COLE-COLE ANALYSIS AND ELECTRICAL CONDUCTION OF NANO $(1-x)\text{Ba}(\text{NO}_3)_2-x\text{KNO}_3$

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ABSTRACT

Complex impedance studies on pure and mixed crystals reveal two partially overlapping depressed semicircles in a complex impedance analysis. The impedance behavior of these samples is interpreted as between the two metal electrodes and can be claimed alike to a combination pertaining to pure R and C. In the variation of DC and AC ionic conductivity (from complex impedance analysis) with reciprocal temperature for pure $\text{Ba}(\text{NO}_3)_2$, KNO_3 and different nano m/o viz. for $_{0.25}\text{Ba}(\text{NO}_3)_2-_{0.75}\text{KNO}_3$, $_{0.19}\text{Ba}(\text{NO}_3)_2-_{0.81}\text{KNO}_3$, $_{0.05}\text{Ba}(\text{NO}_3)_2-_{0.95}\text{KNO}_3$ it is found that the improvement of conductivity resulted in escalation along the mole fraction. That is, the improvement has been extreme in the case of nano 81m/o of KNO_3 in 19m/o of $\text{Ba}(\text{NO}_3)_2$ and has shown to reduce for nano $_{0.05}\text{Ba}(\text{NO}_3)_2-_{0.95}\text{KNO}_3$ (which supports the DC conductivity by two probe method).

Keywords: Composite Solid Electrolytes, Complex Impedance Spectroscopy, Cole-Cole Plots, Grain Boundary
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INTRODUCTION

Physical properties of $\text{Ba}(\text{NO}_3)_2$, KNO_3 is carried out by most of the research scholars earlier. Studies on PbNO_3 comprise AC conductivity adjacent to phase transition points by Y.Govind reddy et al,¹ improvement in dc ionic conductivity of $\text{KNO}_3\text{-Al}_2\text{O}_3$ merged solid electrolyte system by M.V.Madavarao et al,² Structural, electrical conductivity and dielectric behavior of $\text{Na}_2\text{SO}_4\text{-LDT}$ composite solid electrolyte by Mohd Z. Iqbal, et al³ etc. Similarly, Dielectric relaxation of ZnO nanostructure synthesized by Tripathi R et al⁴, temperature variation of lattice parameter by Bichile G K et al⁵, dielectric constant by Sirdeshmukh D B J et al,⁶ temperature dependence of piezo optic behavior by Krishna Rao K V et al,⁷ temperature variation of photoelasticity by Krishna Murthy V G et al,⁸ photoelastic constants by Bhimsen Sachar Seshagiri Rao T et al,⁹ micro hardness by Sirdeshmukh L et al,¹⁰ photo elastic dispersion by Bansigir K G et al¹¹ and ionic conductivity in single crystals of $\text{Ba}(\text{NO}_3)_2$ by K SaiBabu et al.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 To comprehend the defect characteristics, an attempt has been made to study ionic conductivity in pellets of alkaline and pellets of alkali earth nitrates.

EXPERIMENTAL

The impedance measurements of stated compositions were done with the assistance of Hioki Impedance analyzer (model 3532), ensuring a range from 5 Hz to an extent of 10MHz frequency. The sample prepared as a pellet is mounted on the specifically intended sample holder and is kept in the furnace. After connecting, the test leads to the sample holder's connecting points the spot frequency was set for a fixed temperature and values of Z, θ along with capacitance, loss and admittance have been noted down. Impedance plots between Z_i and Z_R have been drawn using the Originpro 7.0 software.

RESULTS AND DISCUSSION

The impedance quantities of stated compositions were done with the assistance of the Hioki Impedance analyzer (model 3532), ensuring a range from 50 Hz to 1 MHz frequency Z (ϕ) are rightly obtained in

correspondence with temperature and frequency. Figure-1,2 and 3 show the Cole-Cole plots corresponding to $\text{Ba}(\text{NO}_3)_2$, KNO_3 mixed systems along with their nanomole percentages viz. $0.25\text{Ba}(\text{NO}_3)_2-0.75\text{KNO}_3$, $0.19\text{Ba}(\text{NO}_3)_2-0.81\text{KNO}_3$, $0.05\text{Ba}(\text{NO}_3)_2-0.95\text{KNO}_3$ at 80°C , 120°C , 160°C , 200°C , 240°C temperatures respectively (Although we have done for other nano mole percentages i.e. for $0.62\text{Ba}(\text{NO}_3)_2-0.38\text{KNO}_3$, $0.37\text{Ba}(\text{NO}_3)_2-0.63\text{KNO}_3$ they have not shown for want of space).

The performance of the Cole-Cole plot is a representation of conducting nature for the considered sample. The impedance facts were scrutinized using circuit software which is equivalent to boukamp and the electrical behavior of the samples was carried out. The $\text{Re}(Z')$ and $\text{Im}(Z'')$ parts of impedance were found with the help of the data available of ϕ , the phase angle and C , the impedance. The complex impedance plots were drawn by taking Z' -real part on X-axis and Z'' -imaginary part on Y-axis.

Fig.-1: Cole-Cole $0.25\text{Ba}(\text{NO}_3)_2-0.75\text{KNO}_3$ mixed Nano System Plots

All these figures reveal two partially overlapping depressed semicircles in complex impedance analysis. A large arc at peak frequencies constitutes the majority resistance of the considered sample and a small arc at low frequencies specifies the grain boundary effect. Consider the arc intercepts on the real axis to get the resistance of grain and the boundary of the corresponding component contributing towards the impedance of the sample. Arrhenius behavior is attributed to a variation in the grain boundary and its resistance along with the relaxation time and inverse temperature. The conduction implicates that it is happening concerning

grain boundaries but not due to grains.¹⁵ It is understood from the figures that the centers of the arcs are slightly depressed, for all the mole percentages. It is also seen from the present figures that the diameter of the arc decreases with temperature, due to the decrease of dc resistance of the sample as temperature increases. The impedance behavior of these samples is interpreted as sandwiched between two metal electrodes and can be considered equivalent to a combination pertaining to R and C. The intercept along the real axis on the small frequency side is normally referred to as the major resistance (R_b) of the sample. The arc intercepts lean towards a lesser value with an upsurge in temperature indicating a decline in major resistance. Therefore, the decrease in the magnitude of Z' with temperature is attributed to an increase in dc conductivity.

Fig.-2: Cole-Cole $_{0.19}\text{Ba}(\text{NO}_3)_2\text{-}_{0.81}\text{KNO}_3$ mixed Nano System Plots

Fig.-3: Cole-Cole $0.05\text{Ba}(\text{NO}_3)_2-0.95\text{KNO}_3$ mixed Nano System Plots Fig.-4: Conductivity V/s Inverse Temperature of pure $\text{Ba}(\text{NO}_3)_2$, KNO_3 and their mixed Nanosystems, from Complex Impedance Analysis

Figure-4 illustrates the variation in dc ionic conductivity (from complex impedance analysis) with reciprocal temperature for pure $\text{Ba}(\text{NO}_3)_2$, KNO_3 and different Nano m/o viz. for $0.62\text{Ba}(\text{NO}_3)_2-0.38\text{KNO}_3$, $0.37\text{Ba}(\text{NO}_3)_2-0.63\text{KNO}_3$, $0.25\text{Ba}(\text{NO}_3)_2-0.75\text{KNO}_3$, $0.19\text{Ba}(\text{NO}_3)_2-0.81\text{KNO}_3$, $0.05\text{Ba}(\text{NO}_3)_2-0.95\text{KNO}_3$ mole percentages obtained from the complex impedance analysis. Improvement of conductivity is found to escalate along mole fraction i.e., the improvement is extreme in the case of nano $0.19\text{Ba}(\text{NO}_3)_2-0.81\text{KNO}_3$ and also found to reduce for nano $0.05\text{Ba}(\text{NO}_3)_2-0.95\text{KNO}_3$ ¹⁶. The present results are in reasonably good agreement with our earlier work by two probes dc technique¹⁷ in which a maximum enhancement was recorded for nano $0.19\text{Ba}(\text{NO}_3)_2-0.81\text{KNO}_3$ and for nano $0.05\text{Ba}(\text{NO}_3)_2-0.95\text{KNO}_3$. It was found decreasing i.e., the improvement found to reduce with the further surge in the mole percent of KNO_3 in $\text{Ba}(\text{NO}_3)_2$.¹⁸ To visualize better the above trend, a plot between conductivity and composition is drawn. Conductivity is optimum at nano $0.19\text{Ba}(\text{NO}_3)_2-0.81\text{KNO}_3$ from Fig.-5.

Fig.-5: Mole Percentages at Different Temperatures of KNO₃ in Ba(NO₃)₂ V/s ln(σT)

CONCLUSION

Complex impedance studies on pure and mixed systems reveal two partially overlapping depressed semicircles in a complex impedance analysis. The impedance behavior of these samples is interpreted as sandwiched between two metal electrodes and can be well-thought-out of equivalence with the 1 combination pertaining to R and C. The incongruence of dc ionic conductivity (from complex impedance analysis) with inverse temperature for pure Ba(NO₃)₂, KNO₃ and different nano m/o viz. for 0.62Ba(NO₃)₂-0.38KNO₃, 0.37Ba(NO₃)₂-0.63KNO₃, 0.25Ba(NO₃)₂-0.75KNO₃, 0.19Ba(NO₃)₂-0.81KNO₃, 0.05Ba(NO₃)₂-0.95KNO₃. It is found that the improvement of conductivity resulted in escalation along the mole fraction. That is, the improvement has been extreme in the case of nano 0.19Ba(NO₃)₂-0.81KNO₃ and has shown to reduce for nano 0.05Ba(NO₃)₂-0.95KNO₃ (which supports the DC conductivity by two probe method.¹⁷

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