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AC conductivity and complex impedance analysis of Ba(NO₃)₂-KNO₃ mixed crystals

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ABSTRACT

Ac conductivity studies and complex impedance spectroscopic studies were carried out on Ba(NO3)2-KNO3 mixed crystals in the temperature range from room temperature to melting points of their respective systems and the frequency range from 50 KHz to 1 MHz. Dielectric constant, loss tangent, capacitance and AC conductivity, in these systems are presented. Dielectric constant, loss , capacitance and AC conductivity are found to increase with temperature and with mole percent of Ba(NO3)2 in KNO3. These dielectric properties are interpreted in terms of space charge polarization and increased concentration of defects in the interfacial layer formed between the host and the dispersoid.

Keywords: Solid electrolytes; Conductivity; Impedance; Space charge polarization; Interface; Alumina

INTRODUCTION

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. Composite solid electrolyte systems based on alkaline and alkali earth nitrates, especially $Ba(NO_3)_2$ and KNO3 exhibit an appreciably high ionic conductivity at ambient temperatures. This nitrate based composite materials has been successfully used as an electrolyte for an intermediate temperature solid state fuel cells. Intermediate temperatures are important for solid state fuel cells [1–3]. Composite Solid Electrolytes (CSE) containing an ionic conductor is a conducting material which can show a dramatic increase in conductivity over that of the pure ionic conductor [4]. The enhancement in conductivity of bi-phase composite electrolytes has been demonstrated for a variety of systems [5–7], and it has become known that the enhancement is due mainly to enhanced electrical conductivity along the interface layer between the ionic and insulating phases. This enhancement in conductivity is dependent on the compositions and micro-structures of the CSE [5–7].

Small-signal AC impedance measurements are gaining in popularity as a technique for investigat- ing the electrochemical properties of materials and used in solid state electrolyte cells. Bauerle first applied it in 1969 to analyse the response of solid electrolyte cells to sinusoidal perturbations. Since then this technique has been used to characterize a wide range of materials which include polymers, oxides, glasses, halides and ceramics and it has been instrumental development of both electrode and electrolyte materials for solid state electro- chemical devices such as batteries, sensors, fuel cells, super capacitors and electrochromics. Several theories were proposed to describe the complex impedance spectroscopy [8–10].

In this paper, we report the dielectric properties and complex impedance spectroscopic studies of Ba(NO3)2-

KNO3 mixed crystals.

MATERIALS AND METHODS

The starting materials were from Qualigens fine chemicals (SQ) of 99.5% purity. Ba(NO3)2 and KNO3 wereobtained 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 approximate diameter 8 mm and thickness 2–3 mm, were painted with silver paste and sandwiched between two flat silver electrodes of the sample holder. These were kept at $^2/_3$ of their melting point for about 4 hrs before the start of an actual experiment. The temperature of the furnace was controlled using a PID type (Indotherm 401D) with an accuracy of $\pm 1^{\circ}$ C. Employing HP 4192A LF impedance analyzer with a HP-16048B test fixture carried out the impedance measurements. The sample was allowed to remain at each temperature for about 30 min in order to attain uniform temperature and the impedance was measured by applying an AC signal of 1 V (peak to peak).

RESULTS AND DISCUSSION

Fig. 1 shows the complex impedance plots, for Ba(NO3)2-KNO3 mixed crystals with 49 m/o, 91 m/o, 95 m/o, at different temperatures. In Fig. 1(a)–(c) an inclined straight line noticed at low frequencies correspond to electrode–electrolyte interface capacitance arising out of the roughness of the surface of the sample [8–9]. Fig. 1(c) indicates that, at higher frequencies the depressed semi-circle does not seem to pass through the origin. This could be due to two reasons. One is that, the semicircle could appear at these frequencies. Secondly, the resistance at high frequencies satisfy R>0 condition. The depressed semi-circle with its origin below the real axis indicates the presence of distributed elements in the material and material electrode systems, which means that the relaxation time is not a single-valued but is distributed continuously or discretely around a mean relaxation time [11,12]. The slope of the line decreases with increasing roughness and for a perfectly flat surface the angle is 90⁰ with real axis. This type of frequency response can be represented by a constant phase element (CPE) which has an impedance $Z = A(j\omega)^{-n}$, where n has values between 0 and 1 and A is a constant. Under these circumstances the system between the electrodes can be equated to an equivalent circuit composing of a parallel combination with the addition of interface capacitance in series.

The temperature dependence of dielectric con-stant(K) in Ba(NO3)2 and KNO3 and their mixed crystals with 49,91, and 95mole percentages are shown in Fig. 2 at frequency 900 KHz. It also shows a very gradual increase in dielectric constant at low temperatures [9,13] up to about 150^oC. Subsequently, the increase in temperature results in a higher rate of increase in dielectric constant due to thermally generated defects. As we proceed, there is a peak at about 200 °C in the case of pure, at 210°C for 49 m/o and at 225°C for 9.5 m/o. This anomaly could be due to the structural phase transition[14]. In the 91 mole percent system the sudden increase in dielectric constant can be seen to take place at a temperature $(190^{0} C)$ which is far the transition temperature (220 °C). This behaviour is akin to the results obtained in the DC ionic below conductivity studies [9]. This mole percent corre- sponds to the threshold where maximum enhance- ment was noticed. It is obvious that increased defect concentration gives rise to larger dielectric constant at the lowest temperature. Fig.3 displays the frequency variation of dielectric constant in 91mole percentage at different temperatures. It can be clearly seen from the figure that the dielectric constant decreases exponentially with frequency to finally become almost constant at very high frequencies. At high temperature and low frequency the large value of dielectric constant is due to ionic migration [15]. The higher value of dielectric constant at low frequencies, for a given temperature, implies that the contributions from different polarizations, namely space charge, dipolar, ionic and electronic are present. At higher frequencies the contribution from space charge polarization diminishes and at very high frequencies (1 MHz) the polarizations present could be ionic and electronic [9].



Fig. 1. Complex Impedance plots for Ba(NO3)2-KNO3 49 m/o,91m/o,95m/o.



Fig. 2. The dielectric constant versus temperature Ba(NO3)2-KNO3 mixed crystals at 900KHz frequency



Fig. 3. The dielectric constant versus Frequency for (91 m/o) at different temperatures.



Fig. 4. The dielectric loss versus frequency Ba(NO3)2-KNO3 for(91 m/o) at different temperatures.

Frequency variation of loss tangent in 91 mole percent of $Ba(NO_3)_2$ in KNO3 at different temperatures are shown in Fig.4. At low temperatures loss tangent variation is almost frequency independent. This is a general behavior of ionic solids where the loss is attributed to both conduction process and space charge polarization of which the latter decreases with frequency.

AC conductivity, $\sigma(\omega)$ of ionic conductors exhibits a frequency independent behaviour at low frequencies. This low frequency 'plateau' is identified with the true DC ionic conductivity [15].

Fig. 5 shows the variation of AC conductivity between the temperatures 80° C and 300° C for pure Ba(NO₃)₂ and KNO₃ and their different mole percentages of 49m/o,91m/o and 95m/o. This data is recorded at 1 MHz for pure and mixed systems. KNO₃ clearly indicates the structural transitions existing at 135, 220 and285 $^{\circ}$ C (which is not completely covered) where conductivity variation becomes sudden at IV–III transition (between 150 and 170 $^{\circ}$ C) then becomes gradual in the III phase, a sudden fall between 200 and 225 $^{\circ}$ C corresponding to III–II transition which once again starts increasing as we go to high temperature. The unusual fall of conductivity during III–II transition could be attributed to the blocking of nitrate ion [16] which prevents the movement of defects, if any. It is quite interesting to note that there is a maximum enhancement of about 2 orders of magnitude in 91 m/o Ba(NO₃)₂ in KNO₃. One more striking feature to be noticed here is that discontinuities corresponding to structural phase transitions existions existing in the pure form disappear in the mixed system [17]. Likewise, absence of these sudden changes is also noticed in case of other mole percentages. However, magnitudes of conductivity are lesser

as compare to that in 91 mole percent system.



Fig. 5. AC condutivity versus temperature for Ba(NO₃)₂ in KNO₃ at 1000KHz frequency.

Capacitance versus frequency for pure $Ba(NO_3)_2$ and KNO_3 and their mixed systems at 49,91 and 95 m/o at 240^oC temperature are shown in fig.6. At low frequencies the capacitance is found to be almost constant for all mole percentages. As the frequency increases the capacitance is found to be increasing for all mole percentages. And it is found to be maximum for 91 m/o where there is found maximum enhancement in conductivity. The increase in capacitance at higher frequencies could be attrib- uted to the lowering of the activation barrier at higher frequencies as compared to that at lower frequencies [18–22].



Fig. 6. Capacitance versus frequency for pure Ba(NO₃)₂ and KNO₃ and their mixed systems at 49,91 and 95 m/o at 240^oC temperature.

CONCLUSION

Complex impedance analysis studies on $Ba(NO_3)_2$ and KNO_3 with different mole percentages showed a significant enhancement in the AC conductivity in mixed systems with respect to the pure. The maximum enhancement observed was about 2 orders of magnitude for 91 m/o. These results lead to the conclusion that the enhanced conductivity in Ba(NO3)2–KNO3 composites is due to the space charge polarization and 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(NO3)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(NO3)2 is less.

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