Thermochimica Acta, 27 (1978) 141–149

THERMOGRAVIMETRIC INVESTIGATIONS OF SOME THIOORTHOPHOSPHATES AND THIOHYPODIPHOSPHATES

M. SCHULTE-KELLINGHAUS AND V. KRÄMER
Kristallographisches Institut der Universität, Hebelstrasse 25, D-7800 Freiburg i.Br. (B.R.D.)
(Received 11 November 1977)

ABSTRACT

By means of a thermobalance the decomposition reactions of the thioorthophosphates of gallium, indium, bismuth, copper and of the thiohypodiphosphates of cadmium, indium, manganese, lead, and tin were determined in order to find their stability regions.

The experiments were performed in atmospheres of flowing nitrogen or oxygen. In nitrogen all compounds decompose into the corresponding metal sulphides and volatile phosphorus sulphides. In oxygen the thioorthophosphates are oxidized into orthophosphates, the thiohypodiphosphates into pyrophosphates. Exceptions are the copper thiophosphates Cu_3PS_4 and Cu_7PS_6 and the analogous copper selenophosphates Cu_3PSe_4 and Cu_7PSe_6 which are oxidized into copper sulphate, selenite and an unknown copper phosphate, respectively.

Some decomposition diagrams indicate by various steps the occurrence of intermediate products. In the case of Cu_3PS_4 (Cu_3PSe_4) the intermediate formation of Cu_7PS_6 (Cu_7PSe_6) was proved. During the oxidation of the thioorthophosphates of gallium, indium and bismuth, the formation of monothioorthophosphates ($MePO_3S$) is supposed.

INTRODUCTION

During recent years preparation and investigation of complex chalcogenides have become important, because many of them exhibit interesting physical properties. Among the metal phosphorus chalcogenides new compounds were synthesized and crystals were prepared by means of chemical vapour transport (CVT). To facilitate synthesis and crystal growth experiments it is desirable to have detailed knowledge about the conditions of formation and decomposition of the compounds, i.e. to evaluate their existence regions. Thermogravimetry represents a versatile method of providing this information.

Furthermore, thermogravimetric often enables the discovery and preparation of new compounds. If the graph of the registered weight change shows various steps the existence of intermediate products is inferred. In most cases these intermediate

TABLE 1

LIST OF INVESTIGATED COMPOUNDS

Formula	*Method of preparation*	*Refs.*
Ga_2PS_4	CVT	1, 2
$InPS_4$	CVT	1, 3, 4
$BiPS_4$	CVT	1, 5
$Mn_2P_2S_6$	CVT	1, 6, 7
$CuInP_2S_6$	CVT	8
$Cd_2P_2S_6$	CVT	1
$In_4(P_2S_6)_3$	CVT	4, 9
$Sn_2P_2S_6$	CVT	1, 10, 11
$Pb_2P_2S_6$	CVT	10, 12
Cu_3PS_4	CVT, SS	1, 6, 13
Cu_4PS_5	SS	14, 15
Cu_7PS_6	SS	16, 17
Cu_7PSe_6	SS	17

products can be isolated for subsequent chemical and physical characterization.

This paper reports the investigation of the substances listed in Table 1.

EXPERIMENTAL

The metal phosphorus sulphides were synthesized by annealing stoichiometric proportions of the elements (SS). Crystals were grown by chemical vapour transport (CVT). Special data thereof are reported in the refs. of Table 1.

To characterize the compounds under investigation and to check their purity as well as to identify the decomposition products, X-ray photographs were taken with a Guinier-de-Wolff-camera (Enraf-Nonius).

The thermogravimetric (TG) measurements were performed on an automatically recording thermobalance (Mettler Thermoanalyzer 1/2). All TG-runs were carried out with a heating rate of 1 °C min^{-1}. Deflection of the curve of weight loss indicates the decomposition temperature T_d (first value in the following equations). If the reactions lead to a definite end, this temperature is also noted (second value). All temperatures are given in °C.

RESULTS AND DISCUSSION

From a structural point of view the metal phosphorus chalcogenides can be divided into two groups: the thio(seleno-)orthophosphates and the thio(seleno-)hypodiphosphates. Many thioorthophosphate structures contain approximately closed packed sulphur sublattices. The phosphorus atoms are tetrahedrally coordinated by sulphur. In the thioorthophosphates of B, Al, Ga, In, and Cu, the metals are also

tetrahedrally coordinated. $BiPS_4$ however shows an eight-fold coordination of Bi. All thio(seleno-)hypodiphosphates contain P_2S_6 (P_2Se_6) groups, in which a pair of phosphorus atoms is octahedraliy coordinated by S (Se). The metals often occupy octahedral voids of closed packed S (Se) layers, e.g. Mg and Fe. Some compounds also show a nine-fold coordination of the metals, e.g. $Sn_2P_2S_6$ and $Pb_2P_2S_6$.

These differences in the structures of the thioorthophosphates and thiohypodiphosphates lead to varying chemical behaviour, as the following experiments indicate.

Decomposition of the thioorthophosphates of Ga, In, and Bi

N_2-atmosphere. The thioorthophosphates are relatively stable compounds, decomposition starts above 450 °C. The following decomposition reactions were found

$$2\ GaPS_4 \xrightarrow{500\text{–}850} Ga_2S_3 + \text{“}P_2S_5\text{”}$$

$$2\ InPS_4 \xrightarrow{450\text{–}700} In_2S_3 + \text{“}P_2S_5\text{”}$$

$$2\ BiPS_4 \xrightarrow{450^*} Bi_2S_3 + \text{“}P_2S_5\text{”}$$

* (Bi_2S_3 decomposes simultaneously)

The reactions always lead to the sulphides of the metals. They are the only possible compounds stable at elevated temperatures, whereas the phosphorus sulphides evaporate because of their higher vapour pressures.

The real composition of these phosphorus sulphides is unknown. For this reason the formula “P_2S_5” should be seen only formal (see also the following reaction formula).

The decomposition of $BiPS_4$ is more complicated because “P_2S_5” evaporates and the arising Bi_2S_3 decomposes simultaneously into Bi and S_2.

O_2 atmosphere. The stability of the thioorthophosphates in air is lower than in inert atmosphere, the oxidation sets in at about 350 °C. The following reactions were found

$$GaPS_4 + 6\ O_2 \xrightarrow{300\text{–}900} GaPO_4 + 4\ SO_2$$

$$InPS_4 + 6\ O_2 \xrightarrow{400\text{–}900} InPO_4 + 4\ SO_2$$

$$BiPS_4 + 6\ O_2 \xrightarrow{440\text{–}800} BiPO_4 + 4\ SO_2$$

It is remarkable that there is no decomposition into the metal sulphide with subsequent oxidation into the corresponding oxide. Only oxidation into the orthophosphate is observed. This reaction becomes plausible considering the structure. In the above compounds phosphorus is tetrahedrally coordinated and appears in its highest oxidation state of +5; therefore no change of coordination is necessary. Hence the reaction can be regarded as a substitution of sulphur by oxygen.

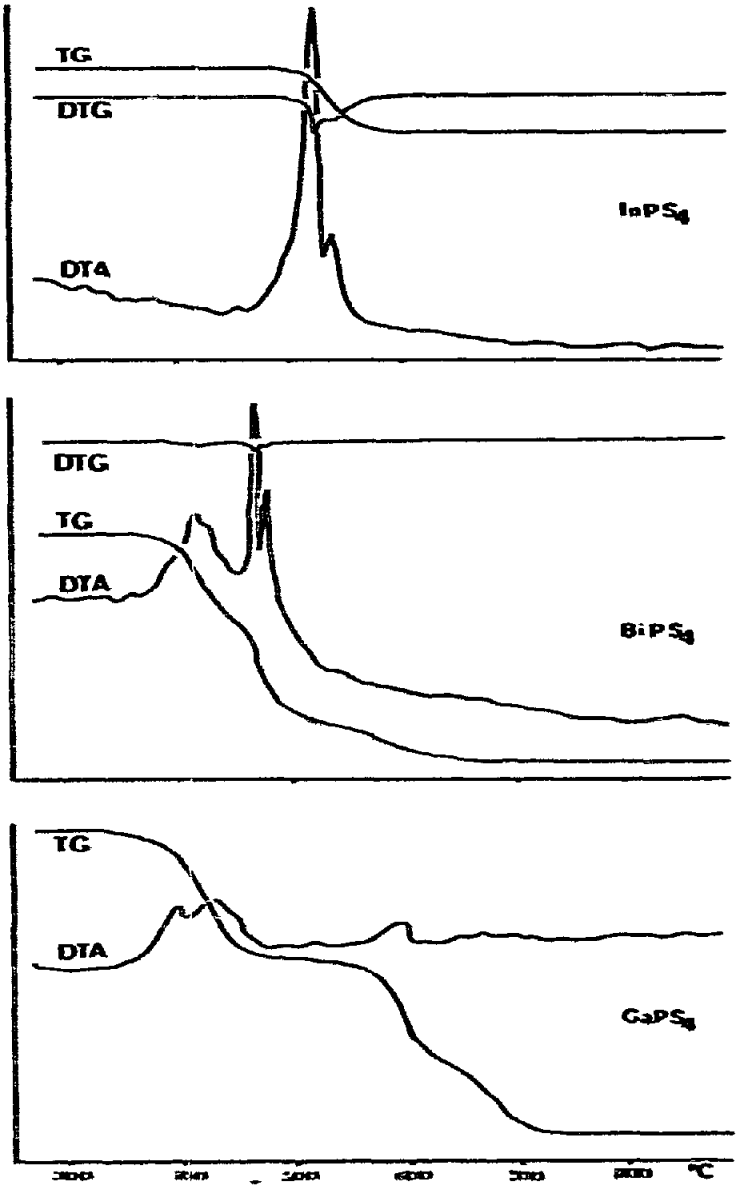

Fig. 1. Thermogram of the oxidation of $InPS_4$, $BiPS_4$, and $GaPS_4$ into the corresponding orthophosphates $InPO_4$, $BiPO_4$, and $GaPO_4$. Sample weight ca. 40 mg; heating rate 1 °C min^{-1}; atmosphere N_2/O_2 = 3/5 (1 h^{-1}).

Intermediate products. The oxidation reactions of the thioorthophosphates leading to the orthophosphates show a very broad TG-step, accompanied by some broad DTA-peaks (see Fig. 1). We tried to isolate the intermediate oxidation products of $BiPS_4$ ($GaPS_4$) responsible for these steps. For this reason, the compounds were heated up to 475°C (480°C) and annealed until the weight remained constant. The most probable formulae calculated from these TG-runs are $BiPO_3S$ ($GaPO_3S$). In the case of $InPS_4$ the symptoms for the existence of an analogous In-compound are less strong.

These compounds are not yet known, but some thioorthophosphorus acids and their alkali salts do exist[18-20]. So far only the Pb salt of H_3PO_3S could be prepared from aqueous solution. All other heavy metal salts decompose below room temperature into the orthophosphates and the sulphides[15]. Contrary to this the Bi- and Ga-compounds seem to be rather stable. Attempts to find a suitable method for growing crystals of the monothioorthophosphates are in progress.

Decomposition of thiohypodiphosphate of Mn, Cu + In, Cd, In, Sn, and Pb

N_2-atmosphere. Here the following reactions were found

$$Mn_2P_2S_6 \xrightarrow{560\text{–}750} 2\,MnS + "P_2S_4"$$

$$CuInP_2S_6 \xrightarrow{490\text{–}700} CuInS_2 + "P_2S_4"$$

$$Cd_2P_2S_6 \xrightarrow{550\text{–}700} 2\,CdS + "P_2S_4"$$

$$In_4(P_2S_6)_3 \xrightarrow{450\text{–}700} 2\,In_2S_3 + "P_2S_4"$$

$$Sn_2P_2S_6 \xrightarrow{520^*} 2\,SnS_2 + "P_2S_4"$$

* (SnS_2 + SnS decomposes simultaneously)

$$Pb_2P_2S_6 \xrightarrow{600^*} 2\,PbS + "P_2S_4"$$

* (PbS decomposes simultaneously)

The stability of the thiohypodiphosphates is similar compared to that of the thioorthophosphates, the decompositions starting between 500 and 600 °C. All reactions run to the corresponding sulphide.

The decomposition reactions of $Sn_2P_2S_6$ ($Pb_2P_2S_6$) show no horizontal end of the TG-curve, because of evaporation of the metal sulphides at higher temperatures. However, in the residue of interrupted reactions there was found SnS plus SnS_2 besides $Sn_2P_2S_6$ (PbS besides $Pb_2P_2S_6$). Under flowing nitrogen of atmospheric pressure, SnS_2 begins to evaporate incongruently at 560 °C, by decomposition into volatile SnS and S_2.

The exact composition of the phosphorus sulphides in this temperature range is unknown, therefore the formula "P_2S_4" is only formally correct (see also the following equations).

O_2-atmosphere. In analogy to the thioorthophosphates the temperatures of decomposition in air are about 100 °C lower compared to those in a N_2-atmosphere. On the other hand the course of the different oxidation is not concordant

$$Mn_2P_2S_6 + 9{,}5\,O_2 \xrightarrow{500\text{–}800} Mn_2P_2O_7 + 6\,SO_2$$

$$Cd_2P_2S_6 + 9{,}5\,O_2 \xrightarrow{470\text{–}800} Cd_2P_2O_7 + 6\,SO_2$$

$$In_4(P_2S_6)_3 + 28{,}5\ O_2 \xrightarrow{330\text{–}850} In_4(P_2O_7)_3 + 18\ SO_2$$

$$Sn_2P_2S_6 + 10{,}5\ O_2 \xrightarrow{380\text{–}680} SnP_2O_7 + SnO_2 + 6\ SO_2$$

$$5\ Pb_2P_2S_6 + 47{,}5\ O_2 \xrightarrow{320\text{–}850} Pb_5P_4O_{15} + P_2O_5 + 30\ SO_2$$

$Mn_2P_2S_6$, $Cd_2P_2S_6$, and $In_4(P_2S_6)_3$ are oxidized to the corresponding pyrophosphates, reactions which were expected after a comparison with the thioorthophosphates. The formal oxidation state of the phosphorus atoms in the P_2S_6 groups is +4, a pair of phosphorus atoms is eight-fold coordinated by sulphur. During the oxidation into the pyrophosphate the oxidation state changes to +5 and therefore the coordination must be changed. One possible way is substitution of the sulphur by oxygen and pushing an additional oxygen between the two phosphorus atoms to form the P_2O_7 group. The exchange of sulphur by oxygen takes place discontinuously, as suggested by a step in the TG-curve of the oxidation of $In_4(P_2S_6)_3$.

Oxidation of $Pb_2P_2S_6$ leads to $Pb_5P_4O_{15}$ in one TG-step. No intermediate formation of the pyrophosphate seems to occur. Oxidation of $Sn_2P_2S_6$ takes place in another way because of the additional oxidation of Sn(II) into Sn(IV).

Decomposition of copper thio- and selenophosphates

N_2-atmosphere. The reactions lead clearly to the copper chalcogenides in analogy to the results with the thiophosphates of Ga, In, and Bi.

In contrast to the other thiophosphates the formation of intermediate products is observed. Each TG-curve shows two steps (see Fig. 2). We tried to isolate the com-

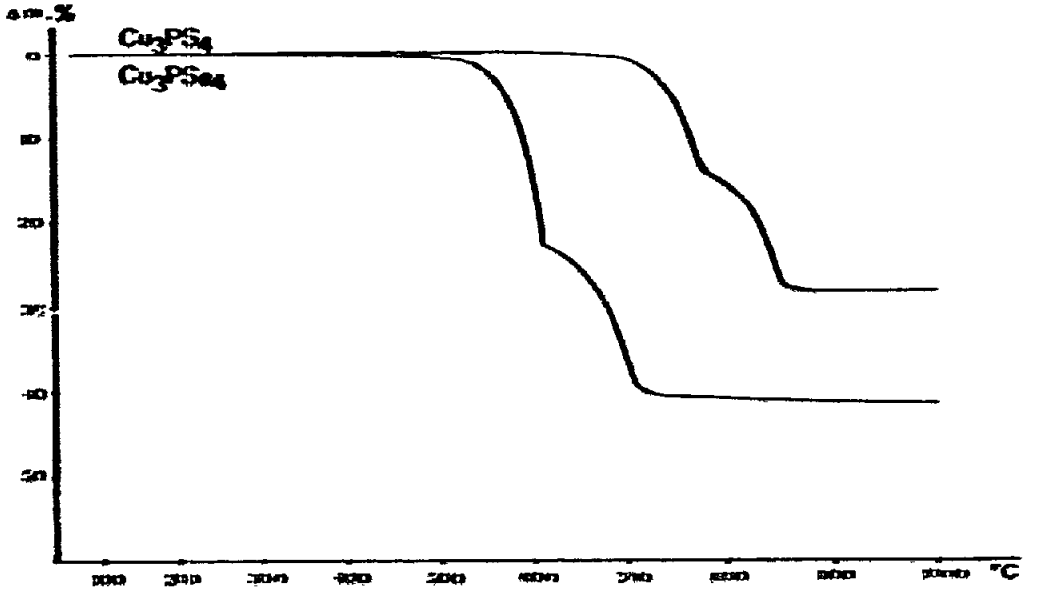

Fig. 2. Thermogram of the decomposition of Cu_3PS_4 and Cu_3PSe_4 into Cu_2S and Cu_2Se. Sample weight ca. 40 mg; heating rate 1 °C min^{-1}; atmosphere N_2 = 6 (l h^{-1}).

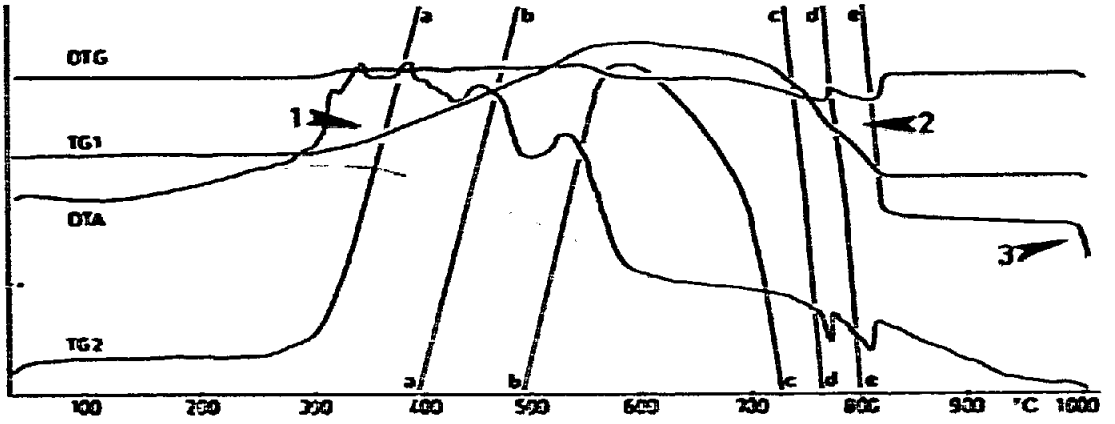

Fig. 3. Thermogram of the oxidation of Cu_3PS_4 into $CuSO_4$ and a Cu-phosphate. TG 1: 100 mg range, TG 2: 10 mg range; sample weight ca. 40 mg; heating rate 1 °C min^{-1}; atmosphere N_2:O_2 = 3/5 (1 h^{-1}).

pounds corresponding to these steps: Cu_3PS_4 (Cu_3PSe_4) were heated up to 575 °C (520 °C) and annealed until the weight was nearly constant. Guinier photographs proved the formation of new compounds, the probable formulae of which were calculated from the weight losses to be Cu_7PS_6 (Cu_7PSe_6). The annealing process yields no pure products, because decomposition into the sulphide (selenide) occurs simultaneously.

Recently it was shown[17] that sintersynthesis is a suitable method for preparing these new compounds, which proves the suggested formula Cu_7PS_6 (Cu_7PSe_6).

The following reactions were found:

$$7\ Cu_3PS_4 \xrightarrow{575^*} 3\ Cu_7PS_6 + 2\ "P_2S_5"$$

$$7\ Cu_3PSe_4 \xrightarrow{290^*} 3\ Cu_7PSe_6 + 2\ "P_2Se_5"$$

* (see following equations)

$$2\ Cu_7PS_6 \xrightarrow{420\text{–}900} 7\ Cu_2S + "P_2S_5"$$

$$2\ Cu_7PSe_6 \xrightarrow{480\text{–}1000} 7\ Cu_2Se + "P_2Se_5"$$

O_2-atmosphere. Contrary to the thioorthophosphates of Ga, In, and Bi, Cu_3PS_4 oxidizes in 3 clear steps with corresponding intermediate products (see Fig. 3). The first step (1, Fig. 3) occurs with increase of weight because of the oxidation into $CuSO_4$ and an unknown copper phosphate. The reason is the higher affinity of copper to sulphur and the change of bond relationships due to the oxidation of Cu(I) into Cu(II).

At higher temperatures a second double step is observed (2, Fig. 3). This weight loss is associated with the well known decomposition of $CuSO_4$ into CuO. The TG- and DTG-curves show the typical form of intermediate formation of CuO -

$CuSO_4$. The copper phosphate begins to decompose in a third step at about 950 °C (3, Fig. 3).

From the second step it is possible to calculate the content of $CuSO_4$ after the first oxidation (57–67%). Therefore, the content of copper of the unknown copper phosphate is 49–44%, the probable formula lies between $2\,CuO \cdot P_2O_5$ and $3\,CuO \cdot P_2O_5$.

During the oxidation of Cu_7PS_6 the same three steps are found. After the first step the Guinier-photograph however shows another intensity ratio of $CuSO_4$ to copper phosphate according to another ratio of Cu:P:S as compared with Cu_3PS_4.

The oxidation of the analogous Se compounds occurs in a similar way. The only difference is their lower stability — decomposition at 130 °C — and the formation of $CuSeO_3$ instead of $CuSeO_4$ ($CuSeO_4$ cannot exist under these condition).

The following reactions were found

$$Cu_3PS_4 + n\,O_2 \xrightarrow{240^*} CuSO_4 + Cu\text{-}P\text{-}O$$

$$Cu_3PSe_4 + n\,O_2 \xrightarrow{130^*} CuSeO_3 + Cu\text{-}P\text{-}O$$

$$Cu_7PS_6 + n\,O_2 \xrightarrow{240^*} CuSO_4 + Cu\text{-}P\text{-}O$$

$$Cu_7PSe_6 + n\,O_2 \xrightarrow{130^*} CuSeO_3 + Cu\text{-}P\text{-}O$$

* ($CuSO_4$ decomposes above 550)

* ($CuSeO_3$ decomposes above 300)

The performed thermogravimetric experiments yielded decomposition mechanisms and thermal stability of the examined thioorthophosphates and hypothiodiphosphates in nitrogen and oxygen atmospheres. Thus hints on appropriate temperature ranges for syntheses and crystal growth of these compounds could be given. During the decomposition reactions intermediate products were found: (a) the copper phosphorus chalcogenides Cu_7PS_6 (Cu_7PSe_6), and (b) two monothioorthophosphates with the probable composition $GaPO_3S$ and $BiPO_3S$. Studies on crystal growth and properties of the latter compounds are in progress.

ACKNOWLEDGEMENT

Financial support of the "Deutsche Forschungsgemeinschaft" is highly appreciated.

REFERENCES

1 R. Nitsche and P. Wild, *Mater. Res. Bull.*, 5 (1970) 419.
2 P. Buck and C. D. Carpentier, *Acta Crystallogr., Sect. B*, 29 (1973) 1564.
3 C. D. Carpentier, R. Diehl and R. Nitsche, *Naturwissenschaften*, 5 (1970) 393.
4 A. Bubenzer, R. Nitsche and A. Rauber, *J. Cryst. Growth*, 29 (1975) 237.

5 H. Zimmermann, C. D. Carpentier and R. Nitsche, *Acta Crystallogr., Sect. B*, 31 (1975) 2003.
6 W. Klingen, G. Eulenberger and H. Hahn, *Naturwissenschaften*, 55 (1968) 229.
7 B. E. Taylor, J. J. Steger and A. Wold, *J. Solid State Chem.*, 7 (1973) 461.
8 W. F. Kuhs, *Diplomarbeit*, Universität Freiburg, 1975.
9 S. Soled and A. Wold, *Mater. Res. Bull.*, 11 (1976) 657.
10 C. D. Carpentier, *Dissertation*, Universität Freiburg, 1974.
11 C. Büchele, *Diplomarbeit*, Universität Freiburg, 1975.
12 W. Klingen, R. Ott and H. Hahn, *Z. Anorg. Allg. Chem.*, 369 (1973) 271.
13 A. Ferrari and L. Cavalca, *Gazz. Chim. Ital.*, 78 (1948) 253.
14 J. Garin and E. Parthé, *Acta Crystallogr., Sect. B*, 28 (1972) 3672.
15 P. Buck, unpublished work.
16 S. T. Teng, *Diplomarbeit*, Universität Freiburg, 1975.
17 W. F. Kuhs, M. Schulte-Kellinghaus, V. Krämer and R. Nitsche, *Z. Naturforsch.*, 32b (1977) 1100.
18 R. Klement, *Z. Anorg. Allg. Chem.*, 253 (1947) 237.
19 R. E. Thilo and G. Ladwig, *Angew. Chem.*, 72 (1960) 636.
20 G. Ladwig, *J. Prakt. Chem.*, 27 (1965) 117.