



Intermetallic compounds in the M–Cu–Sn systems with M = Eu, Sr, Ba

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ABSTRACT

Several samples were prepared in the title systems, starting from the elements sealed under argon in Ta crucibles, melting in an induction furnace and annealing at 823 K. Six ternary phases were found: EuCu_2Sn_2 , $a = 11.100$ (3), $b = 4.307$ (1), $c = 4.824$ (1) Å, $\beta = 108.88$ (1)°, and SrCu_2Sn_2 , $a = 11.197$ (4), $b = 4.322$ (2), $c = 4.859$ (1) Å, $\beta = 108.43$ (1)°, $C2/m$, CaCu_2Sn_2 -type, closely related to the BaAl_4 structure; $\text{Sr}_3\text{Cu}_8\text{Sn}_4$, $a = 9.3280$ (2), $c = 7.8826$ (4) Å, $P6_3mc$, $\text{Nd}_3\text{Co}_8\text{Sn}_4$ -type, ordered variant of the BaLi_4 -type; SrCu_4Sn_2 , $a = 8.176$ (1), $c = 7.799$ (1) Å, $I4/mcm$, CaNi_4Sn_2 -type; SrCu_9Sn_4 , $a = 8.663$ (1), $c = 12.457$ (2) Å, and BaCu_9Sn_4 , $a = 8.717$ (1), $c = 12.545$ (2) Å, $I4/mcm$, LaFe_9Si_4 -type, ordered variant of the NaZn_{13} structure. The structure of the first compound was refined by the Rietveld method, while single crystal data were used for the others. Some remarks are given on the crystal chemistry of the encountered and related structure types.

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1. Introduction

The similar alloying behaviour of the divalent alkaline earth and rare earth M elements ($M = \text{Ca, Sr, Ba, Eu, Yb}$) is known since many years (see for example Ref. [1]). Europium and ytterbium normally behave as divalent elements and often give rise to phases with the same composition and structure as those formed by alkaline earths. Concerning the M–Cu–Sn systems an extensive study was done for the Yb system, where fifteen phases occur [2–5], while in the Ca [6–9] and Eu [10–12] systems eight and five compounds have been structurally investigated, respectively. For the Sr–Cu–Sn and Ba–Cu–Sn systems only the two isotopic compounds SrCuSn_2 and BaCuSn_2 [13] are known, while preliminary data of another compound, $\text{Ba}_3\text{Cu}_3\text{Sn}_7$ were reported in a congress abstract [14]. Examining all these phases we can note several regularities. The compounds $\text{Yb}_3\text{Cu}_8\text{Sn}_4$ [4], $\text{Eu}_3\text{Cu}_8\text{Sn}_4$ [11] and $\text{Ca}_3\text{Cu}_8\text{Sn}_4$ [9] are isotopic. The two compounds $\text{Yb}_4\text{Cu}_2\text{Sn}_5$ [3] and $\text{Ca}_6\text{Cu}_2\text{Sn}_7$ [8] are formed by the same trigonal and quadrangular prisms, but arranged in a different way, and belong to a series with general formula $M_2 + nT_2X_3 + n$ with $n = 2$ and $n = 4$, respectively. Other phases crystallize with structures derived from the BaAl_4 -type, as $\text{Yb}_3\text{Cu}_6\text{Sn}_5$ [4], isotopic with $\text{Dy}_3\text{Co}_6\text{Sn}_5$ [15], whose structure is a periodic intergrowth of Cu_3Au - and BaAl_4 -slabs, or CaCu_2Sn_2 [9], monoclinic distortion of the ThCr_2Si_2 structure (BaAl_4 ternary derivative).

Further phases containing fragments of the same BaAl_4 -type are the ordered EuCuSn_2 [12], SrCuSn_2 and BaCuSn_2 [13], isotopic with CeNiSi_2 . Interestingly, MCu_xSn_2 phases with this last structure are also formed by the trivalent rare earths, but with copper defects ($x < 1$) and homogeneity ranges [16]. A more strict similarity with the trivalent rare earth analogues is found between the MCu_9Sn_4 compounds with $M = \text{Yb}$ [5], Eu [12], Ca [9] and $M = \text{La–Nd}$ [17], all crystallizing with a tetragonal ordered derivative of the cubic NaZn_{13} structure. However, for the rare earth compounds a transition from the ordered tetragonal to the disordered cubic structure is obtained by a small change of composition from MCu_9Sn_4 to $\text{MCu}_{9.4}\text{Sn}_{3.6}$, which appreciably affects the magnetic properties. For instance, only the ordered MCu_9Sn_4 compounds ($M = \text{Ce, Pr, Nd}$) show a ferromagnetic transition at 5.5, 10.5 and 15 K, respectively, as well as EuCu_9Sn_4 that orders ferromagnetically at 10 K.

The present work is devoted to check existence and structure of other intermediate phases in the M–Cu–Sn systems with $M = \text{Sr, Ba, Eu}$, in the region from 7 to 20 at.% of M.

2. Experimental

The elements used were commercial products: europium 99.9 wt.%, strontium 99.85 wt.%, barium 99.5 wt.%, copper 99.99 wt.%, tin 99.999 wt.% pure. Stoichiometric quantities of the metals were handled and weighed in a glove box, closed in tantalum crucibles, arc welded under argon, melted in an induction furnace and usually annealed at 823 K for 2–3 months. The

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homogeneity of the samples, which were stable in air, was checked by standard metallographic techniques.

Differential thermal analyses (DTA) were carried out on a Netzsch apparatus, using molybdenum containers sealed under argon, with cooling rate of 5 °/min.

Powder X-ray diffraction analysis was carried out using both a powder diffractometer (Philips PW1050/81, Cu K α radiation) and a Guinier camera (Cu K α 1 radiation), with silicon as internal standard. Data collection for Rietveld refinement was made with 0.02° 2 θ steps and 20'' time. Single crystals were mounted on a Bruker Nonius MACH3 diffractometer (graphite monochromatized Mo K α radiation). Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), (fax: (49)7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-422453 (SrCu₂Sn₂), CSD-422454 (Sr₃Cu₈Sn₄), CSD-422455 (SrCu₄Sn₂), CSD-422456 (SrCu₉Sn₄), CSD-422457 (BaCu₉Sn₄), the name of the authors, and citation of the paper.

The computer programs used were: LAZY PULVERIX [18] (powder diffraction pattern calculation), SHELXS-97 [19] or SIR97 [20] (structure solution), SHELXL-97 [19] (single crystal structure refinements), STRUCTURE TIDY [21] (crystal data standardisation), DBWS-9807a [22] (Rietveld analysis).

3. Results and discussion

Nine samples were prepared, namely SrCu₉Sn₄, SrCu₄Sn₂, SrCu₂Sn₂, Sr₃Cu₈Sn₄, BaCu₉Sn₄, EuCu₂Sn₂, Ba₃Cu₈Sn₄, BaCu₂Sn₂, BaCu₄Sn₂. In the first five cases the micrographic and X-ray diffraction results confirmed the existence of the corresponding compounds. Also EuCu₂Sn₂ exists, but a complex situation occurs, as described in the following. The last three samples excluded the occurrence of the corresponding compounds, showing a mixture of two or more neighbouring phases. Table 1 reports the crystallographic data of the six new compounds, while the details of the conditions of single crystal intensity data collection are reported in Table 2. The absorption effects were always taken into account by an empirical method (ψ -scans on 3–6 strong top reflections) [23]; in some cases also a spherical correction was applied.

3.1. EuCu₂Sn₂ and SrCu₂Sn₂

Different samples of EuCu₂Sn₂ were prepared and characterized. The corresponding DTA cooling curves showed four exothermic effects at 1083, 1080, 1048 and 943 K, with the peak heights in the ratio 32:100:39:12, respectively. Accordingly, in order to obtain a monophasic sample, different thermal treatments were applied, but a polyphasic appearance of both as cast and annealed samples was always observed. As often found, kinetic factors hindered the attainment of the thermodynamic stable situation. The X-ray powder patterns revealed reflections of three phases: EuCu₂Sn₂, indexed on the basis of the CaCu₂Sn₂-type [9], and the already known EuCuSn₂ (CeNiSi₂-type) and EuCu₉Sn₄ (LaFe₉Si₄-type) [12], in decreasing

quantities. As the search for a single crystal of the 1:2:2 phase was unsuccessful, the Rietveld method was applied to the sample showing the maximum quantity of this phase. The refinement process, carried out on the three phases, gave acceptable results ($R_{wp} = 0.020$; $R_B = 0.062$ for EuCu₂Sn₂; mass percentages 71% for the 1:2:2 phase, 16% for 1:1:2, 13% for 1:9:4), sufficient to support the existence and structure type of EuCu₂Sn₂. Taking into account these results, the highest DTA peak at 1080 K may indicate the formation temperature of EuCu₂Sn₂. Consequently, the value of the annealing temperature already reported [12] for the preparation of EuCu₉Sn₄ (1053 K) allows to assign the 1083 K peak to the formation of this phase. The formation of the EuCuSn₂ phase (prepared by annealing at 853 K [12]), can be tentatively assigned to the 1048 K peak. Concerning the smallest peak at 943 K, two assignments are possible. Since europium forms other three phases in the region around the 1:2:2 composition, namely EuCu₄Sn₂, Eu₃Cu₈Sn₄ and EuCuSn, the fourth thermal effect may indicate the formation of one of these last compounds, not detected in the X-ray diffraction patterns. Alternately, the peak may indicate the occurrence of a ternary eutectic point. This proposed assignment can be confirmed only by a complete thermal study of the system. Table 3 reports the atomic coordinates and displacement parameters of the 1:2:2 phase, while Fig. 1 shows the observed and calculated powder pattern profile.

Single crystal data allowed to assign also the phase SrCu₂Sn₂ to the CaCu₂Sn₂-type. Atomic coordinates and equivalent isotropic displacement parameters are reported in Table 3, while interatomic distances are available as Supplementary material.

Starting from the structural prototype BaAl₄, several binary and ternary types are derived, because of different site occupations (e.g. ThCr₂Si₂), geometrical distortions of the elementary cell (e.g. CaGa₄), deviations from the 1:4 stoichiometry (e.g. La₃Al₁₁). The CaCu₂Sn₂ structure has been already discussed in a previous work [9], and the three CaCu₂Sn₂-type compounds can be compared with other four phases which are geometrically related: EuGa₄ (BaAl₄-type), CaCu₂Ge₂ (ThCr₂Si₂-type), CaGa₄ [13] and CaCu_{0.15}Ga_{3.85} [24] (with their own types). For these MX₄ phases Table 4 reports the interatomic distances within the X substructure, namely the coordination around the basal X_b atom (4d position in the BaAl₄-type cell), and around the apical X_a atom (4e position in the BaAl₄-type cell). As it is known, in the BaAl₄ structure each X_b atom is surrounded by four X_a atoms (in a nearly tetrahedral geometry) and by four X_b atoms (square planar geometry), while each X_a atom is surrounded by four X_b atoms and one X_a atom (square pyramidal coordination). The M–X bonds complete the coordination of all X atoms. In order to evaluate the bond strength [25], the table reports also the values of the ratio $d/\sum r$ between the bond length value and the corresponding sum of the metallic radii. In this discussion, as common basis, the metallic radii for CN12 after Teatum, Gschneidner and Waber [26] will be used to calculate bond contractions and radii ratios.

As can be seen, in all compounds the four nearly tetrahedral bonds around the X_b atom always show a strong linear contraction (from 6% to 11%). The same contractions occur obviously in the four

Table 1
Crystallographic data of the studied compounds.

Compound	Structure type	Space group	Pearson's code	Cell parameters [Å]				Method ^a
				<i>a</i>	<i>b</i>	<i>c</i>	β [°]	
EuCu ₂ Sn ₂	CaCu ₂ Sn ₂	C2/ <i>m</i>	<i>m</i> S10	11.100 (3)	4.307 (1)	4.824 (1)	108.88 (1)	D
SrCu ₂ Sn ₂	CaCu ₂ Sn ₂	C2/ <i>m</i>	<i>m</i> S10	11.197 (4)	4.322 (2)	4.859 (1)	108.43 (1)	G
Sr ₃ Cu ₈ Sn ₄	Nd ₃ Co ₈ Sn ₄	<i>P</i> 6 ₃ <i>m</i> <i>c</i>	<i>h</i> P30	9.3280 (2)		7.8826 (4)		D
SrCu ₄ Sn ₂	CaNi ₄ Sn ₂	<i>I</i> 4/ <i>m</i> <i>c</i> <i>m</i>	<i>t</i> I28	8.176 (1)		7.799 (1)		G
SrCu ₉ Sn ₄	LaFe ₉ Si ₄	<i>I</i> 4/ <i>m</i> <i>c</i> <i>m</i>	<i>t</i> I56	8.663 (1)		12.457 (2)		G
BaCu ₉ Sn ₄	LaFe ₉ Si ₄	<i>I</i> 4/ <i>m</i> <i>c</i> <i>m</i>	<i>t</i> I56	8.717 (1)		12.545 (2)		D

^a D: Powder diffractometer; G: Guinier camera.

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