An Investigation of New Phase Diagram of Ag\textsubscript{2}SO\textsubscript{4} - CaSO\textsubscript{4}

Ravi V. Joat, Pravin S. Bodke, Shradha S. Binani, S. S. Wasnik

Abstract—A phase diagram of the Ag\textsubscript{2}SO\textsubscript{4} - CaSO\textsubscript{4} (Silver sulphate – Calcium Sulphate) binaries system using conductivity, XRD (X-Ray Diffraction Technique) and DTA (Differential Thermal Analysis) data is constructed. The eutectic reaction (liquid $\rightarrow$ a- Ag\textsubscript{2}SO\textsubscript{4} + CaSO\textsubscript{4}) is observed at 10 mole% CaSO\textsubscript{4} and 645°C. Room temperature solid solubility limit up to 5.27 mole % of Ca\textsuperscript{2+} in Ag\textsubscript{2}SO\textsubscript{4} is set using X-ray powder diffraction and scanning electron microscopy results. All compositions beyond this limit are two-phase mixtures below and above the transition temperature ($\approx$ 416°C). The bulk conductivity, obtained following complex impedance spectroscopy, is found decreasing with increase in CaSO\textsubscript{4} content. Amongst other binary compositions, the 80AgSO\textsubscript{4} - 20CaSO\textsubscript{4} gave improved sinterability/packing density.

Keywords—Ag\textsubscript{2}SO\textsubscript{4} - CaSO\textsubscript{4} (Silver sulphate–Calcium Sulphate) binaries system, XRD (X-Ray Diffraction Technique) and DTA(Differential Thermal Analysis).

I. INTRODUCTION

THE sulphate based solid electrolytes have found potential application in electrochemical devices [1], [2]. Particularly, Li\textsubscript{2}SO\textsubscript{4}, Na\textsubscript{2}SO\textsubscript{4} and Ag\textsubscript{2}SO\textsubscript{4} based systems are potential materials from SO\textsubscript{x} galvanic gas sensor viewpoint [2]. The first two materials have been studied extensively as compared to the latter one.

Amongst all the sulphates silver sulphate, a non-alkali metal is an exception that exhibits high Ag\textsuperscript{+} conductivity. The high ionic conductivity, in spite of large size of Ag\textsuperscript{+} (1.26Å), has been suggested to be due to its high quadrupolar polarizability. The Ag\textsubscript{2}SO\textsubscript{4} based solid electrolytes offer additional advantages from SO\textsubscript{x} number, differential thermal analysis and X-Ray powder diffraction techniques [15]. A detailed investigation on Li\textsubscript{2}SO\textsubscript{4} - Ag\textsubscript{2}SO\textsubscript{4} binary phase diagram has been carried out by Oye [16]. Following an extensive work on Ag\textsubscript{2}SO\textsubscript{4} - Me\textsubscript{2}SO\textsubscript{4} (Me = Na and K) Secco et al., in recent past, have proposed Ag\textsubscript{2}SO\textsubscript{4} - Rb\textsubscript{2}SO\textsubscript{4} binary phase diagram [17], [18]. According to these phase diagrams Ag\textsubscript{2}SO\textsubscript{4} forms solid solution in entire compositional range of binary system and their useful utility for SO\textsubscript{x} gas sensor application due to their stable performance as compared to mono-phase. Moreover, the performance of sensor depends considerably on the magnitude of cationic conductivity, the phase and form along with the chemical and thermodynamical stability of solid electrolyte. Most of this information can easily be obtained from the binary-phase diagram and so they are important.

In 1907, Nacken has proposed the equilibrium phase diagrams of Ag\textsubscript{2}SO\textsubscript{4} with mono-valent alkali sulphates (Me\textsubscript{2}SO\textsubscript{4} where Me = Na and K) using the results obtained towards thermal analysis [14]. In a systematic study, Takahashi et al have initially determined the conductivity and later constructed the binary phase diagrams with silver halides (AgX - Ag\textsubscript{2}SO\textsubscript{4} where X = Gland Br) with the help of transport number, differential thermal analysis and x-ray powder diffraction techniques [15]. It is evident from the literature that so far a systematic investigation on the Ag\textsubscript{2}SO\textsubscript{4} - MSO\textsubscript{4} (M = Sr, Ca, Ba) binary systems, which may be potential from SO\textsubscript{x} gas sensor viewpoint, is lacking. All these factors have prompted us to investigate Ag\textsubscript{2}SO\textsubscript{4} - CaSO\textsubscript{4} binary system, using electrical conductivity, differential scanning calorimetry, differential thermal analysis and x-ray powder diffraction techniques, constructing phase diagram to understand the phase and form of solid electrolyte belonging to this system in the vicinity of sensor operating temperature.

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II. EXPERIMENTAL

The initial ingredients Ag₂SO₄ and anhydrous CaSO₄ with purity greater than 99.9% were procured from E Merck. The above chemicals in (100-x)Ag₂SO₄-(x)CaSO₄ (where x = 0.1, 2.5, 5.27, 7.57, 10, 20, ... 100) mole percent were mixed in an agate mortar under acetone for 2 hours. Well ground compositions were then transferred to translucent quartz ampoules and heated to the temperature 20°C above their respective melting point. The melt was allowed to cool, at the rate of 1.50°C min⁻¹, to room temperature. On the other hand, the compositions with more than 60-mole % of CaSO₄ were prepared by fusing the well ground mixture at 800°C in silica ampoules so as to avoid thermal decomposition of silver sulphate. The ingots obtained by breaking the ampoules were finally pulverized to get fine powder. The entire procedure was carried out in a dark room so as to avoid photodecomposition of silver sulphate.

All samples were characterized using X-ray powder diffraction (XRD) (Philips PW 1700 diffractometer attached with PW 1710 controlling unit) using CuKα radiation at room temperature. Whereas, XRD patterns were recorded at 300 and 450°C for a few selected samples viz. 20, 40 and 60 mole % CaSO₄ added to Ag₂SO₄. In order to set the room temperature solid solubility limit, diffraction patterns were recorded for 5.27 mol% CaSO₄ added to Ag₂SO₄ samples prepared by two different techniques viz. (i) initial ingredients Ag₂SO₄ and CaSO₄ in appropriate mole ratio were thoroughly mixed mechanically under acetone for 2 hours and (ii) melting the same thoroughly mixed composition followed by slow cooling the melt to room temperature. The information towards the solid-solid phase transition temperature, the melting point and the heat of transition were obtained by differential scanning calorimetry (DSC) and differential thermal analysis using Mettler TA 4000 DSC 25 and Mettler TA DTA, respectively.

The microstructure of 10, 20 and 30 mol% CaSO₄ added to Ag₂SO₄ clearly indicate the formation of two-phase mixture and in 80Ag₂SO₄ - 20CaSO₄ it shows denser packing as compared to other compositions.

B. Scanning Electron Microscopy (SEM)

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C. Thermal Analysis (DSC/DTA)

A typical DTA thermogram of 80Ag₂SO₄-20CaSO₄ is depicted in Fig. 1. The solid-solid phase transition temperature and the melting point are obtained from the onset of endothermic peak. It is worth mentioning here that the values of Tc obtained following DSC and DTA analyses for all samples were found in agreement within the accuracy of ±2°C. Moreover, they were reproducible. A close look at the insert of Fig. 1 reveals a continuous decrease in the heat corresponding to solid-solid phase transition with an increase in CaSO₄ concentration in Ag₂SO₄. This is due to the decrease in net content of latter in the samples indicating formation of two-phase mixtures.

A phase diagram of Ag₂SO₄-CaSO₄ binary system, constructed using above XRD and DTA/DSC data is shown in Fig. 2. The solid circles represent the thermal discontinuities obtained from DTA/DSC. Thermodynamic features present in this binary system are summarized as follows, (a) the solid-solid phase transformation (α-Ag₂SO₄ → β-Ag₂SO₄) and melting point for Ag₂SO₄ are at 416 and 658°C, respectively, (b) the solid-solid phase transformation and melting point for CaSO₄ are at 1190 and 1450°C, respectively, (c) eutectic reaction (liquid → α-Ag₂SO₄ + CaSO₄) at 10 mole% CaSO₄ and 645°C (d) approximately 5 mole% CaSO₄ is soluble in β-Ag₂SO₄ (e) two phase mixture of (β-Ag₂SO₄ + β-CaSO₄) exists between room temperature and 416°C, (f) two phase mixture...
of $\alpha$-Ag$_2$SO$_4$ and $\beta$-CaSO$_4$ exists between 416 and 655°C for all compositions, (g) melt and solid $\beta$-CaSO$_4$ coexists beyond 30 mole% CaSO$_4$ and above 655°C. Due to experimental limitation it was not possible to investigate thermal behaviour of samples above 1000°C. The dotted line is, however, an extrapolated liquidus curve.

A close look at this phase diagram reveals that $T_c$ slightly decreases with an addition of CaSO$_4$ up to 7.5 mole% and thereafter it remains fairly constant. The initial decrease in $T_c$ with an increase of CaSO$_4$ concentration is due to the formation of solid solution (Table I). Irvine and West have explained the decrease in $T_c$ by assuming that the substitution of alio-valent cation results in the creation of extrinsic vacancies that causes lattice distortion/disorder [22]. According to them, the order-disorder phase transition in solid solution occurs more readily with rising temperature, and $T_c$ displaces to a lower temperature.

**D. Temperature Dependent Conductivity**

The plots of log ($\sigma$) versus $10^3/T$ for (x)Ag$_2$SO$_4$·(1-x)CaSO$_4$ system for x = 0-10, $\nu$ = 10-60 and x = 70-100 mole% are displayed in Figs. 3, 4 (a) and 4 (b), respectively. As seen, in both orthorhombic (stable below 416 °C) and hexagonal (stable above 416°C) modifications of Ag$_2$SO$_4$ conductivity obey the Arrhenius law.

Observed change in conductivity at 416°C, for all samples, accounts for orthorhombic (β) to hexagonal (α) phase transition in Ag$_2$SO$_4$. Notably, this temperature coincides with the $T_c$ obtained from DSC and DTA investigations. The change in slope from 416°C, ascribed to a switch in conduction mechanism due to structural phase-transition, is the manifestation of partial insolubility of CaSO$_4$ in Ag$_2$SO$_4$ and vice-versa. Also, it rules out the formation of new intermediate compound in the entire binary system. These results are in agreement with above discussed XRD and DTA results. The conductivity measurements were restricted to below 560°C due to softening/deformation of samples at this temperature.

Insert of Figs. 3, 4 (a) and 4 (b) display the conductivity behavior (in both the modifications) of samples with CaSO$_4$ addition. In the high temperature modification (Fig. 3), the conductivity exhibits a maximum at 7.57 mole% (= 7% vacancies) CaSO$_4$ within the solid solubility region. Whereas, in two-phase region (Figs. 4 (a) and (b)), it remains fairly invariant. In contrast, the conductivity below the transition temperature decreases (insert of Figs. 3, 4 (a) and 4 (b)).

The maximum in conductivity at 7.57 mole%, corresponding to ≈ 7% vacancies, is in good agreement with the reporting [23]. Since Ca$^{2+}$ (0.99A) is smaller than Ag$^+$ (1.26 A), the partial replacement of latter by former leads to an appreciable lattice contraction (Table II) in room temperature phase of Ag$_2$SO$_4$. Hence, Ca$^{2+}$ addition gives an additional vacancy with deeper potential well that offers large activation energy for Ag$^+$ migration. Therefore, as CaSO$_4$ content increases, conductivity decreases in low temperature phase.

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Fig. 1 DTA thermogram of 80 Ag$_2$SO$_4$-20CaSO$_4$ and insert variation of phase transition enthalpy with the addition of CaSO$_4$ in Ag$_2$SO$_4$.

Fig. 2 The phase diagram for Ag$_2$SO$_4$–CaSO$_4$ binary system. The solid circles represent thermal discontinuity as determined from differential thermal analysis. The indicated bi-phase regions are confirmed by x-ray diffraction. The broken line near Ag$_2$SO$_4$ end indicates the uncertainty of the solid solution range in this phase. The dotted line is expected liquidous curve.

Fig. 3 log ($\sigma T$) versus 1000/T for (l-x) Ag$_2$SO$_4$ - (x) CaSO$_4$ where x = 0 - 10. Insert indicates the variation of conductivity with CaSO$_4$ concentration.

Fig. 4 (a) log ($\sigma T$) versus 1000/T for (1-x) Ag$_2$SO$_4$ - (x) CaSO$_4$ binary system with (a) x = 10 - 60 and (b) x = 70 - 100. Insert indicates variation of conductivity with CaSO$_4$ concentration.
IV. CONCLUSION

The CaSO₄ is sparingly soluble in both the hexagonal and the orthorhombic phases of Ag₂SO₄ and form bi-phase mixtures in entire binary system. The eutectic reaction (liquid $\rightarrow \alpha$-Ag₂SO₄ + CaSO₄) is observed at 10 mole% CaSO₄ and 645°C. The value of conductivity although decreased but 20 mole % CaSO₄ added to AgSO₄ is useful for Sox gas sensor application due to (i) its bi-phase nature at operating temperature, (ii) low activation enthalpy for ion migration, (iii) improved sinterability and (iv) good mechanical strength.

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REFERENCES