

Conductivity pre-exponential factors for some new superionic conductors

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Abstract. The pre-exponential factors obtained from the ionic conductivity studies on $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$, $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$, $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ and $\text{AlPO}_4:\text{Li}^+$ have been analysed. The compensation law has been found to be valid for these materials indicating that the entropy is directly related to the activation energy. The $1/\alpha$ vs β plots show straight lines for most of the superionic materials except for a few and this variation has been discussed.

Keywords. Nasicon analogues; superionic conductors; pre-exponential factor; Meyer-Neldel rule.

1. Introduction

Solid ionic conductors are of immense scientific and technological interest. They are used in fuel cells, oxygen and specific ion sensors and electrochromic displays (Hagemuller and Van Gool 1978; Vashishta *et al* 1979; Takahashi and Kozawa 1980). Many solid electrolytes with high ionic conductivity comparable to that of Na β -alumina have been reported (Liang 1973; Hu *et al* 1977; Bankamp and Huggins 1978). The ionic conductivity and hopping rate data for some Nasicon analogues have been reported earlier (Desai *et al* 1987). In this paper the extrapolation of the pre-exponential factors from the ionic conductivity data has been carried out on a wide range of materials like $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$; $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$, $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ and $\text{AlPO}_4:\text{Li}^+$. The first two compounds have been reported earlier as Nasicon analogues (Byrappa *et al* 1985), the third one as a new fast proton conductor (Byrappa *et al* 1987a) and the last one is an interesting new material reported recently (Byrappa *et al* 1987b). AlPO_4 shows a covalent bonding and has six polymorphic modifications. The seventh polymorphic modification with 100% ionic bonding and a conducting ion like Li^+ in its composition has been reported earlier (Byrappa *et al* 1986a,b). The Meyer-Neldel rule or the compensation law applied to all these materials show that the entropy is directly related to the activation energy.

2. Experimental method

The synthesis and characterization of all these superionics have been reported earlier (Byrappa and Gopalakrishna 1985; Byrappa *et al* 1985, 1987a,b). Similarly the experimental method of complex impedance measurements has been given earlier (Desai *et al* 1987).

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3. Results and discussion

The ionic conductivity in superionics can be expressed as

$$\sigma = \sigma_0 / T [\exp(-E/kT)], \quad (1)$$

where E is the activation energy, T the temperature, k the Boltzman's constant and σ_0 the pre-exponential factor. The conductivity pre-exponential factor σ_0 can be expressed as

$$\sigma_0 = N e^2 a^2 C(1-C) \gamma k^{-1} \omega_0 \exp(S/k) \quad (2)$$

$$\sigma_0 = k \omega_0 \exp(S/k) \quad (3)$$

Therefore $\log \sigma_0 = S/k + \log(k \omega_0), \quad (4)$

where e is the electronic charge, a the hopping rate, γ the constant depending upon the number of possible jumps available for a particular ion, ω_0 the vibrational frequency of the mobile ions, N the number of equivalent sites per unit volume, C the concentration of mobile ions and S the entropy (Almond *et al* 1983). It has been reported that for a wide range of materials the magnitude of the pre-exponential factor σ_0 and the activation energy E are related by the Meyer-Neldel rule

$$\log \sigma_0 = \alpha E + \beta, \quad (5)$$

where α and β are constants (Weichman and Kuzel 1970; Roberts and Thomas 1974; Dosdale and Brook 1978). The study of Meyer-Neldel rule helps to rationally understand the activation entropies. It has been shown that in Ag^+ ion conducting glasses (Almond and West 1986), the entropies and activation energy values for ionic conduction can be expressed as

$$S = E/T_d, \quad (6)$$

where T_d is the effective temperature corresponding to an order-disorder transition in mobile ion sub-lattice. From (1) and (4) we get

$$\alpha = 1/kT \text{ and } \beta = \log \sigma_0 T. \quad (7)$$

Similarly from (4) and (6) we get

$$\log \sigma_0 = (E/kT_d) + \log k\omega_0. \quad (8)$$

By combining these equations with the Meyer-Neldel rule (equation (5)) we get

$$\alpha = 1/kT_d; \beta = \log \omega_0. \quad (9)$$

The applicability of the Meyer-Neldel rule to the materials synthesized by the present authors and the role of α and β in understanding the mobile ion conduction mechanism have been critically examined in this paper. Table 1 gives the values of E and $\log \sigma_0$ for $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$, $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$, $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ and $\text{AlPO}_4: \text{Li}^+$. The values of E have been plotted against $\log \sigma_0$ (figure 1). The linear relationship E vs $\log \sigma_0$ indicates that T_d and C are the same for members of a particular family of superionic materials. The slope of the straight lines in the E vs $\log \sigma_0$ plots can be used to evaluate T_d . The curvatures in the conductivity plots generally indicate an ordered-disordered transition. The pre-exponential factors were obtained for all these compounds from the ionic conductivity data measured within a wide range of temperature (room temperature to 550°K). Similarly the activation

Table 1. Interdependence of the concentration, pre-exponential factor and activation energy.

Compound	Concentration*		$\log \sigma_0$	E (eV)
	(wt %)			
$\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$	25.00	ZrO_2	1.90	0.43
	27.50		2.39	0.55
	28.75		2.69	0.70
	31.25		4.99	1.20
	35.00		7.49	2.22
$\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$	7.18	La_2O_3	0.65	0.15
	7.80		1.30	0.30
	8.12		2.60	0.75
	9.02		3.40	1.00
	9.92		4.99	1.50
	10.78		6.94	2.10
$\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$	2.15	La_2O_3	-0.37	0.75
	3.23		-2.61	0.50
	5.02		5.86	1.50
	5.39		6.29	1.60
	6.46		0.54	0.80
	6.85		-3.80	0.30
$\text{AlPO}_4: \text{Li}^+$	0.55	Li_2O	-3.00	0.30
	0.95		-1.39	0.22
	1.36		1.52	0.15
	1.77		2.30	0.14
	2.18		3.00	0.10

*Concentration of the component in the nutrient

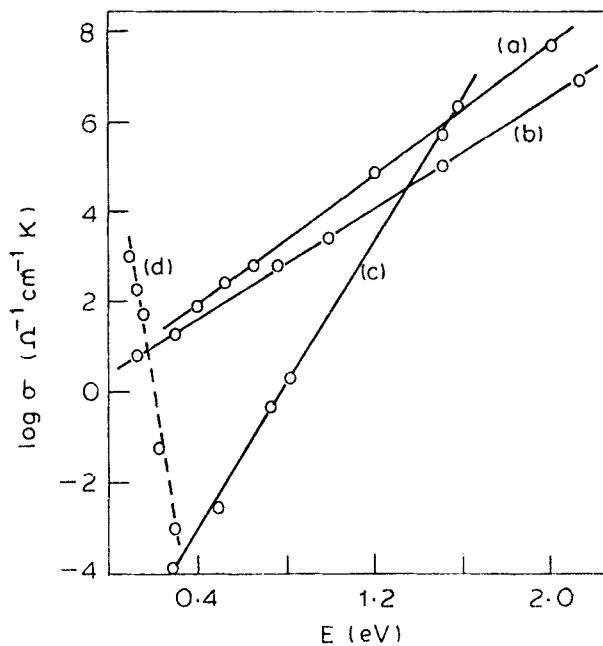
**Figure 1.** $\log \sigma_0$ against E plot for some superionic conductors. a. $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ b. $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$, c. $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$ and d. $\text{AlPO}_4: \text{Li}^+$.

Table 2. Values of α and β for some superionic materials.

Compound	$\alpha = 1/T_d k$	$1/\alpha$	$\beta = \log(k\omega_0)$
$\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$	3.25	0.31	1.00
$\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$	7.76	0.13	-6.00
$\text{Na}(\text{La, Al})\text{ZrP}_3\text{O}_{12}$	2.75	0.36	2.50
AgI-fly Ash	10.00	0.10	-3.50
$\text{Na}_2\text{SO}_4\text{-In}(\text{SO}_4)_3$	6.50	0.15	-1.50
$\text{Na}_2\text{SO}_4\text{-La}(\text{SO}_4)_3$	8.00	0.12	-2.62
$\text{AlPO}_4\text{:Li}^+$	2.90	0.03	6.00
AgI-Ag oxysalt glass	9.00	0.11	2.10
AgI-AgBr	7.60	0.13	-1.50
$\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4$	7.00	0.14	-4.25
$\text{Y:Na}_2\text{SO}_4$	9.99	0.10	0.65
$\text{Li}_{3+x}\text{V}_{1-x}\text{Ti}_x\text{O}_4$	17.36	0.05	-4.06
$\text{AgI} + \text{Pb}^{2+}$	19.53	0.05	-9.12
$\text{Na}_{1+x}\text{Zr}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$	16.50	0.06	-7.82
$\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$	8.69	0.11	-2.17

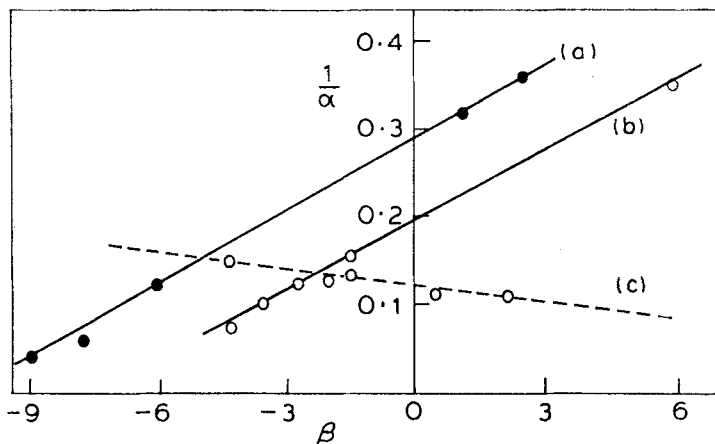


Figure 2. $1/\alpha$ against β plot for some superionic conductors. **a.** $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$; $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$; $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$; AgI-Pb^{2+} ; $\text{Na}_{1+x}\text{Zr}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$ systems. **b.** AgI-fly Ash; $\text{Na}_2\text{SO}_4\text{-La}_2(\text{SO}_4)_3$; $\text{Na}_2\text{SO}_4\text{-In}(\text{SO}_4)_3$; $\text{AlPO}_4\text{:Li}^+$; $\text{Li}_{3+x}\text{V}_{1-x}\text{Ti}_x\text{O}_4$; $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ systems. **c.** $\text{Na}_2\text{SO}_4\text{-Na}_2\text{WO}_4$; AgI-AgBr; AgI-Ag oxysalt glass; Y: Na_2SO_4 systems.

energy values were obtained from the Arrhenius plots given earlier (Byrappa *et al* 1987c). It is found that the Meyer-Neldel rule is applicable to all the four compounds indicating that the pre-exponential factor increases exponentially with E except in the case of $\text{AlPO}_4\text{:Li}^+$ where it decreases exponentially with E . Such a decreasing trend in the $\log \sigma_0$ vs E has been reported for several ion-exchanged β -alumina (Whittingham and Huggins 1972). The decrease in the values of $\log \sigma_0$ with E is attributed to a small negative entropy of the activation. On the other hand, the first three materials showing an increase in the pre-exponential factor with E have been compared to AgI-Ag oxysalt glasses and Lisicon (Almond *et al* 1985). It is interesting to note that $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$, $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$ are the fast ionic conductors and $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ is a fast proton conductor. The positive slope of $\log \sigma_0$ vs E

indicates an increase in the values of conductivity pre-exponential factor with E . The pellets of $\text{Na}_2(\text{La, Al})\text{ZrP}_3\text{O}_{12}$ and $\text{Na}_2(\text{La, Al})\text{TiP}_3\text{O}_{12}$ have been prepared with and without polyvinyl alcohol, but the $\log \sigma_0$ vs E plots are the same for both and hence the binding medium (in this case polyvinyl alcohol) does not hinder the mobility of the ions. Table 2 gives the values of α and β for some known superionics available in the literature (Prakash and Gopalan 1985; Shahi and Wagner 1982; Saito *et al* 1984; Rodger *et al* 1985; Shahi *et al* 1986; Delmas *et al* 1981; Shannon *et al* 1977), as well as for the present compounds. The plots of $1/\alpha$ vs β show three straight lines. Lines (a) and (b) appear almost parallel with a positive slope, whereas line (c) has a negative slope. The positive slope of $1/\alpha$ vs β plot (figure 2) indicates an increase in the disordering temperature T_d with an increase in the values of $\log(k\omega_0)$. On the other hand the negative slope indicates a decrease in T_d with an increase in the values of $\log(k\omega_0)$. These results appear to be surprising and such a behaviour may be explained in terms of the varying concentration of selective cations in the composition, x , C , conduction mechanism, etc.

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