

Thermoelectromotive Power Study of A Superionic Conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$

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Summary: The superionic conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$ was synthesized and characterized. The thermoelectromotive power study on this compound has been carried out in the temperature range from 25 – 80°C. The effect of heat treatment on the material, variation of thermoelectric power with temperature reported which is represented by the equation: $-\theta = 0.218 (10^3/T) - 0.174$.

The theory of Rice and Roth was verified. The material found to be disordered.

Introduction

In previous study the superionic conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$ have been prepared and characterized according to the reported method ^(1, 2) and found to be reproducible. It shows high ionic conductivity $2.3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at room temperature. With important property the conductivity changes very slowly with rise of temperature which leads to the conclusion that the numbers of ions available for electrical conduction remain fixed ⁽²⁾.

The structure of the compound $\text{Ag}_7\text{P}_3\text{S}_{11}$ shows that the material has crystallographically distinct ^{31}P sites; namely that of the isolated PS_4^{-3} ion and those of $\text{P}_2\text{S}_7^{-4}$ group ⁽²⁾. That also approved by standard MAS-NMR spectroscopy, XRD, Raman ^{31}P and ^{109}Ag NMR ⁽²⁻⁷⁾.

It is well known that when a temperature gradient exists between the two ends of a conductor, one end shows a positive potential and the other a negative one. The mobile charges usually move from the hotter to the cooler part. In case of electronic conductors the cooler end acquires negative charge, while in case of ionic conductors it can get either positive or negative charge depending on which ion is mobile the positive or the negative. It was found that in case of AgI- based superionic conductors, silver ions (Ag^+) are always the mobile ones which move to the cooler part under the influence of a temperature field, thereby lower their energy making the cooler end

positive and thus create a potential difference between the ends of the materials. It is known that for a small temperature difference between the ends of the investigated materials, the potential difference ΔV is found to be proportional to the temperature difference ΔT . The ratio $\Delta V / \Delta T$ is termed as thermoelectric power θ ⁽⁸⁻¹⁰⁾.

The thermoelectric power θ and the electrical conductivity (σ) measurements are of importance as they provide information, in general, regarding the number and type of defects, their mobility, the heat transport of each defect etc.^(8 - 12).

As no alkali metal could possibly be used as electrode material, θ_{het} is inherently present in the thermoelectric power measurements on superionic conductor solids in which alkali ions are responsible for the high ionic conductivity of such material. In such a measurement of the thermoelectric power, θ_{total} includes the heterogeneous thermoelectric power θ_{het} , which makes the interpretation of the data from such measurements difficult. However, through thermoelectric power on materials in which silver or copper ion conductor, which are the mobile species, the θ_{het} part of θ_{total} can be eliminated, as an Ag/Cu foil or powder or wires can easily be used in the experimental set up as electrode material.

Apart from conductivity measurements on this material, the thermoelectric power (θ) studies of this materials is of interest, in the sense that it further contributes to understanding the superionic conductor solids. We report in this paper: 1) the effect of the heat treatment 2) the variation of the thermoelectric power with temperature, 3) the verification of the theory of Rice and Roth⁽¹⁴⁾, and 4) indication of a disordered structure of this material.

Experimental

Chemicals

All chemicals used in this work were laboratory pure, silver powder (mesh) from Hopkins & Williams Ltd., England, red phosphorous from Riedel, Hanover, Germany and sulfur from B.D.H. England.

Preparations

$\text{Ag}_7\text{P}_3\text{S}_{11}$ was prepared as reported in the literature^(1, 2). The material was ground to fine powder for about 2 h. The powder was sieved (crystallite size of about 300 μm) which was used to prepare pellets at a pressure of $5 \times 10^5 \text{kPa}$. The thickness of the pellet was 6 mm and 2.5 mm in diameter. The sample holder was the same as that used previously for conductivity measurements^(2, 10, 11) and for thermo - emf studies^(10, 11).

Measurements

Thermoelectric potential difference was measured by digital automatic multimeter PM 2511 from Phillips and the temperature was measured using Ni-Cr-Ni thermocouple in conjunction with a BTV- multimeter No. 941136 and using the same techniques used by Khalifa et al(2). The error involved in the measurement of temperature was $\pm 0.2^\circ\text{C}$. The ambient temperature was controlled by a heater surrounding the sample holder, while a tiny heater located in the lower plate of the holder created the temperature difference between the two end faces of the pellet. For measurement of thermoelectric power (θ), an auxiliary experiment was done first, to study the variation of thermoelectric voltage ΔV with the temperature difference ΔT between the ends of the pellet, while the mean temperature of the pellet was kept constant within $\pm 0.1^\circ\text{C}$. For this material, the variation of ΔV with ΔT was found to be linear with the temperature difference between the two faces of the pellet. The temperature was controlled by heater surrounding the pellet while the temperature difference was created through an auxiliary heater placed at the top flat face of the silver electrode.

Result and Discussion

In this study, it was observed that, even without any temperature difference between the two ends of the pellets, there was a small potential difference ΔV between the faces of the pellet. This effect may be due in part to an uneven distribution of the charge carriers of the samples. In case of superionic conductor solids, the activation energy for ionic movement is very low; therefore the ions are almost free to move in

the solid. If they happen to collect at any one of the ends, the pellet will show a small potential difference between the faces. In order to eliminate this potential difference a temperature difference was created between the two faces to force the positive silver ions (Ag^+) to move to cooler parts in order to lower their energy. The heating was continued till the spurious potential difference decayed to zero. This resulted in almost zero potential difference. Observations were taken when only the steady state had been achieved in each case.

Figure (1) shows the thermoelectric power θ versus the reciprocal of the absolute temperature. This plot shows average values observed during heating and cooling cycle. The results can be represented by the equation:

$$-\theta = 0.218 (10^3/T) - 0.174 \quad (1)$$

This equation yields the heat of transport of Ag^+ ions in the material as 0.217 eV. The activation energy deduced from the conductivity measurement as reported by Khalifa et al⁽²⁾ is 0.29 eV for the same material.

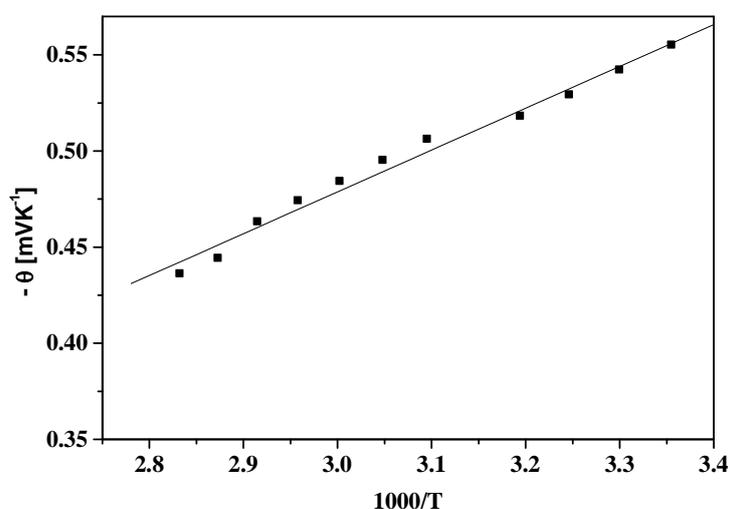


Figure (1) Thermoelectric power (θ) of $\text{Ag}_7\text{P}_3\text{S}_{11}$ (using silver electrode) as a function of inverse of absolute temperature.

Rice and Roth⁽¹⁴⁾ have established theoretically a correlation between thermoelectric power and activation energy for isothermal migration (Δh) obtained from electrical conductivity studies. They have assumed that mobile, cationically disordered ions

possess a 'free-ion' like state. In such a solids there were more lattice sites available than the number of mobile ions. According to Rice and Roth:

$$-\theta_{\text{hom}} = \Delta h/eT^{(14)} \quad (2)$$

Where (Δh) is the activation energy of the mobile ion in the material under investigation (in this case is the Ag^+ ion). It has been shown that in case of superionic conductors, the two transport parameters, namely the heat of transport and the activation energy for migration tend to be the same i.e. $q_{\text{Ag}^+}^* = \Delta h^{(14)}$ so that the heat of transport $q_{\text{Ag}^+}^* = 0.218 \text{ eV}$ and

$$-\theta_{\text{hom}} = \frac{q_{\text{Ag}^+}^*}{eT} \quad (3)$$

Equation 3 shows that the heat of transport of the mobile ions through the immobile lattice is equal to the activation energy of the ion. In particular, for $\text{Ag}_7\text{P}_3\text{S}_{11}$ the close agreement between the heat of transport and the value for the activation energy would suggest that the ions in free-ion-like state in a disordered solid and supports the theory of Rice and Roth⁽¹⁴⁾.

Conclusion

In this study $\text{Ag}_7\text{P}_3\text{S}_{11}$ was synthesized. It was observed that there was a small potential difference ΔV between the faces of the pellet of the material, even without any temperature difference between the two ends of the pellets. This effect may be due in part to an uneven distribution of the charge carriers of the samples. The plot, figure (1), shows average values observed during heating and cooling cycle. The results can be represented by the equation 1. This equation yields the heat of transport of Ag^+ ions in the material as 0.217 eV . The activation energy of the material found to be equal to 0.29 eV . Close agreement between the heat of transport and the value for the activation energy for $\text{Ag}_7\text{P}_3\text{S}_{11}$, equation 3, suggest that the ions in free-ion-like state in a disordered solid and supports the theory of Rice and Roth⁽¹⁴⁾.

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