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Note

THE SYSTEM Ag_2SO_4–$CdSO_4$

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The phase diagram of the binary system Ag_2SO_4–$CdSO_4$ presented here was studied by DTA using sealed ampoule techniques to suppress decomposition of the salts [1].

The only previous work to be reported for this system is the binary section taken from a quaternary system [2] which is reported by Levin et al. [3]. This shows a eutectic at 62 mol% (all compositions are expressed as mol% of Ag_2SO_4) and 583°C. The eutectic horizontal is evident at compositions of 0–80 mol% where a region of solid solution begins. A maximum in the silver sulphate-rich liquidus curve is indicated at 671°C and 90 mol%, and is interpreted as being a maximum melting solid solution. The other liquidus curve extends only as far as 800°C, and there is no evidence of any polymorphic transitions.

Existing DTA studies on $CdSO_4$ [4–8] show two high-temperature phase transitions, $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$, which occur in the temperature ranges 750–843 and 830–897°C, respectively. High-temperature X-ray diffraction [9] has indicated transition temperatures of 754 ± 12 and 820 ± 13°C, and has also shown the structures of the three modifications, α, β, and γ to be orthorhombic ($HgSO_4$ structure), orthorhombic ($CrVO_4$ structure) and hexagonal ($NaKSO_4$ structure), respectively. Ag_2SO_4 transforms from the low temperature α form (orthorhombic) to the β form (Na_2SO_4-I structure) between 425 and 433°C [1,10,11] and melts without decomposition at 660°C.

EXPERIMENTAL

Materials

Reagents used were BDH AnalaR Ag_2SO_4 (99%) while $CdSO_4$ was obtained by heating Aldrich Gold Label $CdSO_4 \cdot H_2O$ (99.999%) to 250°C for 48 h. Mixtures were prepared by gently grinding the salts together for 5 min under $CHCl_3$ (Fisons A.R. grade, 99.9%). Any remaining solvent was removed by heating at 100°C for 30 min before transferring mixtures to

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ampoules. Immediately before evacuating and sealing the quartz ampoules, samples were held at 400°C for 1 h. Sample masses of 100–200 mg were used throughout.

Apparatus

The DTA apparatus has been described previously [1]. In the present study the temperature programmer was replaced by a Control and Readout LTD 802KB/407/505 system.

RESULTS

The phase diagram obtained by DTA (Fig. 1) records the average peak temperatures of transitions on heating at 6 K min^{-1} taken over multiple heating/cooling cycles.

The $\alpha \rightarrow \beta$ transition of $CdSO_4$ is observed at 797 ± 4°C on heating (744 ± 5°C on cooling) over the composition range 0–29 mol% while the transition $\beta \rightarrow \gamma$ occurs at 838 ± 2°C (825 ± 7°C), 0–32 mol%. The eutectic horizontal occurs at 585 ± 2°C (576 ± 3°C) throughout the range 1–80 mol%, the eutectic composition itself being 64 mol%. Pure Ag_2SO_4 transforms at 433°C, melting at 665°C. Two regions of solid solution, corre-

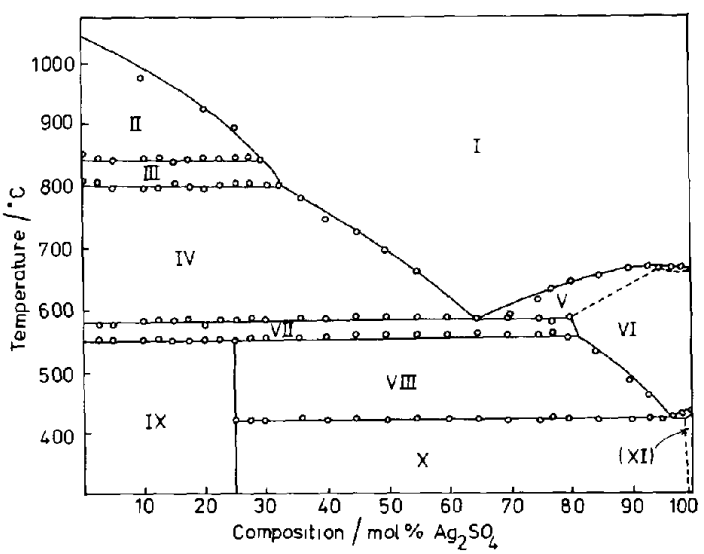

Fig. 1. Phase diagram for the system Ag_2SO_4–$CdSO_4$; (I) l; (II) γ $CdSO_4$ + l; (III) β $CdSO_4$ + l; (IV) α $CdSO_4$ + l; (V) β ss + l; (VI) β ss; (VII) α $CdSO_4$ + β ss; (VIII) $Cd_3Ag_2(SO_4)_4$ + β ss; (IX) $Cd_3Ag_2(SO_4)_4$ + α $CdSO_4$; (X) $Cd_3Ag_2(SO_4)_4$ + α ss; (XI) α ss. where l denotes liquid and ss denotes solid solution.

sponding to the two Ag_2SO_4 structures, are apparent. The low temperature solid solution, α, appears over a composition range so narrow that the sub-solidus curve cannot be detected. A eutectoid is observed at 97 mol%, and the transition temperature for the horizontal is $419 \pm 2°C$ ($395 \pm 10°C$) over the composition range 1–98 mol%. Solidus curves for the β solid solution could not be detected despite making in situ visual observations using an optical furnace [1]. The maximum on the liquidus curve at 670°C, 95 mol% implies a maximum melting solid solution. The double salt, $Cd_3Ag_2(SO_4)_4$, undergoes a solid-state decomposition at $554 \pm 3°C$, the reverse reaction exhibiting considerable supercooling ($491 \pm 9°C$). The composition of this compound is indicated by the absence of the eutectoid horizontal at compositions < 25 mol%, this being determined by the use of a very sensitive thermocouple arrangement capable of detecting small amounts of Ag_2SO_4 (< 1 mol%). Additional evidence is provided by X-ray powder diffraction. Figure 2b shows the characteristic pattern of the compound, while Fig. 2a shows that of the unheated 25 mol% mixture.

No transitions relating to the liquidus curve were apparent between 0 and 10 mol% or in pure $CdSO_4$ itself, over the temperature range 860–1030°C; hence, melting must occur at about 1040°C, this being the value to which the liquidus curve is extrapolated. (Margulis et al. [7] extrapolated the melting point to 1130°C.)

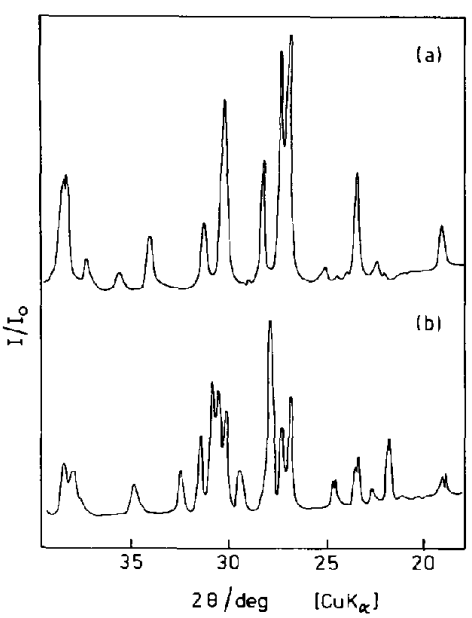

Fig. 2. X-ray powder diffraction patterns of (a) unheated, and (b) heated 25 mol% mixtures.

CONCLUSIONS

The transition temperatures for $CdSO_4$ obtained in the present work fall into the middle range of the literature values, being closest to those of Margulis et al. [6] who reported temperatures of 787 and 837°C. Because the conditions employed in the high-temperature X-ray study approach those of equilibrium the spread of DTA data around those values underlines the importance of the kinetics of phase transitions and of preparation and pretreatment of materials. The present diagram reinforces the results of the earlier study [2], but provides much additional information.

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