fig.5 (b) that the conductivity enhancement in 4.27 m/o $Sr(NO_3)_2$ is only around 5 times (0.5 orders) with respect to pure $NaNO_3$ i.e. a small enhancement, which could be due to the aliovalent substitution. In these systems a restricted solid solution forms in the crystal growth process i.e. the Sr^{+2} ions into $NaNO_3$ structure and Na^+ ions into cubic structure of $Sr(NO_3)_2$.

The significant enhancement of 1-2 orders at 14.68 m/o $Sr(NO_3)_2$ could be directly attributed to the co-existence of two phases. Co-existence of poly phases within one sample allows the creation of phase boundaries or anti-phase domain boundaries. At these phase boundaries degree of disorder is more, because of the mismatching of boundaries. Hence defect concentration enhances due to the easy movements of atoms along the boundaries [17-18]. The increase of number of mobile ions at the phase boundaries enhances the conductivity.

The fall in enhancement of conductivity with m/o $Sr(NO_3)_2$ could be due to the fall of phase boundaries in between the parent phases. This might be also due to fall in free volume for the hoping of sodium ion as the ionic radius of strontium (1.15 A^o) is more than that of sodium (0.95 A^o) [19].

Table 1. Activation Energies and pre–exponential factors of mixed system from the ac data and two probe dc method.

Mole percent (x)		**Pellet**				**Single crystal**	
	Activation Energy in eV			**Pre-exponential factor**		**Activation Energy in eV**	**Pre-exponential factor**
	Two probe	**ac conductivity**	**Hoping frequency**	**Two probe**	**ac conductivity**		
0	1.17	1.16	1.18	4.12	3.95	2.07	17.19
4.27	1.23	--	--	4.97	---	2.13	12.97
9.12	1.48	--	--	7.95	---	2.44	16.77
14.68	1.16	1.11	1.14	5.10	5.31	2.12	15.9
21.12	1.38	1.49	1.39	7.03	7.45	2.32	13.7

4. Conclusions

Sodium nitrate ($NaNO_3$) and strontium nitrate ($Sr(NO_3)_2$) mixed crystals were grown by slow evaporation technique. XRD, FTIR, SEM, dc and ac conductivities have been carried out on so obtained pellets. Analysis of XRD, FTIR and SEM studies of pure and mixed systems show that upto 4.27 m/o $Sr(NO_3)_2$, existing of only $NaNO_3$ structure with Sr^{+2} replacing Na^+ and for higher m/o, it is a coexistence of two phase mixture of $NaNO_3$ containing dissolved $Sr(NO_3)_2$ and $Sr(NO_3)_2$ containing dissolved $NaNO_3$. Conductivity, which is measured from dc two probe method and complex impedance method, is observed to increase with m/o and a peak at 14.68, followed by decrease. The conductivity enhancement in 4.27 m/o $Sr(NO_3)_2$ is only around 5 times (0.5 orders) with respect to pure $NaNO_3$ i.e. a small enhancement, which could be due to the aliovalent substitution. In these systems a restricted solid solution forms in the crystal growth process i.e. the Sr^{+2} ions into $NaNO_3$ structure and Na^+ ions into cubic structure of $Sr(NO_3)_2$.

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