

Growth, characterization and dc ionic conductivity studies on mixed super ionic conductor NaNO_3 : $\text{Sr}(\text{NO}_3)_2$

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ABSTRACT

Mixed systems $[\text{NaNO}_3]_{100-x}:[\text{Sr}(\text{NO}_3)_2]_x$ with $x = 0, 4.27, 9.12, 14.68$ and 21.12 in different mole percentages were grown by slow evaporation method. Pellets of these crystals were prepared by applying suitable pressures and sintered at 200°C for 20 hours. In the present study, the variation of DC ionic conductivity with temperature on these mixed matrix solid electrolytes has been measured in both single crystal and pellet forms and it is found to increase with temperature in all the systems. Enhancement of conductivity is noticed to increase with mole percent (m/o) in NaNO_3 - $\text{Sr}(\text{NO}_3)_2$ mixed systems. The maximum enhancement of conductivity is observed to be nearly one order of magnitude with respect to the host material in single crystals as well as pellets for $x = 14.68$. In all the systems the conductivity in the pellet form is found to be higher than that of single crystal form. Analysis of the X-ray diffraction peaks shows the co-existence of two phases i.e. NaNO_3 in rhombohedra phase and $\text{Sr}(\text{NO}_3)_2$ in fluorite type phase. The experimental data indicating higher conductivity at $x = 14.68$ is interpreted in terms of the increased defect concentration at phase boundaries which are the regions of misfit of disorder, the movements of atoms along the boundaries can be expected to occur easily and also the increase of defect concentration at the phase boundaries. Further, decrease in conductivity is explained in terms of the reduction of phase boundaries and decreasing of free volume available for Na^+ ion transport. Activation energies are obtained from the conductivity data in the extrinsic conduction region.

Keywords: Mixed crystal, Solid electrolyte, Superionic conductor, Phase boundaries, Ionic conductivity.

INTRODUCTION

Focus of research in the field of solid state ionics is gaining importance in recent past because of their potential applications in solid state ionic devices, such as rechargeable batteries, fuel cells, sensors, memory devices and high energy storage batteries [1, 2]. This field involves mainly the study of transport phenomena of ions in solids. The study of ionic conductivity plays an important role in understanding the lattice defects and energy for defects in the crystal structures [3]. In the beginning solid state ionics was highlighted in the crystalline solid electrolytes, subsequently this field expanded to other forms of solid, namely polycrystalline, glassy, mixed and dispersed solid electrolyte systems. In solid electrolytes, conduction due to the migration of ions is not appreciable at room temperature but is substantial at high temperatures. Such materials exhibiting high ionic conductivity, negligible electronic conductivity and low value of activation energy for ion migration at temperatures below their melting point, are called super ionic conductors [4]. The increasing demand for alternative power sources, high energy storage devices and energy conversion systems motivated the researchers to develop novel solid electrolytes by employing various methods of synthesis in order to improve the ionic conduction in these solid electrolytes [5]. However, earlier investigations show that the enhancement of conductivity is not much appreciable by the method of conventional doping [6].

A good amount of work has already been reported on Lithium and Sodium based solid electrolyte systems [7-9]. AC and DC conductivity studies on dispersed and polymer sodium electrolyte systems revealed appreciable enhancement of ionic conductivity [6, 10, 11]. A series of pure and mixed crystals have been studied by several researchers with the aim of identifying new materials [12-16]. Electrical, dielectrical and micro-hardness studies on mixed crystals of alkali and alkaline earth halides, such as KCl - NaCl, KBr - KI, KCl - KBr, KBr - NaI, AgBr - AgCl, and CaF₂ - SrF₂ have been reported extensively [17 - 24]. Survey of literature with a view to identify newer materials with high ionic conduction motivated the authors to look for nitrates of alkali and alkaline earth rather than that of halides.

A normal Na⁺ ionic conductor, NaNO₃ has been chosen and an attempt has been made to improve the conductivity by mixing with Sr(NO₃)₂, another solid ionic conductor, heterogeneously. Study of ionic transport in Sr(NO₃)₂ dispersed with Al₂O₃ showed enhancement in conductivity [25].

In the present study, [NaNO₃]_(100-x):[Sr(NO₃)₂]_x mixed matrices were prepared and characterized by XRD. DC ionic conductivity was recorded and activation energies along with pre-exponential factors were determined.

MATERIALS AND METHODS

The commercially available chemicals of NaNO₃ and Sr(NO₃)₂ (with 99.9% Purity), were taken in different mole ratios and grown them as single crystals by using slow evaporation method. The small transparent single crystals were selected and painted with silver paste for taking conductivity data. The crystal was mounted in the sample holder and current measurements were taken in a slow and constant rate of heating of about 1^oC / min. Throughout the experiment almost same rate was maintained. A constant voltage of 1.5V was applied from a dry battery. The current value was recorded using Agilent (Previously Hewlet Packard) nano ammeter. A chromel-alumel thermo couple, with its hot junction kept very close to the sample was used to measure its temperature. The sample was annealed at about 200 ^oC for 2 hours before the data was recorded. Pellets were obtained by grinding the single crystals and pressed them into pellets by applying a pressure of 4 tons/sq.m. using hydraulic press. These pellets were sintered at 200 ^oC for 20 hours and the conductivity measurements were taken as stated above.

The XRD data of pure and mixed systems [NaNO₃]_(100-x):[Sr(NO₃)₂]_x in the form of powdered samples were recorded by the "Regaku Miniflex" X-ray diffractometer. The FTIR spectra of pure and mixed systems were recorded using FTIR spectrometer in the region 400-3500cm⁻¹ by KBr technique to confirm the presence of different groups.

RESULTS AND DISCUSSION

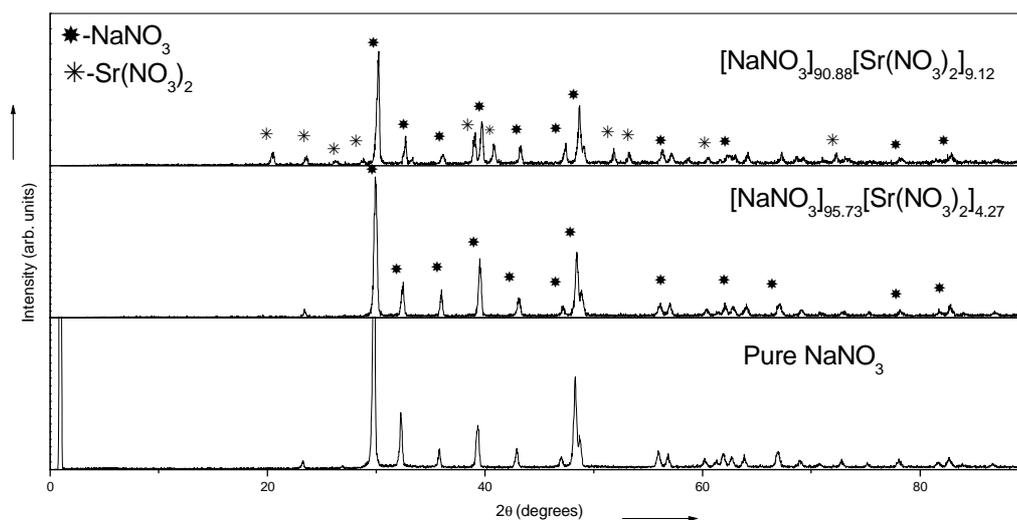


Fig1 (a)

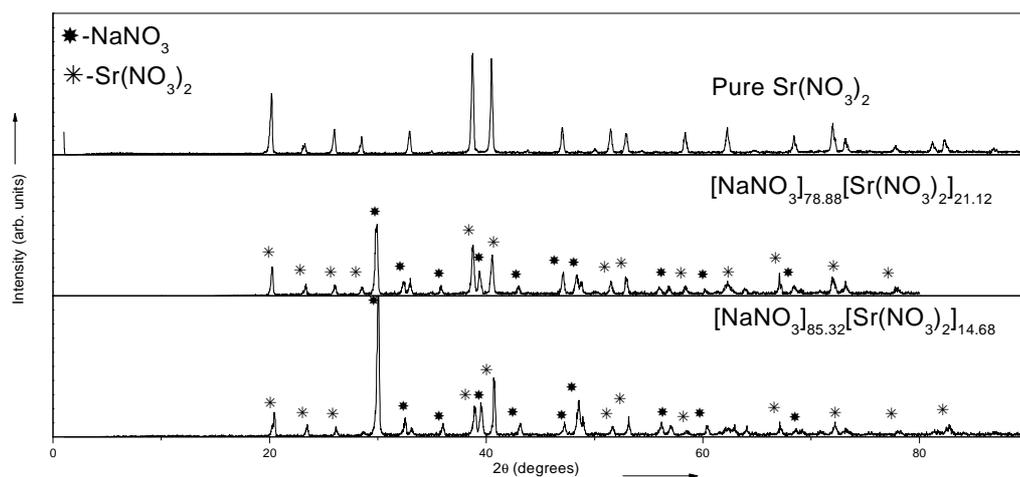


Fig1 (b)

Fig.1. X-ray powder diffraction patterns of $[\text{NaNO}_3]_{(100-x)}:[\text{Sr}(\text{NO}_3)_2]_x$, pure and mixed systems (a) pure NaNO_3 and $x = 4.27, 9.12$ (b) $x = 14.68, 21.12$ and pure $\text{Sr}(\text{NO}_3)_2$.

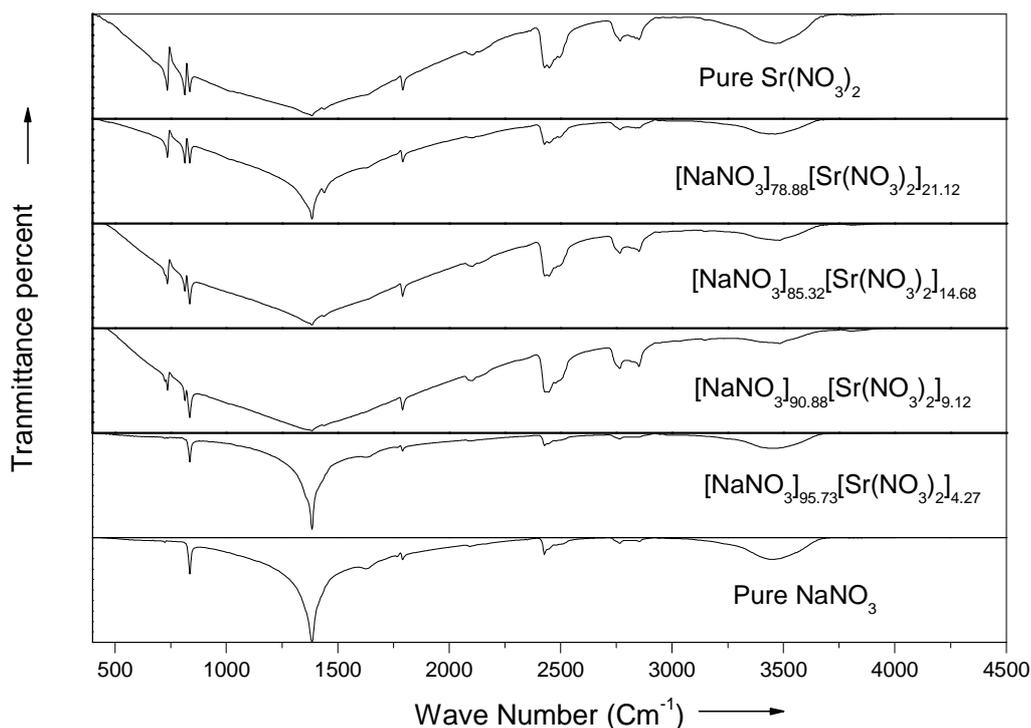


Fig.2. FTIR Spectra of Pure and mixed systems.

XRD patterns of the systems, as shown in Fig.1 (a) and Fig.1 (b), reveal that there are no new peaks but there exist peaks corresponding to each of the nitrates, indicating that there is no new structure formed. Peaks in the diffractograms show the existence of two phases [26-28]. It indicates that the compounds are polycrystalline in nature with mixed rhombohedral structure of NaNO_3 and fluorite type structure of $\text{Sr}(\text{NO}_3)_2$. Sodium nitrate belongs to the rhombohedral calcite structure with a space group $R3c$, with two molecules per unit cell and has an orientational disorder of nitrate ion at 275°C [29]. It is a Frenkel type disordered crystal, with Na^+ ion as the mobile charge carrier [30] and its ionic radius is 0.95 \AA . Strontium nitrate has a fluorite type structure and is an RX_2 type

compound, having cubic structure with a space group Pa3 and belongs to T_h^6 Class [31] and it is an anti-Frenkel disordered crystal, i.e. mobile carriers are anions [3] whose ionic radius is 1.90 \AA^0 .

In order to reconfirm that the new structures are not formed, Fourier Transform Infra Red (FTIR) spectra were recorded on pure and mixed systems which are shown in Fig.2. Sharp peaks were seen at 836 cm^{-1} and 1385 cm^{-1} in pure NaNO_3 and in the case of $\text{Sr}(\text{NO}_3)_2$ the strong and sharp peaks were observed at 734 cm^{-1} and 1385 cm^{-1} . These values are in good agreement with the earlier reported values on similar systems [32]. The presence of bands of both NaNO_3 and $\text{Sr}(\text{NO}_3)_2$ in the mixed systems show the existence of two phases, which was already confirmed by the XRD patterns.

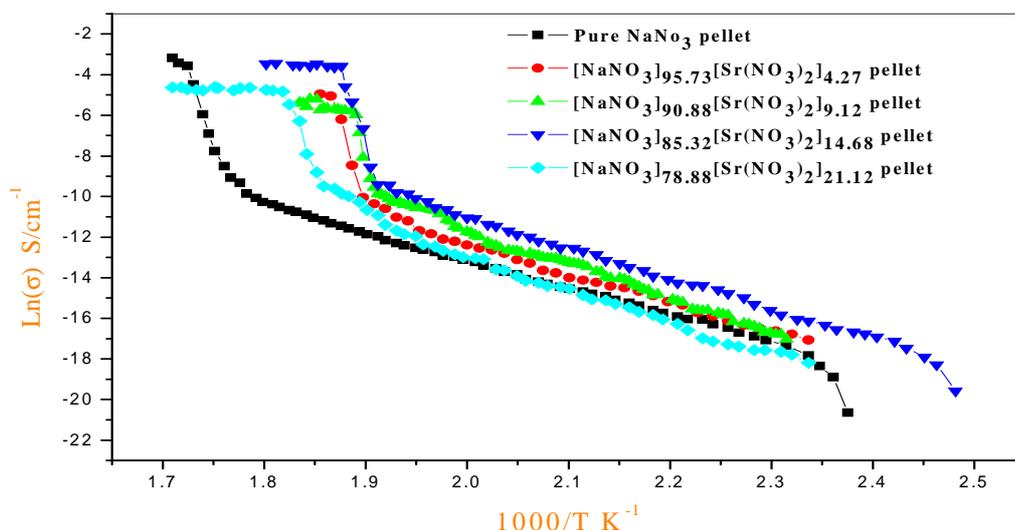


Fig.3. $\text{Ln}(\sigma)$ versus $1000/T$ for NaNO_3 and $\text{NaNO}_3\text{-Sr}(\text{NO}_3)_2$ mixed pellets

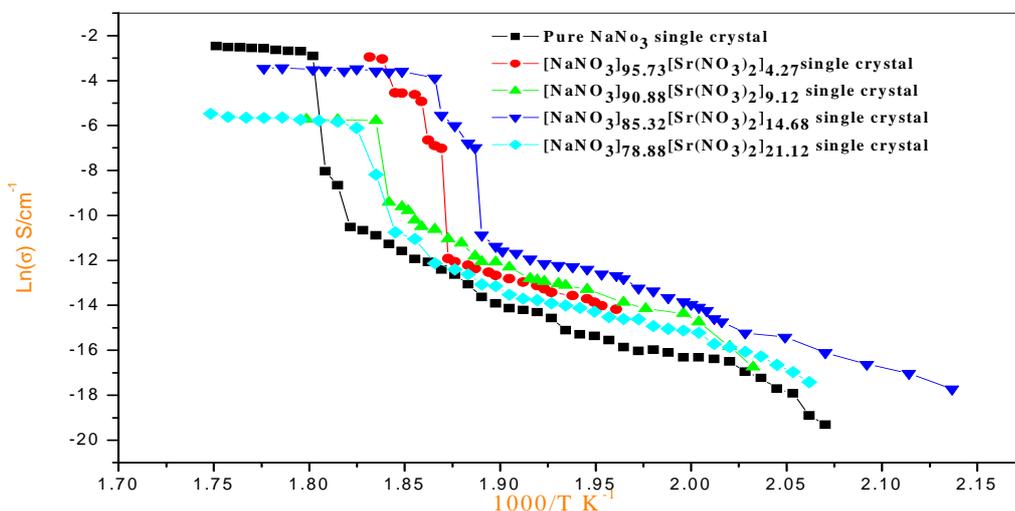


Fig.4. $\text{Ln}(\sigma)$ versus $1000/T$ for NaNO_3 and $\text{NaNO}_3\text{-Sr}(\text{NO}_3)_2$ mixed single crystals.

Fig.3 and Fig.4 show variation of $\text{Ln}(\sigma)$ versus $1000/T$ of $[\text{NaNO}_3]_{(100-x)}\text{:}[\text{Sr}(\text{NO}_3)_2]_x$ mixed systems with $x = 0, 4.27, 9.12, 14.68$ and 21.12 for pellets and single crystals respectively, from room temperature to 310°C . It is observed that the conductivity increases linearly with the increase in temperature for all the compositions. Conductivity of pure NaNO_3 can be seen to increase linearly up to its transition temperature, followed by a deviation from its linearity in both pellets and single crystals. Fig.5 shows variation of $\text{Ln}(\sigma)$ versus mole percent (x) of $[\text{NaNO}_3]_{(100-x)}\text{:}[\text{Sr}(\text{NO}_3)_2]_x$ for single crystals and pellets. The enhancement in conductivity is noticed to increase with mole percent with a threshold at $x = 14.68$, where enhancement recorded was maximum in either forms of the system and starts falling with further increase of m/o . The maximum enhancement at $x = 14.68$ is observed to be nearly one order of magnitude with respect to pure NaNO_3 in the extrinsic region. It may be noticed from Fig.3 that

value of $\text{Ln}(\sigma)$ for pure at about 225 °C is 1.81×10^{-6} S/cm whereas it is 1.54×10^{-5} S/cm for $[\text{NaNO}_3]_{85.32}[\text{Sr}(\text{NO}_3)_2]_{14.68}$. It can be seen that the conductivity in all compositions of $[\text{NaNO}_3]_{(100-x)}[\text{Sr}(\text{NO}_3)_2]_x$ system showed similar behavior as that of NaNO_3 and the entire mixed matrix follows Arrhenius behaviour. It is observed, from Fig.3 and Fig.4, that the conductivity in pellets is more than that in single crystals for all compositions of the system. Activation energies along with pre-exponential factors of pure and mixed systems are shown in Table 1.

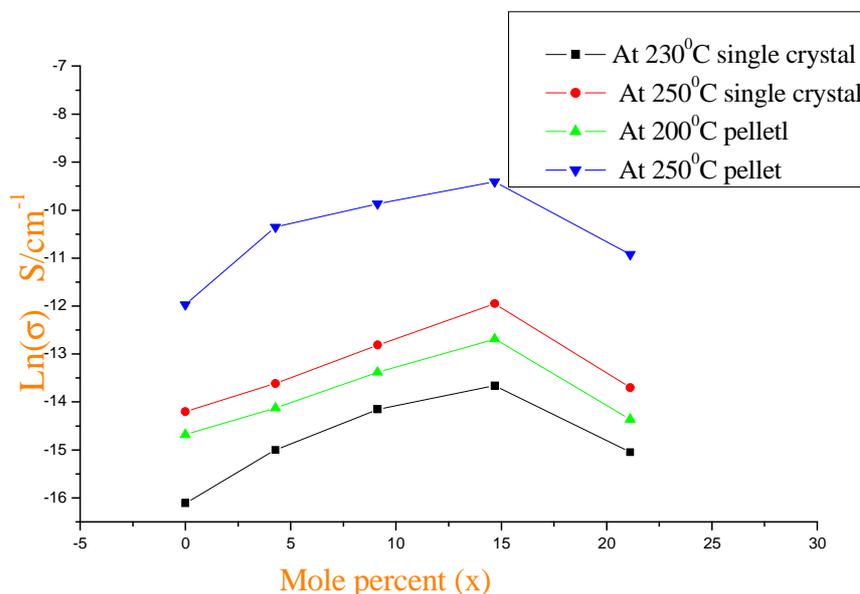


Fig.5. $\text{Ln}(\sigma)$ versus Mole percent (x) at different temperatures of single crystals and pellets

Table 1: Activation Energies and Pre-exponential factors for both pellets and single crystals.

Mole percent (x)	Pellet		Single crystal	
	Activation Energy in eV	Pre-exponential factor	Activation Energy in eV	Pre-exponential factor
0	1.16	13.88	2.07	46.15
4.27	1.21	15.78	2.13	34.47
9.12	1.48	22.91	2.77	49.33
14.68	1.29	19.10	2.35	40.45
21.12	1.44	20.59	2.03	31.70

The ionic conductivity in NaNO_3 follows Arrhenius behavior upto its transition temperature [11], where as ionic conductivity in $\text{Sr}(\text{NO}_3)_2$ was explained with different regions of conduction [33]. The enhancement of conductivity in mixed crystals is interpreted as follows: The significant increase in conductivity of the mixed system with increasing $\text{Sr}(\text{NO}_3)_2$ can be directly attributed to the co-existence of two phases [34]. Careful examination of X ray patterns as seen in Fig.1 (a) and Fig.1 (b) confirms the co-existence of two phases. Presence of two phases in the same sample facilitates the formation of phase boundaries, which are the regions of misfit of disorder and most probable sources of cationic defects. The movements of atoms along the boundaries can be expected to occur easily [35]. The increase of number of mobile ions at the phase boundaries enhances the defect concentration and hence conductivity. Furthermore, the transition temperature in NaNO_3 is lowered (Fig.3) by the introduction of Sr^{2+} ions into NaNO_3 structure i.e. the lowering of the enthalpies of formation of Na^+ ion by the resulting lattice strain [36]. Decreasing of the transition temperature of mixed matrix with increasing m/o of $\text{Sr}(\text{NO}_3)_2$ could be due to the increased concentration of lattice defects as a result of lattice strain produced by heterovalent ion substitution.

Further, decrease in conductivity with increasing m/o of $\text{Sr}(\text{NO}_3)_2$ could be mainly due to the reduction in phase boundaries between sodium and strontium phases. This could also be due the reduction in free volume available for Na^+ ion transport because the ionic radius of Sr^{2+} (1.22 \AA) is greater than that of Na^+ (0.95 \AA) [37].

CONCLUSION

The mixed system $[\text{NaNO}_3]_{100-x}[\text{Sr}(\text{NO}_3)_2]_x$, $x = 0, 4.27, 9.12, 14.68, 21.12$ in different mole percentages were grown by slow evaporation method. X-ray diffractograms were recorded for this mixed matrix. Analysis of the X-ray diffraction peaks shows the co-existence of two phases. The variation of DC ionic conductivity with temperature

on these mixed matrix solid electrolytes has been measured in both single crystal and pellet forms. Enhancement of conductivity is noticed to increase with m/o in mixed matrix of $\text{NaNO}_3\text{-Sr}(\text{NO}_3)_2$ systems. The maximum enhancement of conductivity is observed to be nearly one order of magnitude with respect to the host material in both single crystals and pellets for $x = 14.68$ m/o. Enhancement of conductivity is interpreted in terms of increased defect concentration at phase boundaries. Further, decrease in conductivity is explained in terms of reduction of phase boundaries and free volume available for Na^+ ion transport.

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