Ionic Conductivity Behaviour in K_3AsO_4

Shivendu Tripathi

Department of Physics, Satish Chandra College, Ballia, U.P. -27700, India

Mechanism of electrical transport in Potassium Arsenate (K_3AsO_4) has been investigated with measurements of ac and dc electrical conductivities and thermoelectric power. The contribution of ionic and electronic conductivities to the total electrical conductivity has also been calculated. In the light of existing theories and models, results have been discussed. The paddle wheel mechanism is found appropriate to explain the ion transport phenomena in K_3AsO_4.

1. INTRODUCTION

Solid electrolytes are materials with high ionic conductivity, either of cation or anion but not usually both, and with negligible electronic conductivity. They are treated as the solid state equivalent of molten salts or strong liquid electrolytes. Solid electrolytes are not exclusively crystalline. A wide range of non-crystalline solids, including some glasses and polymers, exhibit high ionic conductivity and in fact, several of the recent advances in solid state Ionics have involved amorphous materials. The properties and application of these advanced materials depend on the close control of structure, composition, texture, dopands and dopand (or defect) distribution [1-6]. Much of the interest and research in solid state Ionics is related to the electrical conductivity properties of solids; new electrochemical cells and batteries are being developed that contain solid, rather than liquid, electrolytes. Hence scientists and technologists have focused their attention for devising new electrochemical cells and batteries that contain solid, rather than liquid electrolytes [7-11]. In view of the above facts, electrical transport properties in alkali metal arsenates namely, potassium arsenate has been studied. Potassium arsenate (K_3AsO_4) is a colourless powder which is used in the textile, tanning and paper industries, and as an insecticide, especially for fly paper. Electrical conductivity and thermoelectric power were investigated for elucidating the transport properties K_3AsO_4.

2. MATERIAL PREPARATION AND EXPERIMENTAL TECHNIQUES

The specimen compound, K_3AsO_4, has been prepared in the laboratory by solid state reaction method. The starting materials for the preparation of K_2CO_3, and AsO_4 are the reactants for preparing K_3AsO_4. Reactants ($K_2CO_3 + AsO_4$) have been taken in the ratio of their molecular weights and they have been thoroughly mixed and fired in the air in a silica crucible at 1000 K for 56 hours for yielding K_3AsO_4, with one intermediate grinding. Preparation of the samples involved the following reaction-

$$3K_2CO_3 + 2AsO_4 \xrightarrow{1000\,K,56\,Hrs} 2K_3AsO_4 + 3CO_2$$
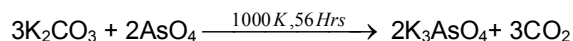
The characterization of this compound has been done using X-rays diffraction data, which revealed that the compounds potassium arsenate possesses orthorhombic structure.

The prepared samples of K_3AsO_4 were subjected to conductivity measurements. The *ac* and *dc* electrical conductivities as a function of various parameters such as *ac* frequency, time and temperature have been investigated. Further, thermoelectric power as a function of temperature has also been examined.

3. ELECTRICAL CONDUCTIVITY MEASUREMENT

An *ac* signal of a small strength is applied on the sample for the measurement of its electrical conductivity. The obtained conductivity is referred to as *ac* electrical conductivity, $\sigma_{ac}(\omega)$. The *ac* conductivity becomes the function of the applied signal frequency if the sample has some sort of dipoles of higher relaxation time or grain boundary or space charge concentration in it. When the sample is subjected to the *dc* signal, the measured conductivity is referred to as *dc* electrical conductivity, σ_{dc}. Most of the methods used for the measurement of $\sigma_{ac}(\omega)$ can also be extended for the measurement of σ_{dc}. However, in case of mixed conduction (ionic and electronic conduction) several complexities are encountered while measuring *dc* because the effective field is reduced due to blocking of ionic charge at the electrodes; so, it becomes time dependent. Due to this, it is often convenient to record instantaneous current through and voltage across the sample. Tentatively, all measurements need certain time hence instantaneous current can not be recorded. Therefore, current through the sample is recorded as the function of time and small extrapolation of the curve on the lower side enables to get instantaneous current. In thermoelectric power (*S*) measurements, no current flows through the sample and thus it becomes a zero current process. Hence it is free from electrode contact problem, grain boundary shape and size of the sample. Results of different types of studies performed on the samples are discussed in the following sections.

3.1. Electrical Conductivity as a Function of Frequency

The conductivity (σ) has been measured at few fixed frequencies with constant temperature. Results are depicted in Figure1. It is apparent from this figure that the value of σ remains constant on the entire frequency range. Further, it is also observed that there exists no difference between σ_{dc} (0) and σ_{ac} values. This indicates that grain boundary effects are minimized and no pore exists in the sample.
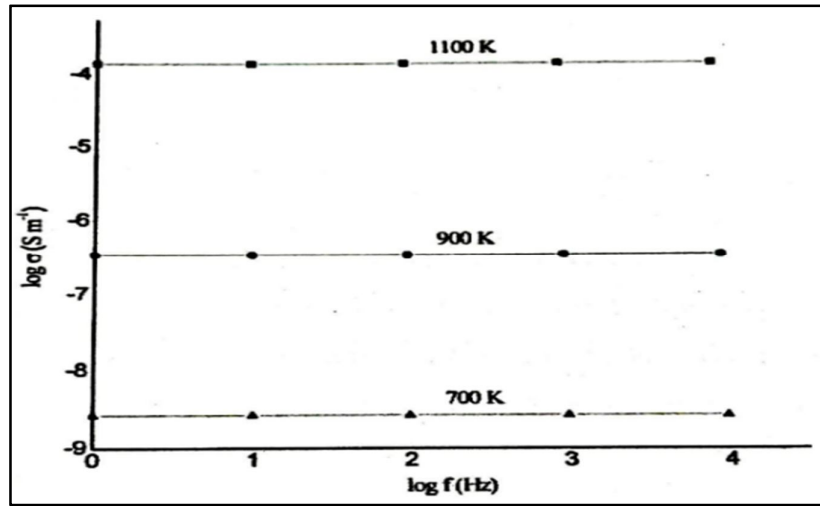
Fig. 1: Plot of logarithm of conductivity (log σ) vs logarithm of frequency (log f).
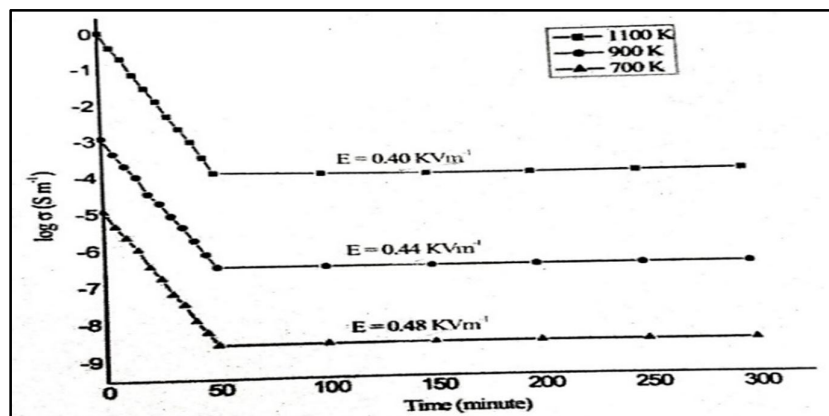
3.2. Electrical Conductivity as a Function of Time

Fig. 2: Plot of logarithm of conductivity (log σ) vs time.

The electrical conductivity occurs due to the migration of ions or electrons or both in the solid. A time dependent de electrical conductivity normally occurs in solids with ionic conduction, if the electrodes used for this measurement are capable of blocking the flow of ions. On applying the electric field, positive ions move in the direction of the applied field and negative ions migrate opposite to it.

Because electrodes are blocking the path of ions, therefore ions are not able to discharge themselves at the electrodes and begin to accumulate at the electrodes. This creates a field opposite to that of the applied field. Thus, the net force acting on the ions

trying to move towards the electrodes decreases and fewer ions are able to reach electrodes. Due to this, *dc* current decreases. With time the opposing field grows and tends to become equal to the applied field after a long time (t→∞). Thus, in pure ionic solids, *dc* current decreases and tends to become zero after a very long time.

In the case of mixed ionic conductors, the current which is continuously decreasing acquires a constant value after a long time. This situation arises because the electric field does not become zero due to the polarization of ions. The transient appears due to ionic charge; hence once these transients have died out, the remaining current of constant value can be totally assigned to electrons. The initial current (at t = 0) is the total current contributed by both ions and electrons [12-16]. Through time-dependent measurement of the current, the total as well as the ionic and electronic parts of the conductivity can be evaluated.

Hence time-dependent studies of a for the compound K_3AsO_4 have been performed at low but constant electric field and temperature, and values of σ_{dc} (0) and σ_{dc} (∞) have been obtained at each temperature. Results are plotted in Fig. 2. As evident from Fig. 2, σ decreases with time and tends to become constant. As temperature increases, electrical conductivity (σ) steeply decreases and becomes constant during a shorter interval of time. The trend of constancy begins to appear after a short interval of time at lower temperatures, but increases at higher temperatures. The constant value of σ_{dc}, after a long time (t→∞) is the electronic part (σ_e) of the conductivity and the value of σ_{dc} for t→0 is the total (ionic + electronic) conductivity. Using the values of σ_i and σ_e, the ratio of ionic conductivity to electronic conductivity is obtained by the relation

$$r = \frac{\sigma_i}{\sigma_e} = \frac{\sigma - \sigma_e}{\sigma_e}$$

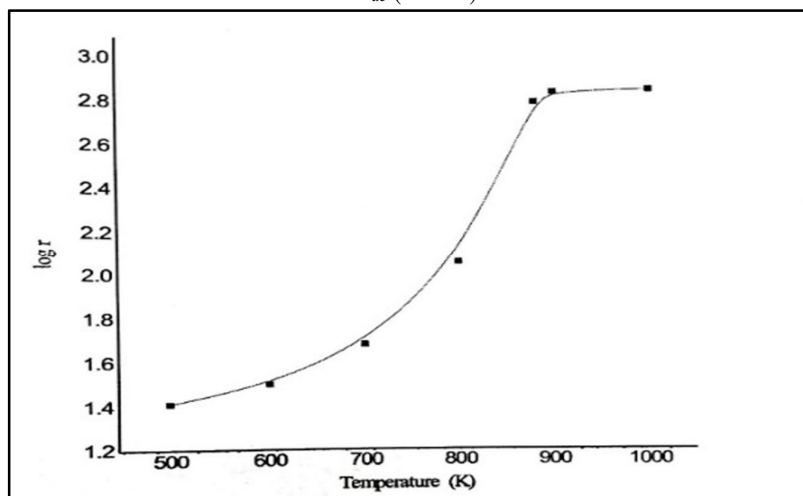$$r = \frac{\sigma_{dc}(t \to 0) - \sigma_{dc}(t \to \infty)}{\sigma_{dc}(t \to \infty)}$$

(1)

Fig. 3: Plot of log r vs temperature.

The variation of log r with temperature (T) is shown in Figure 3. From Figure 3, the contributions of ionic conductivity (σ_i) and electronic conductivity (σ_e) to the total conductivity (σ) at any temperature can be calculated as

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

(2)

The calculated values of ionic contribution (σ_i) and electronic contribution (σ_e) to total electrical conductivity (σ) for the sample compounds at different temperatures are shown in Table 1.

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.

T(K)	σ (Sm^{-1})	σ_e (Sm^{-1})	σ_i (Sm^{-1})	r	log r	% of σ_i
1100	1.14	1.41×10^{-4}	1.13	8.21×10^2	2.89	99.90
1040	6.25×10^{-3}	1.44×10^{-5}	6.24×10^{-3}	8.13×10^2	2.88	99.76
1000	4.24×10^{-3}	1.74×10^{-6}	4.24×10^{-3}	7.14×10^2	2.85	99.20
900	1.28×10^{-3}	3.46×10^{-7}	1.28×10^{-3}	1.20×10^2	2.45	97.20
800	5.24×10^{-4}	4.62×10^{-8}	5.22×10^{-4}	5.12×10^1	1.68	96.04
700	1.23×10^{-5}	2.62×10^{-9}	1.20×10^{-5}	3.23×10^1	1.53	95.00
600	5.44×10^{-7}	4.60×10^{-10}	5.43×10^{-7}	2.45×10^1	1.37	93.29
500	2.14×10^{-9}	2.60×10^{-10}	1.88×10^{-9}	1.90×10^1	1.23	92.10

As evident from Table 1, ionic contribution to total electrical conductivity increases with temperature. It reaches nearly 97% in 1050 K for K_3AsO_4. Afterwards, ionic contribution suddenly increases and becomes more than 99% in the compounds. This clearly indicates that the solid possess two phases: one below and the other above a particular temperature. The particular temperature, at which the two phases of the sample compounds are justified, is termed as phase transition temperature (T_p). The super-ionic and normal ionic phase of the compounds exists above and below this temperature, T, respectively. The phase transition temperature (T_p) for K_3AsO_4 is 1050 K respectively.

Further, electronic conductivity also increases with temperature although it remains very weak (~10^{-4} Sm^{-1}).

3.3. Electrical Conductivity as a Function of Temperature

The electrical conductivity (σ) of K_3AsO_4 has been measured as a function of temperature during heating and cooling cycles. Graphical representation of the results obtained for σ is shown in Fig.4. At higher temperatures, σ and $σ_i$ values are almost the same. However, σ and $σ_i$ slightly differ at lower temperatures. In general, the curve shown in Fig.4 can be divided into three regions: (i) linear region below a certain temperature T_1 (ii) non- linear region for temperature $T_1 < T < T_2$ and (iii) flat and linear region for $T > T_2$ In the linear range the variation of σ can be represented by the equation
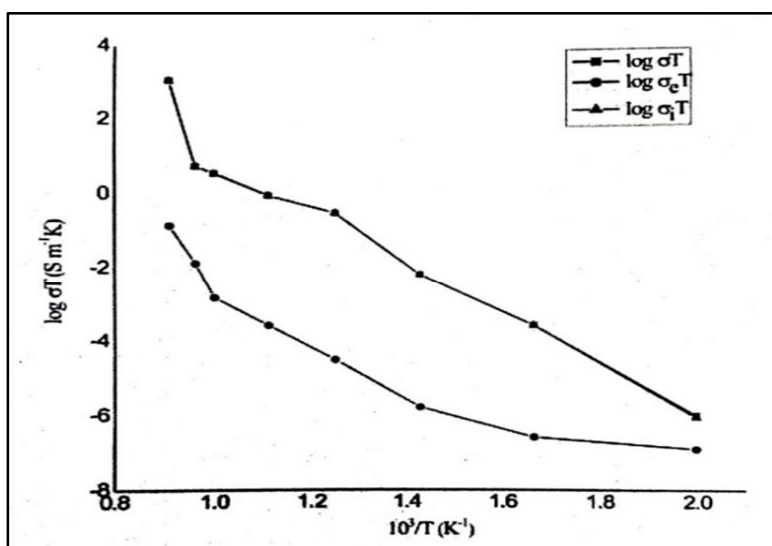
$$\sigma_i T = \sigma_0 \exp^{\frac{-E_a}{kT}} \qquad (3)$$

Fig. 4: Plot of logarithm of conductivity & temperature (log σT) vs inverse of temperature T^{-1}.

In the higher temperature region, $σ_i$ is very high (=1.13 Sm^{-1}).This region, therefore, indicates the super ionic phase of K_3AsO_4 the solid. The nature of log$σ_e$T versus T^{-1} plot is similar to that of the logσT versus T^{-1} plot as shown in Figure 4. Electronic conductivity jumps by several orders of magnitude at a temperature at which one observes a jump in $σ_0$ Thus, there occurs a structural change in the solid at the phase transition temperature. Below this temperature, log$σ_e$ T vs T^{-1} plot is linear and can be expressed by the equation

$$\sigma_e T = \sigma_0 \exp^{\frac{-\omega}{kT}} \qquad (4)$$

The value of ω (0.65 eV for K_3AsO_4) is large but not enough to relate it to the energy band gap of the solids. It seems that electronic conduction occurs due to hopping of trapped electrons at the defect centres of K_3AsO_4 compound [13-16].

4. Thermoelectric Power Measurement

Results of thermoelectric power (S) measurement are graphically presented in the form of Svs T^1 plot in the Figure 5. These plots can also be divided into three regions: (i) a linear region below $T_1(T < T_1)$ (ii) a nonlinear region betweenT_1 and $T_2(T_1< T < T_2)$ and (iii) a linear region above $T_2(T > T_2)$ In the linear region, the results can be expressed by the relation
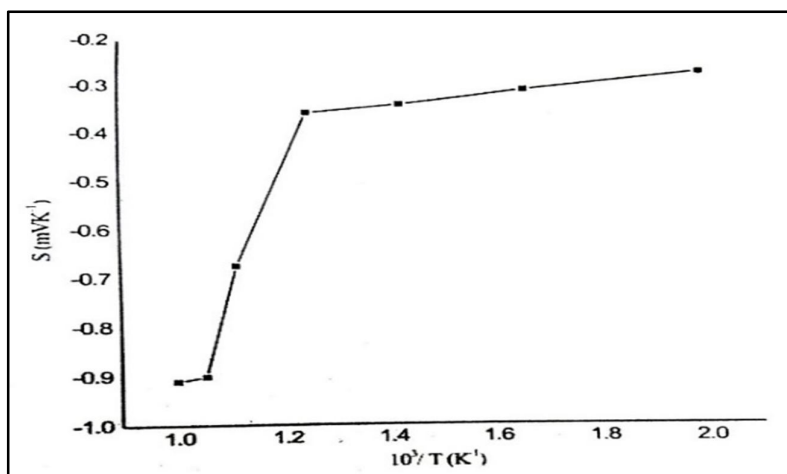
$$S = \frac{Q}{eT} + H \tag{5}$$

Fig. 5: Plot of Thermoelectric power (S) vs inverse of temperature T^{-1}.

Below T_p therefore, the slopes of the S vs T^{-1} and logσ$_i$T vs T^{-1} plots give the heat of transport (Q), H, C and activation enthalpy (h_m) for the mobile ions which are listed in Table 2.

Table 2: Summarised result of activation energy (E_a), C, heat of transport (Q), H and thermoelectric power (S).

Temperature	E_a = h_m (eV)	C = σ$_0$ (Sm^{-1})	Q (eV)	H (mVK^{-1})	S (mVK^{-1}) at 1000 K
High temperature region (T>T_2) K	0.38	6.45 ×10^7	0.40	-0.84	-0.85

Low temperature region (T<T$_1$) K	1.24	5.67 ×10^9	0.94	-0.74	
Here T$_1$ = 1000 K, T$_2$ = 1100 K and T$_p$ = 1050 K					

5. DISCUSSION

In case of both the solids, thermoelectric power (*S*) is found to be negative in the entire chosen range of temperature, which indicates that mobile carriers in the studied compounds are positively charged. Two types of positively charged ions: K^+ and As^{+5} ions in K_3AsO_4 exist. Due to high positive charge, As^{+5} ions are not expected to be mobile, whereas K^+ ions having smaller values of charge as well as dimensions in comparison to As^{+5} ions will exhibit greater mobility. The general transport mechanism of such ions is expected due to hopping. However intrinsic hopping conduction of these ions from normal lattice site to other lattice site is least probable because it will involve high activation energy (5 eV or more). Hence electrical conduction takes place probably due to hopping of defects. Therefore, it appears that there exists a large number of Frenkel defects even in normal ionic phase of the K_3AsO_4 solids and these defects may further be generated at higher temperatures.

In the lower temperature range, which is normal ionic phase, there is an appreciable electronic contribution (2 to 8% for K_3AsO_4) to the electrical conductivity (σ). A high jump in σ (10^3 times) is found at T_p. Above T_p, there is a bending in log $\sigma_i T$ vs T^{-1} plot (Figure 4). The electronic conductivity in this range is negligible. Both σ and *S* should entirely be due to ions. As shown in Table 2, $h_m < Q$ which indicates that K_3AsO_4 compounds belong to the rotator group of solid electrolytes, where not only a large number of equal energy sites are available for K^+ ions as compared to their numbers, but also disorder of the AsO_4 groups helps in enhancing the K^+ ion conductivity. Thus, the Paddle-Wheel mechanism of ionic conduction in super ionic solids seems to be valid for understanding the superionic phase of the samples.

6. CONCLUSION

K_3AsO_4 are typical superionic solids. The phase transition occurs at a particular temperature (T_p) in the samples. T_p is found to be 1050 K for K_3AsO_4. Below phase transition temperature (T_p) the solids behave like a normal ionic conductor in which the electrical conductivity is due to ions with electronic conduction up to 3 to 8% in K_3AsO_4. Above T_p the superionic phase of the compounds comes into existence, which is almost ionic in nature with negligible electronic conductivity approx. 0.1% for K_3AsO_4. In both the phases normal and superionic, electrical conductivity occurs due to Frenkel defects present in the compounds. Further, the Paddle Wheel Mechanism is found suitable for explaining the conduction mechanism of the alkali (K^+) metal arsenates.

REFERENCES

[1] S. Chandra; "Superionic Solids: Principles and Applications", Amsterdam: North-Holland, 1981.

[2]   P.G. Bruce (*ed.*); "Solid State Electrochemistry", No. 5, Combridge University Press, New York, 1995.

[3]   P.P. Kumar and S. Yashonath; "Ionic conduction in the solid state", J Chem. Sci., Vol. 118, pp. 135-154, 2006.

[4]   R.C. Agrawal and R.K. Gupta; "Superionic solid: composite electrolyte phase – an overview", J. Mater. Sci., Vol.34, pp.1131-1162,1999.

[5]   N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto and A. Mitsui; "A lithium superionic conductor", Nature Materials, Vol.10, pp. 682–686, 2011.

[6]   S.A. Suthanthiraraj and V. Methew; "AC Conductivity, XRD and Transport Properties of Melt Quenched Pb- I_2-Ag_2O-Cr_2O_3 System", Ionics, Vol.14, pp. 79-83, 2008.

[7]   K. Padmasree and D.K. Kanchan; "Conductivity and Di- electric Studies on $20CdI_2$-$80[xAg_2O$-$y(0.7V_2O_5$-$0.3B_2O_3)]$ Super Ion Conducting System", J. Non-Cryst. Solids, Vol. 352, pp. 3841-3848, 2006.

[8]   M. Pant, D.K. Kanchan, P. Sharma and M. Jayswal; "Mixed Conductivity Studies in Silver Oxide Based Barium Vanado-Tellurite Glasses", Science and Engineering B, Vol. 149, pp. 18-25, 2008.

[9]   H.B. Lal, K. Gaur and A.J. Pathak; "Electrical transport in the system Li_2SO_4-mLi_2MoO_4-$2mLi_3VO_4J$", Mater. Sci., Vol. 25, pp. 3683-3687, 1990.

[10]   K. Shahi; "Transport studies on superionic conductors", Physica status solidi (a), Vol. 41 (1), pp. 11-44, 1977.

[11]   B.K. Verma and H.B. Lal; "Electrical transport studies on heavy rare-earth tungstates", Mater. Res. Bull., Vol.16, pp. 1579-1591, 1981.

[12]   K.M. Mishra, A.K. Lal and F.Z. Haque; "Ionic and electronic conductivity in some alkali vanadates", Solid State Ionics, Vol.167, pp. 137-146, 2004.

[13]   K. Gaur, A.J. Pathak and H.B. Lal; "Electrical conduction in lithium molybdates", J. Mater. Sci., Vol.5, pp. 785–786, 1986.

[14]   K. Gaur, A.J. Pathak and H.B. Lal; "Some new data on lithium sulphate", J. Mater. Sci. Lett., Vol. 7, pp. 425–427, 1988.

[15]   S. Tripathi, K.M. Mishra and S.N. Tiwari; "Electrical conduction of superionic conductors: Na_2ZrO_3", Emerg. Mater. Res. USA, Vol. 1(4), pp. 205–211, 2012.

[16]   S. Tripathi, K.M. Mishra and S.N. Tiwari; "Mass and Charge Transport in Na_3AsO_4", J. Sci. Tech. Res., Vol. 1, pp. 70-74, 2011.

Shivendu Tripathi