Journal of Thermal Analysis, Vol. 16 (1979) 295–306

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

V. KRÄMER

Kristallographisches Institut der Universität, Hebelstr. 25, D-7800 Freiburg (GFR)

(Received August 20, 1978)

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 $Ag_2S-Ga_2S_3$, $PbS-In_2S_3$, Ga_2S_3 and $In_2S_3-Bi_2S_3$, in which numerous new ternary compounds have been found. Supplementary thermogravimetric measurements on the chalcogenide halide systems $Bi_2S_3-BiX_3$ and $Bi_2O_3-BiI_3$ are added.

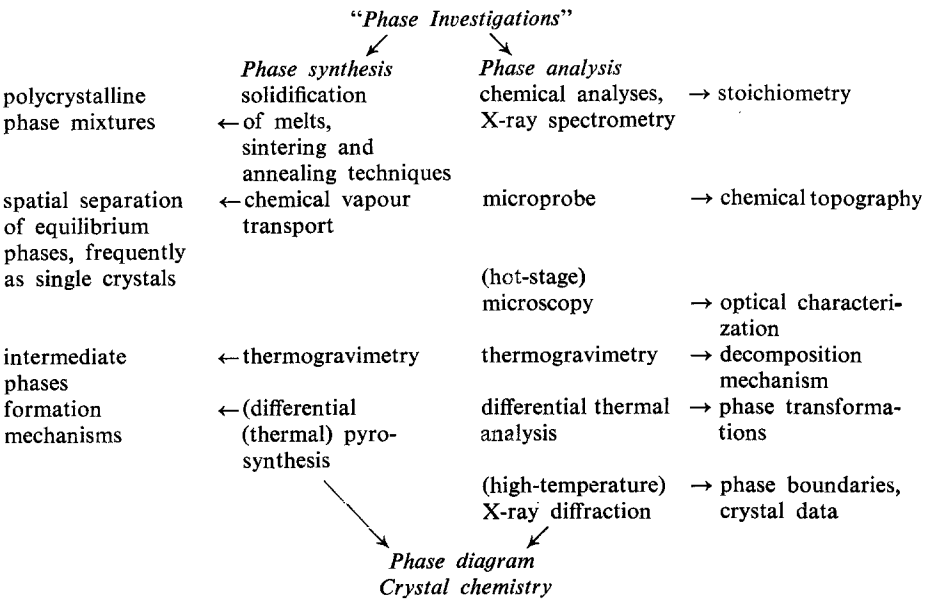
In the past two decades phase investigations of multi-component sulphide systems have undergone stimulation because many of them contain intermediate compounds with interesting physical properties, suitable for technical applications such as semiconductors, frequency doublers, detectors, etc. For a large 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 $Ag_2S-Ga_2S_3$, $PbS-In_2S_3$, $Ga_2S_3-In_2S_3$ and $In_2S_3-Bi_2S_3$.

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

* Partially presented in a paper at the "Journées de Calorimétrie et d'Analyse Thermique", Torino, Italy, 28–30. 6. 1978.

Table 1



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 $Bi_2S_3-BiX_3$ and $Bi_2O_3-BiI_3$.

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 10°/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 2°/min and a nitrogen atmosphere were employed.

Subsolidus studies by CVT

In contrast to time-consuming sinter-annealing processes with pressed pellets of varying compositions and temperatures, CVT in the subsolidus region of sulphide systems has the following, significant advantages (Nitsche [6, 7]):

a) increasing the reaction rates by the mineralizing action of the halogen transport agent,

b) fractionating the equilibrium phases at different parts of the ampoule because of different equilibrium constants and transport rates,

c) enlarging the crystallites to a useful size.

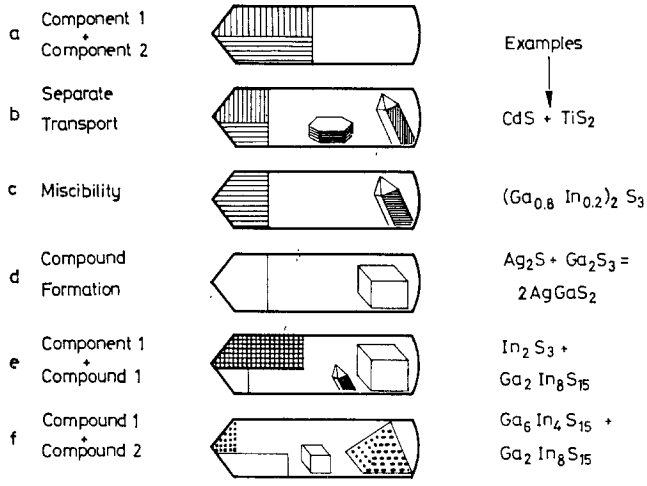


Fig. 1. Possible phase fractionations in binary systems under CVT conditions (Nitsche [6, 7], modified)

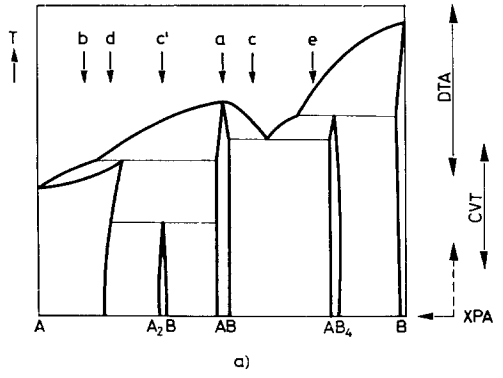


Fig. 2a. T—X phase diagram of a hypothetical binary system: letters *a*—*e* refer to Fig. 2b

Figure 1 exhibits several examples of phase fractionations in binary sulphide systems under chemical transport conditions. In Fig. 2a a hypothetical phase

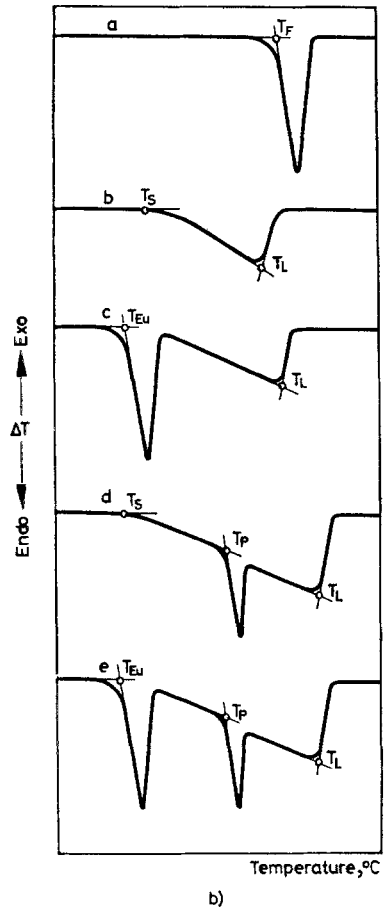


Fig. 2b. Typical DTA heating curves. *a:* congruent melting of a compound at T_F; *b:* melting of a solid solutions (T_S: solidus temperature, T_L: liquidus temperature); *c:* thermal effects due to solidus (T_{Eu}: eutectic temperature) and liquidus temperatures; *c':* curve like "*c*" plus a preceding sharp peak of type "*a*" indicating a peritectoid reaction (not shown, cf. Fig. 2a); *d:* incongruent melting of a component with finite phase width (T_p: peritectic temperature); *e:* incongruent melting of an intermediate compound at T_P

diagram is shown; on the right side the appropriate temperature ranges for DTA and CVT are given. In addition, high-temperature X-ray diffraction permits determination of the phase boundaries at elevated temperatures (XPA: X-ray phase analysis). Figure 2b shows selected DTA heating curves. The eutectic peak area depends on the mole ratio of the components, and thus the positions of solvus curves and eutectic points can be evaluated by a composition versus peak area plot [2].

Discussion of combined DTA and CVT investigations of four characteristic sulphide systems

The system $Ag_2S-Ga_2S_3$ [8] (Fig. 3)

Both methods showed that three intermediate compounds exist: the well-known chalcopyrite-type compound $AgGaS_2$, and two new phases of composition Ag_9GaS_6 and $Ag_2Ga_{20}S_{31}$.

This phase diagram determination stands as an example of where each of the independent methods of investigation confirms the results of the other.

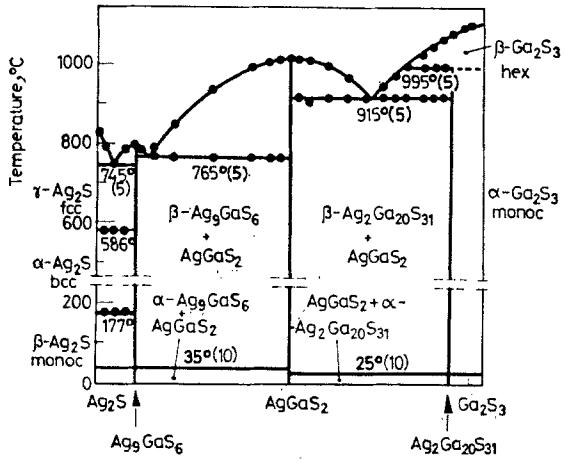


Fig. 3. Phase diagram of the system $Ag_2S-Ga_2S_3$ [8]

The system $PbS-In_2S_3$ [9]

DTA measurements with a heating rate of 5°/min yield a phase diagram which contains only one intermediate compound, $PbIn_2S_4$, in accordance with the results

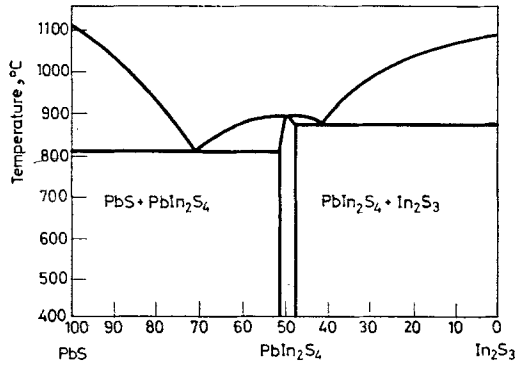


Fig. 4. Preliminary phase diagram of the system $PbS-In_2S_3$ [9, 10]

of Rustamov et al. [10] (Fig. 4). However, CVT experiments in the indium-rich part of the system demonstrated an additional phase besides $PbIn_2S_4$ or In_2S_3. New DTA runs with a low heating rate of 2°/min revealed the existence of a second intermediate phase, located in the immediate neighbourhood of $PbIn_2S_4$. Thus, an improved phase diagram could be proposed (Fig. 5).

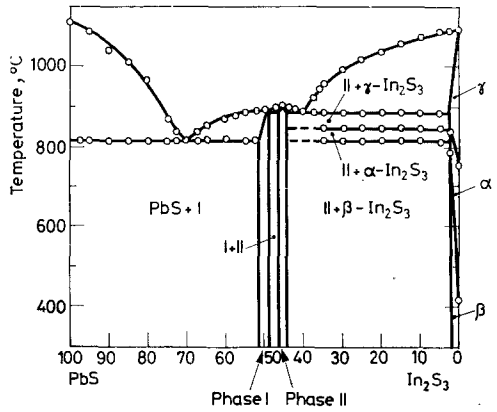


Fig. 5. Improved $PbS-In_2S_3$ phase diagram [9]

The reason for the different results at different heating rates is to be seen in kinetic barriers which are overcome with sufficiently low heating rates.

It should be borne in mind that the phase relationships of this system are rather complicated, because additional phases of similar compositions were found.

The system $Ga_2S_3-In_2S_3$

A phase diagram of this system was published by Muschinsky and Ambross [11] on the basis of DTA measurements (Fig 6). They found one ternary compound, $GaInS_3$, melting incongruently. We investigated this system by means of CVT with iodine and obtained quite different results in the subsolidus region [12] (Fig. 7).

We did not find the $GaInS_3$ phase, but instead three other compositions: $Ga_6In_4S_{15}$, $Ga_2In_4S_9$ and $Ga_2In_8S_{15}$. The first compound seems to have a finite phase width of some mole %. The second phase could be obtained only at temperatures above 700°. At lower temperatures phases I and III were formed.

However, phase II could be kept metastable at room temperature (over many years) without visible decomposition.

This is an example of a system with considerable kinetic barriers which are overcome by the mineralizing action of the transport agent.

DTA studies on the liquidus and solidus temperatures are comparable to those in [11].

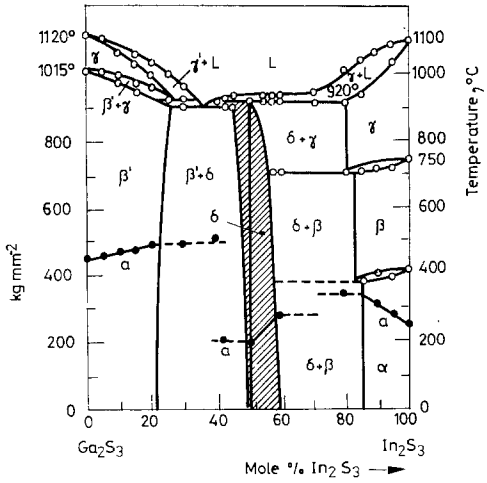


Fig. 6. Phase diagram of the system Ga_2S_3—In_2S_3 (Muschinsky and Ambross [11])

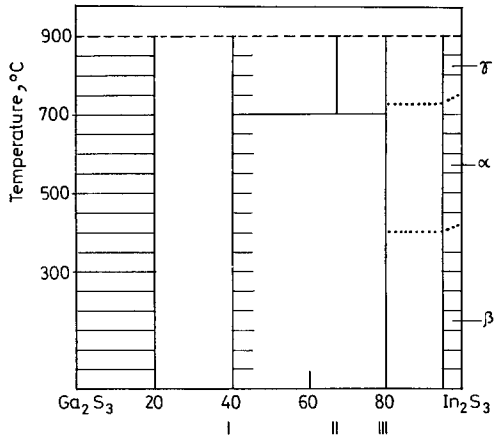


Fig. 7. Subsolidus region of the system Ga_2S_3—In_2S_3 as revealed by CVT. I: $Ga_6In_4S_{15}$, II: $Ga_2In_4S_9$, III: $Ga_2In_8S_{15}$

The system In_2S_3—Bi_2S_3 [1]

CVT with halogens can fail if the transport agent is incorporated as a constituent of thermally stable solid compounds. This is the case in the above system, because bismuth exhibits a distinct tendency to form various sulphide halides.

Four different types of such mixed anion compounds were found:

a) the well-known bismuth sulphide halides, BiSX (X: Cl, Br, I),

b) the ternary bismuth sulphide chloride, $Bi_4S_5Cl_2$ [13, 14],

c) the ternary bismuth sulphide halides, $Bi_{19}S_{27}X_3$ (X: Cl, Br, I) [15, 16],

d) the quaternary indium bismuth sulphide halides, $InBi_2S_4X$ (X: Cl, Br) [17].

Thermogravimetric studies on all sulphide halides showed that the sulphide chlorides have the lowest thermal stability; they decompose below 500°, whereas sulphide bromides and iodides are stable up to about 700°. Therefore, chlorine was regarded as the most promising transport agent for growing halogen-free ternary indium bismuth sulphides.

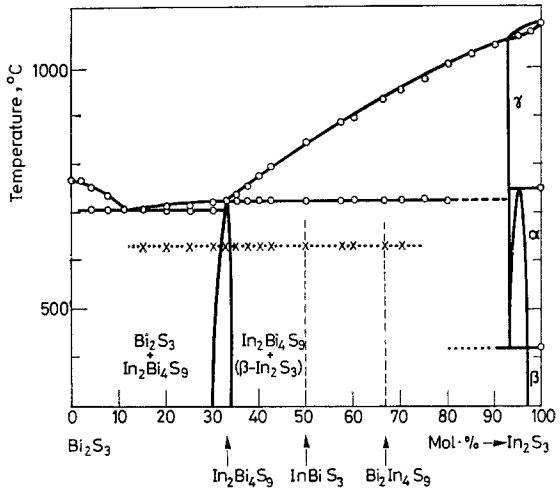


Fig. 8. Phase diagram of the system In_2S_3—Bi_2S_3 [1]

In fact, besides the components of the system, three intermediate compounds could be prepared by chlorine transport. Figure 8 shows the DTA and CVT results. By DTA alone, only $In_2Bi_4S_9$ was found (besides Bi_2S_3 and β-In_2S_3).

CVT with chlorine yields two additional phases, of compositions $InBiS_3$ and $Bi_2In_4S_9$ [18, 19]. Both phases melt incongruently near the solidus temperature of 725°.

Thermogravimetric studies in chalcogenide halide systems

The system Bi_2S_3—BiX_3

The bismuth sulphide halides BiSX (X: Cl Br, I) are well-known compounds. Recently the halogen-poor sulphide halides $Bi_{19}S_{27}X_3$ were described [15, 16]. They can be prepared by thermal decomposition of BiSX (Fig. 9). In the case of BiSCl the decomposition runs over two indistinct steps, indicating that an additional intermediate phase is formed. This phase was isolated when BiSCl was

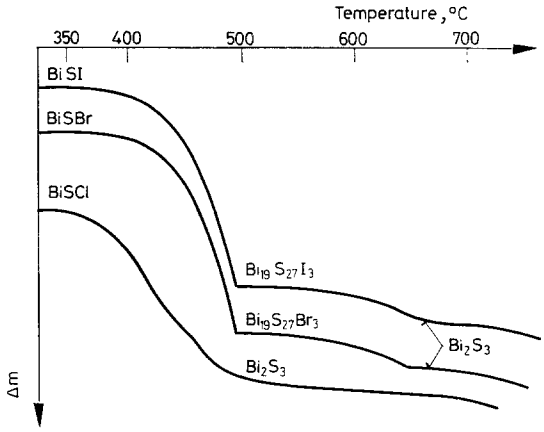


Fig. 9. Thermal decomposition of BiSX compounds [20], N_2 atmosphere, heating rate 2°/min

heated isothermally at 340°; its composition was derived from thermogravimetric data by a weight difference calculation for the decomposition reaction 5 BiSCl → → $Bi_4S_5Cl_2$ + $BiCl_3$ [13]. Subsequent CVT experiments led to the preparation of single-crystals for further studies.

The system $Bi_2O_3 - BiI_3$

Oxide halides such as BiOI exhibit similar decomposition behaviour as for the above-mentioned sulphide halides [20]. BiOI decomposition proceeds in four well-marked steps (Fig. 10). The following reaction mechanism was found by interpreting the thermogravimetric curves:

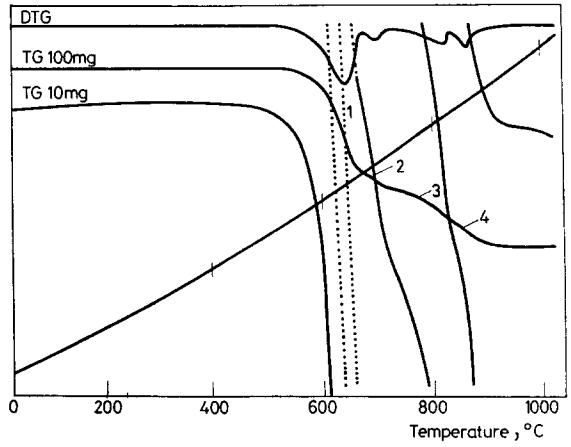


Fig. 10. Thermal decomposition of BiOI [20]; N_2 atmosphere, heating rate 1.5°/min, reduced original plot

$$\text{step 1:5 BiOI} \xrightarrow{500^\circ} Bi_4O_5I_2 + BiI_3\ (g)$$

$$\text{step 2:9 } Bi_4O_5I_2 \xrightarrow{650^\circ} 5\ Bi_7O_9I_3 + BiI_3\ (g)$$

$$\text{step 3:7 } Bi_7O_9I_3 \xrightarrow{700^\circ} 9\ Bi_5O_7I + 4\ BiI_3\ (g)$$

$$\text{step 4:3 } Bi_5O_7I \xrightarrow{800^\circ} 7\ Bi_2O_3 + BiI_3\ (g)$$

These results confirm the existence of the compounds I–III described in a DTA study of the system Bi_2O_3–BiI_3 (Fig. 11) by Klimakov et al. [21]. Obviously, they did not find the additional compound $Bi_4O_5I_2$; this is envisaged as a subsolidus phase which must be formed by a peritectoid reaction during DTA cooling runs. The probably low rate of this solid-state reaction seems to prevent the formation of this compound.

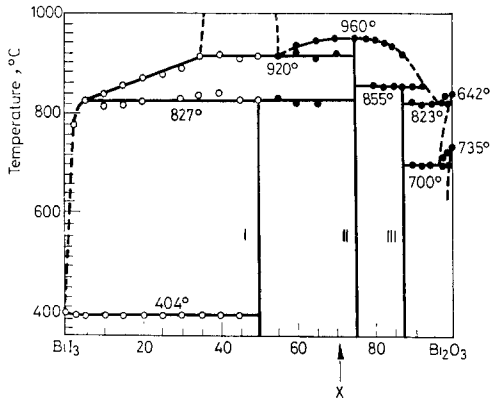


Fig. 11. Phase diagram of the system Bi_2O_3–BiI_3 (Klimakov et al. [21]). I: BiOI, II: $Bi_7O_9I_3$, III: Bi_5O_7I; X: $Bi_4O_5I_2$

Both examples show that thermogravimetry is a rather simple tool to give appropriate information on the existence and thermal stability of intermediate compounds in chalcogenide halide systems.

Conclusion

Four typical sulphide systems were used to show the advantages of parallel studies by DTA and CVT. Three points are of particular interest:

(i) DTA and CVT are independent methods, each of which can confirm the results of the other.

(ii) By CVT, i.e. by the mineralizing action of the transport agent, intermediate phases can be discovered which do not show up in DTA experiments.

(iii) Even if one transport agent leads to the formation of thermally stable sulphides (often new and interesting compounds), other halogens and growth temperatures may be suitable for preparation of ternary sulphides by CVT.

Supplementary thermogravimetric studies are advantageous in systems which at elevated temperatures include a volatile component but thermally-stable intermediate compounds. By the recording of the stepwise decomposition of the compound with the highest content of the relatively unstable component, the series of phases with decreasing amounts thereof can be ascertained. This possibility applies especially to chalcogenide halide systems.

*

The author highly appreciates the encouragement of Dr. W.-D. Emmerich (Netzsch, Selb, Germany) who stimulated the performance of this review.

A considerable part of this work was supported by the Deutsche Forschungsgemeinschaft

References

1. V. KRÄMER, Thermochim. Acta, 15 (1976) 205.
2. A. GÄUMANN, Chimia, 20 (1965) 82.
3. D. E. ETTER, P. A. TUCKER and L. J. WITTENBERG, Thermal Analysis, Academic Press, New York, 1969.
4. B. D. CULLITY, Elements of X-Ray Diffraction, Addison-Wesley, Reading, Mass., 1967.
5. H. SCHÄFER, Chemical Transport Reactions, Academic Press, New York, 1964.
6. R. NITSCHE, J. Cryst. Growth, 9 (1971) 238.
7. R. NITSCHE, J. Phys., 36 C (1975) 3.
8. G. BRANDT and V. KRÄMER, Mater. Res. Bull., 11 (1976) 1381.
9. K. BERROTH and V. KRÄMER, Mater. Res. Bull., in preparation.
10. P. G. RUSTAMOV, Z. D. MELIKOVA and R. S. GAMIDOV, Azerb. Khim. Zh., 6 (1976) 111.
11. V. P. MUSCHINSKY and V. P. AMBROSS, Krist. Techn., 5 K (1970) 5.
12. V. KRÄMER, R. NITSCHE and J. OTTEMANN, J. Cryst. Growth, 7 (1970) 285.
13. V. KRÄMER, Z. Naturforsch. 31b (1976) 1542.
14. V. KRÄMER, Acta Cryst., B, 35 (1979) 139.
15. V. KRÄMER, Z. Naturforsch. 29b (1974) 688.
16. V. KRÄMER, J. Appl. Cryst., 6 (1973) 499.
17. V. KRÄMER, Mater. Res. Bull., 11 (1976) 183.
18. V. KRÄMER, Z. Naturforsch. 26b (1971) 1074.
19. G. CHAPUIS, CH. GNEHM and V. KRÄMER, Acta Cryst., B 28 (1972) 3128.
20. V. KRÄMER, Habilitationsschrift, Universität Freiburg, 1976.
21. A. M. KLIMAKOV, B. A. POPOVKIN and A. V. NOVOSELOVA, Zh. Neorgan. Khim., 19 (1974) 2553.

RÉSUMÉ — Pour choisir les méthodes de croissance des cristaux adaptées aux systèmes à composants multiples, il est avantageux de connaître en détail les diagrammes de phases correspondants. On montre que l'ATD, combinée avec le transport chimique de la vapeur (CVT) représente une méthode souple pour évaluer les diagrammes de phases dont on a besoin. Les courbes du liquidus et du solidus peuvent être établies par ATD. Un aperçu sur les relations de phases dans la région située sous le solidus peut être obtenu par CVT avec les halogènes étant donné que les compositions d'équilibre se présentent souvent comme des phases monocristallines séparées dans l'espace. L'avantage de combiner l'ATD et le CVT est illustré par les systèmes binaires récemment étudiés: $Ag_2S-Ga_2S_3$, $PbS-In_2S_3$, $Ga_2S_3-In_2S_3$ et $In_2S_3-Bi_2S_3$, dans lesquels on a trouvé de nombreux composés ternaires nouveaux. Des mesure, thermogravimétriques supplémentaires ont également été effectuées sur les systèmes chalcogénures-halogénures $Bi_2S_3-BiX_3$ et $Bi_2O_3-BiI_3$.

ZUSAMMENFASSUNG — Zur Auswahl entsprechender Kristallwachstumsmethoden für Verbindungen mit vielen Komponenten ist die eingehende Kenntnis der betreffenden Phasendiagramme eine Voraussetzung. Es wird gezeigt, daß die Differentialthermoanalyse (DTA), gekoppelt mit dem chemischen Dampftransport (CVT) eine vielseitige Methode zur Auswertung der erforderlichen Phasendiagramme darstellt. Mit Hilfe der DTA können Flüssig- und Festphasenkurven ermittelt werden. Die Anwendung des CVT ergibt bei Halogenen einen entsprechenden Einblick in die Phasenverhältnisse des subfesten Gebietes, da die Gleichgewichtszusammensetzungen oft als Einkristall- und räumlich abgesonderte Phasen vorkommen. Der Vorteil der Kopplung der DTA mit dem CVT wird an Hand der vor kurzem untersuchten Binärsysteme $Ag_2S-Ga_2S_3$, $PbS-In_2S_3$, $Ga_2S_3-In_2S_3$ und $In_2S_3-Bi_2S_3$ veranschaulicht, in welchen zahlreiche neue Ternärverbindungen gefunden wurden. Ergänzende thermogravimetrische Messungen an den chalkogeniden Halogenidsystemen $Bi_2S_3-BiX_3$ und $Bi_2O_3-BiI_3$ werden hinzugefügt.

Резюме — При выборе подходящих методов выращивания кристаллов многокомпонентных соединений желательным является знание соответствующих фазовых диаграмм. Показано, что дифференциальный термический анализ (ДТА), совместно с методом химического переноса пара (ХПП), является многосторонним методом для определения требуемых фазовых диаграмм. Посредством ДТА могут быть установлены линии ликвидуса и солидуса. Применение метода химического переноса пара с выходами галогенов, позволяет глубже понять фазовые соотношения подсолидусной области, поскольку равновесные составы часто существуют как монокристаллические и пространственно разделенные фазы. Преимущество комбинированного метода ДТА и химического переноса пара показано на примере недавно изученных бинарных систем Ag_2S—Ga_2S_3, PbS—In_2S_3, Ga_2S_3—In_2S_3 и In_2S_3—Bi_2S_3, в которых были обнаружены новые трехкомпонентные соединения. В дополнение приведены термогравиметрические измерения халькогенид-галогенидных систем Bi_2S_3—$Bi\,X_3$ и Bi_2O_3—BiI_3.