

Silver Ion Conducting Properties And Differential Thermal Analysis Of AgI Family Super Ionic Conductor

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ABSTRACT

Super ionic material KAg_4I_5 was synthesized by two methods i.e 'solution evaporation method' and 'firing method'. Highly pure AgI and KI were used as raw materials for synthesis. The powder obtained by 'solution evaporation method' was dried, ground and then heated at 162°C for 14 hours in air, then ground before characterisation studies. In 'firing method' mixture was heated and quenched and then ground followed by heating at 162°C for 18 hours before final grinding and characterisation studies. Present investigation is undertaken to compare two methods of preparation of super ionic conductor KAg_4I_5 since very little work has been done on this compound. Lattice constant of the material was obtained from diffraction photographs obtained from Debye-Scherrer camera. Differential thermal analysis(DTA) shows, *greater* proportion of super ionic compound obtained when synthesized by first method. Though the measured electrical conductivity obtained by first method is higher than that of second method, activation energy of charge transport is found to be the same in both.

KEY WORDS:

DTA; Debye-Scherrer camera; Firing method; KAg_4I_5 ; Solution evaporation method; Super ionic conductor

INTRODUCCION:

Crystalline super ionic conductors attract much attention for its fundamental studies on ion transport mechanism and their applications in solid state batteries and solid state electro chemical devices[1]. Super ionic conductors are characterised by the high ionic conductivities and low activation energies of their charge carriers at near ambient temperature. The ionic conductivity of these materials at room temperature is as high as that of aqueous electrolytes or ionic melts [2]. There are three types of super ionic materials. They are AgI, PbF₂ and Na-β-Al₂O₃ [3]. Of these three types of super ionic conductors AgI forms the basis of a whole family of silver ion conductors which exhibit the highest solid state ionic conductivities known at low temperatures [3]. Super ionic conductivity at temperatures close to room temperature is exhibited by the first three of the following four major classes of compounds which have been investigated for their temperature dependant physical properties including structural, thermal and magnetic properties. (i) AgX family (AgI, AgBr, CuBr and CuI) including Ag₃SBr, Ag₃SI and RbAg₄I₅, (ii) MX-Al₂O₃ composites (MX = AgI, AgCl, LiI etc), (iii) glasses in the system AgI-Ag₂O-MxOy (M = B, x = 2, y = 3; M = Te, x = 1, y = 2 etc) and (iv) polymeric systems such as LiClO₄-polyethylene oxide [4]. The motivation for the study of these compounds is their challenging physics and application potential in the areas of secondary electro chromic batteries, electrochemical sensors, fuel cells and devices. The ionic-covalent nature of the Ag-I bond is invoked in an electronic theory of super ionic conductors [5]. AgI undergoes a first order phase transition at 149⁰C accompanied by a large jump in ionic conductivity. The high temperature α-phase is super ionic with an activation energy of 0.05 eV. In an attempt to stabilize the high conductivity phase at ambient temperatures, many structural modifications have been tried. Rubidium substituted compound RbAg₄I₅ has been found to be the best super ionic conductor, which undergoes phase transition at -151⁰ C to achieve super ionic state [6,7]. The room temperature conductivity of this fast ion conductor is 0.21(Ω cm)⁻¹ with an activation energy of 0.1eV[8]. It has been also suggested that substitution of potassium and ammonium ions in AgI would also lead to the formation of super ionic conductors namely ;KAg₄I₅ and NH₄Ag₄I₅. But very little work has been done on these compounds. Moreover two methods of preparation of these types of sample have been suggested by Bradley and Greene[9,10] and Owens and Argue [11]. Ball milling method of the Synthesis of RbAg₄I₅ and KAg₄I₅ Crystals was suggested by Peng H Machidan N Shigematsut[12]. When AgI is heated, local changes occur in Ag-I bonding and these changes play a leading role in the phase transition to the super ionic state. Local fluctuations of bonding create field of forces that cause ion movement. The transition to the super ionic state occurs when the bond fluctuations go critical resulting in a collapse of the Ag⁺ sub lattice [4]. The conductivities in the present investigation were found to be almost same as those of the RbAg₄I₅ and KAg₄I₅ crystalline phases reported by Owens et al. With a view to study the relative efficacy of above mentioned first two methods that the present

investigation was undertaken, in which KAg_4I_5 was prepared by different methods and its lattice constant and electrical conductivity are measured and compared.

MATERIALS AND METHOD

The super ionic material KAg_4I_5 was prepared by the “solution evaporation method” suggested by Bradley and Greene [9,10] as well as by “firing method” suggested by Owens and Argue[11]. Highly pure AgI (98%) and KI (99.8%),GR-grade obtained from Sarabhai M Chemicals were used without further treatment. The samples prepared by the “solution evaporation method” and the “firing method” are designated as “A” and “B” respectively. The powder thus prepared were made into thin wires and used for diffraction photographs using the Debye-Scherrer camera. The lattice constant of materials were calculated from these photographs assuming cubic structure. Differential thermal analysis (DTA) of the prepared samples was carried out using a MOM Derivatograph with a heating rate of 10^0 C min^{-1} up to 200^0 C . For the measurement of electrical conductivity, powders were pressed into pellets of $1.057 \pm 0.002 \text{ cm}$ in diameter and $0.45 \pm 0.06 \text{ cm}$ in thickness at a pressure of 350 kg cm^{-2} at 80^0 C . To ensure the good electrical contact the circular surfaces were pressed with micro-thin silver foil. The sample was then placed between two silver electrodes in the conductivity cell. The conductivity was measured in the temperature range from RT to 200^0 C .

RESULT AND DISCUSSION

Lattice constants of samples A and B are found to be 1.035 nm and 1.088 nm respectively. Lattice constants of A and B samples obtained from the present measurement agree closely to the value of 1.115 nm reported by Bradley and Greene [9,10]. Though the lattice constants of A and B samples are similar, the photographs of samples show, the sample A exhibits lines of strong intensity and sample B exhibits weak intensity under identical conditions of X-irradiation. The DTA curves of the samples prepared by both methods are shown in Fig. 1a and Fig 1b. The sample A shows the only endothermic peak at 85^0 C and the sample B shows at 85^0 C and 125^0 C . It is known that K_2AgI_3 is also formed together with KAg_4I_5 during synthesis which is stable up to 130^0 C [12] and transform into super ionic KAg_4I_5 phase at high temperatures. The 125^0 C Peak in the sample B is due to transformation of K_2AgI_3 to KAg_4I_5 , showing that this sample contains K_2AgI_3 . Hence in the method of ‘firing’, conversion is not complete during heating at 170^0 C . Thus proportion of super ionic compound KAg_4I_5 is greater in the sample A than in the sample B. The temperature variation of conductivity is shown in Fig. 2a and b for samples B and A respectively. Data of conductivity vs temperature is shown in table-I. From table and figure we can understand Conductivity increases with temperature in super ionic conductor. Though conductivity of sample A is higher than that of sample B through out the whole temperature range, the activation energy of charge transport is calculated to be same in both i.e 0.04 eV . Also the DTA measurements show that the sample A contains comparatively more KAg_4I_5 than the sample B.

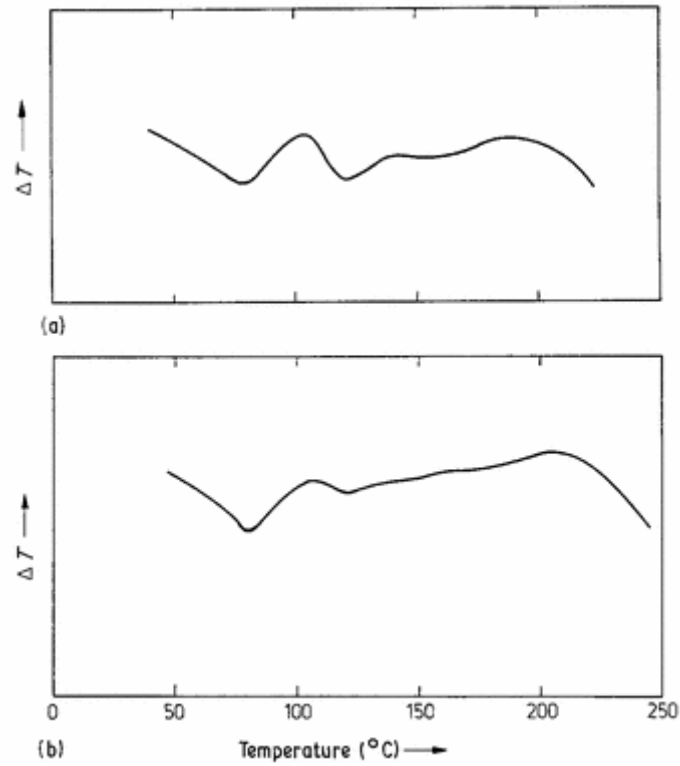


Figure 1 Differential thermal analysis of KAg_4I_5 samples: curve (a) for the B sample and (b) for the A sample

TABLE-I Conductivity data with variation of temperature of both the samples

$1/T(\times 10^{-3})\text{K}$	\log_{10}^{ot}	
	Sample B	Sample A
1.9	1.525	1.55
2.0	1.5	1.54
2.1	1.49	1.51
2.2	1.48	1.5
2.3	1.46	1.49
2.4	1.45	1.47
2.5	1.42	1.45
2.6	1.41	1.42
2.7	1.381	1.4
2.8	1.38	1.39
2.9	1.344	1.37
3.0	1.343	1.36
3.1	1.31	1.34
3.2	1.30	1.325
3.3	1.25	1.31

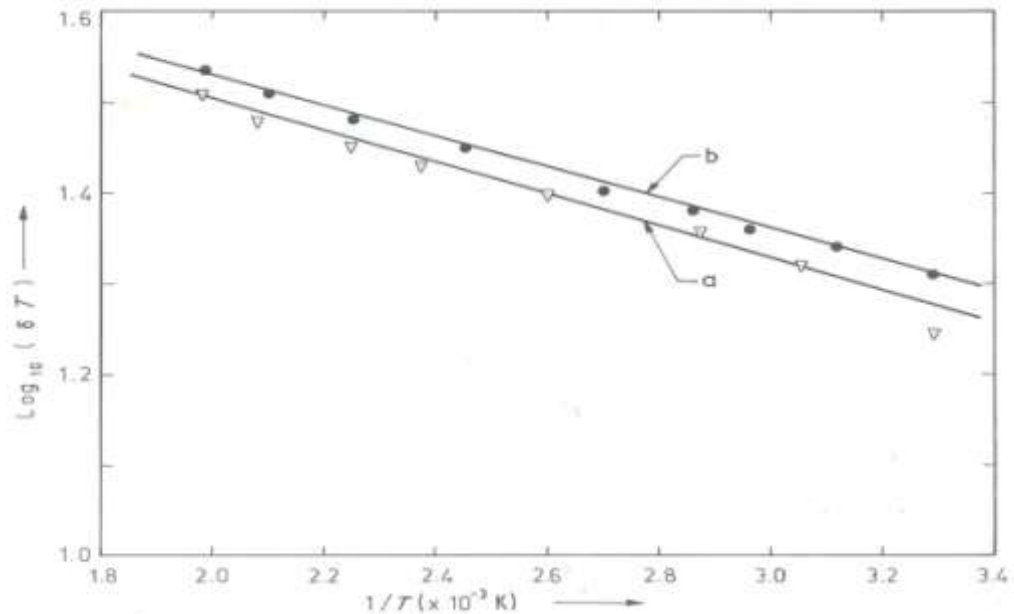


Figure 2 Temperature dependence of the electrical conductivity of KAg_4I_5 pellets: curve (a) for B sample and curve (b) for A sample

The activation energy 0.04eV obtained from the present measurement agrees closely with the value (0.05eV) reported by Hooper[1]. The conductivity at room temperature was found to be $0.068(\Omega \text{ cm})^{-1}$ for sample A, and $0.064(\Omega \text{ cm})^{-1}$ for B which is similar to $0.05(\Omega \text{ cm})^{-1}$ as reported by Bradley and Greene [9,10] but differs from the value of $0.21(\Omega \text{ cm})^{-1}$ reported by Owens and Argue [11]. It is also seen from literature that the values of activation energy and conductivity for the same super ionic compound reported by various authors [9-11, 13-15] vary two to four times. It depends on temperature and pressure during pallet formation.

CONCLUSION

As KAg_4I_5 is a super ionic conductor its presence in higher proportion in the sample A is responsible for its higher conductivity. The value of conductivity and activation energy show that both the “solution evaporation” and “firing” methods of preparation lead to formation of the super ionic compound KAg_4I_5 . But solution evaporation method is relatively more effective in producing this type of super ionic compound (MAg_4I_5 where $M=Rb, K, NH_4$) than the firing one. Further work along this line under progress.

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