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NONSTOICHIOMETRY IN $PbCuSbS_3$ COMPOUND

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The $CuSbS_2$–PbS system has been studied in the interval 0–100 mol.% PbS composition and its diagram state has been ploted. The formation of the quartenary compound $PbCuSbS_3$ congruently melting at 1125±5 K has been proved. It is established that the compound $PbCuSbS_3$ is a phase of changing composition and its field homogeneousity is in the interval 46–52% PbS.

Keywords: *nonstoichiometry, phase diagram, X-ray analysis, density.*

Introduction

During the investigation of the systems $CuSbS_2$–$LnSbS_3$, $FeSb_2S_4$–$FeLn_2S_4$, PbS–$EuBi_2S_4$ and $CuBiS_2$–$LnBiS_3$ several compounds have been characterized. This work is devoted to the structural study of one of than: Cu_2LnSbS_7, $FeLnSbS_4$, $PbLnBi_2S_5$ and $Cu_2LnBi_3S_7$ compounds [1–5].

Experimental part

A part of the samples for measurements was synthesized by method [6], their composition was calculated from the weight change during equilibration. In addition, the samples were prepared separately by mixing the appropriate amounts of the pure elements in powder form weighed on a semi-microbalance to an accuracy of ±0.0001 mg. Starting materials were Pb (99.99%), Cu (99.999%), Sb (99.999%) and sulfur (99.99999%). The sample mass was about 1–3 g, for the density measurements, where larger samples about 3–4 g were necessary.

The mixtures were placed into quartz ampoules, which were evacuated to about 10^{-2} Pa, flushed several times which Ti guttered Ar, and finally scaled under vacuum. They were slowly (within one day) heated up to about 1220 K, kept at this temperature for one week, and cooled in the furnace. The alloys were then ground in an agate mortar, scaled again in quartz ampoules as described above, and homogenized at an appropriate. A number of samples were chemically analyzed; the deviation from the nominal composition was negligible.

DTA-measurements were performed using a thermal analyzer (NTR-70) with samples of about 1–3 g scaled under vacuum in special quartz containers. The heating rate was 5^0/min, and an identical quartz crucible containing pure chromium was used as a reference. The Pt/Pt 10 at.% Rh-thermocouples were calibrated at the melting points of high purity zinc, antimony and cupper. Additionally heating curve determinations were performed on six large samples (about 5 g) with compositions in the vicinity of the melting point maximum of the 3-phase using especially designed quartz crucibles [7]. They were prepared from one master alloy whose composition was changed after the measurement several times by adding either lid, cupper or antimony. After sealing the mixture was masted to get a homogeneous alloy. The samples were heated in an electric furnace, changing the temperature by the power input, the thermo-emf signal of a Pt/Pt 10% Rh-thermocouple was simplified and recorded using the registration equipment of the DTA-apparatus described above.

X-ray measurements were made with a "Dron-3" using filtered CuK_α-radiation. The lattice constants were obtained by linear regression and extrapolation to zero using the function $(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)/2$.

For the density measurements a pycnometer with 2 ml volume was employed using water as displacement liquid. Between 3 and 4 g of the finely powdered samples were weighed into the pycnometer cell, which was then filled with water. The measurements were performed at temperature between 295 and 300 K.

Results and discussions

Phase diagram.

The results of the DTA-measurements for 25 samples between 0 and 100 mol.% of PbS are collected in Table 1; all data points were evaluated from the heating curves except for a few liquidus point, where the temperatures of the effects are listed both on heating and cooling. However, because of considerable super cooling, even then the liquidus temperature cooling could only be estimated by extrapolation. Table 1 contains the solidus and liquidus temperatures for eight compositions obtained from heating curve determinations as described above.

The corresponding part of the phase diagram is shown in Figure 1.

There invariant arrests are observed in the investigated composition range, whose temperatures were fixed by additional data points outside this range.

Table 1. Results of the DTA-measurements in the $CuSbS_2$–PbS system.

Composition, mol.% PbS	Solidus, K	Liquidus heating cooling, K	Mikrohardness ($\times 10^7$ Pa)	Pycnometric density, g/sm^3
0.0	775	825	230	6.25
2.0	745	810	235	6.22
5.0	710	800	240	6.20
6.0	675	780	244	6.14
10	680	770	244	6.05
15	675	730	244	6.02
20	675	675	274	–
25	675	800	268	6.00
30	675	900	264	–
35	675	970	260	–
40	675	1035	256	5.98
45	–	1080	254	5.97
46	830	1090	253	5.98
48	950	1100	251	5.84
50	–	1125	250	5.75
51	–	1120	255	5.80
52	1050	1110	255	5.90
55	–	1100	255	5.91
60	955	1070	255	–
65	950	1040	75	5.92
70	950	950	72	5.94
75	960	1080	72	6.25
80	955	1190	70	6.40
85	960	1240	74	6.58
90	960	1310	72	6.60
100	–	1400	72	6.61

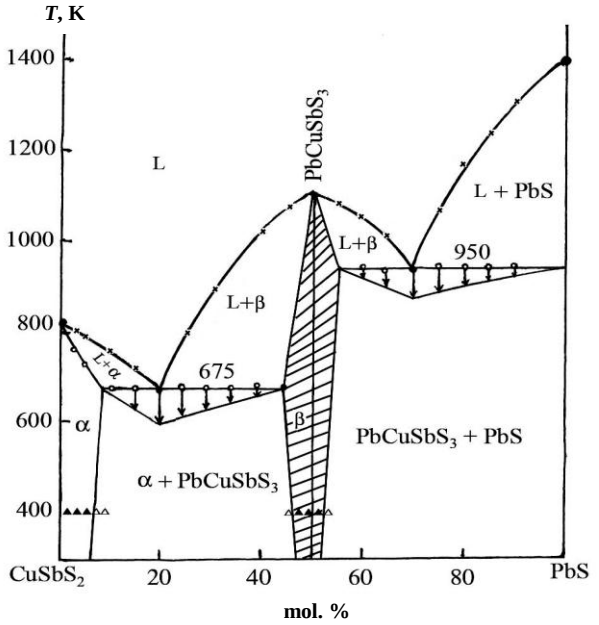

Fig.l. Phase diagram of the $CuSbS_2$–PbS system (o – solidus, × – liquidus on heating or cooling resp, ▲ – one phased alloys, Δ – two phased alloys).

On the $CuSbS_2$-rich side, the effect at 675 K corresponds to the eutectic between α($CuSbS_2$) and β($PbCuSbS_3$). The congruent melting point of $PbCuSbS_3$ was found at 50 mol.% PbS and 1125± 5 K. The temperatures of the invariant arrests are in good agreement with the volume given in [8].

As far as the position of the congruent melting point is conserved, the present results agree very well with those of Bayramova et al. [8], however, their temperature maximum of 1300 K seems to be somewhat too low.

The homogeneity range of the 3-phase ($PbCuSbS_3$) was determined [8] by based on lattice parameter measurements. As can be seen from Figure l, our $PbCuSbS_3$-rich phase boundary is in perfect agreement with their data. Since the extension of the phase can be estimated from the first appearance of the invariant arrests at 675 K, the present results are through to be more reliable.

As possible explanation for the displacement of the melting point maximum away from the stoichiometric composition we suggest that the minimum in the integral Gibbs energy of the liquid phase is shifted considerably to the PbS-rich side.

Lattice parameters.

The lattice parameters (Table 2) were determined by X-ray measurements for two series of samples: one quenched from 675 K

and one from 400 K which was also used for the density measurements.

Table 2. Lattice parameters of the phase β($PbCuSbS_3$)

Composition, mol.% PbS	Quenching temperature, K	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
44	675	8.165	8.725	7.833	557.68
46	675	8.164	8.715	7.830	557.09
46	400	8.161	8.700	7.800	553.80
48	675	8.164	8.705	7.828	556.70
48	400	8.163	8.700	7.810	554.65
50	675	8.162	8.700	7.830	556.00
50	400	8.164	8.730	7.827	557.34
51	675	8.164	8.720	7.831	557.49
51	400	8.162	8.710	7.830	556.64
52	675	8.166	8.740	7.840	560.83
52	400	8.163	8.720	7.840	559.34
53	675	8.168	8.712	7.846	561.31

From the composition dependence shown in Figure 2 the PbS-rich phase boundary was obtained at 45 mol.% PbS (675 K) and 54 mol.% PbS (950 K). Regardless of the quenching temperature a maximum value is observed around 43.5 mol.% PbS. The values remain constant below about 43 mol.% PbS which is not quite in agreement with the results of the thermal analyses. Therefore the concentration where the slope changes should clearly indicate the beginning of the filling of the interstitial positions. Although this particular composition cannot be accurately pinpointed in Figure 2, the change of slope occurs somewhere around 52 mol.% PbS rather than exactly at the equimolecular ratio.

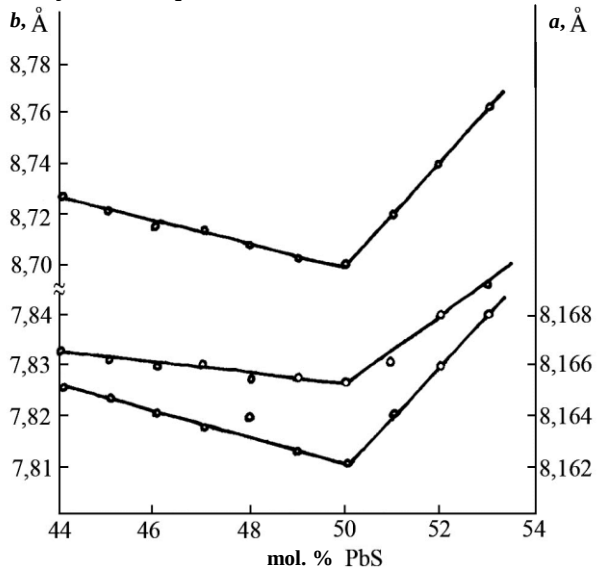

Fig.2. Lattice parameters of β(solution solidus on bases $PbCuSbS_3$) samples quenched from 675 K.

Density.

The composition dependence of the pycnometric density for samples quenched from 600 K is shown in Figure 3.

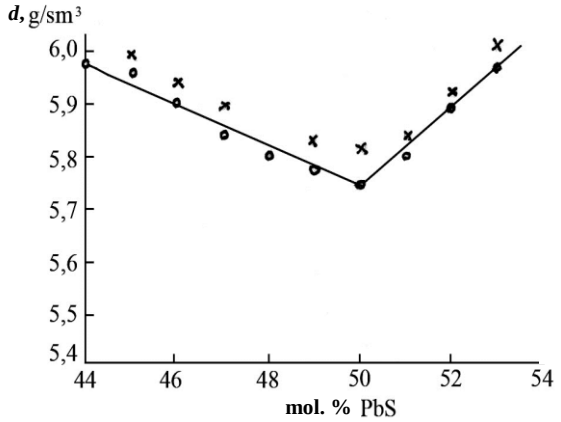

Fig.3. Density as a function of composition from samples quenched from 675 K (o – experimental data, × – calculated from the X-ray data).

The values are in good agreement with the results of [8–10]. It would be rather unusual if the experimentally determined densities should be higher than lattice parameters in Figure l.

Here again the curve consists of two more or less linear branches which intersect at a composition between 50.5 and 51.0 mol.% PbS rather than exactly at 50 mol.% PbS.

Also shown in Figure 3 are the theoretical densities, calculated from the lattice parameters under the assumption that above 50 mol.% PbS vacancies exist in regular cupper positions, whereas below stoichiometry interstitial positions are filled with cupper atoms. It can be clearly seen that the experimental curve is shifted to lower density values.

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$PbCuSbS_3$ BİRLƏŞMƏSİNDƏ QEYRİ-STEXİOMETRİYA

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$CuSbS_2$–PbS sistemi 0–100 mol.% PbS qatılıq intervalında öyrənilmiş və onun hal diaqramı qurulmuşdur. Sistemdə 1125±5 K-də konqruent əriyən $PbCuSbS_3$ birləşməsinin əmələ gəldiyi sübut edilmişdir. Müəyyən edilmişdir ki, $PbCuSbS_3$ birləşməsi qeyri-stexiometrik olub, dəyişən tərkibli fazadır. Onun həllolma sahəsi 46–52 mol.% PbS intervalında dəyişir.

Açar sözlər: *qeyri-stexiometriya, faza diarqamı, rentgenoqrafik analiz, sıxlıq*.

НЕСТЕХИОМЕТРИЯ В СОЕДИНЕНИИ $PbCuSbS_3$

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Система $CuSbS_2$–PbS изучена в интервале концентраций 0–100 мол.% PbS и построена её диаграмма состояния. Доказано образование в системе четверного соединения $PbCuSbS_3$, плавящегося при 1125±5 K конгруэнтно. Установлено, что соединение $PbCuSbS_3$ является фазой переменного состава, и область его гомогенности находится в интервале 46–52 мол.% PbS.

Ключевые слова: *нестехиометрия, фазовая диаграмма, рентгенографический анализ, плотность.*