

Electrical and Thermoelectric Properties of NaAlO₂

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The electrical conductivity (σ) with ionic (σ_i) and electronic (σ_e) conductivity and thermoelectric power (S) of NaAlO₂ have been separated over the entire temperature range from 450K to just below its melting point with the help of time dependent study of dc electrical conductivity. Superionic phase has been observed well below the melting point in which the conductivity is almost purely ionic. The phase transition temperature below which the solid transform from superionic to normal phase has been obtained from electrical conductivity (σ) and thermoelectric power (S) measurement. In normal ionic phase, the solid NaAlO₂ shows mixed conduction (ionic and electronic) behavior. The variation of σ_i and σ_e with temperatures has been shown in various plots and the conduction mechanism is explained by extended lattice gas model.

Keywords: Ionic conductivity; Electronic conductivity; Thermoelectric power, Phase Transition temperature

1. INTRODUCTION

The solid electrolytes, having low activation energy for ion migration and an electrical conductivity of the order of 10^{-1} to 10^{-6} Scm⁻¹, show high ionic conductivity and negligible electronic conductivity at ambient temperature. Such electrolytes are very interesting due to their ionic behavior and have wide technological aspects. Electrochemical applications are one of the most important use of these electrolytes as in battery due to having high energy density, no leakage problem, long life and ease in handling in comparison to liquid electrolytes. The alkali-based super-ionic solid electrolytes are a very promising material because of its light weight, high electrochemical potential and easy in carry for these batteries [1-6]. There have been carried out a lot of study for alkali-based solid electrolytes in which most of these are confined either to the super-ionic α -phase just below the melting point or to the low conducting β -phase [7,8,9]. In alkali, the softness of sodium metal is expected to promote good contact with the components in solid state ionic devices such as batteries, during repeated cycles. The simple sodium based ion conducting solid electrolytes has been studied by many workers [10-14]. In view of this, the present work is directed towards the systematic study of the electrical conductivity (σ) and thermoelectric power (S) of NaAlO₂ solidified melt which is necessary to judge their potentialities in electrochemical applications.

2. MATERIAL PREPARATION AND EXPERIMENTAL TECHNIQUES

The specimen compound NaAlO₂ was prepared in the laboratory by solid state reaction method. The starting materials for the preparation of NaAlO₂ are Na₂CO₃ and Al₂O₃,

both with stated purity of 99.99% (M/s Rare and Research Chemicals, Bombay, India) were taken in the ratio of their molecular weight which have been thoroughly mixed and fired in the air in a silica crucible for 60 hours at 1000K with one intermediate grinding. A self-designed sample holder was taken for the measurement of electrical conductivity. It consists of a corning flat-bottom test tube in which two flat silver electrodes of equal size and area are fixed parallel to each other and joined by two thick silver wires for external connection. The compound, which conductivity is to be measured, is poured into sample holder and pressed. It is heated along with the salt inside, firstly it melts, then allowed to cool slowly at room temperature and made a small cylindrical shape pellets of smooth faces. The measuring instrument was connected to the outer electrodes of the sample [10, 11]. For thermo-emf, the thin silver foil pressed on the faces of the pellets served as electrodes and sufficient time was allowed after applying the temperature gradient (ΔT) before recording the thermo-emf. ΔT was measured using a chromel-alumel thermo couple.

3. RESULTS AND DISCUSSION

The electrical conductivity (σ) and thermoelectric power (S) of NaAlO₂ prepared have been measured as a function of temperature in both heating and cooling cycles as shown in Table 1. The dc electrical conductivity (σ_{dc}) has been measured as a function of time with the help of an electrode that blocks ionic conduction but not the electronic conduction. A time dependent dc electrical conductivity normally occurs in solids with ionic conduction, if the electrodes used for this measurement are capable of blocking the flow of ions. The positive ions move in the direction of the applied field and negative ions opposite to it through the electrodes. Since ions have been blocked by electrodes, so they are begin to accumulate at electrodes instead of discharging and creates a field opposite to that of the applied field. The ions, trying to move towards the electrodes, decrease. Thus in pure ionic solid, dc current decreases with time and tends to become zero due to opposing field which is equal to applied field after a very long time Since the electric field does not become zero therefore, in mixed conduction, a current arises due to polarization of ions which are continuous decreasing current and acquire constant value after a long time. When the transient have died out which appears due to ionic charges, the electronic parts of the conductivity dominates the ionic part of the conductivity. Therefore total current will be assigned to electronic conductivity [12,13,14]. Since both ions and electrons contribute in total current at initial state ($t = 0$). Hence by time-dependent measurement of the current, the total as well as the ionic and electronic parts of the conductivity can be obtained.

Table 1: Total conductivity (σ), ionic conductivity (σ_i), electronic conductivity (σ_e), ratio of ionic to electronic conductivity (r) and percentage contribution of ionic conductivity at different temperatures for NaAlO₂.

T(K)	σ ($\Omega^{-1}\text{m}^{-1}$)	σ_e ($\Omega^{-1}\text{m}^{-1}$)	σ_i ($\Omega^{-1}\text{m}^{-1}$)	r	Log r	% of σ_i
1000	4.82	5.03×10^{-3}	4.8149	9.57×10^2	2.98	99.96
900	3.43	3.73×10^{-3}	3.4262	9.18×10^2	2.96	99.93
850	3.23	3.63×10^{-3}	3.2263	8.88×10^2	2.94	97.54
800	4.03×10^{-1}	2.03×10^{-3}	4.0097×10^{-1}	1.97×10^2	2.29	95.20
700	5.73×10^{-2}	8.37×10^{-4}	5.6460×10^{-2}	6.74×10^1	1.82	92.58
600	6.23×10^{-3}	1.65×10^{-4}	6.0700×10^{-3}	3.67×10^1	1.56	91.99
500	3.23×10^{-4}	1.08×10^{-5}	3.1200×10^{-4}	2.89×10^1	1.46	91.66

3.1.1 Ionic Conductivity

The variation of electrical conductivity (σ) and thermoelectric power (S) with inverse of the temperature has been shown in Figure 1 and Figure 2 as $\log \sigma T$ vs T^{-1} and $\log S$ vs T^{-1} plots respectively. There is almost no difference between σ and σ_i at higher temperatures but they differ slightly at lower temperatures. The conductivities (σ and σ_i) show variation at some temperature ranges as: linear region below certain temperature T_1 , non-linear region between T_1 and T_2 ($T_1 < T < T_2$), and flat and linear region for $T > T_2$. The Thermoelectric power plot also has same behavior as ionic conductivity plot. For linear range, the σ and S can be represented by the equations-

$$\sigma_i T = c \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

$$S = \frac{\eta}{eT} + H \quad (2)$$

where c is the temperature-independent constant and E_a is the activation energy, η is the slope of the S vs T^{-1} plot and H is a constant.

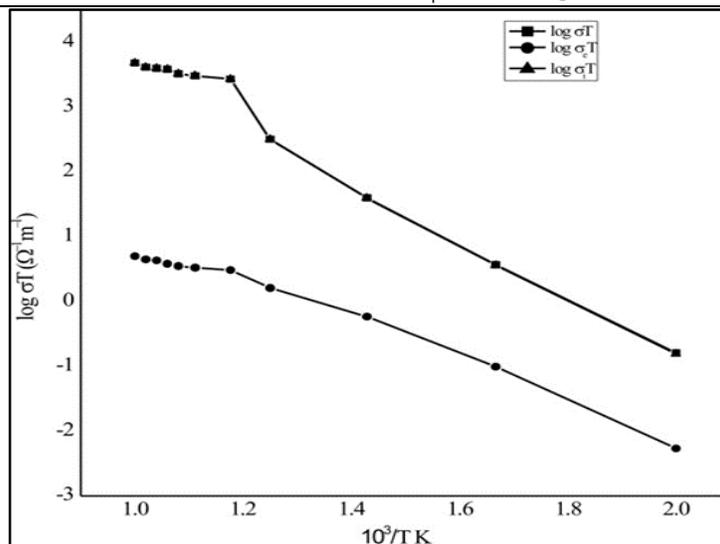


Fig. 1: Plot of logarithm of product of conductivity and temperature ($\log \sigma T$) vs inverse of temperature (T^{-1}) of NaAlO₂.

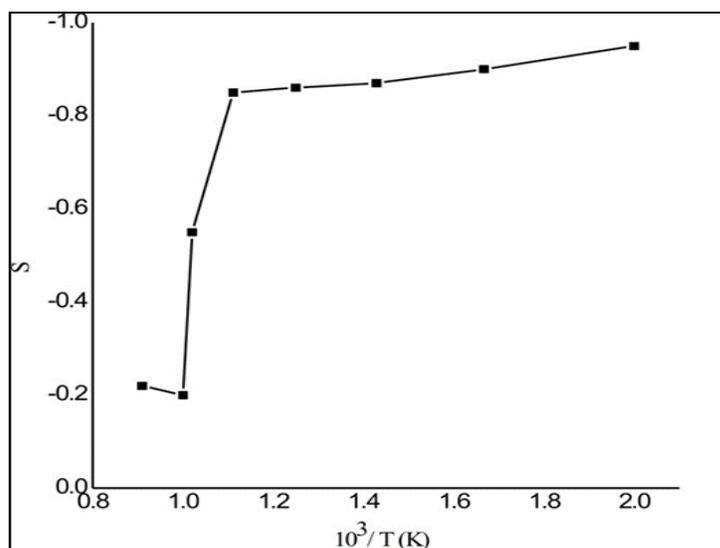


Fig. 2: Plot of thermoelectric power (S) vs inverse of temperature ($10^3/T$) of NaAlO₂.

In the higher temperature region, σ_i are very high ($\sim 4.82 \Omega^{-1}m^{-1}$) and activation energy is very small as listed in Table 2 which is the superionic phase of the solid. There exists a high jump in σ (103 times) and shows a bending in $\log \sigma_i T$ vs T^{-1} plot at 820 K. The

contribution of electronic conductivity in this range is negligibly small ($\approx 0.04\%$). From lower temperature to below 820 K, which is normal ionic phase, there is an appreciable (≈ 1 to 9%) electronic contribution to electrical conductivity (σ). Since the thermoelectric power (S) is negative in the entire studied temperature range and thus the mobile carriers are positive charged. There are two types of positive charged ions in NaAlO_2 namely Na^+ ions and Al^{3+} . Since Na^+ ions having low positive charge and small size in comparison to Al^{3+} , therefore it shows high mobility. The conduction mechanism happens due to hopping of ions. Since in intrinsic hopping of these ions from normal lattice site to other lattice site will involve high activation energy (≈ 5 eV or more) which is least probable because activation energy is very small. Therefore, the electrical conduction occurs probably due to hopping of defects. It indicates that there exist a large number of Frenkel defects even in normal ionic phase of the NaAlO_2 which may further be generated at higher temperatures. In the non-linear region, σ jumps around a particular temperature which is the phase transition temperature ($T_p = 820\text{K}$). Since both σ and S should arise entirely due to ions, therefore the heat of transport (Q) and activation enthalpy (h_m) for the mobile ions can be calculated from the S vs T^{-1} and $\log \sigma_i$ vs T^{-1} plots which has also been reported in Table 2.

Table 2: Summarised results of electrical conductivity and thermoelectric power of NaAlO_2 .

Temperature	E_a (eV)	σ_0 ($\Omega^{-1}\text{m}^{-1}$)	η (eV)	H (mVK ⁻¹)
High temperature region ($T > T_2$) K	0.34	1.78×10^5	-0.29	-0.41
Lower temperature region ($T < T_1$) K	0.91	1.26×10^8	0.17	-0.45

Here $T_1 = 815$ K, $T_2 = 825$ K, and $T_p = 820$ K

From Table 2, since the heat of transport (Q) is less than activation energy (E_a). Therefore the extended lattice gas model is suitable for explaining the conduction mechanism. In this approach, it is assumed that a large number of mobile ions, comparable to or less than the number of their sites, are available and a molten sublattice-like situation exists. The mobile ions (Na^+) while hopping from one site to another can interact with each other and modify the diffusion or transport activation energy. A repulsive interaction exists between the nearest neighbours and the mobile (hopping) ions interact with the lattice. As the ion moves, it polarizes the host crystal and carries the polarization cloud with it. Interaction between hopping ions and lattice vibrations, mediated via optical phonon, provides a sink or source of energy, which is coupled to the mobile ions, and hence contributes activation energy to the conductivity [14]. Thus the extended lattice gas model should be suitable for ionic conduction in super ionic phase of this compound.

3.2 Electronic conductivity

The $\log \sigma_e T$ vs T^{-1} is similar to $\log \sigma T$ vs T^{-1} plot and shows similar behavior as electrical conductivity (σ) as shown in Figure 1. It increases by several orders of magnitude at same temperature as in electrical conductivity (σ). Thus it appears that there occurs a structural change in the solid at the phase transition temperature. Below this temperature the $\log \sigma_e T$ vs T^{-1} plot is linear and expressed by the equation-

$$\sigma_e T = \sigma_0 \exp\left(\frac{w}{kT}\right) \quad (3)$$

where σ_0 is constant and w is the activation energy for electronic conduction.

The value of w is large but not enough to relate it to the energy band gap of the solid as shown in Table 3. The electronic conduction occurs due to hopping of electrons trapped at defect centers. The electrical conductivity (σ) has been performed with time at low but constant electric field and temperature as shown in Figure 3.

Table 3: Results of electronic contribution to electrical conductivity of the sample NaAlO₂.

w (eV)	σ_0 ($\Omega^{-1}\text{m}^{-1}$)	T_P (K)
0.74	1.10×10^5	980 ± 5

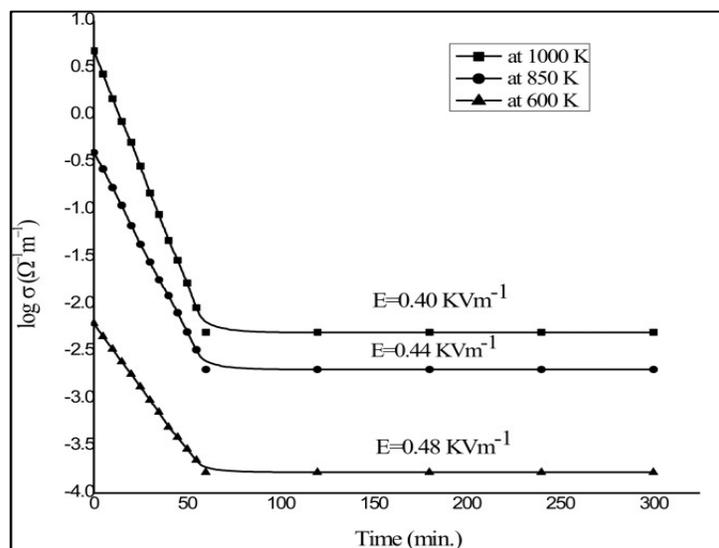


Fig. 3: Plot of logarithm of electrical conductivity ($\log \sigma$) vs time of NaAlO₂.

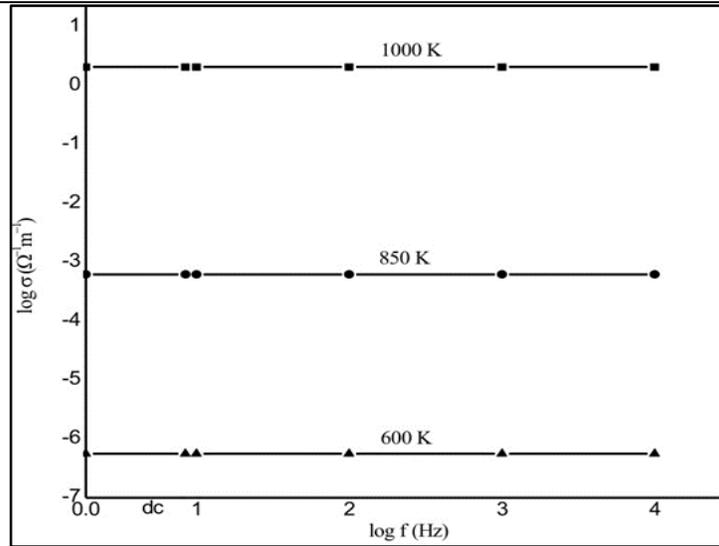


Fig. 4: Plot of logarithm of conductivity ($\log \sigma$) vs logarithm of frequency ($\log f$) of NaAlO_2 .

The electrical conductivity (σ) decreases with time and tends to become constant. At lower temperature the trend of constancy begins to appear after a short interval of time, but it increases with increasing temperature. After a long time ($t \rightarrow \infty$), the electronic part (σ_e) of the conductivity and the value of σ_{dc} for $t \rightarrow 0$ is the total (ionic + electronic) conductivity. The variation of frequencies with electrical conductivity (σ) has been depicted in Figure 4. There exists no difference between $\sigma_{dc}(0)$ and σ_{ac} . This indicates that grain boundary is not important and no pore exists in the sample. A time-dependent study of σ_{dc} has been performed at widely separated temperatures and $\sigma_{dc}(0)$ and $\sigma_{dc}(\infty)$ have been obtained at each temperature. Using these values, the ratio of ionic to electronic conductivities has been obtained by using the relation-

$$\begin{aligned}
 r &= \frac{\sigma_i}{\sigma_e} \\
 &= \frac{\sigma - \sigma_e}{\sigma_e} \\
 &= \frac{\sigma_{dc}(0) - \sigma_{dc}(\infty)}{\sigma_{dc}(\infty)} \quad (4)
 \end{aligned}$$

From Fig.5 the contribution of ionic and electronic conductivity to the total conductivity at any temperature has been obtained by using the relation-

$$\sigma_i = \left(\frac{r}{r+1} \right) \sigma \quad (5)$$

$$\sigma_e = \left(\frac{1}{1+r} \right) \sigma \quad (6)$$

The percentage of ionic and electronic contribution to electrical conductivity (σ) in the NaAlO₂ at different temperatures has been calculated and given in Table 1 which gives clear idea about both the conductivities. The contribution of ionic conductivity (σ_i) in electrical conductivity increases as temperature rises up to just far below the melting point of the compound and becomes approximately up to 100% at a particular temperature. Using log r vs T plot as shown in Figure 5, the ionic (σ_i) and electronic (σ_e) parts of conductivity are differentiated.

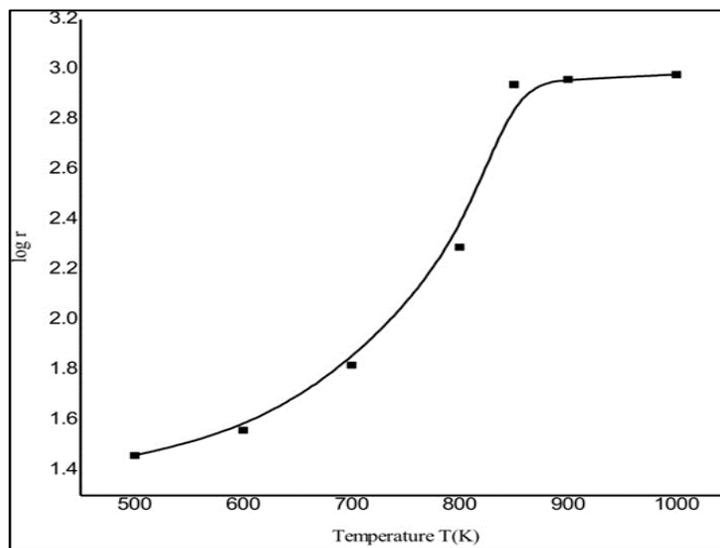


Fig. 5: Plot of log r Vs. temperature (T) of NaAlO₂.

4. CONCLUSION

It may reasonably be concluded that NaAlO_2 is a typical superionic solid and shows phase transition at a particular temperature ($T_p = 820 \text{ K}$). Below T_p , it behaves like a normal ionic conductor in which the electrical conductivity is governed by ions with electronic conduction up to 1% to 9%. Above T_p , the superionic phase of the compound has been observed which is almost ionic with negligible small electronic conductivity ($\approx 0.04\%$). In both the phases electrical conductivity occurs due to Frenkel defects and the extended lattice gas model is suitable for explaining the conduction mechanism of the sample.

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