INVESTIGATIONS OF SULPHIDE SYSTEMS
BY THERMAL ANALYSIS AND CHEMICAL VAPOUR TRANSPORT*

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For the selection of appropriate crystal growth methods for multi-component compounds, a detailed knowledge of the corresponding phase diagrams is desirable. It will be shown that differential thermal analysis (DTA) combined with chemical vapour transport (CVT) represents a versatile method for evaluation of the required phase diagrams. By means of DTA, liquidus and solidus curves can be established. The application of CVT with halogens yields suitable insights into the phase relationships of the subsolidus region, because the equilibrium compositions frequently occur as single-crystalline and spatially separated phases. The advantages of combining DTA and CVT are illustrated by the recently studied binary systems Ag₂S—Ga₂S₃, PbS—In₂S₃, Ga₂S₃ and In₂S₃—Bi₂S₃, in which numerous new ternary compounds have been found. Supplementary thermogravimetric measurements on the chalcogenide halide systems Bi₂S₅—BiX₃ and Bi₂O₃—BiI₃ are added.

In the past two decades phase investigations of multi-component sulphide systems have undergone stimulation because many of them contain intermediate compounds with interesting physical properties, suitable for technical applications such as semiconductors, frequency doublers, detectors, etc. For a large number of applications single-crystals are necessary. Crystal growth of the desired compound requires a knowledge of the corresponding equilibrium phase diagram. Common methods of studying phase relationships (not restricted to sulphide systems) are shown in Table 1. The aim of this work is to demonstrate the advantages of combining DTA and CVT for determining the phase diagrams of sulphide systems, illustrated by the systems Ag₂S—Ga₂S₃, PbS—In₂S₃, Ga₂S₃—In₂S₃ and In₂S₃—Bi₂S₃.

DTA represents a versatile method for examination of phase transformations, e.g. solid–solid transformations or melting points. DTA is less suitable in studying subsolidus regions of a system, because it is a dynamical method, which often prevents equilibrium adjustment.

In addition, CVT is not only an established method for preparing sulphide compounds but is also highly suitable for subsolidus studies, because in most

cases the equilibrium compositions can be obtained as single-crystalline and spatially separated phases.

Furthermore, if a compound decomposes gradually on increase of the temperature, additional information on the intermediate phases can be obtained by means of a thermobalance. Such thermogravimetric studies are illustrated on the chalcogenide-rich parts of the system Bi₂S₃–BiX₃ and Bi₂0₃–BiI₃.

Experimental

The DTA measurements were carried out with a Netzsch DTA apparatus using a block holder for sealed quartz ampoules as described elsewhere [1]. Samples of 500 mg were examined with heating rates of 2, 5 and 10⁰/min. The thermal effects appearing in the DTA curves were interpreted following the directions of Gäumann [2] and Etter et al. [3]. After the run, the samples were powdered and examined with a Guinier-de Wolff X-ray camera to identify the phases and to establish the phase boundaries at room temperature by the parameter and disappearing-phase methods [4].

The CVT experiments were performed in sealed quartz ampoules (length 15 cm, diameter 15 mm), starting from high-purity elements and small amounts of a halogen, especially iodine, to induce chemical transport (Schäfer [5]). Crystal growth experiments in horizontal two-zone furnaces lasted for two or three days.

Thermogravimetric measurements were made with a Mettler thermobalance. A heating rate of 2⁰/min and a nitrogen atmosphere were employed.

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