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Dielectric and DC conductivity studies and of Al_2O_3 dispersed $NaNO_3$ Solid Electrolytes for battery applications

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Abstract: *solid electrolyte system of chemical compositions (100-x) $NaNO_3$- xAl_2O_3 (where x=0.0, 10,15, and 20 mole%) were prepared by fast evaporation technique. The synthesized electrolytes were characterized and investigated through AC conductivity and dielectric studies. AC conductivity was studied at high frequency and temperature up to 250^oC depends on the Tg. The conductivity of the pure sample was found good and it was increased with the dopant molar content Al_2O_3. AC conductivity varied upto three orders in the low frequency region for most of the samples and in the high frequency range it varied upto two orders. Cole-Cole impedance plots have shown semicircular patterns. The bulk resistance was decreased with increasing doping concentration which is an indication of increasing trend of conductivity.*

Keywords: *AC conductivity, Cole-Cole plots, fast evaporation, bulk resistance*

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I. Introduction

Developing new electrolytic materials is an essential need for various applications in the recent days [**1**]. The composites of solid electrolytes are the superior tools to develop electrolytic materials for energy storage devices, fuel cells, super capacitors, chemical sensors, electro chromic devices [**2-3**]. It will reduce the losses arising from the high internal resistances in electro-chemical devices with aqueous solutions. Fast evaporation technique is very convenient and effective method for the enhancement of conductivity when dispersing an insulating oxide in a host ionic conductor. Since Frenkel type defect solids seem to be more promising materials to enhance conductivity by the dispersion of insulating oxides, we considered $NaNO_3$with rhombohedral calcite structure as host material and Al_2O_3 as dispersion for the purpose of enhancement of conductivity. [**4-5**]. Alumina is an important insulating and ceramic material, which has unique properties such as thermal and chemical stability, high strength, toughness etc. Alumina is familiar for its outstanding performance under tension or bending conditions.

Y.Govinda Reddy et.al[**6**] studied $Pb(NO_3)_2$based Al_2O_3,CuCl-Al_2O_3,Na_2SO_4-Al_2O_3,Li_2SO_4-Al_2O_3,CsCl-Al_2O_3doped solid electrolyte system and its transport studies for various applications. P.S Ananthaet al.[**7**]studied on $NaNO_3$-Al_2O_3et.al using melt quench method, also M.V. Madhavarao [**8**] et.al through slow evaporation technique. Due to the wide range of applications Al_2O_3can be used in various fields.

The present study is an attempt to disperse $NaNO_3$ with fine insulating oxide nano powder Al_2O_3 to make it dispersed solid electrolyte system. In general, it is believed that no chemical reaction is formed to occur between the host material and the dispersoid in composite solid electrolyte system [**9**]. The aim of the present work is to synthesize solid electrolytes through fast evaporation technique and to study their conductivity properties using AC and D.C conductivity.

II. Experimental

Sample preparation & Characterization techniques

The starting materials sodium nitrate and aluminum oxide with particle size <50nm (TEM) are of AR grade from sigma Aldrich (USA). For the synthesis of ionic solids required chemicals according to molar ratio were dissolved in double distilled water and heated on magnetic stirrer at 60^{0}C. to get the homogeneous solution after half an hour, desired mole% of alumina was added to the initial solution, and heated the solution till 90^{0}C with continuous stirring. Then the solution was taken to 110^{0}C so as to obtain dry gel. Figure 1 shows the synthesis pattern flow chart of (100-x) $NaNO_3$- xAl_2O_3 (where x=0.0, 10,15, and 20). The final mixture was collected and grinded in an agate mortar and piston for 2hrs subsequently characterization is done on these powders through AC and DC conductivity measurements. AC conductivity was studied in the frequency range 50Hz to 35MHz and temperature from RT to 250^{0}C.

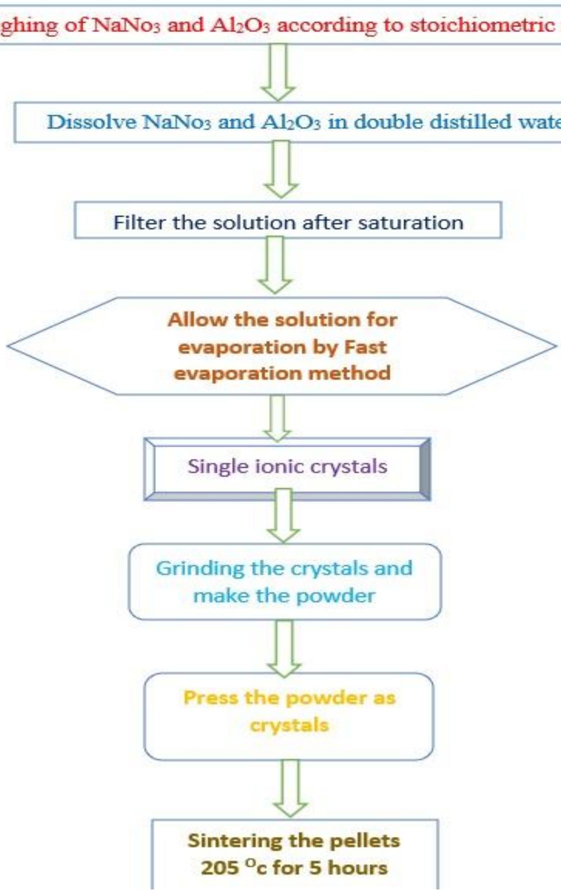

Figure 1 Flow chart for sample preparation

III. Results and Discussions

AC Conductivity of Aluminium (Al_2O_3) doped $NaNO_3$:

Synthesized (100-x) $NaNO_3$- xAl_2O_3 (where x=0, 10,15,20 mole%)solid electrolytes were characterized for AC conductivity measurements. AC conductivity measurement used to understand the conduction mechanism and its nature in materials like ceramics, glasses, solid electrolytes and polymers. AC conductivity studies can provide an important electric transport mechanism of the electrolytes doped with different metal oxides. AC conductivity also depends on the thermal treatments of materials [**10**]. There are several models to analize the frequency dependent AC conductivity and dielectric properties of different materials like polymers, glasses, ferrites and ceramics. The following models are widely used. They are quantum mechanical tunnelling (QMT) model, hopping over barrier (HOB) model and correlated barrier hopping (CBH) model.

Generally, the AC conductivity have been discussed as frequency dependent as well as temperature-dependent. The plots drawn between logσ (vs.) logf for getting the conductivity. Total AC Conductivity is the sum of two regions i,e plateau region (DC region) and curved surface region. The first region (plateau) is also known as DC conductivity region and, curved zone also known to be frequency dependent AC conductivity. The dispersion behaviour may be attributed to the sample-electrode polarization of the composites at lower temperatures. At high temperature, the electrode polarization might decreases and frequency independent regime increasing. It is also observed that with increase in temperature causes enhancement of conductivity in the high frequency region. Jonscher's universal power law used to analyze the conductivity as

$$\sigma(\omega) = \sigma(0) + A\omega^n ,$$

where, σ(0) is frequency independent (dc region) conductivity of the material, A is the dispersion parameter and n is frequency exponent[**11**].

In the present investigation, the variation of AC conductivity with applied AC frequency have been discussed. It is also discussed with temperature variation. At the room temperature the results of AC conductivity was found to be in the lower order. The σ_{ac}conductivity is low at lower temperature due to the migration of cations from interstitials to the vacancies, recombination of schottkey defects or migration of vacancies. [**12**]. In the low frequency segment $\sigma_{ac}$is almost constant and linear. In the high frequency segment it was shown significant enhancement up to several orders.

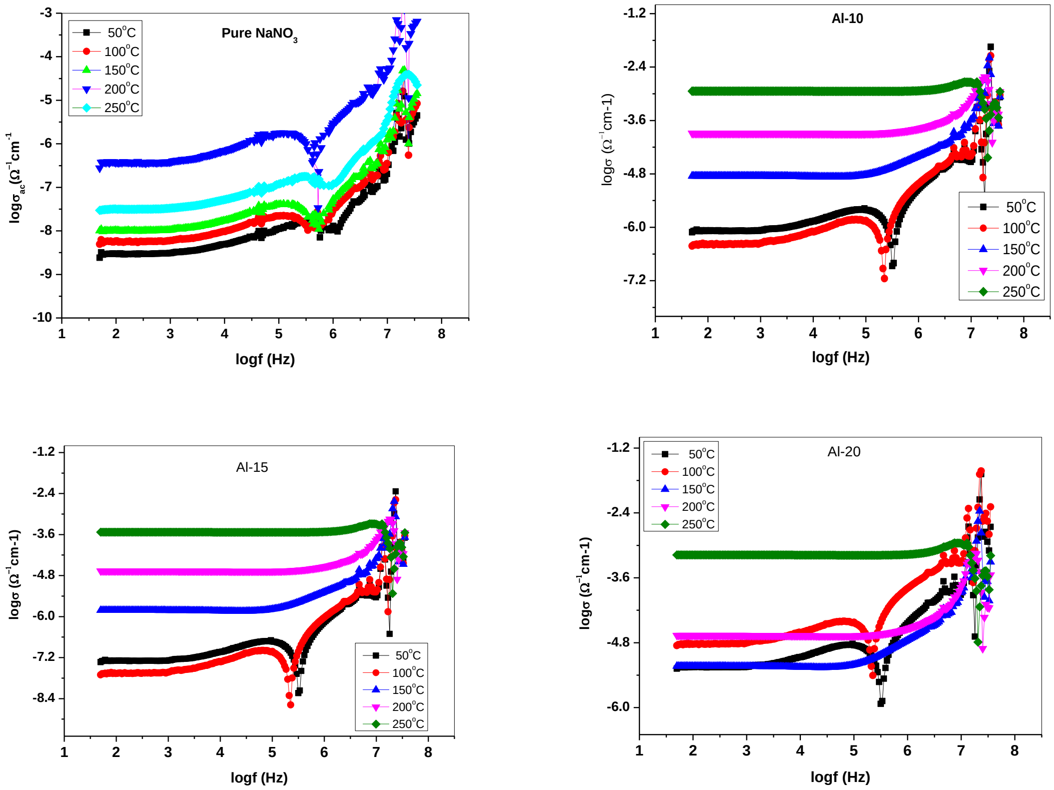

Figure.2.Variation of σ_{ac} with applied frequency of different mol% Al_2O_3

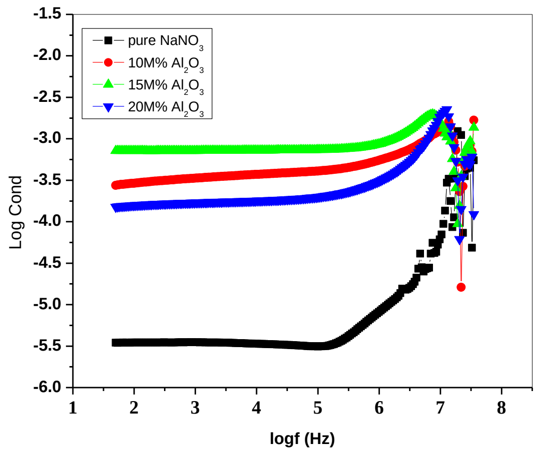

Figure.3.Comparison of σ_{ac} with applied frequency of different mol% Al_2O_3 (At 250°C)

AC conductivity of Al_2O_3 doped $NaNO_3$ electrolytes with (1-x)$NaNO_3$-xAl_2O_3 compositions varied with applied frequency and temperature increment. It was shown linearity at lower temperatures. It may due to the non-homogeneities present in the sample as well as hygroscopic nature of the electrolytes. It also found that the AC conductivity is purely frequency independent (dc conductivity) in the low frequency domain and also observed dispersion behaviour in the high frequency region for all the studied solid electrolytes. The behaviour of the conductivity at different temperatures might be due to the short-range coupling of hopping of adjacent sites [**13**].

Figure.2a represents the variation of conductivity σ_{ac} with applied AC frequency of pure $NaNO_3$ sample. It is very clear that the AC conductivity is almost constant at low frequency region and increased rapidly with increasing the frequency. The AC conductivity found the highest at high frequency region. The AC conductivity varied up to three orders with the increase of temperature.

The AC conductivity $\sigma_{ac}$of 10mol% of Al_2O_3 sample varied one orderfor the variation of temperatures taken from 50^{o}C to 250^{o}C in the low frequency region as shown in **Fig.2b**. At high frequencies it varied upto three orders while the transformation from DC to AC region. It also increased up to one order in the high frequency segment.

The conductivity $\sigma_{ac}$of 20mol% of Al_2O_3 sample varied from 10^{-7}-10^{-5} $\Omega^{-1}cm^{-1}$ for the variation of temperatures from 50^{o}C to 250^{o}C in the low frequency region as shown in. At high frequencies it varied from 10^{-5}-10^{-2} $\Omega^{-1}cm^{-1}$. The conductivity is increased up to three orders in the high frequency segment.

The AC conductivity (σ_{ac}) of 15mol% of Al_2O_3 sample varied four orders for the variation of temperatures taken place from 50^{o}C to 250^{o}C in the low frequency region as shown in **Fig.2c**. At high frequencies it varied from 10^{-7}-10^{-3} $\Omega^{-1}cm^{-1}$ while the transformation from DC to AC region. It also increased up to two orders in the high frequency segment.

The AC conductivity (σ_{ac}) of all the studied electrolytes was compared at 250^{o}C as shown in the **Figure.3**. It is clearly observed that the ac conductivity varied upto three orders with dopant mole percentages. Pure $NaNO_3$ has shown the log of conductivity value around 5.5 and varied upto 3.0 for highest Al_2O_3 content. At high frequencies it varied up to two orders.

$Z^/$ vs $Z^{//}$ Cole-Cole plots:

Complex impedance behaviour of the Al_2O_3 doped solid electrolytes at different temperatures werediscussed in terms of real and complex impedance components $Z^/$ and $Z^{//}$. It was found that the real and imaginary impedance parts werehigh at low temperatures andCole-Cole plots were shown single semicircle behaviour. It may occur due to the major contributionsby grain boundary and grain interior. At low frequency, spikes were found due to the electrode-sample (electrolyte) interface.It was also found that the centre of semicircles always lies below the real axis of impedance plots, which confirms the domination of non-Debye relaxation in composites [**6,14**]. As the increase of mole concentration of dopant Al_2O_3, the radius of depressed semicircle decreased, which confirms the enhancement of conductivity. **Fig.5**depicts the Cole-Cole plotsof Al_2O_3 doped samples at 250^{o}C for different mole percentages.It clearly shows that the addition of dopant Al_2O_3causes the decrease of impedance, which also causes the enhancement of the ac conductivity.

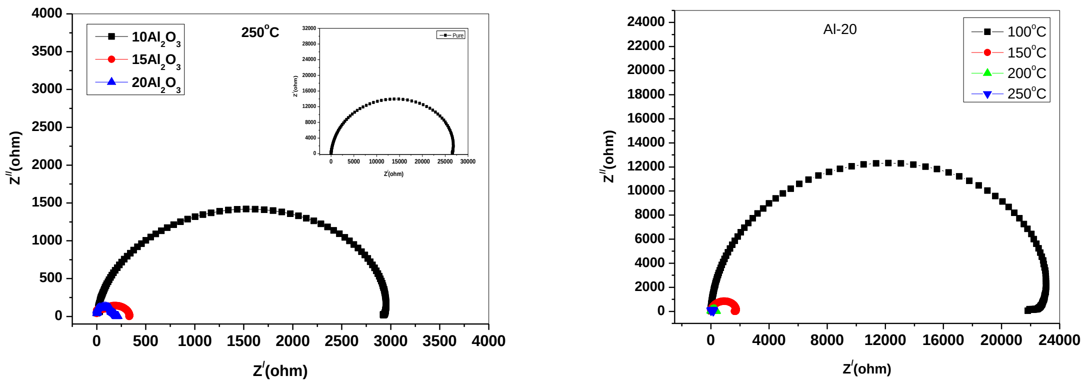

Figure.4.Variation of Z/ and Z// with different Al_2O_3mol% at 250^{o}C.

Fig.4depicts the Cole-Cole plots of 20mol% Al_2O_3 doped sample at different temperatures. It is very clear that the increase of temperature causes the decrease of impedance, which also causes the enhancement of the ac conductivity. The plots at higher temperatures (200°C and 250°C), clearly indicates that the semicircle started away from origin. With further increase in temperature, the semicircle has become almost parallel to y-axis. These observations indicate variation of contributions of grain interior, grain boundary to the total conductivity at higher temperatures. The depressed arc in the high frequency region is due to combination of bulk resistance R_b and capacitance C_b of the sample. The arc corresponding to interface polarization is fitted within experimental frequency window by forming depressed semicircle at higher temperatures. The conductivity in these systems could be due to the combination of grain interior and grain boundary at lower temperatures, and it showed higher capacitive nature at higher temperatures.

D.C. ionic conductivity

D.C. ionic conductivity of the studied electrolytes found to increase with temperature and also observed that it was increased with molar percentage of dopant up to 15mol%. Further,it was decreased due to blocking effect of the dispersoid particles[**15**]. In the present study, the dc conductivity was increased more than three orders of magnitude with respect to host material insertion in the extrinsic region. The increment in the dc conductivity can be explained with the help of the following models:

According to Jow and Wagner model[**16**] and Kliewer theory the dispersoid Al_2O_3 when introduced into $NaNO_3$ a space charge region is created at host dispersoid interface boundary. According to Maier's space charge model the solid electrolyte is enriched with defects at the interface in the space charge region [**17,18**]. $NaNO_3$ being a Frenkel type disordered crystal, conductivity is thought to be due to cation migration [**19**]. As the mole content of dopant increases, the total surface area increases which leads to an increase in the enhancement of conductivity. Further increasing of Al_2O_3, host is not enough to surround the dispersoid particles individually. This leads to clustering of particles of the dispersoid hence a fall of total effective surface area of contact between them [**20, 21**].

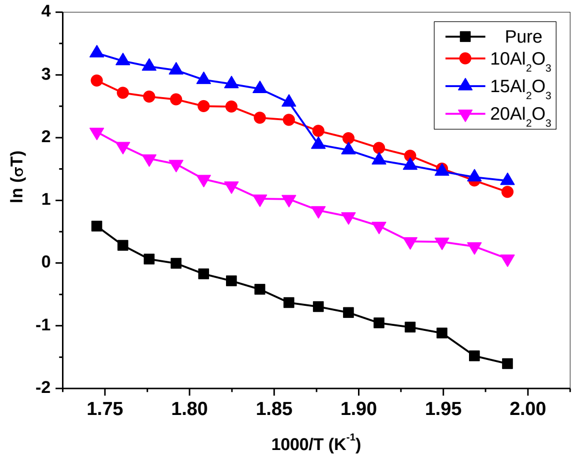

Figure.5.Variation of D.C. ionic conductivity with temperatures

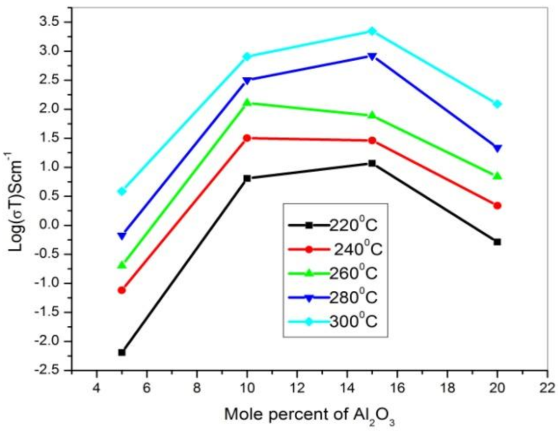

Figure 6. Variation of DC ionic conductivity with different Al_2O_3 content

The enhancement in the dc conductivity in the dispersed electrolyte system mainly observed due to the increase of mole percent and it attains maximum at 15mol%,further, it was falls down.

IV. Conclusions

- Solid ionic electrolytes of (100-x) NaNO3- xAl2O3 (where x=0.0, 10,15, & 20 mole%) were synthesized successfully from fast evaporation technique.
- AC conductivity increased with Al_2O_3 mole percentages.
- AC conductivity increased upto three orders in DC region(low frequency)
- AC conductivity increased upto two orders in AC region

- Cole-Cole plots have shown semicircular behavior and bulk resistance decreased with increasing Al_2O_3 content
- Higher order conductivity of the studied electrolytes make them prominent materials for battery applications
- DC conductivity also increased with dopant content

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