

DC Ionic Conductivity Study by Two Probe Method on $(1-X)\text{Pb}(\text{NO}_3)_2:X\text{CeO}_2$ Composite Solid Electrolyte

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ABSTRACT

Lead Nitrate composite solid electrolyte system in different compositions was synthesized by dispersing nano particles of CeO_2 in the host $\text{Pb}(\text{NO}_3)_2$. These systems were characterized by XRD, DSC and FTIR. X-ray diffraction patterns have shown peaks corresponding to pure lead nitrate and cerium oxide in all the compositions with varying intensities and no additional or shifting of peaks were observed. DSC studies indicate uniform melting point in host and dispersed composites. FTIR studies ruled out the chemical reaction between host and dispersoid. Dc ionic conductivity studies were carried out in the temperature range 100°C to 400°C. Ionic conductivity was found to increase with mole percentage of the dispersoid with increase in temperature. Maximum enhancement was observed for 8mole% dispersed system as against the pure $\text{Pb}(\text{NO}_3)_2$ in the extrinsic region of conductivity. Enhanced conductivity in dispersed systems was thought to be due to the presence of Space Charge Layer between the host and dispersoid.

Key words: Composite Solid Electrolyte, Space Charge Layer, Ionic conductivity, Fluorite structure.

INTRODUCTION

The enhancement of ionic conductivity in inorganic ionic solids by dispersion of fine insulating and insoluble particles has been reported by several authors¹. The presence of high ionic conductivity with negligible electronic conductivity of these systems has attracted a great deal of interest from industry and researchers due to their potential applications in solid state ionic devices in the recent past. These dispersed solid electrolyte materials have become promising candidates for devices in solid state technology. In the field of fast ionic conductors or super ionic conductors efforts are being continued for newer materials along with existing electrolyte materials to improve performance of solid state ionic devices.

Ionic conducting materials are broadly classified into two categories namely, cation based

conductors and anion based conductors. In both the categories of composite solid electrolytes, the non conducting materials such as Al_2O_3 , CeO_2 , SiO_2 and ZrO_2 are used as second phase particles for enhancement of conductivity. These second phase dispersoid particles are nearly insoluble in host under the preparation conditions. Several theories have been proposed to explain the enhancement of conductivity by forming a layer called Space Charge Layer (SCL) between the matrix of host and dispersoid. Due to enrichment of charge carriers at the host and interface interaction region in the matrix which forms as a highly conducting layer is treated as Space Charge Layer². Two probe method is one of the important techniques to study ionic transport parameters through dc conductivity technique³.

The enhancement of ionic conductivity in nitrates of alkali and alkaline earth dispersed composites have been reported in the literature⁴⁻⁶.

The structures of $\text{Ba}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ were reported to be fluorite type structure forming an isomorphous group⁷. They have a cubic structure with a space group $\text{Pa}\bar{3}$ and belong to T_h class and reported that anti-Frenkel disorder is predominant in these nitrates⁸. For the present study $\text{Pb}(\text{NO}_3)_2$ was chosen as the host matrix material because of non-hygroscopic and does not exhibit any solid-solid transformation. Our survey of literature indicates that no systematic investigation has not been reported so far on $\text{Pb}(\text{NO}_3)_2\cdot\text{CeO}_2$ composite system. The aim of present work is to study enhancement in host $\text{Pb}(\text{NO}_3)_2$, with the dispersion of nano size CeO_2 insulating particles, and to interpret the obtained results with suitable models/theories.

obtained from sigma Aldrich. $\text{Pb}(\text{NO}_3)_2$ and CeO_2 powders taken in particular composition were mixed in the presence of acetone for homogeneous mixing of both the constituents. Pellets of 12mm diameter and 1-2mm thickness were prepared by using steel die by applying a pressure of 0.26 GPa and they were sintered at 300°C for about 15 hours. Silver paint was employed to ensure good electrical contacts with electrodes. To study ionic conductivity by two probe method, pellets were mounted in between the electrodes of sample holder and annealed at 100°C for 3hrs prior to the actual data recording. The temperature was measured with the help of Cr-Al thermocouple. A fixed voltage of 1.5V was applied and the current measurement was done by using Agilent digital multi meter.

Experimental procedure

Single crystals of $\text{Pb}(\text{NO}_3)_2$ were grown by solution growth technique from the starting material (99% purity) which was obtained from Merck chemicals (USA). The crystals obtained by this method were ground in an agate mortar and then sieved to obtain uniform particle size ($> \mu\text{m}$ size). The dispersoid CeO_2 (nano size $< 25\text{nm}$) used was

Structural characterizations were performed on Expert Pro X-ray Diffractometer (XRD) with $\text{CuK}\alpha$ radiation and Bruker Optics, Germany Tensor 27 model spectrometer (FTIR) respectively. The thermal properties have been carried out by DSC on Q20, a computer interfaced system, with continuous heating rate of $10^\circ\text{C min}^{-1}$.

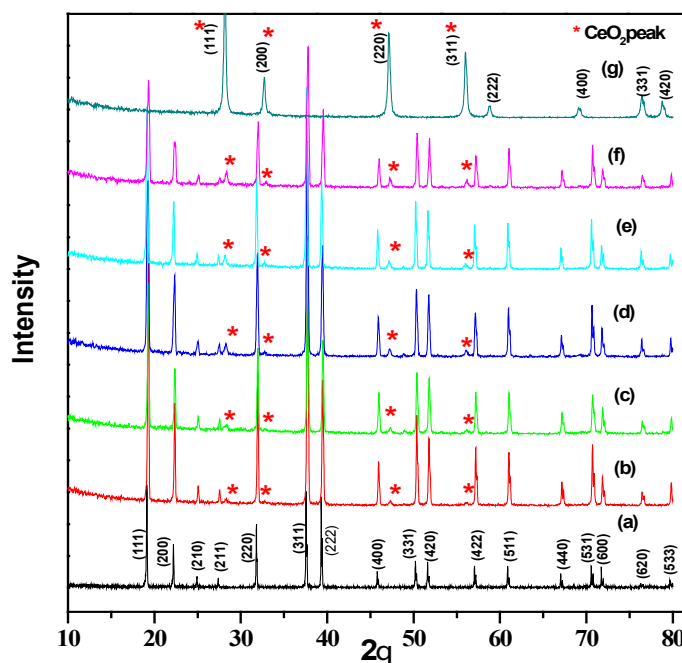


Fig.1 : X-ray diffraction patterns of (a) Lead Nitrate pure (b) Lead Nitrate pure + 4 mole % of CeO_2 (c) Lead Nitrate pure + 6 mole % of CeO_2 (d) Lead Nitrate pure + 8 mole % of CeO_2 (e) Lead Nitrate pure + 10 mole % of CeO_2 (f) Lead Nitrate pure + 14 mole % CeO_2 (g) Pure CeO_2

RESULTS AND DISCUSSION

X-ray diffractograms of various compositions are shown in Fig.1 and peaks indicate that the

system is in crystalline form and no new peaks were noticed except those belong to host and dispersoid which reveals that CeO_2 remains as a separate phase in $(1-x)\text{Pb}(\text{NO}_3)_2:\text{xCeO}_2$ composite. This XRD

Table1: Comparison of calculated XRD data and reported JCPDS data

Calculated data from 2θ		Reported JCPDS data		Crystallite size Calculated from XRD(nm)
Lead Nitrate Pure (JCPDS 36-1462)				
2θ	(hkl)	2θ	(hkl)	
19.13	111	19.56	111	149.23
22.2	200	22.61	200	190.23
24.92	210	25.33	210	155.37
27.37	211	27.78	211	99.19
31.79	220	32.2	220	277.14
37.67	311	37.94	311	242.89
39.43	222	39.69	222	373.33
45.91	400	46.15	400	276.12
50.33	331	50.58	331	301.66
51.62	420	51.99	420	310.16
57.19	420	57.39	420	266.54
61.04	511	61.24	511	298.28
67.2	440	67.34	440	369.79
71.11	531	70.88	531	460.71
76.3	620	76.61	620	813.1
Cerium Oxide Pure (JCPDS 81-0792)				
28.15	111	28.54	111	72.93
32.7	200	33.07	200	52.32
47.15	220	33.07	220	43.16
56.03	311	56.33	311	78.8
58.79	222	59.07	222	84.97
69.17	400	69.4	400	99.06
76.47	331	76.68	331	125.2
78.81	420	79.06	420	124.01

Table 2: Ion Transport parameters Viz. the Pre-exponential factor (σ_0) and the Activation Energy (E_a) of $\text{Pb}(\text{NO}_3)_2:\text{CeO}_2$ composites.

Mole percentage	Temperature range ($^{\circ}\text{C}$)	Activation Energy (eV)	Pre exponential factor (σ_0)
0	250-350	0.56	1.36
4	250-350	0.46	3.68
6	250-350	0.29	1.4
8	250-350	0.19	0.41
10	250-350	0.37	1.99
14	250-350	0.51	3.33

is observed nearly at 454°C. The endothermic peak remains unaffected, except slight shifting with increase of dispersoid concentration. This suggest that there is no solubility of CeO_2 in $\text{Pb}(\text{NO}_3)_2$ and thus $\text{Pb}(\text{NO}_3)_2\text{:CeO}_2$ system form a two phase system, which is in conformity with XRD results. DSC curves of pure Lead Nitrate and its various compositions shows no phase transitions occur before its melting. The Endothermic peaks in pure Lead Nitrate after melting point indicates decomposition nature of it.

FTIR spectra of pure and composite samples have been recorded in the wave number range 600-4000 cm^{-1} (shown 600-2500 cm^{-1}) shown in Fig.3. FTIR is a powerful tool to identify functional groups present in composites by monitoring the vibrational energy levels of molecules and to identifying the nature of bonding between molecules ¹⁰. The spectrum of $\text{Pb}(\text{NO}_3)_2$ shows a strong absorption band at 721 (ν strong), 803(ν strong), 1013,1072,1287,1770 cm^{-1} . These values are in good agreement with earlier reported values and these bands are ascribed to presence due to isotopically different NO_3^- ions ¹¹. And beyond 2600 cm^{-1} a few very weak absorptions are observed (not shown in graph) are due to weak interaction of hydrogen bond with pure Lead Nitrate. The other compositions also show similar absorption peaks at corresponding wave numbers, except with slight fluctuation at 1287 cm^{-1} .

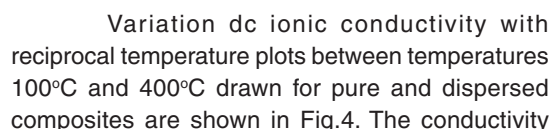


Fig. 2 : DSC Plots of pure and various compositions of CeO₂



data were represented by Arrhenius relation given by $\sigma = \sigma_0 \exp(-E_a/K_B T)$, where σ_0 is pre-exponential factor, E_a is activation energy, K_B is Boltzmann's constant and T is absolute temperature. From conductivity graph it is clear that, while increasing the concentration of CeO_2 the enhancement of conductivity was found increase and reaching to a saturation value at 8mole% of dispersoid and there onwards decrement of conductivity was recorded. The maximum enhancement of conductivity recorded was about one order with respect to pure $\text{Pb}(\text{NO}_3)_2$ system. Fig.5 shows variation of conductivity with different mole% of CeO_2 dispersed systems for few typical temperatures indicates a systematic variation of conductivity as a function of CeO_2 . Similar

observations made on some anion-Frenkel defect systems such as CaF_2 , PbF_2 , $\text{Ba}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ ¹²⁻¹⁶ where the conductivity varied systematically as function of dispersoid for different insulating particles.

From the above observation, it is clear that dispersion of CeO_2 in host $\text{Pb}(\text{NO}_3)_2$ responsible for considerable enhancement in conductivity. To interpret the enhancement in conductivity with CeO_2 dispersion in host $\text{Pb}(\text{NO}_3)_2$, Random Resistor Network [RRN] model taken into account, out of available models.¹⁷ According to this model, from the macroscopic point of view at interface region a highly conducting layer exist between host and dispersoid and predicts the existence of two critical concentrations, namely, P_c' and P_c'' . At P_c' the high conducting layers begin to form connected pathways and at P_c'' the connected pathways get disrupted as they begin to form closed loops due to increased concentrations of insulating bonds. Fig.5 shows that conductivity raises initially, passes through maximum at 8mole% of CeO_2 composite and subsequently drops to higher mole% of CeO_2 composite. This appears to be consistent with RRN model for $(1-X)\text{Pb}(\text{NO}_3)_2:X\text{CeO}_2$ composite system.

The transport parameters are given in Table.2 for all $\text{Pb}(\text{NO}_3)_2\text{-CeO}_2$ composites studied in this work. The variation of activation energy (E_a) is consistent with the generally observed relation for ionic conductors i.e. the increase in conductivity is almost invariably associated with a decrease in activation energy. The activation energy initially decreases from pure $\text{Pb}(\text{NO}_3)_2$ to 8mole% of CeO_2 composite, where conductivity is maximum in

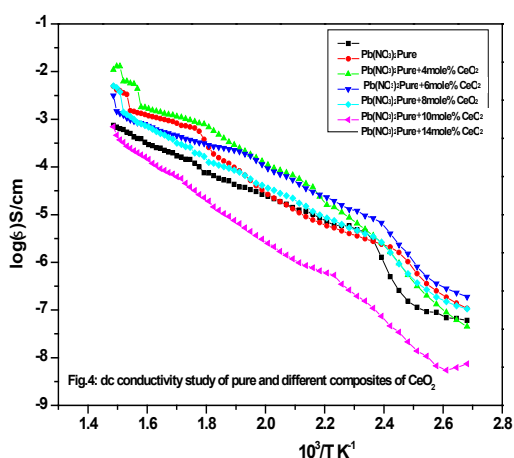


Fig.4: dc conductivity study of pure and different composites of CeO_2

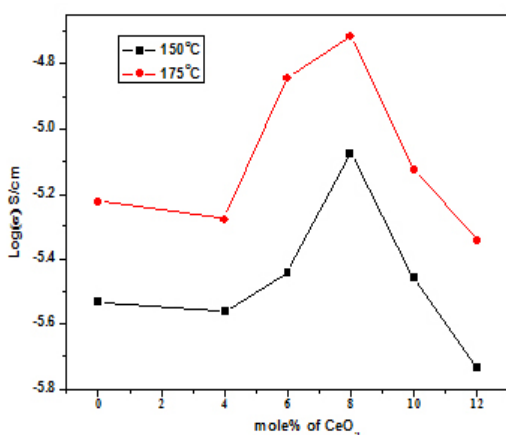


Fig. 5: mole% of CeO_2 Vs $\text{Log}(\sigma)$ at different temperatures

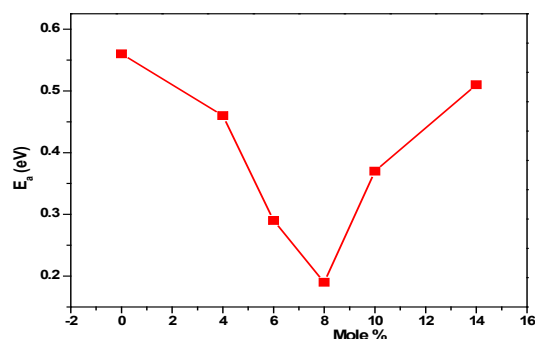


Fig. 6: Variation of Activation energy with different mole percentages of CeO_2

extrinsic region and there after enhancement of activation energy is observed, where the conductivity recorded decrement. The variation of activation energy (E_a) vs. mole percentage is shown in Fig.6.

In composite solid electrolytes, it is widely believed that the presence of excess defects at the host matrix and dispersoid particle interface contributes to high conductivity in composite solid electrolytes. Formation of space charge layer between host and dispersed particles is thought to be responsible for conductivity enhancement process. In Fluorite structured ionic solids, ionic mobility requires anti-Frenkel defects^{7, 18}. The enhancement in conductivity with heterogeneous dispersion can be explained within the frame work of space charge model proposed by Maier's semi quantitative model¹⁹. Macroscopically generation of excess anion vacancies at matrix-particle interface due to formation of space charge layer is more appropriate for this composite solid electrolyte system.

CONCLUSION

XRD and DSC studies confirm that the composite $(1-x)\text{Pb}(\text{NO}_3)_2 \cdot x\text{CeO}_2$ is biphasic system. FTIR studies show the presence of NO_3^- ion. The maximum enhancement of conductivity is about one order of magnitude for 8mole% dispersed electrolyte with respect to host $\text{Pb}(\text{NO}_3)_2$. The conductivity enhancement in extrinsic region due to formation of space charge layer between host $\text{Pb}(\text{NO}_3)_2$ and CeO_2 is thought to be responsible. With the formation of space charge an internal field developed at interface which causes acceleration in transport of conducting ions.

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