Enhancement of dc ionic conductivity with particle size of dispersoid in xKNO$_3$ – $_{1\text{-}x}$Ba(NO$_3$)$_2$

S. Shashi Devi [1], T.Vijay Kumar[3], S.Narender Reddy[2], A.Sadananda Chary[3]

[1]Department of physics, University college of Science, Osmania University, Hyderabad-500007, Andhra Pradesh, (INDIA).
[2]Department of physics, University college of Engg, Osmania University, Hyderabad-500007, Andhra Pradesh, (INDIA).
[3]Department of physics, University college of Science, Osmania University, Hyderabad-500007, Andhra Pradesh, (INDIA).

Tel :+ 91-9676101151

E-mail : devishashi5@gmail.com

Abstract

The ionic conductivity of xKNO$_3$ – $_{1\text{-}x}$Ba(NO$_3$)$_2$ mixed crystals, σ_x, has been measured from nearly 360K to close to their melting points. The conductivity in the extrinsic region of Ba(NO$_3$)$_2$ increased as the m/o of KNO$_3$ is increased up to 91m/o and then for 95 m/o the conductivity falls. The further enhancement in conductivity of about three orders is found with the dispersion of Al$_2$O$_3$ to the 91 m/o of KNO$_3$ in Ba(NO$_3$)$_2$. DSC and XRD studies reveal that no new phase is formed. The enhanced conductivity is attributed to the excess cation vacancies generated in the space charge region of the matrix phase surrounding the alumina particles as a consequence of stabilization of cations at the dispersoid surface due to internal absorption.

INTRODUCTION:

The conductivity of many ionic conductors is increased by up to several orders of magnitude when the material is prepared as a composite with a finely dispersed second phase. Ionic conductors containing dispersed second phase particle (DSPP) are called "composite ionic conductors". The addition of DSPP to normal ionic conductors causes an increase in the conductivity. This phenomenon has attracted a great deal of attention from both chemists and physicists, since the pioneer work by Liang in 1973[1]. Conductivity of composites is governed mainly by the ionic transport via interface regions of the ionic crystal [2]. In most cases, the second phase consists of a non conducting material

such as Al$_2$O$_3$ or SiO$_2$ which is insoluble in the host material under the fabrication conditions. Since the discovery of the enhancement in ionic conductivity in LiI due to dispersion of alumina [1], several other

researchers have observed the enhancements in various other composites such as polymer electrolytes [3], electrolytes formed by eutectic compounds [4], dispersed solid electrolyte systems of Silver, Lithium, Calcium halides[5], dispersed systems of some alkali nitrates and halides [6-10], silver halides dispersed with different insulating particles [11] and in many other super ionic solids dispersed with insulating second phase [12], alkaline earth nitrate based dispersed systems[13] and in many other cation and anion based conducting solid electrolyte systems[14-20]. Composite solid ionic conductors may not only offer enhanced ionic conductivity, but also superior mechanical properties and low cost. In the previous study we have seen increase in conductivity in the extrinsic region of $Ba(NO_3)_2$ as the m/o of KNO_3 increased up to 91 m/o and it showed fall of conductivity for 95 m/o. In the present work, we have aimed at enhancing the conductivity of 91 m/o of KNO_3 in $Ba(NO_3)_2$ by studying the influence of composition , and form of alumina with different particle size. An attempt has been made to identify the conductivity enhancement mechanisms operating in this system.

Experimental :

$Ba(NO_3)_2$ and KNO_3 were from Qualigens fine chemicals (SQ) of 99.5% purity, is first dissolved in double distilled water and then allowed to grow single crystals. The crystals so obtained are crushed in an agate mortar, sieved and the average size of the particles was estimated to be nearly 50μm. The dispersoid Al_2O_3 of different particle sizes viz 0.06μm, 0.3μm, 1μm of 99.8% was used, as received from Adolf Meller Co. USA. Both the powders taken in a particular composition were mixed in the presence of acetone for an hour, manually, until the acetone got evaporated completely. Pellets were prepared by using a steel die at a pressure of 0.89GPa and were sintered at 2/3 of their melting point for 24 hrs. After cleaning the surfaces an electrode material (silver) was applied for good electrical contact.

Pellet was then mounted in a spring loaded sample holder and annealed at about 150°C for 4 hrs before the data was recorded. A constant rate of heating of 2° C/min was maintained throughout the experiment. The temperature was recorded by Cr-Al thermocouple. A small dc voltage of 1.5V was applied across the sample and the current was measured on a digital dc nano ammeter. Data was recorded on at least three to four samples each of pure and mixed pellets, running a minimum of three cycles on each sample. Similar experimental conditions were maintained for all the samples and the data showed a reasonably good reproducibility.

Results and discussion :

X-ray diffraction data, on pure mixed system ($Ba(NO_3)_2$ - 91 m/o of KNO_3) and dispersed with 1.1, 5.3, 10.8 and 20 mole percentages of Al_2O_3(0.06μm) are shown in Fig1. On comparing the patterns of pure mixed system and dispersed systems in figure 1 that there are no new peaks which indicate that no solid solution is formed in these systems. Such observations in case of NaCl- Al_2O_3 [20], KCl- Al_2O_3 [21], CsCl- Al_2O_3 [22], and $NaNO_3$- Al_2O_3 [23] solid electrolyte systems have also ruled out the formation of solid solutions in them.
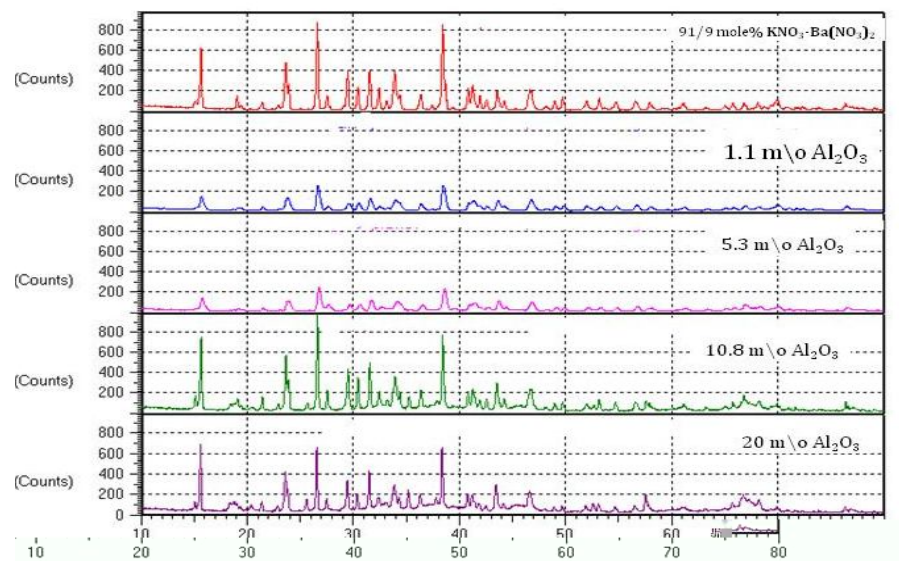
Fig 1: X-ray powder diffraction for 0.06µm Al$_2$O$_3$.

DSC traces of all the said compositions are shown in figure 2. From the figure it is clear that the melting point is practically unaffected in the dispersed systems. Two small humps are observed one at nearly 133°C and other at 210°C [24]. The first hump is a known transition and the second could be due to the formation of an amorphous phase within the space charge layer that is expected to form between the host material and the dispersoid particles [25-27]. Similar results were seen when the same system was dispersed with other particle in 0.3µm Al$_2$O$_3$ and 1µm Al$_2$O$_3$. All these results indicate that no new structure is formed in the dispersoid material and the melting point is unaffected.
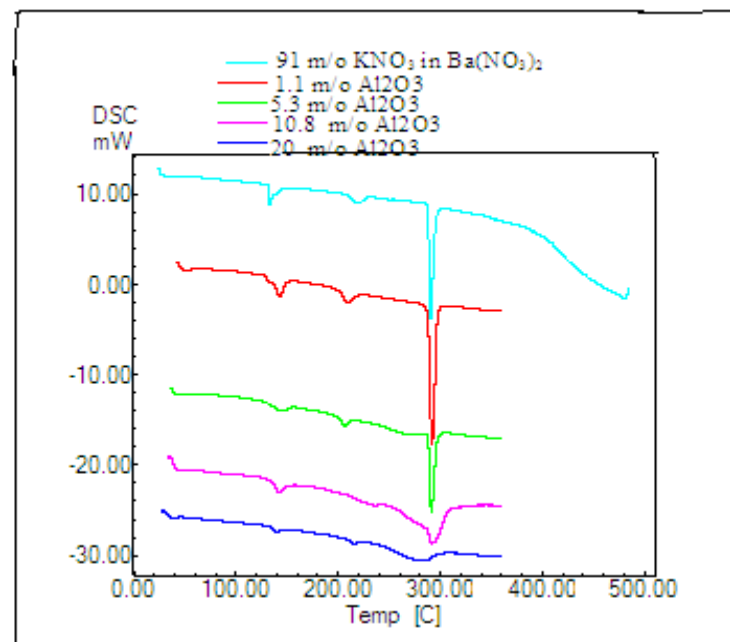

Fig 2: DSC Curves for 0.06µm Al$_2$O$_3$.

The temperature dependence of dc ionic conductivity from room temperature to nearly the melting point of pure and dispersed with various particle sizes(0.06µm, 0.3µm, 1µm) of Al$_2$O$_3$ are shown in figures 3,4 and 5 respectively.

Conductivity in pure(91 m/o of KNO$_3$ in Ba(NO$_3$)$_2$) can be seen to increase linearly with temperature up to its transition temperature(137°C)

followed by a bend in the conductivity plot. In the dispersed systems the enhancement in conductivity is observed to increase with mole percentage of Al_2O_3 for all particle sizes.
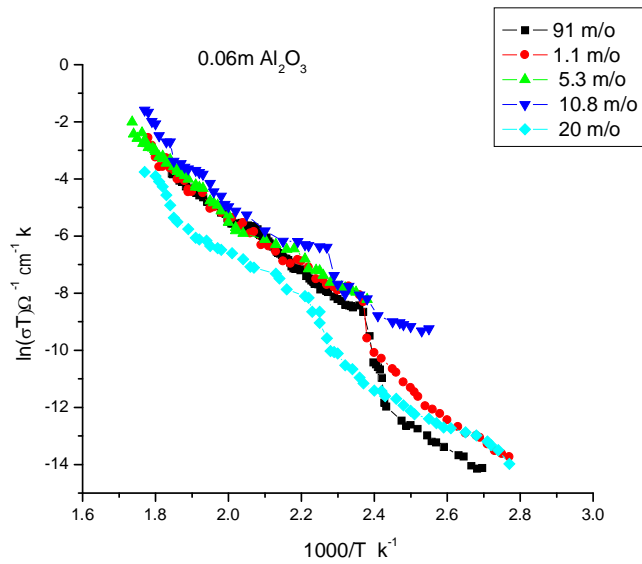

Fig 3. ln(σT) versus 1000/T for 91 m/o of KNO$_3$ in Ba(NO$_3$)$_2$ and different mole percentages of 0.06μm Al$_2$O$_3$.
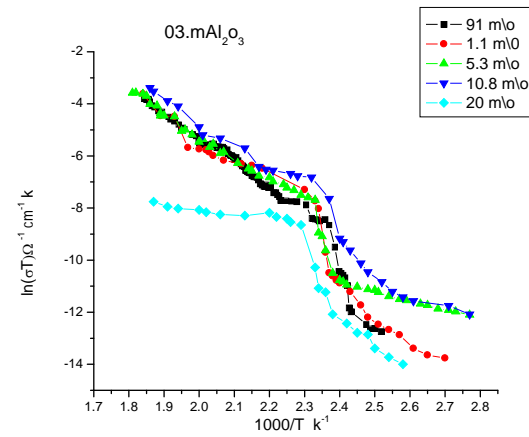
Fig4. Ln(σT) versus 1000/T for 91 m/o of KNO$_3$ in Ba(NO$_3$)$_2$ and different mole percentages of 0.3μm Al$_2$O$_3$.
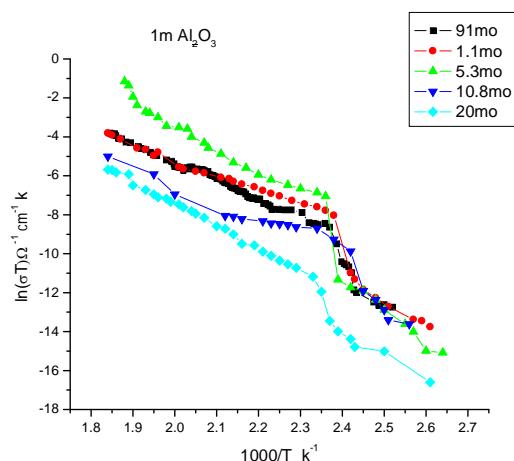
Fig5. ln(σT) versus 1000/T for 91 m/o of KNO₃ in Ba(NO₃)₂ and different mole percentages of 1μm Al₂O₃.

In case of 0.06μm Al₂O₃ (fig. 3) the enhancement in conductivity is observed to increase with mole percent with a threshold at 10.8 mole percent where from enhancement starts falling with further increase in mole percent i.e for 20 mole percent. The maximum enhancement at 10.8 mole percent is observed to be about 1 order of magnitude with respect to pure mixed system in the extrinsic conduction region. In case of 0.3μm Al₂O₃ (fig. 4) the enhancement in conductivity is observed to increase with mole percent with a threshold at 10.8mole percent where from enhancement starts falling with further increase in mole percent i.e for 20 mole percent. The maximum enhancement at 10.8 mole percent is observed to be about 1 order of magnitude with respect to pure mixed system in the extrinsic conduction region. And in case of 1 μm Al₂O₃ (fig. 5)

the enhancement in conductivity is observed to increase with m/o with a threshold at 5.3 mole percent where from enhancement starts falling with further increase in mole percent. The maximum enhancement at 5.3 mole percent is observed to be about 3 order of magnitude with respect to pure mixed system in the extrinsic conduction region.

Conductivity versus m/o of the 0.06μm Al₂O₃, 0.3μm Al₂O₃ and 1 μm Al₂O₃ at different temperatures are shown in figures 6, 7 and 8 respectively. The maximum enhancement in conductivity occurs at 10.8 m/o of alumina in 0.06μm Al₂O₃, 10.8 m/o of alumina in 0.3μm Al₂O₃, and 5.3 m/o of alumina in 1μm Al₂O₃. It may be noticed from the plots the conductivity values at 10.8 m/o in 0.06μm Al₂O₃ are 7.68 Ω^-cm^{-1} k, 6.3 Ω^-cm^{-1} k, 5.82 Ωcm^{-1} k and at 10.8 m/o in 0.3μm Al₂O₃ are 6.82 Ω^-cm^{-1} k, 6.56Ω^-cm^{-1} k, 5.7 Ω^-cm^{-1} k and 5.3 m/o in 1μm Al₂O₃ are 6.86 Ω^-cm^{-1} k, 5.95Ω^-cm^{-1} k, 4.87 Ω^-cm^{-1} k respectively.
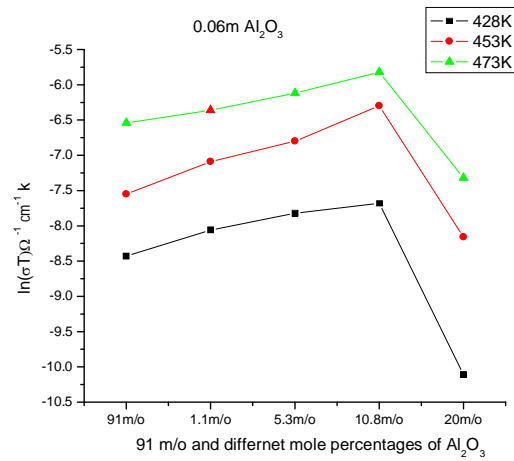
Fig6. Conductivity versus m/o of the 0.06μm Al$_2$O$_3$ at different temperatures.
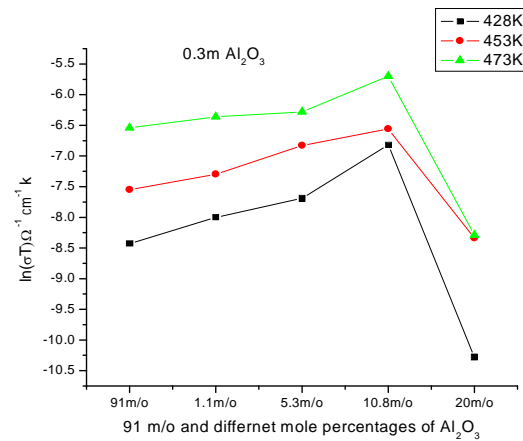

Fig7. Conductivity versus m/o of the 0.3μm Al$_2$O$_3$ at different temperatures.
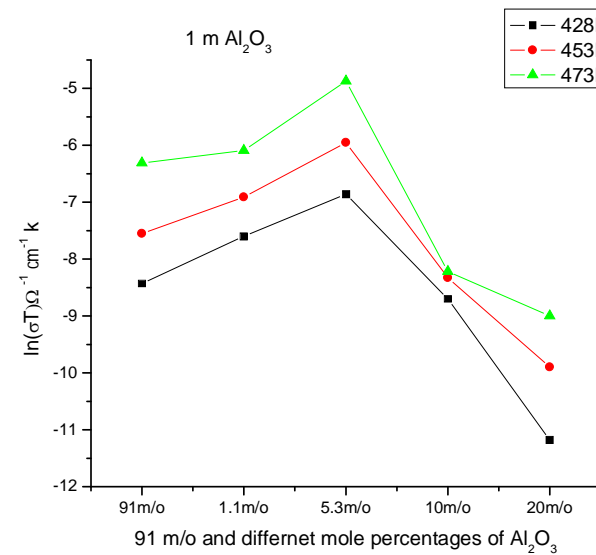
Fig8. Conductivity versus m/o of the 1μm Al$_2$O$_3$ at different temperatures.

The observed enhancement in the conductivity in these dispersed systems are interpreted in terms of the formation of space charge layer at the interface between the host matrix and the dispersoid. The mechanism of formation of space charge layer is understood as follows. The defect species, which is involved in ionic conduction of the matrix, may be repelled from or attracted to the interface resulting in the formation of a

space charge region [11, 13, 28, 29]. Thus in the present system being a Frenkel solid, if the cations are attracted to the interface, the vacancy concentration in the space charge region will be increased relative to the bulk value. Repulsion of cations by the inert phase will increase the concentration of interstitials in the space charge region. Thus space charge region is associated with an increased concentration of defects. Thus additional contribution to the total conductivity from the space charge region accounts for the enhancement in ionic conductivity. The activation energies calculated for pure and dispersed systems erived from $\log \sigma T$ versus 1000/T plots are shown in table-I.

TABLE - I

Mole percentages	0.06μm Al_2O_3	0.3μm Al_2O_3	1μm Al_2O_3
91 m/o of KNO_3 in $Ba(NO_3)_2$	0.8ev	0.8ev	o.8ev
1.1 m/o	0.6ev	0.78ev	0.66ev
5.3 m/o	0.67ev	0.79ev	0.5ev
10.8 m/o	0.41ev	0.64ev	0.82ev
20 m/o	1.11ev	0.85ev	1.47ev

The activation energies are calculated in the extrinsic region of temperature. It may be noticed from the table that the activation energy is minimum for 10.8m/o in case of 0.06μm Al_2O_3 and 0.3μm Al_2O_3. It is found

minimum for 5.3 m/o Al_2O_3 in 1μm Al_2O_3 where we got the maximum enhancement in conductivity. These results lead to the conclusion that the enhanced conductivity in 91 m/o of KNO_3 in $Ba(NO_3)_2$- Al_2O_3 composites is due to the increased concentration of cation vacancies [30-31].

When the concentration of Al_2O_3 is low, all the particles are completely surrounded by the host matrix. Conductivity of the system increases with increasing concentration of Al_2O_3 because it amounts to the increase in the highly conducting bonds between dispersoid particle and host matrix. Subsequently, when the total volume of the interface layers is most effectively linked together, the total number of highly conducting bonds become maximum, consequently sample would show maximum conductivity.

As the concentration of Al_2O_3 further increase, Al_2O_3 particles cannot be completely covered by the interface layers simply because the available host cannot envelope all the Al_2O_3 particles, number of non-conducting bonds increase and therefore conductivity decreases[11,29,32-34].

CONCLUSIONS

The composite solid electrolyte 91 m/o of KNO_3 in $Ba(NO_3)_2$ dispersed with alumina has been investigated through XRD, DSC and two probe dc ionic conductivity techniques. The composite containing 10 m/o of 0.06μm Al_2O_3 and 0.3μm Al_2O_3 has the maximum conductivity of about 1 order of magnitude higher than of 91 m/o of KNO_3 and in case of 1μm Al_2O_3 the maximum enhancement in conductivity of 3 orders is found in 5.3 m/o Al_2O_3. The enhancement of conductivity is interpreted in terms of

the formation of space charge region between the host matrix and dispersoid. The formations of cation vacancies are more probable than the interstitials in the interfacial region.

ACKNOWLEDGMENTS

REFERENCES

[1] A.R.West; Solid state Chemistry and its Applications, John Wiley and Sons, New York, **(1984).**

[2] C.C.Liang; J Electrochem. Soc.,**120,** 1298**(1973).**

[3] W.Wieczorek; Solid State Ionics **53-56,** 1064 **(1992).**

[4] J.B. Wagner Jr., Mater; Res. Bull. **15**, 1691 **(1980)**.

[5] A.K. Shukla, N. Vaidehi, K.T. Jacob; Proc. Ind. Acad. Sci. (Chem.Sci) **96** 533 **(1986)**.

[6] N.F. Uvarov, E.F Hairetdinov, N.B. Bratel; J. Electrochem. **29** 1231 **(1993)**.

[7] N.F. Uvarov, V.P. Isupov, G.V. Lavrova, E.F. Hairetdinov; Solid State Ionics **74** 15 **(1994)**.

[8] V.G Ponomareva, N.F. Uvarov, G.V. Lavrova, E.F. Hairetdinov; Solid State Ionics **55** 83 **(1996)**.

[9] V.G. Ponomareva, G.V. Lavrova; Solid State Ionics **55** 83 **(1996)**.

[10] N.F. Uvarov, I.V. Skobelev, B.B. Bokhonov, E.F. Hairetdinov, J.Mater; Synth. Process. **4** 391 **(1996)**.

[11] J.Maier; Prog. Solid State Chem. **23** 171 **(1995)**.

[12] R.C. Agarawal, R.K. Gupta, J. Mater; Sci. **34** 1131 **(1999)**.

[13] S. Narender Reddy, A. Sadananda chary, Ch. Gopal Reddy, M.V. Madavarao Rao; Mater. Lett. **58** 2949 **(2004)**.

[14] G.V. Lavrova, V.G. Ponomareva, E.B. Burgina; Solid State Ionics **176** 767 **(2005)**.

[15] B. Kumar, C. Chen, Chakrapani, Varanasi, J.P. Fellner; J. Power Sources **147** 128 **(2005)**.

[16] J.E. Diosa, A. Solis, R.A. Vargas, B.E. Mellander; Solid State Ionics **175** 459 **(2004)**.

[17] P.S. Anantha, K. Haraharan; J. Phys. Chem. Solids **64** 1131 **(2003)**.

[18] S. Narender Reddy, A. Sadananda chary, K.Saibabu, T. Chiranjivi; J. Mater. Sci. Lett. **11** 980 **(1992)**.

[19] K. Shahi, Ashok Kumar, Mater; Res. Bull. **31**(7) 877 **(1996)**.

[20] K. Shahi, Ashok kumar Kumar, in: B.V.R. Chowdhary, et al.; (Eds.), Solid State Ionics: Mater. Appl., World Pub. Co., 433 **(1992)**.

[21] K. Shahi, Ashok kumar Kumar, in: B.V.R. Chowdhary et al.; Solid State Ionics Materials, World Scientific Pub.Co., **14-153 (1994).**

[22] Ashok kumar, K. Shahi; Material Research Bulletin, **31(7),** 877-886 **(1996)**.

[23] P.S. Anantha, K. Hariharan; J.Of Physics and chemistry of Solids, **64,** 1131-1137 **(2003)**.

[24] S. Shashi Devi, B.L.Aruna , S.Narender Reddy, A.Sadananda Chary; Pelagia Research Library, **3(6),** 1337-1342 **(2012)**.

[25] N.F. Uvarov, P.Vanek et al.; Solid State Ionics, **90**, 201-207 **(1996).**

[26] N.F. Uvarov, P.Vanek, M.Savinov, V.Zelenzy, V.Studnicka, J.Pezelt; Solid State Ionics**, 127**, 253-267 **(2000).**

[27] N.F. Uvarov, P.Vanek,; J.of Material Synthesis and Processing, **8(5/6),** 319-326 **(2000).**

[28] M.V. Madavarao Rao, S. Narender Reddy, A. Sadananda chary; Physica B: Condensed Matter, **362,** 193-198 **(2005).**

[29] M.V. Madavarao Rao,; Ph.D. Thesis, Osmania University, India, **(2004).**

[30] Prakash Gopalan, P.Bhandari, A.R.Kulkarni, V.R.Palkar; Materials Research Bulletin, **37,** 2043-2053 **(2002).**

[31] M.V. Madavarao Rao, S. Narender Reddy, A. Sadananda chary; Physica B: Condensed Matter, **369**, 181-186 **(2005)**.

[32] Shusheng Jiang, J.Bruce Wagner, (Jr.); J.Phys.Chem.Solides, **56(8),** 1101-1111 **(1995)**.

[33] Shusheng Jiang, J.Bruce Wagner, (Jr.); J.Phys.Chem.Solides, **56(8),** 1113 **(1995).**

[34] M.V. Madavarao Rao, S. Narender Reddy, A. Sadananda chary; J.of Non-Crystalline Solids, **352(2)**, 155-159 **(2006).**