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Impedance spectroscopy studies of PVA/PEG based polymer blend electrolytes

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ABSTRACT

A magnesium ion conducting polymer blend electrolytes based on polyvinyl alcohol (PVA) and polyethylene glycol (PEG) complexed with magnesium acetate ($(CH_3COO)_2Mg$) was prepared using solution cast technique. The typical complex impedance spectrum of the optimum sample at different temperatures comprises of a broadened semicircle in the high frequency region followed by a tail in the lower frequency region. The ionic conductivity increased with increasing dopant concentration. The 30 wt. % $(CH_3COO)_2Mg$ doped system has a maximum conductivity of 3.23×10^{-5} S/cm at 373 K. The frequency dependent ac conductivity of optimum conducting composition (OCC) at different temperatures shows a frequency independent plateau in the low frequency region and exhibits dispersion at higher frequencies. The ionic conductivity of polymer blend electrolyte was measured by varying the temperature ranging from 303 to 373 K. The temperature dependence of ionic conductivity reveal that conduction mechanism is Arrhenius type thermally activated process. The dielectric and modulus studies were studied at different temperatures.

KEYWORDS

Polymer blend;
Polyvinyl alcohol;
Polyethylene glycol;
Ionic conductivity;
Magnesium acetate.

INTRODUCTION

Now a days polymer materials are of great interest because, when it is combined with suitable metal salts, they give electrolytes which are useful for the development of advanced high energy electrochemical devices, e.g. batteries, fuel cells, electrochromic display devices, photo electrochemical solar cells, etc[1-4]. Compared with systems based on liquid or gel electrolytes solid polymer electrolytes are much more stable and have long life characteristics. Poly (ethylene) oxide (PEO) has been a popular choice of polymer matrix for magnesium ion conductors[5-8], but very less work has done based on polymer blends.

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties[9]. The significant advantages of polymer blends are often exhibit properties that are superior compared to the properties of each individual component polymer[10]. However, the manifestation of superior properties depends upon the miscibility of blend. Blending can, however, have profound and sometimes unexpected effects on thermal stability, which cannot simply be predicted on the basis of behavior of the components and their relative proportions[11].

In the present work, the Mg^{2+} ion conducting polymer blend electrolytes based on polyvinyl alcohol and Polyethylene glycol complexed with $(CH_3COO)_2Mg$ have been prepared by solution cast technique. The polymer electrolytes have been characterized by complex impedance spectroscopic analysis in the temperature range 303-373 K.

EXPERIMENTAL

Polyvinyl alcohol (PVA) from CDH, India has molecular weight 1,25,000 and polyethylene glycol (PEG) from CDH, India has molecular weight 4,000 were used as received. Equal quantity of PVA and PEG (50/50) by weight was added to doubly distilled water with stirring the solution at room temperature to complete dissolution. Required quantity (0, 10, 20,30 and 40 wt. %) of $(CH_3COO)_2Mg$ was also dissolved in doubly distilled water and added to the polymeric solution with continuous stirring for about 12 hours. The solution was poured into cleaned Petri dishes and evaporated slowly at room temperature under vacuum to ensure removal of the solvent traces. After drying, the films were peeled from Petri dishes and kept in vacuum desiccators until use. The thickness of the obtained films was in the range of 90–120 μm.

When the polymer electrolyte films have formed they were placed between the blocking stainless steel electrodes of the conductivity cell with leads connected to a HIOKI 3532-50 LCR meter interfaced to a computer for conductivity measurements. The measurements were made over a frequency range of 60 Hz to 5 MHz at different temperatures. The temperature dependent conductivity studies were carried out for PVA-PEG-x wt. % of $(CH_3COO)_2Mg$ (x= 0, 10, 20, 30 and 40 wt. %) polymer electrolyte films. Conductivity measurements were carried out over the same frequency range for temperatures ranging from room temperature to 373 K. The conductivity cell with connecting lead wires were placed in an oven with temperature control facilities.

RESULTS AND DISCUSSION

Impedance analysis

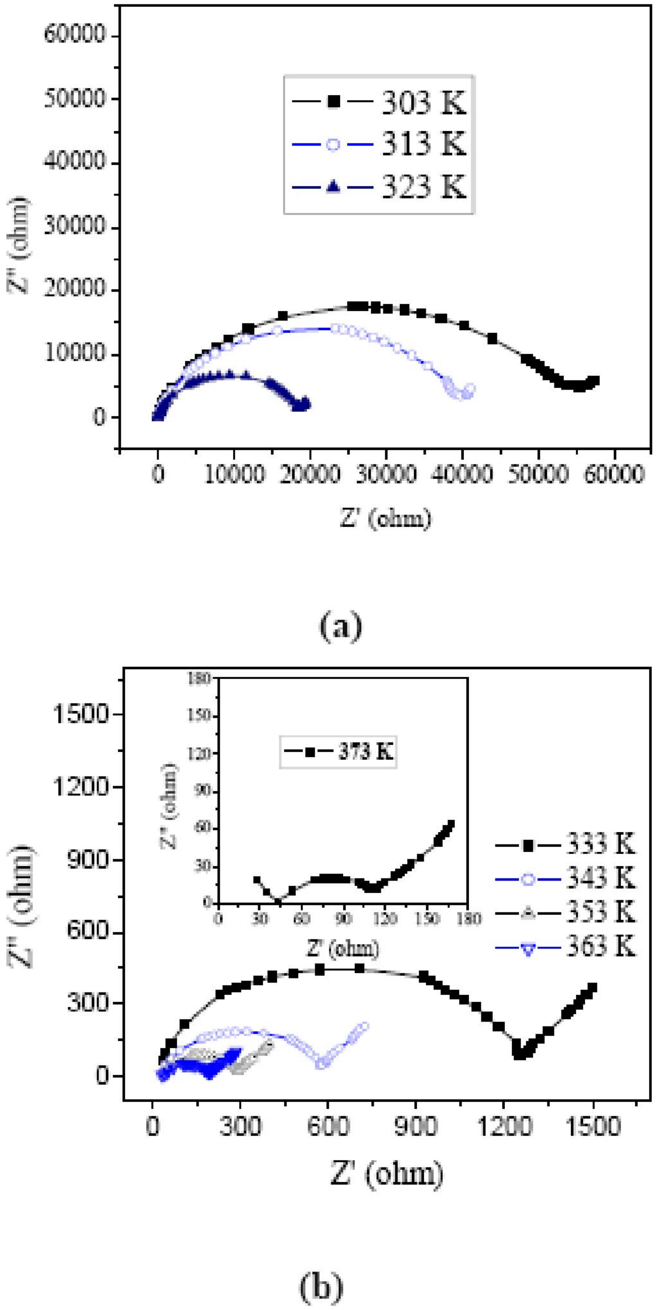

Figure 1 : Complex impedance plots for the (PVA-PEG-30 wt % of $(CH_3COO)_2Mg$) polymer electrolyte (a) at low temperatures from 303 K to 323 K (b) at high temperatures from 333 K to 373 K (inset at 373 K).

Figure 1a and 1b shows the typical result of the complex impedance plots for PVA-PEG-$(CH_3COO)_2Mg$ (50-50-30 wt %) at different temperatures.

This plot shows a high frequency semicircle which corresponds to the bulk resistance and a spike (a lower frequency region) which is due to the effect of electrode/electrolyte interface. If the electrodes and electrode/electrolyte interface were ideal, vertical spikes at the low frequency end should have been obtained. Semicircles are significantly broadened and electrode spikes at the low frequency end of the spectrum are distinctly non-vertical, as it is evident from Figure 1. Spikes inclined at an angle of less than 90° to the real axis are obtained in the present study, and this is due to roughness of the electrode/electrolyte interface[3, 12]. Ionic conductivity was determined from the bulk resistance (R_b) where the semicircle crossed the Z'-axis. It can be observed from the plots that as the temperature increases, the diameter of the semi-circle at higher frequency decreases implying that the bulk resistance (R_b) decreases. By knowing the bulk resistance (R_b) along with the dimensions of the sample, the conductivity of the sample has been calculated by using the relation $\sigma = L/R_bA$, where L is the thickness of the sample and A is the electrode area respectively.

Conductivity analysis

The variation of logarithmic conductivity as a function of magnesium acetate concentration in PVA-PEG-$(CH_3COO)_2Mg$ at various temperatures is given in Figure 2.

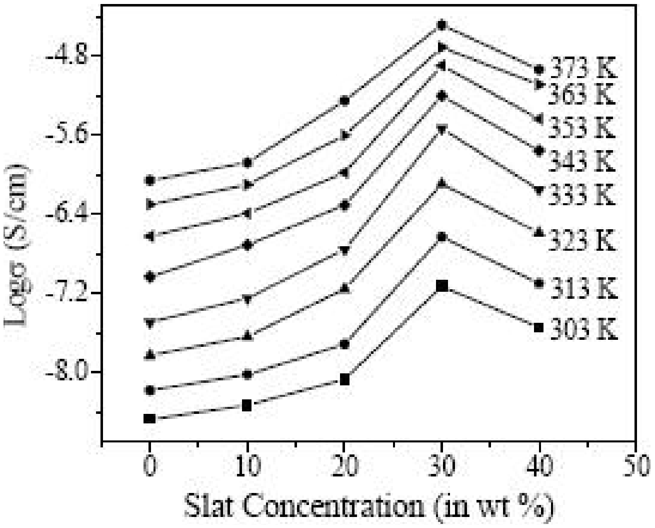

Figure 2 : Composition dependence conductivity of PVA-PEG-$(CH_3COO)_2Mg$ system at various temperatures.

The following conclusions can be drawn. The conductivity of pure (PVA-PEG) is found to be of the order of 10^{-9} S/cm at room temperature and its variation with composition of magnesium acetate is very weak. At higher temperatures, however, the variation is found to be appreciable. The conductivity values at different temperatures are listed in TABLE 1. The conductivity increases with temperature in pure (PVA-PEG) and also for all compositions of the (PVA-PEG-$(CH_3COO)_2Mg$) polymer blend electrolyte systems. The conductivity increases with the increase of the number of charge carriers by the addition of $(CH_3COO)_2Mg$ and the conductivity has been found to be high ($\sigma \sim 3.23 \times 10^{-5}$ S/cm) for 30 wt. % of $(CH_3COO)_2Mg$ doped polymer electrolyte at 373 K. This increase in conductivity with increasing temperature can be related to the increase in the number of mobile charge carriers contributing to the transport of ions. The higher the number of charge carriers (n) and higher the mobility (μ), the higher is the conductivity (σ).

TABLE 1 : Ionic Conductivity values of PVA/PEG-Mg acetate polymer blend electrolytes at different temperatures.

Temperature in Kelvin	Ionic Conductivity in S/cm				
	0 wt % of salt	10 wt % of salt	20 wt % of salt	30 wt % of salt	40 wt % of salt
303	3.38 x 10^{-9}	6.69 x 10^{-9}	8.58 x 10^{-9}	7.44 x 10^{-8}	2.86 x 10^{-8}
313	8.63 x 10^{-9}	9.54 x 10^{-9}	1.94 x 10^{-8}	9.34 x 10^{-8}	7.94 x 10^{-8}
323	1.49 x 10^{-8}	2.31 x 10^{-8}	7.02 x 10^{-8}	1.98 x 10^{-7}	2.58 x 10^{-7}
333	3.23 x 10^{-8}	5.65 x 10^{-8}	1.74 x 10^{-7}	2.91 x 10^{-6}	6.98 x 10^{-7}
343	9.30 x 10^{-8}	1.95 x 10^{-7}	4.91 x 10^{-7}	6.24 x 10^{-6}	1.74 x 10^{-6}
353	2.38 x 10^{-7}	5.05 x 10^{-7}	1.05 x 10^{-6}	1.26 x 10^{-5}	3.64 x 10^{-6}
363	4.99 x 10^{-7}	7.91 x 10^{-7}	2.48 x 10^{-6}	1.92 x 10^{-5}	8.06 x 10^{-6}
373	8.71 x 10^{-7}	1.32 x 10^{-6}	5.58 x 10^{-6}	3.23 x 10^{-5}	1.15 x 10^{-5}

As seen from the Figure 3, the frequency dependent conductivity plots show two distinct regions. The first region observed at low frequencies corresponds to the frequency independent conductivity. This conductivity value has been assigned to the bulk conductivity of the sample. In the high frequency region, the conductivity increases with the frequency. The extrapolation of the plateau region to the Y-axis gives the values of σ_{dc}. The maximum conductivity has been found to be 3.23 x 10^{-5} S/cm at 373 K for PVA-PEG- 30 wt. % of $(CH_3COO)_2Mg$ polymer blend electrolyte.

It has been found that the dc conductivity increases with increase of temperature which suggests that the free volume around the polymer chain causes the increase in mobility of ions, polymer segments and hence the conductivity[13]. As the temperature increases, the low frequency dispersion region becomes prominent and shifts to higher frequency region and the frequency independent plateau region increases. Hence, the polarization effect becomes dominant as the temperature increases.

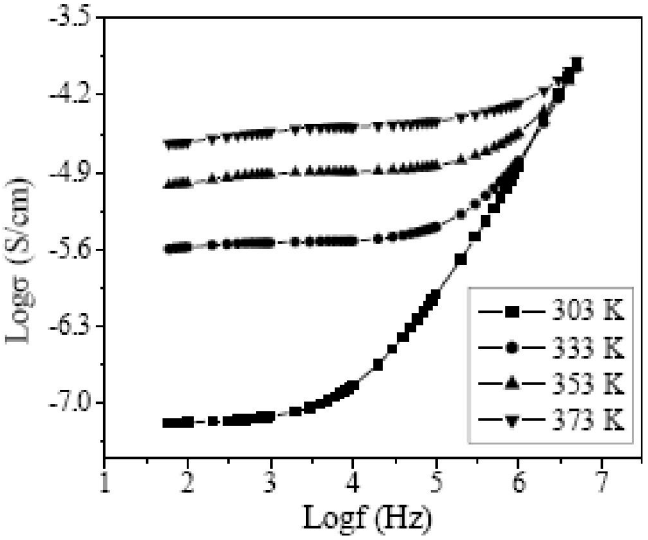

Figure 3 : Conductance spectra of (PVA-PEG-30 wt. % of $(CH_3COO)_2Mg$) polymer electrolyte at different temperatures.

The variation of conductivity as a function of temperature for pure (PVA-PEG) and for different compositions of (PVA-PEG-$(CH_3COO)_2Mg$) polymer electrolytes over the temperature range 303-373 K is shown in Figure 4.

Linear relations are observed in all polymer electrolytes and this meant that there is no phase transition in polymer matrix by the addition of salt in the temperature range studied. These results suggested that there is no dynamic conformational change in polymer matrix. The temperature dependence of dc conductivity, studied from conductivity spectra has been found to obey Arrhenius relation

$$\sigma = \sigma_0 \exp(-E_a/KT) \qquad (1)$$

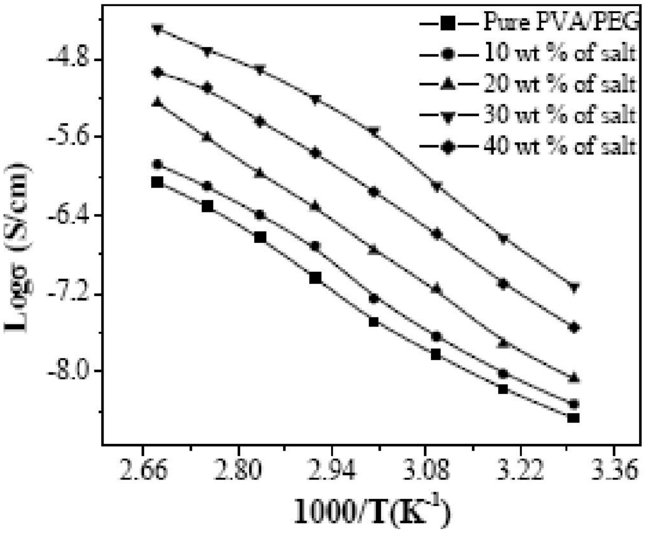

Figure 4 : Temperature dependent conductivity of 50PVA-50PEG-x wt. % of $(CH_3COO)_2Mg$ (x= 0, 10, 20, 30 and 40).

Where σ_0 is the pre-exponential factor; Ea is the activation energy; K is the Boltzmann constant.

The experimental data indicate that the ionic conductivity of all the samples is enhanced with increase of temperature. When the temperature is increased, the mobility of polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilities the translational motion of ions. The segmental motion either allows the ions to hop from one site to another site or provides a pathway for ions to move. Hence, the ionic motion in the polymer electrolyte is due to hopping of ions from one site to another site and the dynamic segmental motion of the polymer, which leads to an increase in the ionic conductivity of the polymer electrolyte.

Dielectric analysis

The dielectric behavior of the polymer electrolyte system is described by using the dielectric function, ε*. Figures 5a and 5b shows the plots of dielectric constant ε' and dielectric loss ε" against the logf at different temperatures. The higher dielectric loss is observed at lower frequencies and it decreases when the frequency increases. The large dielectric loss at lower frequency is due to free charges builds up at the interface between the electrolyte and the electrodes[14]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the values of ε' and ε" at high frequencies. The decrease of dielectric constant with frequency shows that the system is of non- Debye type.

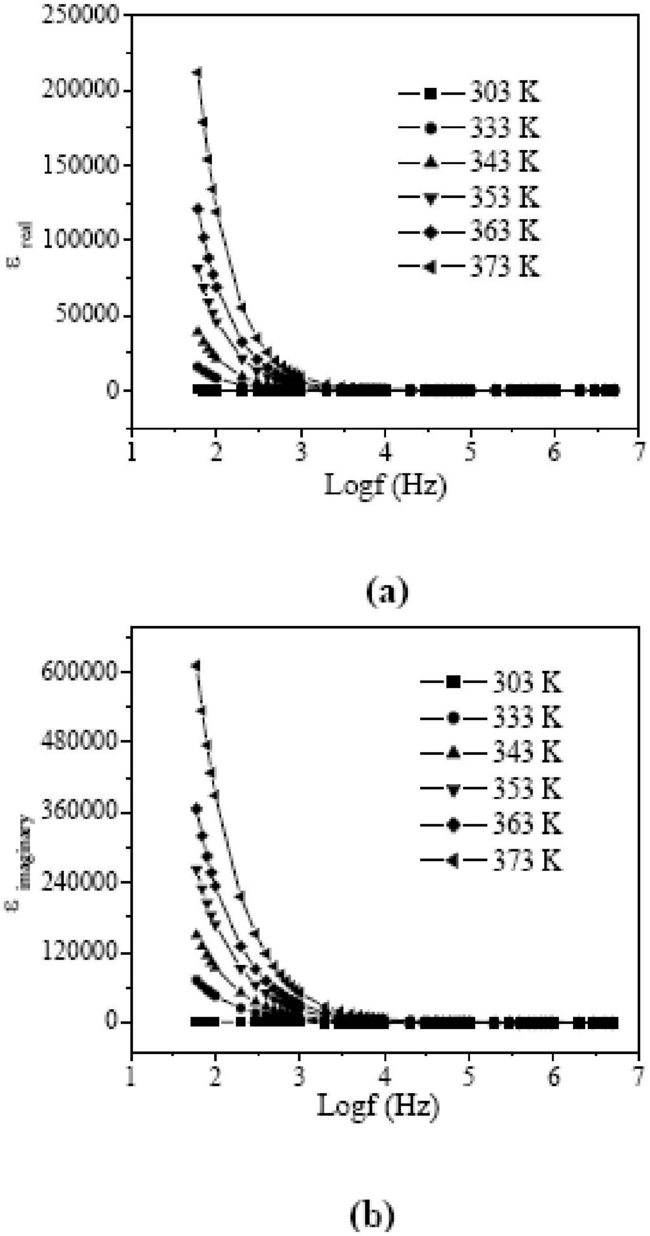

Figure 5 : Typical plots of the variation of (a) real part (b) imaginary part of dielectric constant with frequency for sample 30 wt % of salt at different temperatures.

Modulus analysis

Figure 6 shows the variation of imaginary part of modulus with logarithmic frequency for 30 wt % of magnesium acetate at different temperatures.

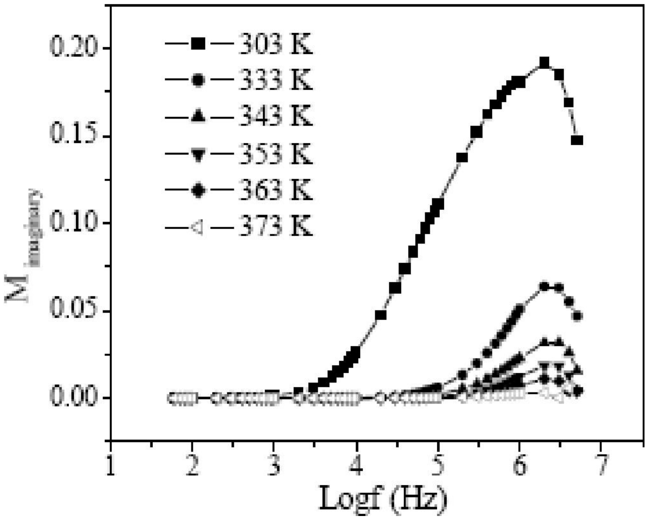

Figure 6 : Variation of imaginary part of modulus with logarithmic frequency for sample 30 wt % of salt at different temperatures.

The M″ shows an increased peak at the high frequency end. The peaking curve at higher frequencies may be attributed to the bulk effect. The strength of peak height decrease with increase in temperature suggesting a plurality of relaxation mechanisms[15]. The long tail present in the plot is due to the large capacitance associated with the electrodes at the low frequency region which confirms the non-Debye behavior[16, 17].

CONCLUSIONS

It is possible to prepare PVA–PEG based polymer blend electrolyte by a simple solvent casting technique. The maximum ionic conductivity of 3.23×10^{-5} S/cm is observed when the polymer blend electrolyte is complexed with 30 wt. % of magnesium acetate at 373 K. The conductance spectrum shows two distinct regions: a dc plateau (low frequency region) and a high frequency dispersive region. The temperature dependence of ionic conductivity reveal that conduction mechanism is Arrhenius type thermally activated process. The dielectric and modulus studies show the non-Debye nature.

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REFERENCES

[1] B.L.Papke, D.F.Shriver, M.A.Ratner, M.Brodwin, R.Duppon, T.Wong; Solid State Ionics, **5**, 83 **(1981)**.

[2] M.B.Armand; Ann.Rev.Mater.Sci., **16**, 245 **(1986)**.

[3] D.F.Shriver, M.A.Ratner; Chem.Rev., **88**, 109 **(1988)**.

[4] A.L.Laskar, J.R.Owen, S.Chandra; Superionic Solids and Solid Electrolytes - Recent Trends (Academic Press, New York), 111 **(1989)**.

[5] D.Srinivas Reddy, E.Laxminarsaiah, M.Jaipal Reddy, S.Ramalingaiah, U.V.Subba Rao; Materials Letters, **29**, 285 **(1996)**.

[6] G.Girish Kumar, N.Munichandraiah; Journal of Electroanalytical Chemistry, **495**, 42 **(2000)**.

[7] M.Jaipal Reddy, Peter P.Chu; Journal of Power Sources, **109**, 340 **(2002)**.

[8] M.A.K.L.Dissanayake, P.Ekanayake; J.Solid State Electrochem., **13**, 1825 **(2009)**.

[9] L.A.Utracki; Polymer Alloys and Blends Carl Hanser Verlag Munich FRG., **(1990)**.

[10] D.A.J.Rand; J.Power Sources, **4**, 101 **(1979)**.

[11] S.Ahmad, S.Zulfiqar; Poly.Degr.Stab., **65**, 243 **(1999)**.

[12] A.M.Stephan, N.G.Renganathan, N.Muniyandi, P.Ramamoorthy, R.Gangadharan, R.Thirunakaran, S.Pitchumani, V.Sundaram; J.Power Sources, **752**, 81-82 **(1999)**.

[13] K.Shibayama, T.Miyamoto; J.Appl.Phys., **44**, 5372 **(1973)**.

[14] C.A.Vincent, J.R.MacCallum; Polymer Electrolyte Reviews I Elsevier Applied Science Publishers Ltd, London and New York, 2 **(1987)**.

[15] K.J.Rao, N.Baskaran, P.A.Ramakrishnan, R.Mishra; Solid State Ionics, **112**, 261 **(1998)**.

[16] J.Kawamura, N.Kuwata, R.Baskaran, S.Selvasekarapandian, T.Hattoriac; Mater. Chem.Phys., **98**, 55 **(2006)**.

[17] D.Mangalaraj, K.Narayandass, K.Prabakar; Mater.Sci.Eng.B., **98**, 225 **(2003)**.