ELSEVIER

Journal of Alloys and Compounds 414 (2006) 113–117

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Isothermal section of the Y_2S_3–Cu_2S–GeS_2 system at 870 K and crystal structures of the $Y_3Ge_{1.25}S_7$ and Y_3CuGeS_7 compounds

L.D. Gulay [a,*], O.S. Lychmanyuk [a], J. Stępień-Damm [b], A. Pietraszko [b], I.D. Olekseyuk [a]

[a] *Department of General and Inorganic Chemistry, Volyn State University, Voli Ave 13, 43009 Lutsk, Ukraine*
[b] *W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna str. 2, P.O. Box 1410, 50-950 Wrocław, Poland*

Received 5 July 2005; accepted 19 July 2005
Available online 26 August 2005

Abstract

The Y_2S_3–Cu_2S–GeS_2 system was investigated using X-ray single crystal and powder diffraction. The existence of the compounds $YCuS_2$ ($YCuS_2$ structure type, space group $P2_12_12_1$) and $Y_{0.84}Cu_{1.48}S_2$–$Y_{2/3}Cu_2S_2$ ($Er_{2/3}Cu_2S_2$ structure type, space group $P\bar{3}$) was confirmed in the Y_2S_3–Cu_2S section. The formation of the $Y_3Ge_{1.25}S_7$ ($Dy_3Ge_{1.25}S_7$ structure type, space group $P6_3$) compound in the Y_2S_3–GeS_2 section was confirmed using X-ray single crystal diffraction ($a = 0.9730(1)$ nm, $c = 0.5826(1)$ nm, $R_1 = 0.0428$). The formation of the compounds Cu_8GeS_6 (β'-Ag_8GeSe_6 structure type, space group $Pmn2_1$), Cu_4GeS_4 (Cu_4GeS_4 structure type, space group $P2_1/c$) and Cu_2GeS_3 (Cu_2SnS_3 structure type, space group Cc) was confirmed in the Cu_2S–GeS_2 section. The isothermal section of the Y_2S_3–Cu_2S–GeS_2 system at 870 K was constructed based on data of the phase analysis of 48 samples. The formation of the new quaternary Y_3CuGeS_7 compound (La_3CuSiS_7 structure type, space group $P6_3$, $a = 0.9835(1)$ nm, $c = 0.5765(1)$ nm), $R_1 = 0.0373$) was established in the Y_2S_3–Cu_2S–GeS_2 system.

Keywords: Chalcogenides; Y compounds; Cu compounds; Ge compounds; S compounds; Isothermal section; Crystal structure; Phase diagram; X-ray single crystal diffraction; X-ray powder diffraction

1. Introduction

The crystal structure of the Y_2S_3 compound (Ho_2S_3 structure type, space group $P2_1/m$, $a = 1.75233$ nm, $b = 0.40107$ nm, $c = 1.01736$ nm, $\beta = 98.601^\circ$) has been determined in Ref. [1].

Several modifications of the phases with composition close to Cu_2S have been established. The crystal structure of $Cu_{31}S_{16}$ ($Cu_{31}S_{16}$ structure type, space group $P2_1/n$, $a = 2.6897$ nm, $b = 1.5745$ nm, $c = 1.3565$ nm, $\beta = 90.13^\circ$) has been investigated in Ref. [2]. Low chalcocite Cu_2S (Cu_2S structure type, space group $P2_1/c$, $a = 1.5246$ nm, $b = 1.1884$ nm, $c = 1.3494$ nm, $\beta = 116.35^\circ$) has been investigated also in Ref. [2]. High chalcocite Cu_2S (Cu_2S structure type, space group $P6_3/mmc$, $a = 0.395$ nm, $c = 0.675$ nm) has been investigated in Ref. [3]. A cubic unit cell has been determined at high temperatures for $Cu_{1.8}S$ (Cu_2Se structure type, space group $Fm\bar{3}m$, $a = 0.5582$ nm) [4]. The crystal structure of the Cu_7S_4 compound (Cu_7S_4 structure type, space group $Pnma$, $a = 0.789$ nm, $b = 0.784$ nm, and $c = 1.101$ nm) has been investigated in Ref. [5].

Two modifications of GeS_2 are known. The crystal structure of low temperature modification (LT) (GeS_2 structure type, space group Pc, $a = 0.6875$ nm, $b = 2.255$ nm, $c = 0.6809$ nm, $\beta = 120.45^\circ$) has been investigated in Ref. [6]. High temperature modification crystallizes also in a monoclinic unit cell (GeS_2 structure type, space group $P2_1/c$, $a = 0.6720$ nm, $b = 1.6101$ nm, $c = 1.1436$ nm, $\beta = 90.88^\circ$) [7].

The crystal structure of the $YCuS_2$ has been described as $ErAgSe_2$ type of structure (space group $P2_12_12_1$, $a = 0.631$ nm, $b = 1.366$ nm, $c = 0.394$ nm) [8]. Only the lattice parameters have been determined for this compound in Ref. [8]. A complete crystal structure investigation of the $YCuS_2$

* Corresponding author.
E-mail address: gulay@lab.univer.lutsk.ua (L.D. Gulay).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.07.035

compound has been performed in Ref. [9] ($YCuS_2$ structure type, space group $P2_12_12_1$, $a = 0.62756$ nm, $b = 1.33863$ nm, $c = 0.39704$ nm). The $Y_{2/3}Cu_2S_2$ compound ($Er_{2/3}Cu_2S_2$ structure type, space group $P\bar{3}$) has also been investigated in Ref. [8]. For this compound a homogeneity range exists.

The existence of the $Y_3Ge_{1.25}S_7$ compound in the Y_2S_3–GeS_2 system has been established in Ref. [10]. The $Ce_6Al_{10/3}S_{14}$ type of structure (space group $P6_3$) has been proposed for this compound and the lattice parameters have been determined: $a = 0.973$ nm, $c = 0.582$ nm.

The existence of the compounds Cu_8GeS_6 (β'-Ag_8GeSe_6 structure type, space group $Pmn2_1$, $a = 0.70445$ nm, $b = 0.69661$ nm, $c = 0.98699$ nm) [11], Cu_4GeS_4 (Cu_4GeS_4 structure type, space group $P2_1/c$, $a = 0.9790$ nm, $b = 1.3205$ nm, $c = 0.9942$ nm, $\beta = 100.90°$) [12] and Cu_2GeS_3 (Cu_2SnS_3 structure type, space group Cc, $a = 0.6449$ nm, $b = 1.1319$ nm, $c = 0.6428$ nm, $\beta = 108.37°$) [13] has been established in the Cu_2S–GeS_2 section.

No quaternary compounds have been reported for the Y_2S_3–Cu_2S–GeS_2 system in the literature.

The isothermal section of the Y_2S_3–Cu_2S–GeS_2 system at 870 K and the crystal structures of the $Y_3Ge_{1.25}S_7$ and Y_3CuGeS_7 compounds are presented in this paper.

2. Experimental details

The samples were prepared by melting of the high purity elements (the purity of the ingredients was better than 99.9 wt.%) in evacuated silica ampoules. The synthesis was realized in a tube furnace. The ampoules were heated with a heating rate of 30 K/h to the maximal temperature, 1420 K. The samples were kept at the maximal temperature during 4 h. After that they were cooled slowly (10 K/h) to 870 K and annealed at this temperature during 240 h. After annealing the ampoules with the samples were quenched in cold water.

Diffraction-quality single crystals of the $Y_3Ge_{1.25}S_7$ and Y_3CuGeS_7 compounds for the crystal structure investigation were selected from the samples of the respective compositions. The X-ray intensities data were collected on a KUMA diffraction KM-4 four-circle single crystal diffractometer equipped with CCD camera using graphite-monochromatized Mo Kα radiation ($\lambda = 0.071073$ nm). The intensities of the reflections were corrected for Lorentz and polarisation factors. Semi-empirical absorption correction was applied. The crystal structure was solved by Patterson methods [14] and refined by full matrix least squares method using SHELX-97 program [15].

X-ray powder diffraction patterns of the samples were recorded using a DRON-4-13 powder diffractometer (Cu Kα radiation, $10° \le 2\Theta \le 80°$, step scan mode with a step size of 0.05° and counting time of 1 s per data point). Phase analysis was carried out. X-ray powder diffraction patterns of the samples for the crystal structure determination were recorded using a DRON-4-13 powder diffractometer (Cu Kα radiation, $10 \le 2\Theta \le 100°$, step scan mode with a step size of 0.05° and counting time of 10 s per data point). Lattice parameters were calculated using least-square method realized in the CSD program [16].

3. Results and discussion

3.1. Investigation of the Y_2S_3–Cu_2S system

The existence of the $YCuS_2$ compound ($YCuS_2$ structure type, space group $P2_12_12_1$) was confirmed in the

Table 1
Crystal data and structure refinement details of the $Y_3Ge_{1.25}S_7$ and Y_3CuGeS_7 compounds

Empirical formula	$Y_3Ge_{1.25}S_7$	Y_3CuGeS_7
Formula weight	581.89	627.28
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions	$a = 0.9730(1)$ nm; $c = 0.5826(1)$ nm	$a = 0.9835(1)$ nm; $c = 0.5765(1)$ nm
Volume	0.4776(1) nm^3	0.4829(1) nm^3
Number of formula units per unit cell	2	2
Calculated density (g/cm^3)	4.046	4.314
Absorption coefficient (mm^{-1})	23.384	24.510
F(0 0 0)	538	580
Crystal size	0.06 mm × 0.08 mm × 0.10 mm	0.07 mm × 0.10 mm × 0.12 mm
Θ Range for data collection	4.19–30.46	4.14–30.50
Index ranges	$-11 \le h \le 13$; $-13 \le k \le 11$; $-7 \le l \le 7$	$-14 \le h \le 13$; $-11 \le k \le 14$; $-7 \le l \le 7$
Reflections collected	7240	7360
Independent reflections	943 [R(int.) = 0.1284]	976 [R(int.) = 0.0869]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	943/0/37	976/0/37
Goodness-of-fit on F^2	1.099	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428$; $wR2 = 0.0733$	$R_1 = 0.0373$; $wR_2 = 0.0796$
R indices (all data)	$R_1 = 0.0612$; $wR2 = 0.0779$	$R_1 = 0.0478$; $wR_2 = 0.0869$
Extinction coefficient	0.008(1)	0.014(1)
Largest diff. peak and hole × 10^{-3} (e/nm^3)	0.890 and −1.015	1.046 and −0.983