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Note

THE SYSTEM Ag_2SO_4—$BeSO_4$

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The phase diagram for the system Ag_2SO_4—$BeSO_4$ was studied by DTA and quenching techniques using a flowing atmosphere of SO_3 to suppress decomposition.

Existing data [1,2] show that Ag_2SO_4 transforms from the orthorhombic to the Na_2SO_4 (I) structure around 412°C and melts without decomposition at 660°C. $BeSO_4$ obtained by dehydrating the tetrahydrate may show either poorly resolved [2] transformations or none at all [3] and decomposes above 650°C. DTA of $BeSO_4$ held at 400°C for 60 h, however, reveals two well-defined peaks, starting at 588°C ($\alpha \rightarrow \beta$) and 639°C ($\beta \rightarrow \gamma$), on heating [2]. On cooling, the latter peak resolves into two, separated by 4°C, indicating the presence of a fourth polymorph over a narrow temperature range. The structures of the other three phases have been determined by Bosik et al. [4] as tetragonal (α), orthorhombic (β) and cubic (γ).

MATERIALS

BDH analytical grade Ag_2SO_4 (99%) and reagent grade $BeSO_4 \cdot 4\,H_2O$ (98%) were used. $BeSO_4$ was obtained by dehydration of the tetrahydrate at 300°C for 24 h and was stored over P_2O_5 in a vacuum desiccator. Mixtures were prepared by grinding together the salts under CCl_4 for 5 min removing the solvent under vacuum.

APPARATUS

The DTA apparatus with a flowing SO_3 atmosphere was essentially as described previously [5]. For the present work, however, the 300 mg sample was contained in a Pt rather than a silica cup. Heating/cooling rates of 5°C min^{-1} were found most satisfactory. Two quenching methods were employed: a 7 mm diameter Pt cup containing the sample was withdrawn rapidly from the furnace and either plunged into CCl_4 or splat-cooled by inserting a Cu rod pre-cooled in liquid N_2. Sample masses of 50—500 mg were quenched in under 4 sec and examined microscopically in both polarized and non-polarized light.

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RESULTS

A transition is characterized here by its DTA peak temperature. The $\alpha \rightarrow \beta$ transition of Ag_2SO_4 occurred at 425 ± 3°C on heating all compositions in the range 0—97 mole % $BeSO_4$ and was followed by the eutectic transition at 441 ± 2°C (Fig. 1). Only at compositions of >20 mole % $BeSO_4$ were these two peaks completely resolved. On cooling compositions of <35 mole % $BeSO_4$, the eutectic transition was detected only as a shoulder on the Ag_2SO_4 $\beta \rightarrow \alpha$ peak, and this latter showed increasing supercooling as the mole % of $BeSO_4$ decreased. For example, pure Ag_2SO_4, which melted reversibly at 661 ± 1°C, cooled to 392°C before transforming and raising its temperature to 420°C. On cooling compositions with >35 mole % $BeSO_4$, the eutectic and Ag_2SO_4 $\beta \rightarrow \alpha$ peaks were resolved and occurred at 421 ± 4°C and 395 ± 7°C.

The $BeSO_4$ $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions were detected at 609 ± 2°C and 646 ± 1°C on heating in the composition range 48—97 mole % $BeSO_4$ (Fig. 1). On cooling, peaks occurred at 587 ± 2°C and 636 ± 2°C, and there was an additional peak at 640 ± 2°C which became gradually undetectable at >80 mole % $BeSO_4$. Pure $BeSO_4$ showed no transformations on heating or cooling and decomposed above 800°C. X-Ray powder diffraction showed that the recrystallization of $BeSO_4$ from a 98 mole % mixture above the eutectic temperature is accompanied by an irreversible change from a metastable to the stable (tetragonal) structure.

In the composition range 0—25 mole % $BeSO_4$, the liquidus line was detected on cooling but not on heating, and extrapolation gave a eutectic composition of 30 mole % $BeSO_4$ (Fig. 1). The other liquidus line was detected neither on heating nor cooling, despite varying the heating/cooling rate from 5 to 15°C min^{-1} and increasing the sample mass to 600 mg. The disappearance of the $BeSO_4$ transitions near 50 mole %, however, allowed

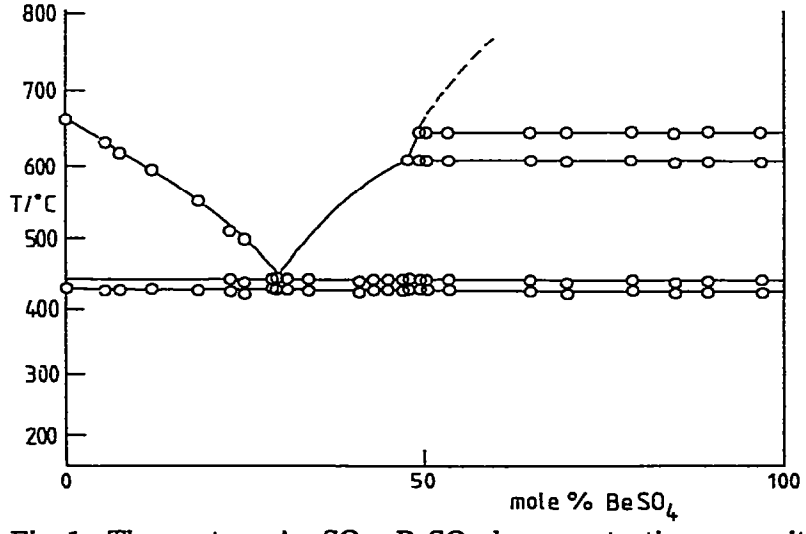

Fig. 1. The system Ag_2SO_4—$BeSO_4$ has a eutectic composition of 30 mole % $BeSO_4$. $AgSO_4$ exhibits one transformation, just below the eutectic temperature, and $BeSO_4$ shows two above it.

parts of this liquidus line to be estimated. Many samples were held for up to 20 h in the vicinity of the estimated liquidus line and quenched by the methods described. While melts 25°C above and below the line gave, respectively, glass and $BeSO_4$ crystals in a glass matrix, crystallization was not reproducible near the line.

All points presented in Fig. 1 were obtained on heating, except the left-hand liquidus line.

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