

# Ion transport studies on $\text{Pb}(\text{NO}_3)_2:\text{Al}_2\text{O}_3$ composite solid electrolytes: Effect of dispersoid particle size

Y Govinda Reddy<sup>1,3</sup>, M Chandra Sekhar<sup>2</sup>, A Sadananda Chary<sup>1</sup>, S Narender Reddy<sup>1\*</sup>

<sup>1</sup>Dept. of Physics, University College of Science, Osmania University, Hyderabad-500007, India.

<sup>2</sup> Dept. of Physics and Astronomy, NIT Rourkela, Odissa- 769008, India.

<sup>3</sup>Dept. of Physics, Vardhaman College of Engg, Shamshabad, Hyderabad- 501218, India.

\*Corresponding author email: snreddy\_sattineni2000@yahoo.com

**Abstract.** Composites of Alumina dispersed Lead Nitrate of different particles sizes (0.3 $\mu\text{m}$ , 36.9 $\mu\text{m}$ ) were prepared through mechanical mixing process. These composites have been characterized by using XRD and SEM. Transport properties of these systems have been studied by means of impedance spectroscopy in the frequency range 100Hz to 4MHz in the temperature range from room temperature to 300°C. Temperature dependent conductivity spectra for composites with different mole percentages of alumina and with different particle sizes (0.3 $\mu\text{m}$ , 36.9 $\mu\text{m}$ ) studied. The contact surface area between host and dispersoid increases with the decrease in particle size. These studies indicate that the conductivity in these systems is mainly due to the contribution enhanced concentration of mobile ions at the interfacial regions of host and dispersoid materials and increased mobility of charge carriers along the grain boundaries. It is believed that mechanism of conductivity through anti-Frenkel disorder ( $\text{NO}_3^-$  ions) in these composites.

**Key Words:** Composite solid electrolyte, Fluorite structure, conductivity spectra, Lead nitrate.

## 1. Introduction

Energy storage devices such as batteries, fuel cells, super capacitors are playing an important role in portable and non portable electronic devices. Electrolytic material plays a vital role in these devices, with high ionic conductivity. The Enhancement of ionic conductivity in these electrolytes and its influencing factors has been drawing the attention in the recent past. Wide range of materials reported in literature as electrolytes, however inorganic ionic salts with insoluble oxides as dispersoids are some of promising candidates as solid electrolytes [1-3]. The magnitude of conductivity enhancement is sensitive to nature of the dispersoid, its concentration, and particle size of dispersoid and also the method of preparation [4]. However the role of particle size of dispersoid is significant to increase the surface area in contact between host and dispersoid which ultimately leads to enhancement of conductivity in composite solid electrolytes [5]. The size of dispersoid may also leads to influence the mechanical strength of material, object oriented control of electrolytic properties, along with enhancement in ionic conductivity of composite [6].

In two phase composite systems the enhancement of conductivity increases with dispersoid concentration up to certain mole percentage (mol %) and there after decreases due to blocking effect [7]. Several models have been proposed in the literature, in order to explain the enhancement of conductivity in variety of composite systems [8]. The present study is aimed at the role of dispersoid ( $\text{Al}_2\text{O}_3$ ) with two



different particle sizes namely  $0.3\mu\text{m}$  and  $36.9\mu\text{m}$  in the host  $\text{Pb}(\text{NO}_3)_2$  and a systematic analysis of conductivity studies by varying the mol% and temperature in the wide frequency range.

## 2. Preparation of composites and Experimental techniques

The composites of  $\text{Pb}(\text{NO}_3)_2:\text{Al}_2\text{O}_3$  with two different particle sizes ( $0.3\mu\text{m}$  and  $36.9\mu\text{m}$ ) of different mole percentages (6, 8, 10 and 14 mol %) are synthesized through direct mixing method. The starting material  $\text{Pb}(\text{NO}_3)_2$  obtained in powder form (Merck chemicals with purity > 99%). Lead nitrate single crystals are grown by slow evaporation method and these crystals are crushed into fine powder with the help of an agate mortar. The finely sieved powder with uniform particle size is mixed with dispersoid of different particle sizes in different mole fractions in the presence of acetone for about an half an hour. The uniformly mixed powders of different compositions were made into pellets by using hydraulic press and subsequently they were sintered at  $300^\circ\text{C}$  for  $\approx 20$  hours. Silver paste was applied on both sides of disc to measure conductivity of composites.

X-ray Diffractograms of all the systems have been taken on Xpert-pro X-ray diffractometer with  $\text{CuK}\alpha$  radiation between  $10$  to  $80^\circ$  range at room temperature. Scanning Electron Microscopy (SEM) studies (ZEISS EVO18) were carried out on sintered pellets to understand change in microstructure of pure  $\text{Pb}(\text{NO}_3)_2$  and composites. Elemental analysis has been done by applying EDS. Ac conductivity measurements have been carried out by employing impedance analyzer [Hioki-3579] in the frequency range  $100\text{Hz}$  to  $5\text{MHz}$  between the temperatures  $30^\circ\text{C}$  and  $300^\circ\text{C}$ . The above experimental process is shown below by using flowchart.



## 3. Results and Discussion

### 3.1 Structural and Morphological studies

Fig.1 shows XRD patterns of pure  $\text{Pb}(\text{NO}_3)_2$ , 10mol%  $\text{Al}_2\text{O}_3$  ( $0.3\mu\text{m}$ ) and 14mol%  $\text{Al}_2\text{O}_3$  ( $36.9\mu\text{m}$ ) dispersed composites at room temperature. For two phase systems, individual phases must reflect in XRD patterns. However the phase corresponding to  $\text{Al}_2\text{O}_3$  dispersoid as second phase is not reflecting implicitly in XRD patterns of composites. It is reported that, to reflect  $\text{Al}_2\text{O}_3$  phase in composites its mol% should be high and sintering temperatures of composites around  $1400^\circ\text{C}$  [9]. Due to this the phase corresponding to  $\text{Al}_2\text{O}_3$  is not reflected for the present investigated composites. Whereas second phase in title composites detected implicitly with  $\text{CeO}_2$  dispersoid [10].

Morphological studies are conducted on present composites to understand engineering between grain and grain boundary, density variations for an applied temperature during sintering process. Fig.2 (a, b and c) shows SEM images of host, 10mol% of  $\text{Al}_2\text{O}_3$  ( $0.3\mu\text{m}$ ), 14mol% of  $\text{Al}_2\text{O}_3$  ( $36.9\mu\text{m}$ ) dispersed composites respectively which are sintered at  $300^\circ\text{C}$ . SEM images shows clear change in surface morphology between host [ $\text{Pb}(\text{NO}_3)_2$ ] and  $\text{Al}_2\text{O}_3$  dispersed composites. In case of pure  $\text{Pb}(\text{NO}_3)_2$  unequal sized grains clearly seen due to sintering effect with less porosity. The SEM images of composites [Fig.2b

and 2c] show enhanced porosity due to dispersion of  $\text{Al}_2\text{O}_3$  particles. Uniform distribution of dispersoid in composites clearly seen in agglomerated form (Fig.2c circular part region and its surroundings). EDS studies are conducted to verify the presence of starting elements or not [pictures are not shown]. It is noticed that presence of all starting elements detected and its proportion increased with increase in mol% of dispersoid.

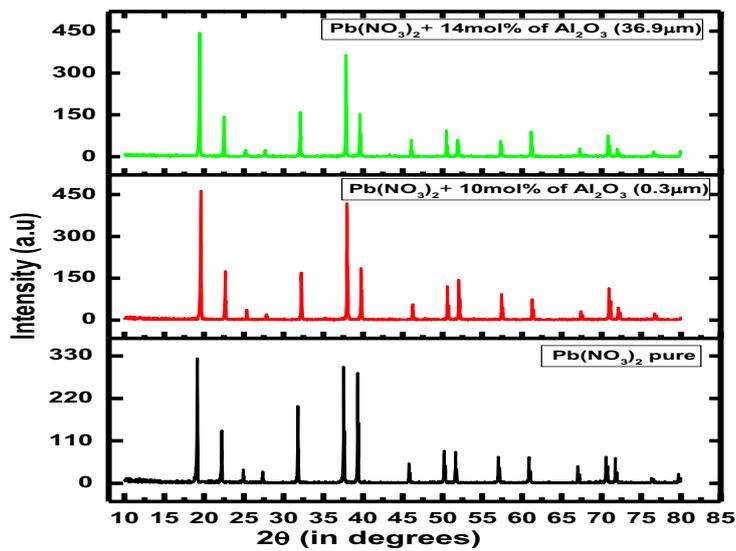


Figure 1. XRD patterns of host and different mol% dispersed composites.

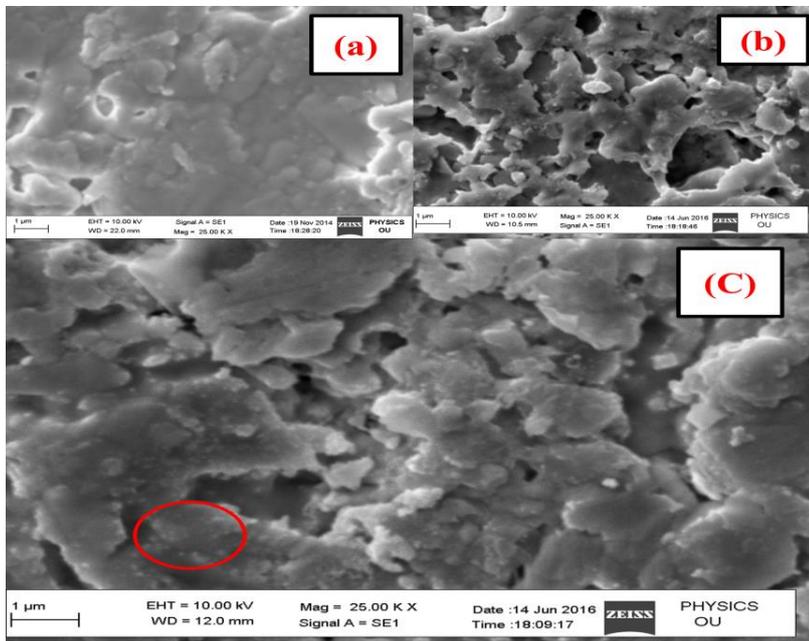
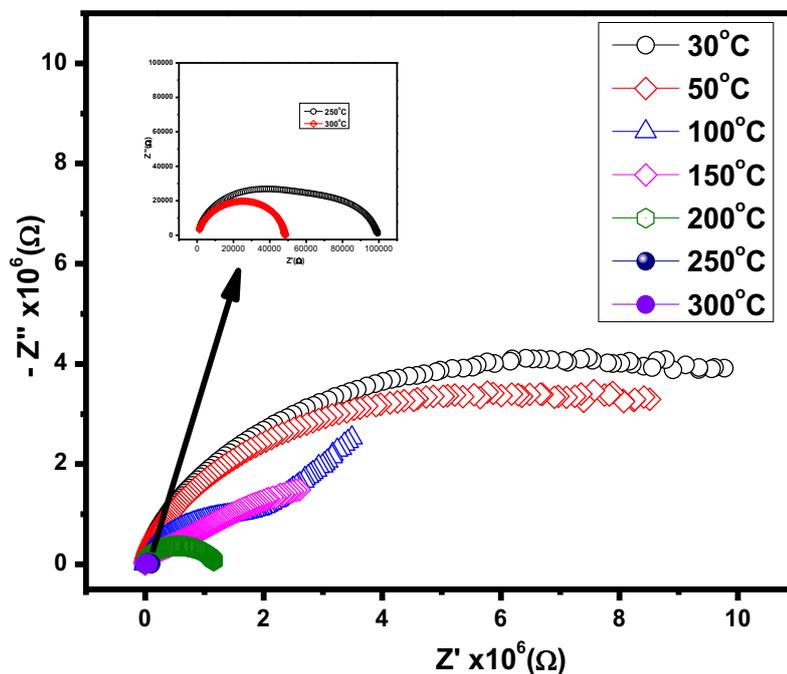


Figure 2. SEM images of (a) host (b) 10mol% of  $\text{Al}_2\text{O}_3$  ( $0.3\mu\text{m}$ ) (c) 14mol% of  $\text{Al}_2\text{O}_3$  ( $36.9\mu\text{m}$ ) composites.

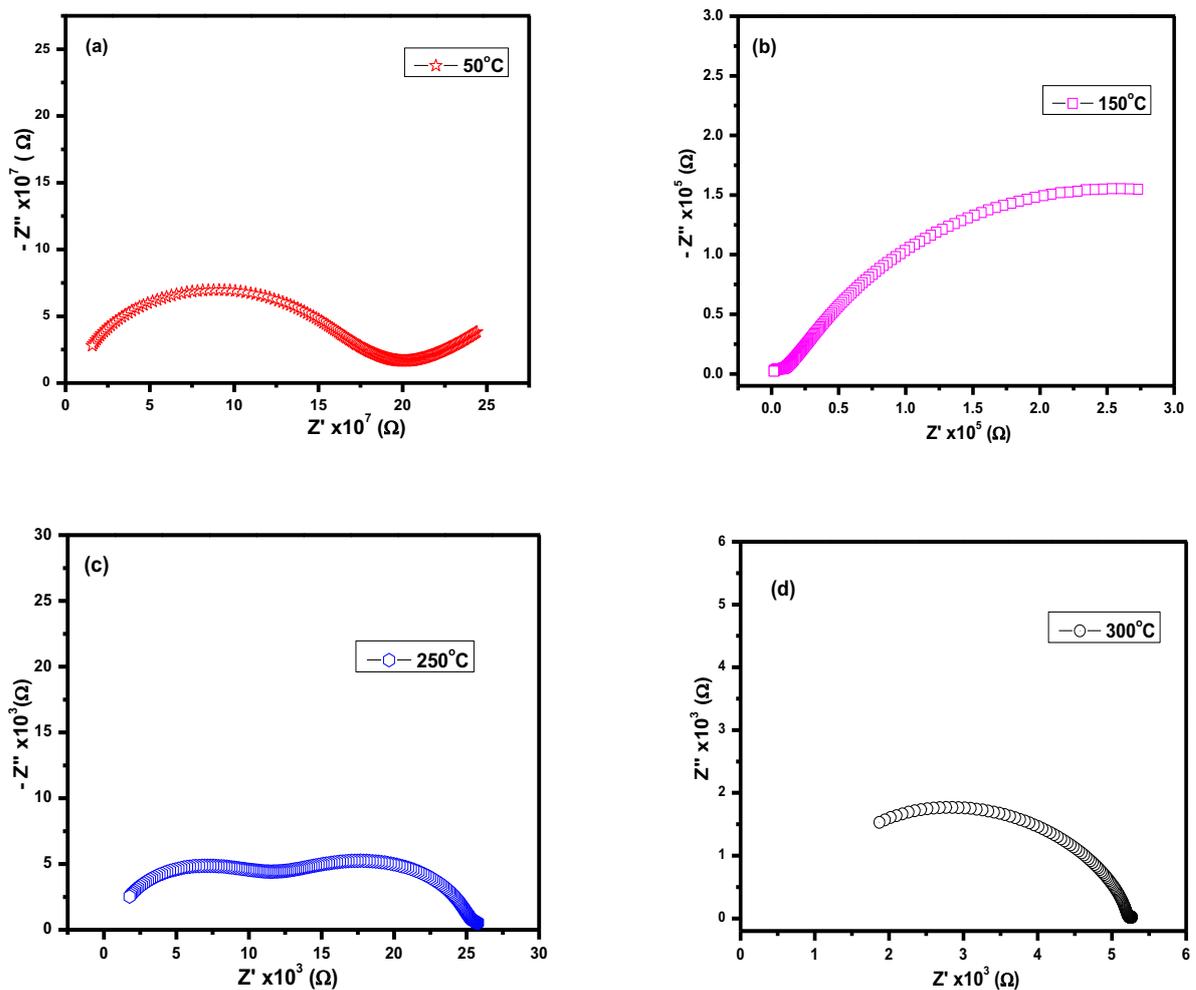
### 3.2 Impedance studies

Impedance spectroscopy is versatile technique to study ionic conductivity, nature of interfaces (due to grain, grain boundary and electrode), characterization of wide variety of solid state devices and measure of corrosion etc [11]. To study ionic conductivity properties of composites Nyquist plots are drawn between real and imaginary parts of impedance response as a function of frequency for an applied input sinusoidal signal across sample. In generally at ideal conditions Nyquist plots consists of three semicircles due to contribution of grain, grain boundary and interfacial polarization phenomena. Mathematically complex impedance can be represented as  $Z^* = Z' - jZ''$  where  $Z'$  is real part of impedance along X-axis,  $Z''$  is imaginary part of impedance on Y-axis and 'j' value is  $(-1)^{1/2}$ . Fig.3 shows Nyquist plots for 10mol% of  $Al_2O_3$  where maximum enhancement is obtained for  $0.3\mu m$  particle size dispersoid composite, throughout experimental frequency range at selected temperatures. From this at room temperature ( $30^\circ C$ ) Nyquist plot shows depressed semicircle whose centre of semicircle lies below  $Z'$  axis. It is observed with increase in temperature the radius of depressed semicircle decreased and shifted towards origin. The decrease in radius of depressed semicircle with increase in temperature indicates increase of ionic conductivity for a particular mol% with increase in temperature. Apart from this with increase in temperature the contribution of grain boundary along with grain clearly visible at  $100^\circ C$ . It can be understood from the shape of Nyquist plots, with increase in temperature grain contribution decreases and grain boundary contribution increases for total ionic conductivity.



**Figure 3.** Nyquist plot for 10mol%  $Al_2O_3$  ( $0.3\mu m$ ) dispersed composite

To understand implicitly various contributions (grain, grain boundary, electrode polarization) to conductivity Nyquist plots are drawn at individual temperatures for 14mol%  $\text{Al}_2\text{O}_3$  ( $36.9\mu\text{m}$ ) dispersed composite and are shown in fig. 4 [a to d]. At  $50^\circ\text{C}$  (Fig a) shows depressed semicircle along with electrode polarization. With increase in temperature electrode polarization disappeared and contribution of grain and grain boundary clearly visible. At  $300^\circ\text{C}$  temperature (fig.4d) depressed semi circle, corresponds to high frequency region withdrawn from origin and it indicates contribution of grain is marginal for total ionic conductivity. Similar response is observed in other mol% dispersed composite solid electrolytes. The grain boundary contribution to total ionic conductivity is also reported for other ionic conducting materials [12].



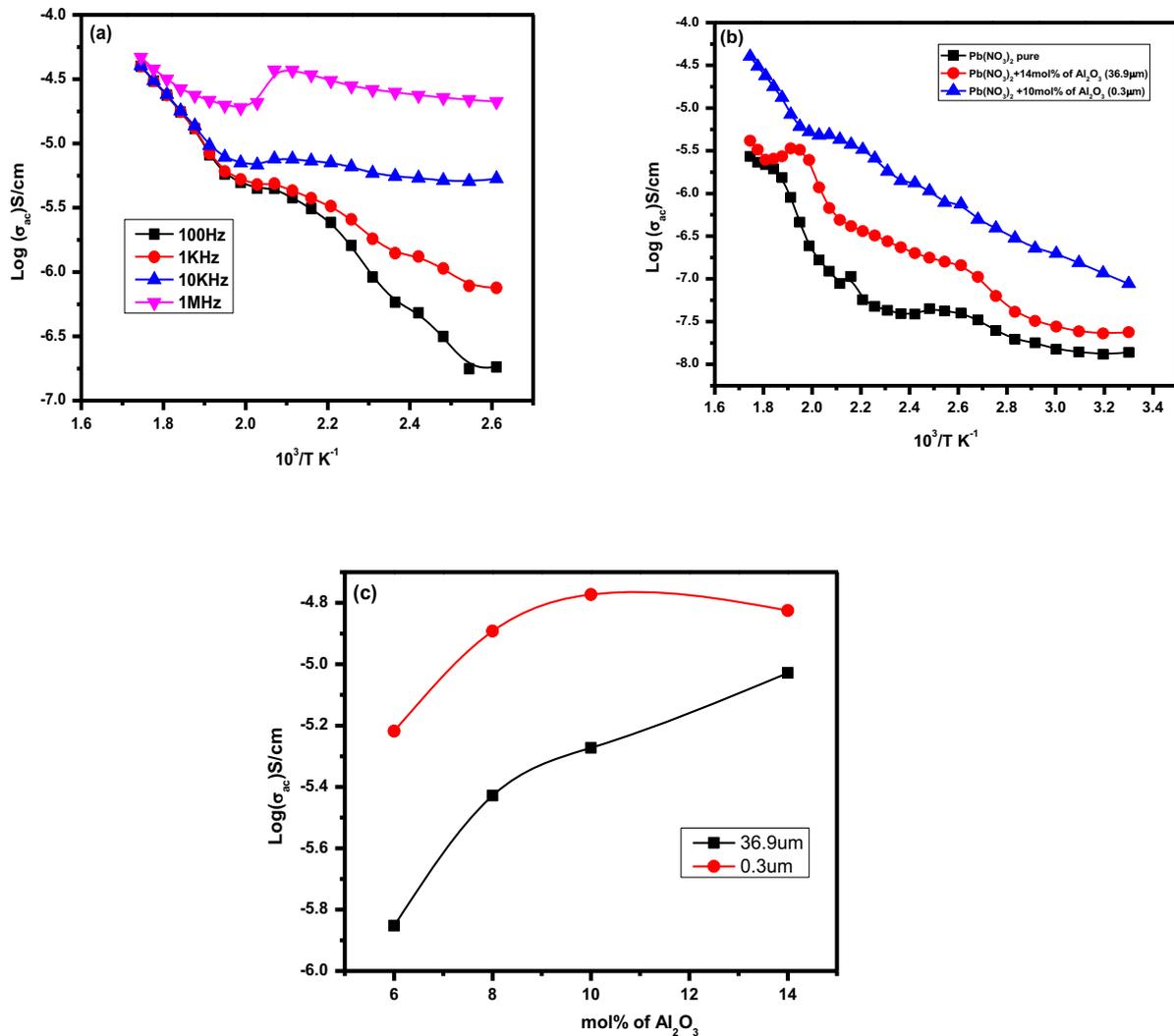
**Figure 4.** Nyquist plots for 14mol%  $\text{Al}_2\text{O}_3$  ( $36.9\mu\text{m}$ ) dispersed composite at different temperatures.

### 3.3 Ionic Conductivity studies

To understand ionic conductivity response of investigated systems under the influence of frequency and temperature, graphs are plotted between ac conductivity Vs inverse of temperature. Fig.5 (a) shows ac conductivity Vs temperature in between 100 to 300°C at different frequencies for 10mol% Al<sub>2</sub>O<sub>3</sub> (0.3µm) dispersed composite. It is observed that conductivity increases with increase in frequency. It can be understood as conductivity is sensitive to temperature and frequency for the present composites, which is general trend of solid electrolytes. The highest conductivity observed for the present composites in the order of 10<sup>-5</sup> S/cm at 300°C. These plots show Arrhenius behavior for an applied constant frequency. The increase in conductivity observed with increase in frequency, however the rate of increase is not uniform throughout experimental temperature range. The rate of increase of conductivity is high at lower experimental temperatures, moderate at mid temperatures and marginal at high temperatures. Similar response is observed for other different mol% dispersed composites with different particles sizes. Fig.5 (b) is drawn between ac conductivity Vs temperature for pure Pb(NO<sub>3</sub>)<sub>2</sub>, 14mol% Al<sub>2</sub>O<sub>3</sub> (36.9µm) composite and 10mol% Al<sub>2</sub>O<sub>3</sub> (0.3µm) composite at 2MHz frequency. The maximum conductivity obtained for 10mol% Al<sub>2</sub>O<sub>3</sub> (0.3µm) composite incorporative to 14mol% Al<sub>2</sub>O<sub>3</sub> (36.9µm) composite and pure Pb(NO<sub>3</sub>)<sub>2</sub>. The variation of conductivity with mol% for two different particle sizes of dispersoids is shown in fig.5(c). It indicates maximum conductivity obtained for 10mol% Al<sub>2</sub>O<sub>3</sub> (0.3µm) in comparative to 14mol% Al<sub>2</sub>O<sub>3</sub> (36.9µm).

The response of composites at various mole percentages with different particle sizes of dispersoid for applied frequency and temperature is due to interaction between ionic salt and insulating oxide. To explain increase of ionic conductivity for heterogeneous doping systems several models are proposed in literature [8]. Out of available models, it is commonly agreed that the concept of formation of 'space charge region' between host (ionic salt) and dispersoid to explain conductivity effects in two phase mixtures [13]. SEM images clearly shows formation of clustering nature of composites. Formation of clusters, leads to formation of highly conducting channels within the composites. So it is more appropriate to explain conductivity enhancement for the present composites by considering the concept of space charge layer. According to space charge model it is assumed that ions are trapped at the interface regions due to driving force provided by dispersoids. It is reported that most of the oxide surfaces (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and SiO<sub>2</sub>) filled with nucleophilic groups [OH<sup>-</sup>] [14]. As a result the opposite charge ions formed around it to maintain charge neutrality at the interfaces which leads to formation of increased defect concentration within the space charge region. For the present host literature studies reveal that, it consists of fluorite structure [15], thereby conduction mechanism in composites due to formation anti-Frenkel defects. So the ionic conductivity due to conduction of NO<sub>3</sub><sup>-</sup> ions is more appropriate for these composites. Formation of defect concentration with in space charge region leads to increase conductivity of composites with dispersion of Al<sub>2</sub>O<sub>3</sub> insulating particles.

The drop in conductivity can be understood due to blocking effect by excess volume fraction of oxide particles at higher mole percentages. This is common phenomena in heterogeneous doping composites.



**Figure 5.** (a) Variation of conductivity at different frequencies for 10mol% Al<sub>2</sub>O<sub>3</sub> (0.3µm) composite (b) Variation of conductivity for host and different mol% of composites with different particle sizes (c) Variation of conductivity with mol%.

**4. Conclusions**

Transport properties studied on title composites with different particle sizes (0.3µm, 36.9µm) of Al<sub>2</sub>O<sub>3</sub> dispersed into Pb(NO<sub>3</sub>)<sub>2</sub>. The particle size of dispersoid influence contact surface area between host and dispersoid thereby conductivity influences. Surface reactive nature of dispersoid plays important role for enhancement of conductivity. For the present investigated systems 0.3µm particle size Al<sub>2</sub>O<sub>3</sub> shows maximum conductivity at 10mol% and also higher than 14mol% Al<sub>2</sub>O<sub>3</sub> (particle size 36.9µm) composite. The total ionic conductivity due to contribution of grain and grain boundary for the present two phase systems.

## Acknowledgement

Authors would like to thank the Head, department of physics, Osmania University for allowing to use central facilities in the department.

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