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Investigation of the R_2Se_3–Cu_2Se–In_2Se_3 (R = La, Pr, Y and Er) systems at 870 K and crystal structure of the $R_2CuInSe_5$ (R = La, Ce and Pr) compounds

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Abstract

Phase equilibria in R_2Se_3–Cu_2Se–In_2Se_3 (R = La, Pr, Y and Er) systems at 870 K were determined using X-ray powder diffraction. The existence of the $RCuSe_2$ ($LaCuS_2$ structure type, space group $P2_1/c$) and $La_5Cu_{13}Se_{14}$ (unknown structure) compounds was confirmed in the R_2Se_3–Cu_2Se (R = La, Pr) sections. The formation of the solid solutions $R_{(2+x)/3}Cu_{2-x}Se_2$ ($0 \le x \le 1$) ($Er_{2/3}Cu_2S_2$ structure type, space group $P\bar{3}$) and the $ErCu_5Se_4$ compound with unknown structure was confirmed in the R_2Se_3–Cu_2Se (R = Y, Er) sections. The existence of the $La_3In_{1.67}Se_7$ ($Ce_3Al_{1.67}S_7$ structure type, space group $P6_3$) and $La_4In_{4.67}Se_{13}$ ($La_4In_{4.72}Se_{13}$ structure type, space group *Pbam*) compounds in the La_2Se_3–In_2Se_3 system and the Pr_3InSe_6 (Pr_3InSe_6 structure type, space group *Pnnm*) compound in the Pr_2Se_3–In_2Se_3 system was confirmed. No ternary compounds exist in the Er_2Se_3–In_2Se_3 and Y_2Se_3–In_2Se_3 sections. The formation of the $CuInSe_2$, $CuIn_3Se_5$, $CuIn_5Se_8$, $CuIn_7Se_{11}$ and $CuIn_{11}Se_{17}$ compounds in the Cu_2Se–In_2Se_3 section was observed. The crystal structure of new quaternary $R_2CuInSe_5$ (R = La, Ce and Pr) compounds (space group *Pnma*, $a = 1.20382(6)$ nm, $b = 0.41185(2)$ nm, $c = 1.7556(1)$ nm (for $La_2CuInSe_5$), $a = 1.19997(7)$ nm, $b = 0.40855(2)$ nm, $c = 1.7464(1)$ nm (for $Ce_2CuInSe_5$) and $a = 1.1973(3)$ nm, $b = 0.40649(9)$ nm, $c = 1.7408(4)$ nm (for $Pr_2CuInSe_5$)) was determined.

Keywords: Chalcogenides; Rare earth compounds; Cu compounds; In compounds; Se compounds; Crystal structure; Phase diagram; X-ray powder diffraction

1. Introduction

Production of the compounds with increasingly complex compositions, such as ternary, quaternary, etc., has become a principle direction in a modern science of materials [1]. Among the multicomponent systems an important place belongs to the complex rare earth chalcogenides. The rare-earth chalcogenides are being extensively studied during last years due to their specific thermal, electrical and optical properties, which e.g. make them prospective materials in the field of infrared and nonlinear optics. Therefore the investigation of the phase relations in the multicomponent systems and the determination of the crystal structures of new complex chalcogenides is an important step in a search for new materials.

The crystal structure of the La_2Se_3 and Pr_2Se_3 compounds (Th_3P_4 structure type, space group $I\bar{4}3d$, $a = 0.9037$ nm for La_2Se_3 and $a = 0.89117$ nm for Pr_2Se_3) has been determined in Refs. [2,3], respectively. The formation of several modifications of Y_2Se_3 and Er_2Se_3 has been reported in literature. The low temperature modification crystallizes in Sc_2S_3 type of structure (space group *Fddd*, $a = 1.145$ nm, $b = 0.818$ nm, $c = 2.438$ nm for Y_2Se_3 and $a = 1.135$ nm, $b = 0.810$ nm, $c = 2.417$ nm for Er_2Se_3) [4]. The cubic unit cell (Th_3P_4 structure type, space group $I\bar{4}3d$, $a = 0.86626$ nm for Y_2Se_3 and $a = 0.8581$ nm for Er_2Se_3) has been determined for high temperature modification in Refs. [5,6], respectively. Additionally the UAs_2 structure type (space group $P4/nmm$, $a = 0.3985$ nm, $c = 0.8228$ nm) has been reported for Er_2Se_3 in Ref. [7]. The formation of two modifications of the Cu_2Se compound has been established. The crystal structure of low temperature modification is not determined yet. Monoclinic unit cell ($a = 1.4087$ nm, $b = 2.0481$ nm, $c = 0.4145$ nm, $\beta = 90.38°$) has been proposed in Ref. [8]. Cubic unit cell has been determined for high temperature modification (*anti*-CaF_2 structure type, space group $Fm\bar{3}m$, $a = 0.5759$ nm [9] or Cu_2Se

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structure type, space group $Fm\bar{3}m$, $a = 0.5787$ nm [10]). Four modifications of In_2Se_3 have been identified in Ref. [11]: α-In_2Se_3 (space group $R\bar{3}m$, $a = 0.4025$ nm, $c = 2.8762$ nm; space group $P6_3/mmc$, $a = 0.4025$ nm, $c = 1.9235$ nm), β-In_2Se_3 (space group $R\bar{3}m$, $a = 0.4000$ nm, $c = 2.833$ nm), γ-In_2Se_3 (space group $P6_122$ or $P6_522$, $a = 0.713$ nm, $c = 1.958$ nm) and δ-In_2Se_3 (hexagonal unit cell, $a = 0.4014$ nm, $c = 0.964$ nm). Complete crystal structure determinations have been reported for some of them: In_2Se_3 (own structure type, space group $P6_5$, $a = 0.711$ nm, $c = 1.930$ nm) [12], In_2Se_3 (Al_2S_3 structure type, space group $P6_1$, $a = 0.711$ nm, $c = 1.934$ nm) [13], In_2Se_3 (Bi_2Te_3 structure type, space group $R\bar{3}m$, $a = 0.405$ nm, $c = 2.941$ nm) [14], In_2Se_3 (own structure type, space group $R3m$, $a = 0.405$ nm, $c = 2.877$ nm) [14].

The existence of the $RCuSe_2$ compounds ($LaCuS_2$ structure type, space group $P2_1/c$, $a = 0.673$ nm, $b = 0.753$ nm, $c = 0.718$ nm, $\beta = 97.68°$ for $LaCuSe_2$; $a = 0.668$ nm, $b = 0.745$ nm, $c = 0.712$ nm, $\beta = 97.13°$ for $PrCuSe_2$) in the R_2Se_3–Cu_2Se (R = La, Pr) systems hve been reported in Ref. [15]. Additionally the formation of the $La_5Cu_{13}Se_{14}$ compound (orthorhombic unit cell, $a = 0.774$ nm, $b = 2.467$ nm, $c = 0.701$ nm) has been also reported in Ref. [15]. The formation of the solid solutions $Y_{(2+x)/3}Cu_{2-x}Se_2$ ($0 \le x \le 1$) ($a = 0.4038$–0.4068 nm, $c = 0.6597$–0.6454 nm) and $Er_{(2+x)/3}Cu_{2-x}Se_2$ ($0 \le x \le 1$) ($a = 0.4023$–0.4043 nm, $c = 0.6561$–0.6456 nm) with $Er_{2/3}Cu_2S_2$ type of structure (space group $P\bar{3}$) in the R_2Se_3–Cu_2Se (R = Y, Er) systems has been reported in Refs. [15,16]. The existence of the $ErCu_5Se_4$ compound with hexagonal unit cell ($a = 1.187$ nm, $c = 0.660$ nm) has been established in Ref. [17]. The existences of the Pr_3InSe_6 compound (own structure type, space group $Pnnm$, $a = 1.74130$ nm, $b = 1.4275$ nm, $c = 0.4109$ nm) in the Pr_2Se_3–In_2Se_3 section has been reported in Ref. [18]. The formation of the $RInSe_3$ compounds with hexagonal unit cell ($a = 0.685$ nm, $c = 0.400$ nm for $LaInSe_3$; $a = 0.684$ nm, $c = 0.394$ nm for $PrInSe_3$) in the R_2Se_3–In_2Se_3 (R = La, Pr) sections and the $RInSe_3$ compounds with cubic unit cell ($a = 1.1375$ nm for $YInSe_3$; $a = 1.137$ for $ErInSe_3$) in the R_2Se_3–In_2Se_3 (R = Y, Er) sections has been reported in Ref. [1]. Additionally the formation of the $La_3In_{1.67}Se_7$ compound ($Ce_3Al_{1.67}S_7$ structure type, space group $P6_3$, $a = 1.050$ nm, $c = 0.650$ nm) in the La_2Se_3–In_2Se_3 system has been also reported in Ref. [1]. The formation of new $La_4In_{4.72}Se_{13}$ compound (own structure type, space group $Pbam$, $a = 1.2442$ nm, $b = 2.2146$ nm, $c = 0.41969$ nm) in the La–In–Se system has been reported recently in Ref. [19]. The existence of the $CuInSe_2$ ($FeCuS_2$ structure type, space group $I\bar{4}2d$, $a = 0.5785$ nm, $c = 1.1573$ nm) [20], $CuIn_3Se_5$, (Cu_2FeSnS_4 structure type, space group $I\bar{4}2m$, $a = 0.57581$ nm, $c = 1.15359$ nm) [21], $CuIn_5Se_8$ (unknown structure) [22], $CuIn_7Se_{11}$ ($CuIn_7Se_{11}$ structure type, space group $P3m1$, $a = 0.40263$ nm, $c = 1.62992$ nm) [23] and $CuIn_{11}Se_{17}$ (unknown structure) [24] compounds in the Cu_2Se–In_2Se_3 section has been reported.

No quaternary compounds in the Y_2Se_3–Cu_2Se–In_2Se_3, La_2Se_3–Cu_2Se–In_2Se_3, Pr_2Se_3–Cu_2Se–In_2Se_3 and Er_2Se_3–Cu_2Se–In_2Se_3 systems have been reported in literature.

This paper is a part of a systematic investigation of ternary and quaternary rare earth chalcogenides. Phase diagrams of the R_2Se_3–Cu_2Se–In_2Se_3 (R = La, Pr, Y and Er) systems at 870 K and crystal structure of the $R_2CuInSe_5$ (R = La, Ce and Pr) compounds are given.

2. Experimental

Sixty-three, 45, 31 and 33 samples were prepared for the investigation of the phase equilibria in the La_2Se_3–Cu_2Se–In_2Se_3, Pr_2Se_3–Cu_2Se–In_2Se_3, Y_2Se_3–Cu_2Se–In_2Se_3 and Er_2Se_3–Cu_2Se–In_2Se_3 systems, respectively. The samples were prepared using high purity elements (the purity of the ingredients was better than 99.9 wt.%). The calculated amounts of the components were sealed in evacuated silica ampoules. The synthesis was realized in a tube furnace. The ampoules were heated with the heating rate of 30 K/h to maximal temperature 1420 K. The samples were kept at maximal temperature during 3 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.

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 pattern of the $R_2CuInSe_5$ (R = La, Ce and Pr) compounds 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 20 s per data point). Crystal structure determination was performed by Rietveld method with the DBWS-9411 program [25].

3. Result and discussion

3.1. Investigation of the R_2Se_3–Cu_2Se (R = La, Pr, Y and Er) systems

The existence of the $RCuSe_2$ ($LaCuS_2$ structure type, space group $P2_1/c$) and $La_5Cu_{13}Se_{14}$ (unknown structure) compounds was confirmed in the R_2Se_3–Cu_2Se (R = La, Pr) sections. The formation of the solid solutions $R_{(2+x)/3}Cu_{2-x}Se_2$ ($0 \le x \le 1$) ($Er_{2/3}Cu_2S_2$ structure type, space group $P\bar{3}$) and the $ErCu_5Se_4$ compound with unknown structure was confirmed in the R_2Se_3–Cu_2Se (R = Y, Er) sections.

3.2. Investigation of the R_2Se_3–In_2Se_3 (R = Y, La, Pr, Er) systems

The existence of the $La_3In_{1.67}Se_7$ ($Ce_3Al_{1.67}S_7$ structure type, space group $P6_3$) and $La_4In_{4.67}Se_{13}$ ($La_4In_{4.72}Se_{13}$ structure type, space group $Pbam$) compounds in the La_2Se_3–In_2Se_3 system was confirmed. The formation of the Pr_3InSe_6 (Pr_3InSe_6 structure type, space group $Pnnm$) compound in the Pr_2Se_3–In_2Se_3 system was also confirmed. No ternary compounds were observed in the Er_2Se_3–In_2Se_3 and Y_2Se_3–In_2Se_3 sections.

3.3. Investigation of the Cu_2Se–In_2Se_3 system

The formation of the $CuInSe_2$, $CuIn_3Se_5$, $CuIn_5Se_8$, $CuIn_7Se_{11}$ and $CuIn_{11}Se_{17}$ compounds in the Cu_2Se–In_2Se_3 section was observed.