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Electrical transport in $CsNO_3$: Complex impedance spectroscopy method on single crystals and pressed pellets

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ABSTRACT

Complex impedance plots on single crystals and polycrystalline $CsNO_3$ are presented in the temperature range 110-350^{0}C. Comparison of dc ionic conductivity in these two forms of $CsNO_3$ reveal that the conductivity in polycrystalline samples is higher by nearly one order of magnitude than that of single crystals. This is attributed to the presence of surface space charge, grain boundaries and dislocation densities.

KEYWORDS

Impedance plots;
Ionic conductivity;
Surface space charge.

INTRODCUTION

The study of d.c. ionic conductivity in solid electrolyte systems is very useful in understanding the defect properties of the systems. And a number of such systems are useful in modern solid state ionics devices. In these applications it is observed that the solid electrolytes are used in the form of pellets rather than as single crystals, because of the flexibility of fabrication with the former[1]. In this study we made an attempt to compare the results of ionic conductivity obtained from complex impedance spectroscopy method on single crystals and pellets of nominally pure cesium nitrate. Not much work has been published in which such a comparative study was undertaken on solid electrolytes in general and cesium nitrate in particular.

EXPERIMENTAL

The starting host material, $CsNO_3$, was from Aldrich chemical (U.S.A). Single crystals were grown by the slow evaporation method after dissolving the starting material in double distilled water. The crystals so obtained were crushed in an agate mortar to obtain a fine powder and then sieved through mesh (#240) for uniform size of the particles. The method of preparation of the pellets and the details of recording and analyzing the data were described in[2-3]. The density of the pellets was found to be nearly 80 per cent of that of the single crystals.

RESULTS AND DISCUSSION

Figure 1 shows the complex impedance plots for single crystals of $CsNO_3$ at four different temperatures namely, 120^{0}C, 233^{0}C, 281^{0}C and 326^{0}C. For want of space we have not included all the plots taken at different temperatures. It can be seen from figure 1(a), corresponding to 120^{0}C, that there is an inclined straight line near the origin that pertains to high frequencies and the impedance data could not be recorded because of the limitation of the instrument for lower frequency side

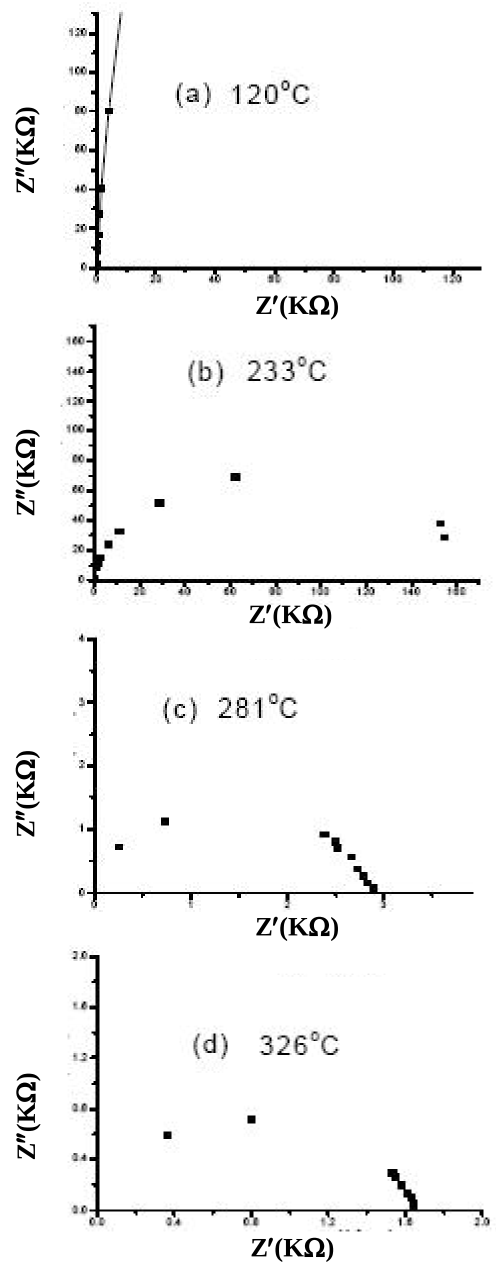

Figure 1 : Complex impedance plots for single crystal of $CsNO_3$ at different temperatures

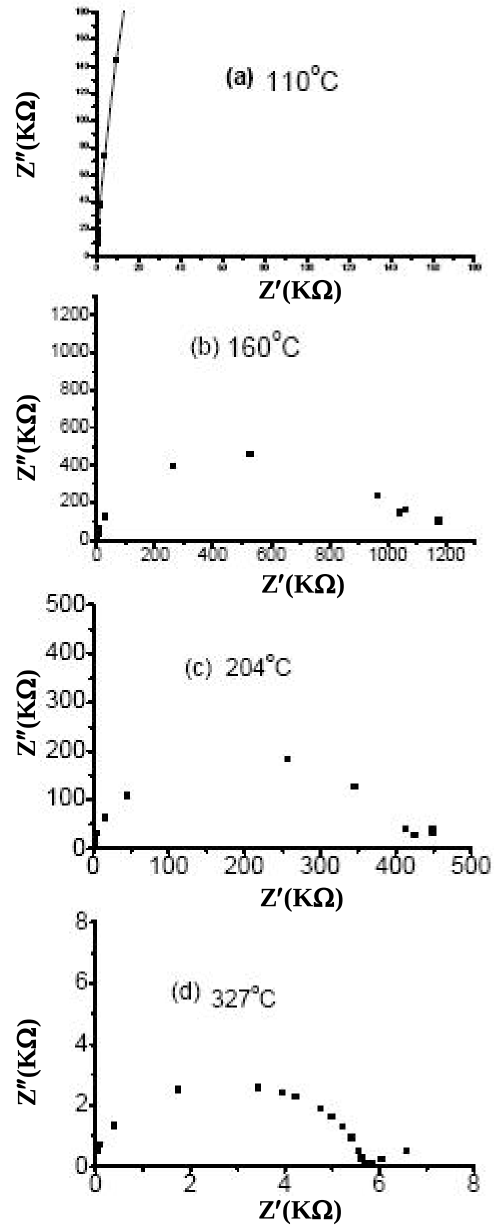

Figure 2 : Complex impedance Plots for pure $CsNO_3$ pellets

of the spectrum. In the subsequent higher temperatures this line gradually becomes a semi circle as shown in figures 1(b-d), which intersects at different values on X-axis. Usually the intercept on X-axis gives the dc resistance of the sample. The values of this intercept are found to decrease with temperature, which implies that dc conductivity of the sample increases.

Similar plots for $CsNO_3$ pellets are shown in figure 2 at different temperatures. As the temperature increases, figures 2(a and d), the intercepts on real axis giving dc resistance can be seen to decrease with temperature here also. Comparison of figures 1 and 2 reveals that the semicircles for pellets are slightly more depressed than those of single crystals, which happens to be a general observation[4,5] due to the presence of constant phase element that arises out of grain boundaries present in them. The appearance of a small line at the low frequency end [figure 2(d)] for $CsNO_3$ pellet may be due to the presence of electrode/electrolyte interface[6-10].

Figure 3 shows the variation of dc ionic conductiv-

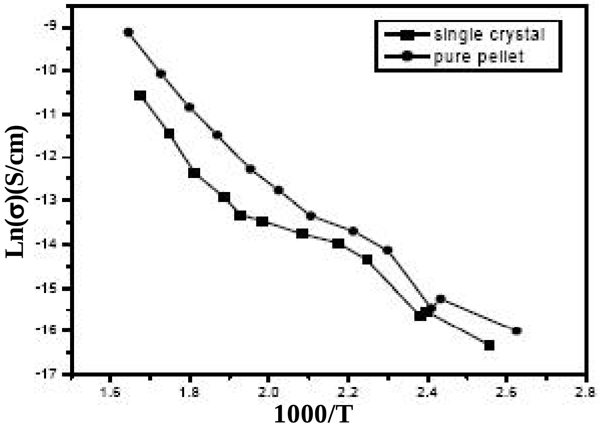

Figure 3 : Ln(σ) versus reciprocal temperature for $CsNO_3$

ity, obtained from complex impedance study, with temperature in single crystal and polycrystalline samples of $CsNO_3$ from 110^{0}C to 350^{0}C. Squares indicate the data on single crystals and circles that of polycrystalline samples. The differences noticed in the value of conductivity in the extrinsic regions (as temperature covered is not up to the melting point i.e. 410^{0}C) can be attributed to the differences in dislocation densities and grain boundaries, the latter being normally associated with surface space charge[4,5,11-13]. Similar observations have also been made in $RbNO_3$[3], CaF_2[14] and $Ba(NO_3)_2$[2]. The conduction mechanism in this system was attributed to Frenkel disorder involving cesium ion vacancies and interstitials[5]. Further studies in this direction are necessary for a better and fuller understanding of the phenomenon involved.

CONCLUSIONS

The cole-cole plots reveal that the intercepts of semicircles on real axis decrease with the increase in temperature indicating the lowering of the dc resistance. The enhancement of conductivity in pressed pellets over single crystals was observed to be nearly one order of magnitude in the extrinsic conduction region. This could be due to increase in the concentration of defects at the grain boundaries that normally arise due to the surface space charge and due to the surface conduction of the sample.

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