

Ionic Conductivity Studies of KNO_3 : KCl solid composite electrolyte system

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ABSTRACT

Composite solid electrolyte system $(1-x) \text{KNO}_3-x\text{KCl}$ (with $x=0.05,0.1,0.15,0.2,0.25,0.3$) is prepared by melt quench method. Characterization is done through XRD and FT-IR. D.C ionic conductivity is studied from room temperature to about 330°C . XRD peaks in the diffractograms show the existence of two phases. It indicates that the compounds are polycrystalline in nature with mixed orthorhombic structure of KNO_3 and Cubic structure of KCl . KNO_3 is a Frenkel type disordered crystal, with K^+ ion as the mobile charge carrier. Conductivity in the system increases with mole percent (m%) of the KCl , reaching a maximum enhancement of more than one order of magnitude with respect to that of pure KNO_3 at 15 m% and more than two orders with respect to KCl . Enhancement of conductivity in the mixed system is interpreted in terms of the formation of space charge layer between KNO_3 and KCl in which defect concentration increases. Activation energy is calculated from conductivity data. Transport number is also evaluated.

Keywords – Composite solid electrolyte, Conductivity, defect concentration, magnitude, phase boundary

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I. INTRODUCTION

Solid electrolytes are drawing the attention of researchers because of their applications in rechargeable batteries, memory devices, fuel cells, sensors, high energy storage batteries. The ionic conductivity in these materials rises by several orders of magnitude when the material is prepared as composite [1]. Several researchers reported that the work on multiphase mixed crystals with the aim in identifying newer materials. Electrical, dielectrical and micro-hardness studies on mixed crystals of alkali and alkaline earth halides, such as $\text{KBr}-\text{KCl}$, KI , $\text{NaCl}-\text{KCl}$, $\text{KCl}-\text{KBr}$, $\text{KBr}-\text{NaI}$, $\text{AgBr}-\text{AgCl}$, and $\text{CaF}_2-\text{SrF}_2$ have been reported extensively [2,3,4]. Shashi devi et al reported on electrical and dielectrical properties of mixed $\text{Ba}(\text{NO}_3)_2$ and KNO_3 . Vijay kumar et al reported on enhanced ionic transport in $\text{NaNO}_3-\text{Sr}(\text{NO}_3)_2$ mixed and nano dispersed multiphase solid electrolyte systems.

Potassium nitrate exhibits an interesting phase sequence. At room temperature it has orthorhombic structure (α -phase) with space group $Pm\bar{c}n$. In the heating cycle, it undergoes a transition at 128°C to trigonal structure (β -phase), which is supposed to be dynamically disordered with nearly

free rotations of the NO_3^- ions. On cooling it has another phase γ between 124 to 110°C , which is ferroelectric with the spontaneous polarization along the c axis in its [5,8].

γ -Phase K^+ ions occupy corners whereas NO_3^- ion lies near its body center. The plane of the NO_3 group is perpendicular to the c -axis and it does not exist exactly at the body center [6].

Potassium chloride has cubic structure (Space group $\text{Fm}\bar{3}m$) with anions (Cl^-) arranged in cubic closed packing with all the interstitial octahedral sites occupied by the cations (K^+).

Survey of literature with a view to identify newer materials with high ionic conduction motivated the authors to look for mixed matrices of alkali nitrates and halides. Cationic conductor, KNO_3 , has been chosen and an attempt has been made to improve the conductivity by mixing with anionic conductor KCl .

II. EXPERIMENTAL

The potassium nitrate, obtained from Aldrich and potassium chloride from Ranbaxy Laboratories Limited, both AR grade are used for the present study. The composite solid electrolyte is described by the general formula $(1-x)\text{KNO}_3-x\text{KCl}$ (with $x=0.05,0.1,0.15,0.2,0.25,0.3$). The samples

were mechanically mixed in an agate mortar for three hours. The powder mixtures of KNO_3 and KCl were heated in an electric furnace at 350°C which is above the melting point of KNO_3 and quenched at room temperature. The quenched samples were ground finely for five hours for further characterization. The finely ground samples were pressed into pellets of 12 mm diameter using a hydraulic press at a pressure of 3.5 tons. These pellets were sintered at $2/3^{\text{rd}}$ melting point of the host material for 24 hours. The pellet was painted with silver paste, mounted in sample holder and annealed at about 150°C for 2 hours before the data was recorded. The current measurements were taken in a slow and almost constant rate of heating throughout the experiment, by applying voltage of 1.5V from a dry battery, 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” [7,8].

The crystalline structure was analyzed with X-ray diffraction (XRD) by a Bruker optics with $\text{Cu-K}\alpha$ radiation at 40 kV and 30 mA in the 2θ range ($10^\circ - 80^\circ$). Fourier Transform Infra-Red spectroscopic (FT-IR) measurements were made using Buker IR spectrometer in the wave number range from $400\text{-}4000\text{cm}^{-1}$.

III. RESULTS AND DISCUSSION

A. X-ray diffraction:

XRD data is shown in fig.1. From the figure it is evident that the peaks of the mixed system can be seen to match with the individual XRD patterns of KNO_3 and KCl . These peaks of pure and mixed systems are sharp and having high intensity, confirming that all the samples are of crystalline nature. It can also be seen from the figure that there is a slight shift at peak position towards high angles indicating a slight change in the lattice parameter. This change in the lattice parameter could be due to the replacement of a bigger NO_3^- ion by smaller Cl^- ions [9] and there are no extra peaks observed in the composite systems.

Peaks in XRD patterns reveal the existence of two phases. It indicates that the compounds are polycrystalline in nature with mixed orthorhombic structure of KNO_3 and cubic structure of KCl . It can also be seen from the figure that the peaks referring to 15 mole percent of KCl are found to be of slightly increased in intensity with respect to the other mole percentages.

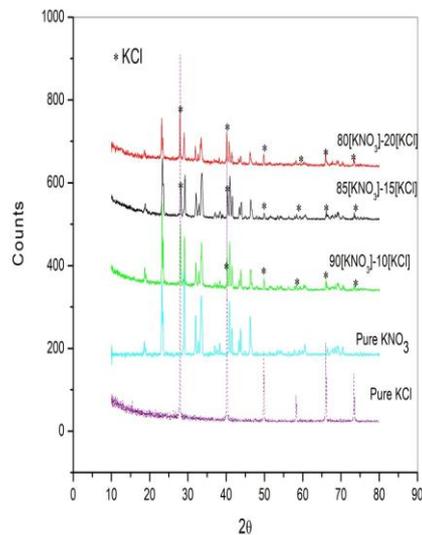


Fig.1. X-ray diffraction patterns of pure and mixed systems, (*) indicates KCl peaks.

B. FT-IR Study:

FT-IR spectra of the mixed system are shown in fig.2.

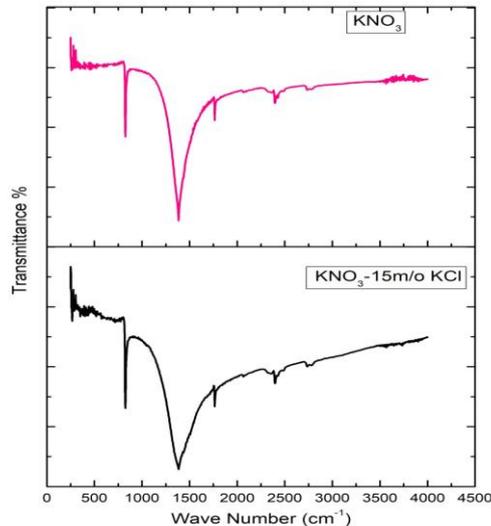


Fig.2. FT-IR Spectra of mixed systems.

The sharp peak observed at 835cm^{-1} is attributed to the vibration of nitrogen in and out of NO_3 plane and the strongest absorption at 1385cm^{-1} is due to asymmetric N-O stretch [10]. There is no evidence of forming a new peak or a shift in the position of peak in mixed systems, indicating that there is no formation of new compound in this process.

C. D.C. Conductivity:

The D.C conductivity was evaluated using the relation $\sigma_{dc} = t / (R \times A)$, where R is the resistance, t is thickness of the sample and A is the area of the sample. It is observed from fig.3 that the conductivity increases linearly with the increase in temperature for all the compositions. Conductivity of KNO_3 is higher than conductivity of KCl. In the mixed system, enhanced conductivity is observed to increase with mole percent of KCl, reaching to a maximum of one order magnitude at a threshold mole percent 15, and is observed to fall with further increase in m/o of KCl .Fig.3 also reveals that the conductivity in all compositions of pure and mixed matrix follows Arrhenius relation.

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E}{k_B T}\right)$$

Where k_B is the Boltzman’s constant, T is the absolute temperature and σ_0 is a Pre-exponential factor[8].

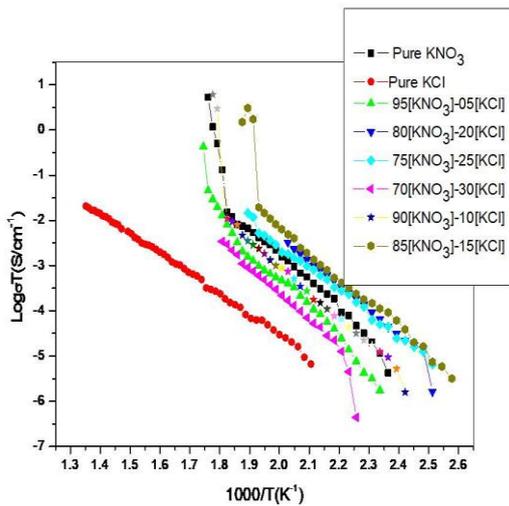


Fig.3. Log (σT) versus 1000/T for KNO_3 ,KCl and mixed system.

Variation of conductivity with mole percent is shown in fig.4 and the activation energies (E_g) are evaluated from the plots of fig.3 and are shown in table.1. Increase of conductivity in the present mixed system with m/o KCl could be due to the enhanced defect concentration at the phase boundaries between the two phases.

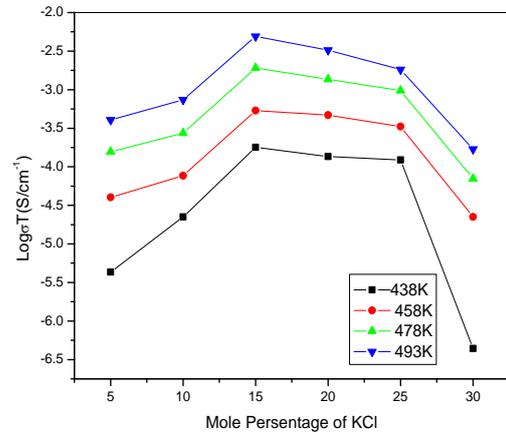


Fig.4. Log(σT) versus mole percent (x) at different temperatures of mixed system

The co-existence of these two phases has been confirmed by XRD [11].

Table 1: Activation energy of all compositions

Compositions	Activationenergy (eV)
Pure KNO_3	1.28
Pure KCl	0.89
95(KNO_3)-5(KCl)	1.33
90(KNO_3)-10(KCl)	1.29
85(KNO_3)-15(KCl)	1.08
80(KNO_3)-20(KCl)	1.14
75(KNO_3)-25(KCl)	1.12
70(KNO_3)-30(KCl)	1.38

Enhancement of conductivity in the mixed system could be due to the creation of either a cation vacancy or an interstitial anion at the phase boundaries. For the creation of an interstitial anion more energy and more space is needed but activation energy in the present system was found to decrease with increase in m/o up to threshold value. Hence, the formation of cation vacancy is more probable than the other, which results in the enhancement of ionic conductivity [12-16].

Further decrease in conductivity with increase in m/o of KCl could be mainly due to the reduction in phase boundaries between two phases. This could also be due to the reduction in free volume available for K^+ ion transport [17].

D. Transport studies:

The transport number offers evidence of ionic and electronic participation in overall conductivity. The overall ion transport number (t_i) and the electronic transport number (t_e) were determined using Wagner’s DC polarization

technique by sandwiching the sample between graphite and silver electrodes.

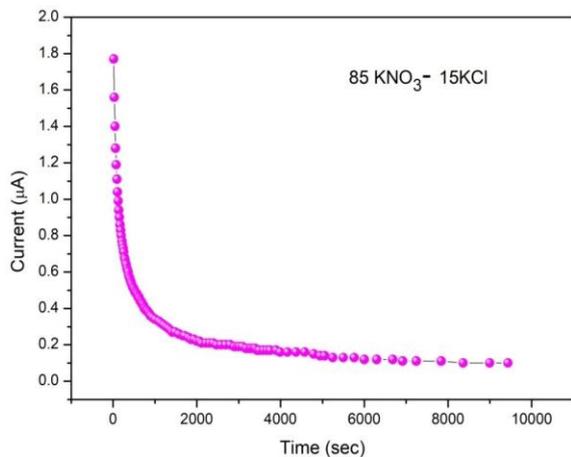


Fig.5. Plot of current versus time for 85KNO₃-15KCl sample

The polarization current was observed as a function of time by applying fixed DC voltage through the sample. t_i and t_e have been calculated from the plot using the following relation

$$t_i = \frac{I_i - I_f}{I_i}$$

$$t_e = 1 - t_i$$

Where I_i is initial current, I_f is final stabilized current. Figure 5 shows the plot of current versus time for 85KNO₃-15m/o KCl sample. The total ionic transport number was found to be 0.99. This value suggests that the charge transport in 85KNO₃-15m/o KCl composite electrolyte system is predominantly due to ions [18].

IV. CONCLUSION:-

Composite solid electrolyte system (1-x)KNO₃-xKCl with various compositions were prepared by melt quench method. Characterization was done through XRD and FT-IR. XRD confirms that there is a slight shift at peak position towards higher angles indicating a slight change in the lattice parameter. This could be due to the change in lattice parameter and provides the facility for the replacement of a bigger NO₃⁻ ion by smaller Cl⁻ ions. FT-IR also confirms the same, as there is no new peak or no shift in the peak positions in all mixed systems. D.C ionic conductivity was measured from room temperature to about 330°C. D.C. Conductivity enhancement was observed to increase with mole percent of KCl, reaching to a maximum of one order of magnitude with respect to the pure KNO₃ at a threshold mole percent 15, and is observed to fall subsequently. In this system, the

creation of K⁺ ion vacancies is thought to be the main cause for the enhancement of conductivity. The total ionic transport number value was found to be 0.99.

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