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RESEARCH ARTICLE

Electrical Impedance and Structural Studies of Fast-Ion Conducting System $(SbI_3)_x$ - $(Ag_2WO_4)_{1-x}$ $(0.1 \leq x \leq 0.5)$

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Abstract: This paper deals with the preparation and characterization of silver ion conducting system composed of $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$ to identify the superionic conducting compositions. Powder samples of various compositions containing x=0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction respectively were synthesized by rapid melt-quenching method. These samples were characterized using x-ray diffraction (XRD) and differential scanning calorimetry (DSC) studies. Their electrical transport properties were studied using complex impedance analysis. The realization of the typical ionic conductivity values of 5.7×10^{-2}, 5.5×10^{-3} and 1.8×10^{-3} S cm^{-1} for the compositions $(SbI_3)_{0.4}$ – $(Ag_2W0_4)_{0.6,}$ $(SbI_3)_{0.2}$ – $(Ag_2W0_4)_{0.8}$ and $(SbI_3)_{0.3}$ – $(Ag_2W0_4)_{0.7}$ respectively at room temperature has been discussed in terms of the observed characteristics.

Keywords: Complex impedance, Electrical conductivity, XRD, Superionic solids, Transport properties

Introduction

The field of solid state ionics plays a pivotal role in overcoming the problems of energy storage and management for a major part of the future generation. Solid electrolytes have several advantages over their liquid counterparts such as feasibility of miniaturization, spill-proof, long shelf –life, lack of corrosion, absence of evolution of toxic substances and wide temperature range of operation and various applications like energy storage, analog memory devices, electrochemical capacitors and electro- chromic displays.

The class of solids usually known as superionic conducting glasses exhibits an appreciably high conductivity. In particular, silver-based materials are found to exhibit high ionic conductivities in the range 10^{-3}-10^{-1} S cm^{-1} at room temperature and possess enormous applications due to their ease of preparation in different forms, large values of room temperature ionic conductivity, *etc*.,[1]. Even though in the majority of the known fast Ag^+ conducting glasses, AgI has been used as a host salt, the replacement of AgI with other metal halides such as PbI_2, CuI, CdI_2 *etc*.,[2-4] was carried out. Such electrolyte systems exhibited electrical conductivities comparable to that of their AgI-doped counterparts. In recent years, investigations on systems with second cation namely Cd^+, Cu^+, Pb^{2+} or Sb^{3+} tend to coordinate with the oxygen atom in the oxy anion framework and leave the Ag^+ ions in an iodine-rich environment[5] and highest conductivities in these systems were realized with the lesser concentration of metal halides and lead to a possibility of having cost effective system[6].

The role of SbI_3 in developing superionic solid electrolytes with conductivity values of 3.2×10^{-2} S cm^{-1} respectively for the composition $(SbI_3)_{0.3}$ - $(Ag_2Cr0_4)_{0.7}$ at room temperature has been established in our laboratory in the previous mixed system $(SbI_3)_x$ - $(Ag_2Cr0_4)_{1-x}$[7].

The role of the silver oxysalt Ag_2WO_4 has also been well established in the literature by many researchers[8-9] owing to its applications in ambient temperature oxygen sensor, chemical sensor and as electron beam recording material[10]. In view of the above facts, the present work has been undertaken with an aim of arriving at a new series of silver ion conducting superionic solids by appropriately substituting SbI_3 for AgI into a typical silver oxysalt namely Ag_2WO_4.

In this context, we report, the preparation of $(SbI_3)_x$ - $(Ag_2WO_4)_{1-x}$ as a new mixed system and its structural and conducting properties characterized through x-ray diffraction, differential scanning calorimetry and electrical conductivity studies.

Experimental

Analar grade chemicals of antimony triiodide, SbI_3 and silver tungstate, Ag_2WO_4 were used as raw materials. Appropriate amounts of these raw materials were taken as per the stoichiometric composition of the new binary system $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$, where x=0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction respectively. Samples were prepared by rapid melt-quenching method as described elsewhere[11].

Characterization

X-ray diffraction (XRD) measurements were carried out on powdered samples at room temperature using a Siefert x-ray diffractometer with Cu $K\alpha_1$ radiation. (λ=1.541 A°). Thermal phase transitions were measured in terms of heat flow in the temperature range 323–573 K using a Perkin Elmer model DSC-7 differential scanning calorimeter at a heating rate of 20º min^{-1} with platinum as the reference material and aluminum sample containers. Their electrical characterization was carried out using powder samples pelletized at a pelletizing pressure of 5 ton cm^{-2} and made into circular pellets of 8 mm diameter. It was then mounted between silver electrodes whereby the complex impedance measurements were carried out using a computer controlled Hewlett-Packard model HP4284A Precision LCR Meter with an applied 500 mV a.c voltage in the frequency range 20 Hz–1 MHz from room temperature (301 K) to 437 K. The temperatures of the samples were measured using a Chromel-Alumel thermocouple attached to the sample compartment.

Results and Discussion

Phase identification-XRD data

Figure 1 shows the room temperature XRD patterns obtained for nine different compositions containing x= 0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction respectively and designated as a, b, c, d and e respectively.

The detection and identification of reflection lines in the XRD patterns have been carried out carefully through the XRD analysis software aided by JCPDS-International Center for diffraction data in order to find out the various phases present in the system.

The experimentally obtained XRD pattern of the present system $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$ reflects the solid state exchange reaction between the starting materials SbI_3 and Ag_2WO_4, because of which AgI phase is formed in certain favorable compositions as evidenced from the observed peaks at 2θ=23.02, 39.2 and 46.3° with *h k l* planes (1 1 1), (2 2 0) and (3 1 1) respectively[12] which may influence the electrical properties. The intensity of these observed peaks increases from the compositions having *x*=0.1 up to 0.5 and in the case of compositions having *x*=0.4, the peaks are found to be less intense and broad indicating its disordered nature which may be accounted for higher ionic conductivity.

The XRD pattern depicted in Figure 1 also witnesses the formation of intermediate phases in addition with AgI phase as a result of the solid state reaction between SbI_3 and Ag_2WO_4 in the case of compositions having *x*=0.3, 0.4 and 0.5 with less intense peaks at 2θ=25.9, 27.9 and 29.9 ° with *h k l* planes (1 0 3), (0 0 4) and (1 1 2) respectively identified as Sb_5O_7I phase[13]. Also less intense peaks at 2θ=26.92, 29.97 and 36.64° with *h k l* planes (1 1 1), (1 1 2) and (0 2 0) respectively[14] corresponding to the Sb_2WO_6 phase for the compositions having *x*=0.1, 0.2, 0.3 and 0.4 respectively. In the case of *x*=0.1, peaks observed at 2θ=38.1, 44.2[15] and 64.2° indicate the presence of traces of metallic silver. Similar peaks are also observed in *x*=0.2 but with lesser intensity. During the melting of starting materials, the initial decomposition of Ag_2O may most probably be the reason for the formation of elementary silver in samples. Therefore, during the preparation process, the formation of elemental silver in traces is unavoidable[16].

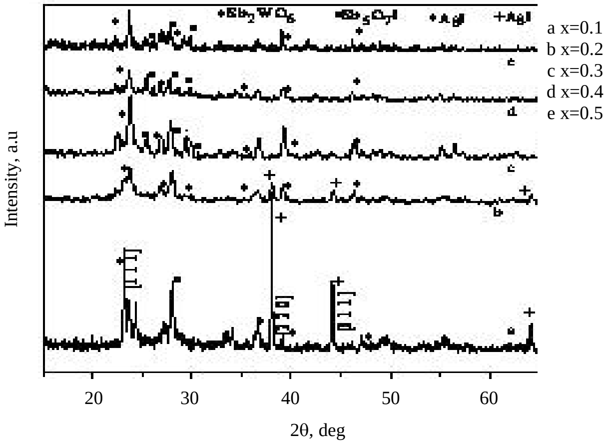

Figure 1. XRD patterns of five different compositions of the mixed system $(SbI_3)_x$-$(Ag_2WO_4)_{1-x},$ $0.1 \leq x \leq 0.5$

Differential scanning calorimetric analysis

The differential scanning calorimetry results obtained for five different compositions having *x*=0.1, 0.2, 0.3, 0.4 and 0.5 mole fraction respectively are shown in Figure 2 and their respective endothermic peak positions are tabulated in Table 1. DSC traces recorded for compositions having *x*=0.1, 0.3 0.4 and 0.5 exhibit endothermic peaks at 418, 423 422, 424 ±3 K respectively, which may correspond to the $\beta \rightarrow \alpha$ phase transition of pure AgI (420 K) phase[17] in good agreement with the XRD results. This observation confirms the formation of AgI as a solid state exchange reaction product between SbI_3 and Ag_2WO_4. In the case of compositions having *x*=0.2, an endothermic peak is observed at around 428 K. The fact that this is not exactly matching with the exact phase transition of AgI may be due to the presence of intermediate compounds as discussed in XRD.

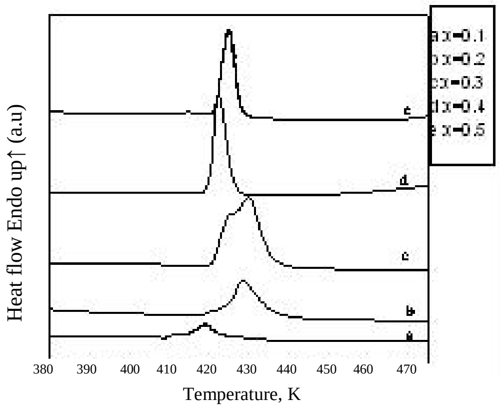

Figure 2. DSC curves obtained for the five different compositions of $(SbI_3)_x$ - $(Ag_2WO_4)_{1-x}$.

Table 1. DSC peaks observed for five different compositions of the mixed system $(SbI_3)_x$-$(Ag_2WO_4)_{1-x}$

Composition (x)	Endothermic peak position, K
0.1	418
0.2	428
0.3	423
0.4	422

Electrical conductivity results

Figure 3 depicts the typical complex impedance Nyquist plots obtained for the composition having x=0.4 at room temperature comprising a portion of a semicircle whose intersection on the real axis corresponds to the bulk resistance (R_b). Similar pattern is observed for the remaining compositions also. Using the value of bulk resistance as evaluated from the impedance plot using the internally incorporated Boukamp equivalent circuit software, electrical conductivity values were estimated from the general relationship.

$$\sigma = t / (A * Rb) \qquad (1)$$

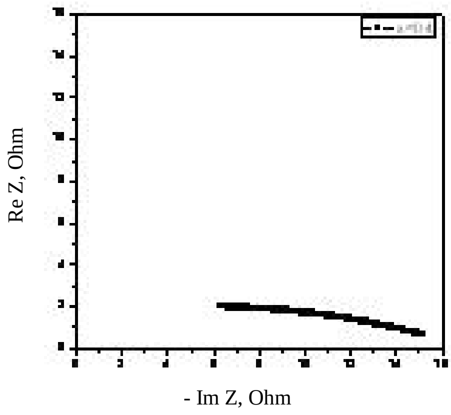

Figure 3. The complex impedance plot obtained for the typical composition of the mixed System $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$ having x = 0.4 mole fraction at room temperature

Where *t* denotes the thickness of the sample pellet and *A* its area of cross-section. The calculated room temperature electrical conductivity values (σ_{301} K) from the complex impedance plots for five different compositions of the present system having *x*=0.1,0.2,0.3, 0.4 and 0.5 mole fraction respectively were found to be 4.1×10^{-4}, 5.5×10^{-3}, 1.74×10^{-3}, 5.7×10^{-2} and 6.4×10^{-4} S cm^{-1} respectively as shown in Table 2. The observed conductivity values reveal the possibility of obtaining typical conductivity (σ) values of the order of 10^{-2}-10^{-4} S cm^{-1} and may be attributed to the presence of AgI in these samples formed as a reaction product of solid state reaction between SbI_3 and Ag_2WO_4 according to (HSAB) principle[3] which states that soft acids would prefer to bind to soft or polarizable bases and that hard acids would prefer to bind to hard or non polarizable bases.

Table 2. Summary of electrical transport data for the system $(SbI_3)_X$ - $(Ag_2WO_4)_{1-X}$

Composition (x)	Room temperature Electrical conductivity $\sigma_{301\ K}$ (S cm^{-1})
0.1	4.1×10^{-4}
0.2	5.5×10^{-3}
0.3	1.7×10^{-3}
0.4	5.7×10^{-2}
0.5	6.4×10^{-4}

The observed conductivity values with respect to the concentration of SbI_3, show a systematic variation when concentration increases from *x*=0.1, room temperature conductivity value increases and reaches a maximum value of 5.7×10^{-2} S cm^{-1} for the composition having *x*=0.4 mole fraction and further increase in *x,* leads to decrease in conductivity values as revealed in the case of effective conductivity values estimated for the composition having x= 0.5 mole fraction.

The most probable reason for this kind of trend in variation of conductivity may be ascribed to the formation and concentration of AgI in these samples and highly disordered nature of the composition having *x* = 0.4. With further increase in SbI_3 content, the tendency of crystallization was found to increase leading to a decrease in ionic conduction[18]**.** Similar results were also reported in the case of systems such as PbI_2-Ag_2O-V_2O_5[2], CdI_2-Ag_2O-V_2O_5-B_2O_3[4], (0.5AgI–0.2SbI_3–0.3Sb_2S_3)[5], PbI_2-Ag_2O-P_2O_5, PbI_2-Ag_2O-TeO_2[6], *x*CuI-(100-*x*) [2Ag_2O-0.7V_2O_5 -0.3B_2O_3][18] and CdI_2-Ag_2O-MoO_3[19]. As reported by Damrawi *et al*[6], SbI_3 as iodine ion source contributes three I^- ions to the Ag_2WO_4 network whereas in the conventional AgI- Ag_2WO_4 system[8], only one I^- ion is contributed to the Ag_2WO_4 network.

Also, the appreciably high conductivity value of 5.5×10^{-2} S cm^{-1} was achieved for the composition $(AgI)_{0.75}$- $(Ag_2WO_4)_{0.25}$ whereas in the present system, maximum conductivity value of 5.7×10^{-2} S cm^{-1} is obtained for the composition $(SbI_3)_{0.4}$- $(Ag_2WO_4)_{0.6}$ with lesser amount of iodide. This appears to suggest that the substitution of SbI_3 as an alternate metal halide into the AgI- Ag_2WO_4 network has resulted in a cost effective system.

Conclusion

The formation of superionic solids in the system $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$ and a typical composition namely $(SbI_3)_{0.4}$-$(Ag_2WO_4)_{0.6}$ and yet another composition $(SbI_3)_{0.2}$-$(Ag_2WO_4)_{0..8}$ exhibiting the high silver ion conductivity of 5.7×10^{-2} and 5.5×10^{-3}S cm^{-1} at 301 K respectively has been discussed. XRD analysis has revealed the formation of multiphase nature of superionic solids in the present system whereas DSC results have shown the $\beta\rightarrow\alpha$ phase transition of pure AgI (420 K) phase. Therefore, the present investigation has demonstrated that addition of SbI_3 as a dopant salt in the $(SbI_3)_x$- $(Ag_2WO_4)_{1-x}$ solid electrolyte system has a significant role in improving the conductivity and indicated their potential as superionic solids suitable for solid state device applications.

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