THE SYSTEM Bi_2S_3 — Sb_2S_3

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ABSTRACT

The phase relations in the system Bi_2S_3–Sb_2S_3 were determined at temperatures between 200 and 800°C by means of quenching and DTA experiments using silica tubes as sample containers. Complete solubility between Bi_2S_3–Sb_2S_3 was found in the solid as well as the liquid states. Since compositions between $(Bi_{0.45}Sb_{0.55})_2S_3$ and Sb_2S_3 have not been detected among naturally occurring members of this solid solution series it is presumed that the deposition of stibnite (Sb_2S_3) and bismuthinite (Bi_2S_3) occurs under completely dissimilar conditions in nature.

INTRODUCTION

The minerals bismuthinite (Bi_2S_3) and stibnite (Sb_2S_3) have the same crystal structure $(D5_8$-type). The dimensions of their orthorhombic unit cells differ by at most 3.5% and one would therefore expect that complete solubility between the two phases is possible in the solid state. Hayase (1955) found that an intermediate form of bismuthinite containing 36-55 mole % Sb_2S_3 does indeed exist and he named this mineral horobetsuite. Subsequently, electron-probe analyses of various bismuthinites revealed that all degrees of substitution of bismuth by antimony can occur up to 42 mole % Sb_2S_3, and this was taken as evidence that there is solid solubility at least up to that limit (Springer 1969). On the other hand, no bismuth could be found in stibnite although material from several localities was studied. The lack of compositions intermediate between horobetsuite and stibnite indicates that there might be a break in the solid solution series Bi_2S_3–Sb_2S_3. In order to explain these analytical results it appeared necessary to determine the phase relations in the synthetic system Bi_2S_3–Sb_2S_3.

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EXPERIMENTAL PROCEDURE AND RESULTS

A study of the system BiS–Sb$_2$S$_3$ was carried out by Takahashi (1920) who found complete solid solubility between these components. As the compound BiS does not exist it is highly likely that he investigated in fact the Bi$_2$S$_3$–Sb$_2$S$_3$ system; his reports of excess bismuth in the synthetic samples support this conjecture. However, apart from the uncertainty about the components there is the objection that the charges were heated in open crucibles which left the system subject to reactions with the furnace atmosphere and to losses of vapour phase.

For the present study the customary evacuated and sealed silica glass tubes were employed as sample containers. This method obviates the disadvantages of the open-crucible technique and furthermore, the vapour pressure inside the capsules is fixed insofar as it corresponds to the equilibrium pressure of the system at a particular temperature (condensed system). The capsules were heated in horizontal tube furnaces for periods of several days to months and then rapidly quenched to the temperature of ice water.

The charges were made up by mixing varying proportions of Bi$_2$S$_3$ and Sb$_2$S$_3$ which in turn had been previously synthesized from the pure elements. The elements were purchased from the American Smelting and Refining Company, New York, and were of high purity (99.999%).

At 500°C and higher, the diffusion rates are sufficiently fast that equilibrium is attained within a few days. At 400°C a few weeks are necessary for equilibrium, but at 300°C not even a 90 day run can produce complete equilibrium. For the runs at and below 300°C a flux was therefore added to the charge. It consisted either of a eutectic mixture of 44.2% NH$_4$Cl and 55.8 wt. % LiCl which has a melting point of 267°C, or a eutectic mixture of AlCl$_3$ (76.9 wt. %) and KCl (23.1 wt. %) which was tried at 200°C. In some of the latter samples the salt decomposed the sulphides and the final product was a brown amorphous powder. It appears that the successful application of the AlCl$_3$–KCl flux depends very much on how well the AlCl$_3$ is dehydrolysed. The sulphide/salt weight ratio was about 1:4.

Melting temperatures were determined by differential thermal analysis. For these measurements the samples were enclosed in silica glass tubes that had a co-axial thermocouple well. The charge consisted of sulphide that had been homogenised at 500°C for several days and an admixture of quartz from Brazil whose inversion temperature of 573°C was used as a calibration point. 100 mg of sulphide and 30 mg of quartz were used in each case to ensure that the heat effects of various samples
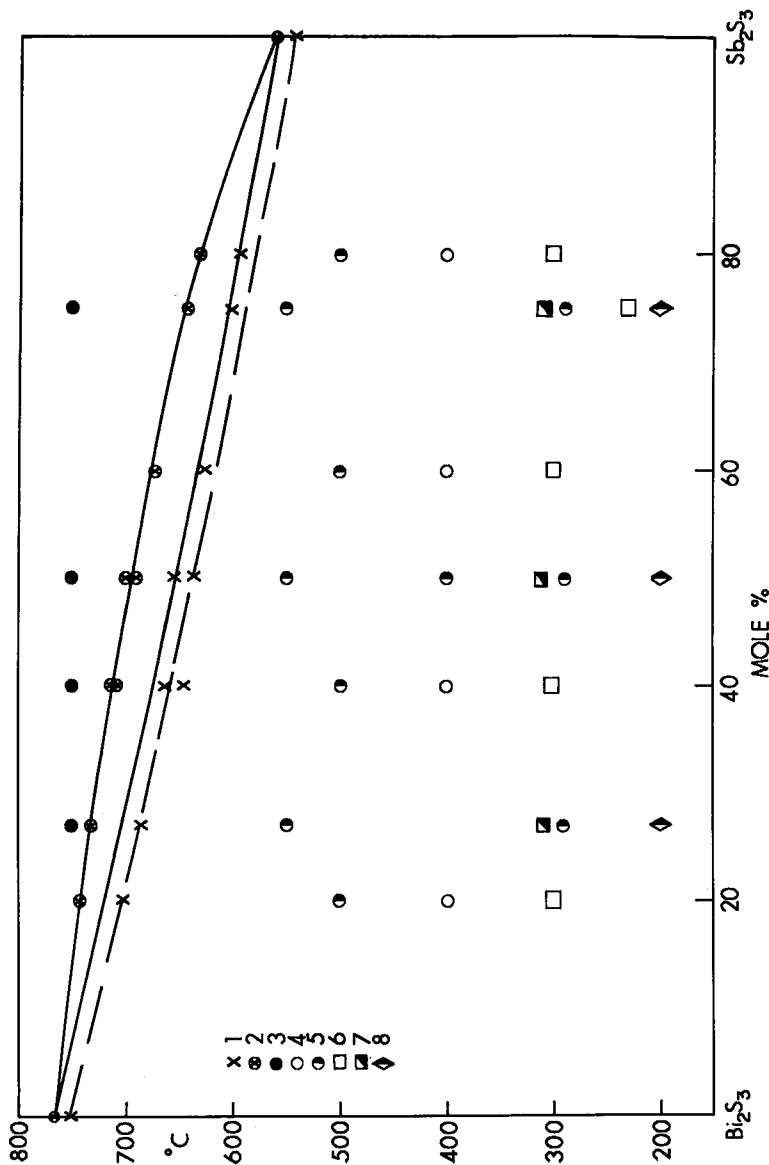
FIG. 1. Experimental points in the determination of the Bi_2S_3–Sb_2S_3 system. DTA experiments: 1 = beginning; 2 = maximum of endothermic peak. Static experiments: 3 = melt, yielding one phase (solid solution) upon quenching; 4 = starting material for the run was a solid solution produced at a higher temperature; 5 = starting material was a mechanical mixture of Bi_2S_3 and Sb_2S_3; 6 = as 4, but with NH_4Cl–$LiCl$ flux; 7 = as 5, but with NH_4Cl–$LiCl$ flux; 8 = as 5, but with $AlCl_3$–KCl flux. The final products in all runs of type 4–8 indicated solid solubility between Bi_2S_3 and Sb_2S_3.

could be compared quantitatively. A constant heating rate of about 3°C per minute was applied.

The conditions and results of the experiments are presented graphically in Figs. 1 and 2. It was found that there is indeed complete solubility between Bi_2S_3 and Sb_2S_3 in the liquid as well as the solid state and this conclusion is summarized in the phase diagram of Fig. 2.

The phases present in the reaction products were identified both by microscopic examination of polished mounts and by x-ray diffraction
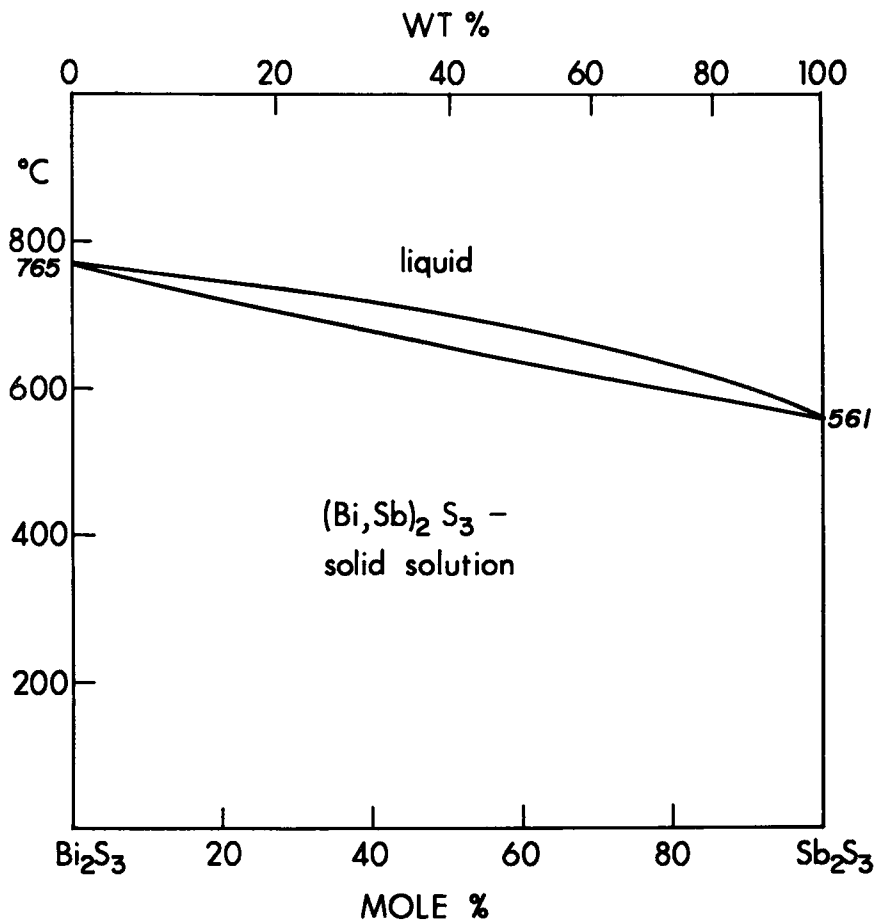

FIG. 2. Summary of the phase relations in the condensed system Bi_2S_3–Sb_2S_3. Vapour is present with all phases.

analysis using a Guinier-de Wolff camera (Enraf-Nonius, Delft, Holland). The powder diffraction patterns of Bi_2S_3 and Sb_2S_3 are very alike. However, due to the differences in the lattice constants, reflections from different lattice planes are at somewhat different positions. The lines for members of the solid solution series are intermediate between those of the pure end members and it was found that a linear relationship exists between lattice spacing and composition within the error of measurement. For instance, the d-value of the 231-reflection of Sb_2S_3 is 2.427Å according to the PDF card index.* With reference to that line stibnites with 20, 40, 60, 80 and 100 mole % replacement of Sb_2S_3 by Bi_2S_3 had d-values of 2.434, 2.439, 2.446, 2.453 and 2.458Å respectively. The last value may be compared with 2.456Å which is the 231-value for Bi_2S_3 in the PDF file. The error in the measurements is estimated at about 0.002Å. A similar linear relation between composition and lattice spacing was found to hold for the reflections 221, 301 and 311.

As mentioned earlier, attainment of equilibrium is very slow at 300°C and below. However, even if the two end members are mixed without a fluxing agent and left to react for 90 days and longer, a clear indication can be obtained from the x-ray pattern that solid solubility is being approached. The film area between the two lines corresponding to identical lattice planes of Bi_2S_3 and Sb_2S_3 becomes increasingly darkened the longer the mixture is left to react. If a flux is added, the lines due to the pure end members become very faint after 9 weeks at 300° and 12 weeks at 200°C, and one single pattern arises instead witnessing the formation of a solid solution. On the other hand, if a solid solution that has been produced at a higher temperature is annealed at a lower one, absolutely no splitting of x-ray lines is observable even if a flux is employed.

The derivation of the solidus and liquidus curves from the DTA results requires some explanation. The beginning of appearance of an endothermic peak on the heating curve, and the maximum of the peak are plotted in Fig. 1. In the case of Bi_2S_3 and Sb_2S_3 there is, of course, a distinct melting point, but depending on the geometry and heat capacity of the samples, this point is spread out into a range. The width of the endothermic peak is 18°C both for Bi_2S_3 and Sb_2S_3 and this is taken to be the minimum melting interval as displayed on the DTA plot. A solid solution has by nature a melting interval and therefore a wider endothermic peak is expected to be visible on the DTA curve. The extent

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* *Powder Diffraction File*, published by the Joint Committee on Powder Diffraction Standards, 1845 Walnut St., Philadelphia, Pa. 19103.

of the peak in excess of 18°C is a measure of the actual melting interval provided the weight of the charge is the same for the entire solid solution series and also the heat absorbed by the melting process is constant. The former requirement has been met by the experimental conditions but the latter is fulfilled only to a first approximation and an uncertainty in the determination of the melting interval is a consequence. However, The beginning of the endothermic effect cannot be read to a precision better than ± 10°C and this imposes a much more serious restriction on the accuracy of the results. The maxima of the peaks can be measured fairly accurately (appr. ±3°C). In the case of Bi_2S_3 and Sb_2S_3 these peaks correspond to the actual melting points and are at 768±3°C and 560±3°C respectively, in the other cases they indicate the end points of the melting ranges.

Alternatively, the melting points of the end members can be determined by placing a sample into the furnace and increasing the temperature stepwise. The appearance of the charge at each step indicates whether or not melting has occurred. By this method the melting points of Bi_2S_3 and Sb_2S_3 were found to be 763±2 and 563±3°C respectively.

During cooling an exothermic effect commences about 30-40°C below the maximum of the endothermic peak. This effect is very strong and distinct and seems to be common among DTA runs of sulphides (Kullerud 1969, p. 241). It is probably due to supercooling and delayed condensation from the vapour phase.

GEOLOGICAL IMPLICATIONS

It was shown in the preceding paragraph that there is a full range of solid solubility between Bi_2S_3 and Sb_2S_3 at temperatures above 200°C. It is possible, though highly unlikely, that a break in the solid solution series exists at a lower temperature. On the other hand, there is a clear indication of a gap in the naturally occurring compositions of that series. A possible explanation for this observation is that during ore-forming processes bismuth was deposited at an earlier stage than antimony and that the ore-bearing fluids were virtually bismuth-free when stibnite crystallized. It is indeed rare to find stibnite deposits that also contain bismuth minerals. The break in the naturally occurring solid solution series is thus not due to the phase relations in the system Bi_2S_3–Sb_2S_3 but to different conditions under which bismuthinite and stibnite are deposited in geological environments.

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Manuscript received August 1970.