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The $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ and $Tb(Cu_{0.58}Al_{0.42})_{11}$ aluminides and their crystal structures

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Abstract

The crystal structure of the new compound $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ with Th_2Zn_{17}-type structure (space group $R\bar{3}m$, $a = 8.767(3)$, $c = 12.824(3)$ Å) has been determined using single crystal X-ray diffraction leading to $R = 0.036$ for 407 independent F_{hkl} values. The crystal structure of $Tb(Cu_{0.58}Al_{0.42})_{11}$ has been established from X-ray powder data with atomic parameter refinement by the Rietveld method (space group *Fddd*, $a = 14.2792(6)$, $b = 14.8916(6)$, $c = 6.5644(3)$ Å). Both structures are characterized by an icosahedral coordination of the smallest atoms.

Keywords: Tb–Cu–Al compounds; Single crystals; Crystal structure; Site preference

1. Introduction

The isothermal sections of phase diagrams of most Ln–Cu–Al systems containing heavy rare-earth metals (except terbium and thulium) have recently been reported [1]. During our investigation of the interaction in the Tb–Cu–Al system at 870 K (the results will be submitted for separate publication) we have found new compounds with the approximate composition $Tb_{0.08}Cu_{0.52}Al_{0.40}$. The present work is devoted to the crystal structure determination of the aforementioned compounds.

2. Experimental

The samples for this investigation were obtained by arc melting pieces of the constituent components with the following purity: Tb, 99.5 wt.%; Cu, 99.99 wt.%; Al, 99.9 wt.%. The samples were homogenized in evacuated silica tubes at 870 K for 600 h and subsequently quenched without breaking the ampoules. Single crystals were obtained by heating a sample with the initial composition $Tb_{10}Cu_{50}Al_{40}$ at 1470 K in an alumina crucible contained in an evacuated silica tube. After this heat treatment the sample was cooled to 870 K, then kept at this temperature for 300 h before cooling to room temperature.

3. Results

Preliminary testing of the single crystal has revealed a rhombohedral unit cell with lattice constants listed in Table 1. A total of 407 independent reflections were used for the structure determination from 1067 obtained experimental intensity values (Table 1). The crystal structure of the compound has been solved by direct methods using the MULTAN program which belongs to CSD software [2]. Atomic positional parameters, thermal anisotropic parameters and statistical distribution of copper and aluminium atoms have been refined by a least squares method after absorption correction of the intensities (Tables 2–4). The composition of the investigated compound corresponds to the chemical formula $Tb_2(Cu_{0.47}Al_{0.53})_{17}$. The reliability factor for final atomic parameters is 0.036 (Table 2). These results show that the investigated single crystal belongs to an already known compound with Th_2Zn_{17}-type structure.

Differential thermal analysis and X-ray diffraction analysis of samples annealed at different temperatures have shown that two compounds with the approximate composition $Tb_{0.08}Cu_{0.52}Al_{0.40}$ are formed only by solid state reaction at 1100 K. The attempts to find *hkl* values for the most clear 16 reflections in the $\sin\theta/\lambda$ range 0.13–0.30, using the automatic indexizing program INDP (part of the CSD software [2]), gave the

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Table 1
Crystal data of the structure refinement for $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ and $Tb(Cu_{0.58}Al_{0.42})_{11}$

	$Tb_2(Cu_{0.47}Al_{0.53})_{17}$	$Tb(Cu_{0.58}Al_{0.42})_{11}$
Space group	$R\bar{3}/m$	*Fddd*
Lattice parameter (Å)	$a = 8.767(3)$	$a = 14.2792(6)$
	$c = 12.824(3)$	$b = 14.8916(6)$
		$c = 6.5644(2)$
Cell volume (Å^3)	853.6(8)	1395.9(2)
Number of atoms in cell	57.0	96.0
Diffractometer	DARTCH	Powder (DRON 3M)
Radiation	Mo Kα	Cu Kα
Mode of refinement	*F(hkl)*	Full profile
2θ limits	3–70	15–120
Number of variables	26	14
Number of measured reflections	1067	262
Number of unique reflections	407	250
R	$R_I = 0.036$	$R_I = 0.072$
	$R_W = 0.036$	$R_P = 0.128$

Table 2
Positional and thermal parameters for $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ and $Tb(Cu_{0.58}Al_{0.42})_{11}$

Atom[a]	Position	*x/a*	*y/b*	*z/c*	B_i (Å^3)
$Tb_2(Cu_{0.47}Al_{0.53})_{17}$					
Tb	6(c)	0	0	0.31064(7)	0.63(1)
T_1	6(c)	0	0	0.10007(3)	0.72(7)
T_2	9(d)	1/2	0	1/2	0.57(9)
T_3	18(h)	0.4987(1)	2*x*	0.1537(1)	0.60(4)
T_4	18(f)	0.7072(2)	0	0	0.61(4)
$Tb(Cu_{0.58}Al_{0.42})_{11}$					
Tb	8(b)	1/8	1/8	5/8	0.65(6)
Al	8(a)	1/8	1/8	1/8	0.7(3)
Cu1	16(c)	0	0	0	0.70(8)
Cu2	32(h)	0.2876(2)	0.0867(2)	0.9335(5)	0.86(8)
T[b]	32(h)	0.3297(4)	0.0373(5)	0.5769(9)	0.74(15)

[a] $T_1 = 1.20(6)$ Cu + 4.80(6)Al; T2 = 8.10(9) Cu + 0.90(9)Al; $T_3 = 7.65(12)$ Cu + 10.35(12)Al; $T_4 = 6.95(14)$ Cu + 11.05 (14)Al.
[b] T = 3.2(3)Cu + 28.8(3)Al.

Table 3
Anisotropic parameters (Å^3) for $Tb_2(Cu_{0.47}Al_{0.53})_{17}$

Atom	*B*11	*B*22	*B*33	*B*12	*B*13	*B*23
Tb	0.62(2)	0.62(2)	0.67(3)	0.31(1)	0	0
T_1	0.76(9)	0.76(9)	0.65(13)	0.38(5)	0	0
T_2	0.53(4)	0.78(6)	0.48(5)	0.39(3)	0.05(2)	0.10(4)
T_3	0.44(1)	0.67(6)	0.77(5)	0.39(3)	−0.04(2)	−0.08(4)
T_4	0.84(5)	0.51(6)	0.37(5)	0.26(3)	−0.05(2)	−0.10(4)

best correlation between experimental and calculated values for a face centered orthorhombic cell with $a = 14.261$, $b = 14.825$, $c = 6.556$ Å. All other experimental 2θ values coincide with calculated angles for these lattice parameters in a satisfactory way. This confirms that the results obtained are correct. The terbium atom location was found by the heavy atom method and the aluminium and copper atoms by calculation of the electronic density. Refinement of atomic parameters was carried out by the Rietveld method, taking into consideration a texture factor along the [001] direction. The final reliability factor of this structure refinement is 0.073 (Table 2). The structure of this compound is characterized by a statistical occupation of the crystallographic positions by copper and aluminium atoms and its composition corresponds to the chemical formula $Tb_8Cu_{51.2(3)}Al_{38.8(3)}$ (or $Tb(Cu_{0.58}Al_{0.42})_{11}$. A powder pattern of the compound is shown in Fig. 1.

Interatomic distances in the structure of

Table 4
Interatomic distances (Å) in $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ and $Tb(Cu_{0.58}Al_{0.42})_{11}$

$Tb_2(Cu_{0.47}Al_{0.53})_{17}$	
Tb	$3T_3$ – 3.345(2); $3T_2$ – 3.374(1); $3T_3$ – 3.282(2); $3T_3$ – 3.135(2); $6T_4$ – 3.117(2); $1T_1$ – 3.077(4)
T_1	1Tb – 3.077(4); $6T_4$ – 2.873(3); $3T_3$ – 2.745(4); $3T_2$ – 2.669(1); $1T_1$ – 2.582(6)
T_2	2Tb – 3.374(2); $2T_1$ – 2.669(1); $4T_3$ – 2.546(2); $4T_4$ – 2.512(1)
T_3	1Tb – 3.345(2); 1Tb – 3.282(2); 1Tb – 3.135(2); $1T_1$ – 2.745(3); $2T_4$ – 2.681(2); $2T_4$ – 2.657(2); $2T_2$ – 2.546(2); $2T_3$ – 2.533(3)
T_4	2Tb – 3.117(2); $2T_1$ – 2.873(3); $2T_3$ – 2.681(2); $2T_3$ – 2.657(2); $2T_4$ – 2.567(2); $2T_2$ – 2.512(2)
$Tb(Cu_{0.58}Al_{0.42})_{11}$	
Tb	3Cu1 – 3.5652; 4Cu2 – 3.412(3); 2A1 – 3.2822; 4T – 3.217(6); 4T – 3.176(7); 4Cu2–3.133(3)
Al	2Tb – 3.2822; 4T – 2.831(7); 4Cu1 – 2.7063; 4Cu2 – 2.701(3)
Cu1	2Tb – 3.5652; 2Al – 2.7063; 2T – 2.545(6); 2Cu2 – 2.528(3); 2Cu2 – 2.504(3); 2T – 2.492(6)
Cu2	Tb – 3.412(3); Tb – 3.133(3); T – 2.828(7); Cu2 – 2.761(5); Al – 2.701(3); Cu2 – 2.611(4); T – 2.608(7); T – 2.570(7); Cu1 – 2.528(3); T – 2.526(7); Cu1 – 2.504(3); T – 2.494(7)
T	Tb – 3.217(6); Tb – 3.176(7); T – 2.950(8); Al – 2.831(7); Cu2 – 2.828(7); T – 2.687(9); Cu2 – 2.608(7); Cu2 – 2.570(7); Cu1 – 2.545(6); Cu2 – 2.526(7); Cu2 – 2.494(7); Cu1 – 2.492(6)

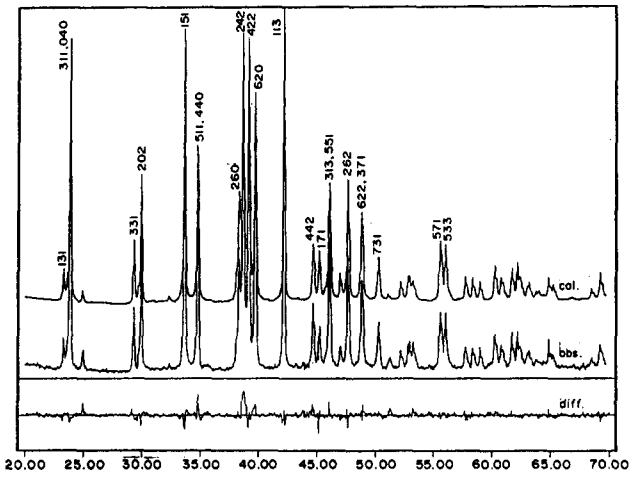

Fig. 1. Observed and calculated profiles of $Tb(Cu_{0.58}Al_{0.42})_{11}$ and the difference between them. Only the strongest indices are shown.

$Tb_2(Cu_{0.47}Al_{0.53})_{17}$ and $Tb(Cu_{0.58}Al_{0.42})_{11}$ are listed in Table 4; they are close to the sum of the atomic radii of the respective components.

4. Discussion

The structure of Th_2Zn_{17} may be considered as a derivative of the $CaCu_5$-type structure in which part of the larger R atoms are replaced by pairs of the smaller X atoms:

$$9RX5 = \frac{6R}{3R}45X = \frac{6R}{6X}45X = 6R51X = 3R_2X_{17}$$

The R atoms have a coordination number (CN) of 20 (as in the initial $CaCu_5$ structure) and the various X atoms have CN = 14, 13 or 12 [3]. The investigated compound $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ is the first one of Th_2Zn_{17}-type found in ternary systems containing RE, copper and aluminium, for which a complete crystal structure determination (including atomic parameters and their statistical distribution refinement) has been presented on the basis of single crystal data. As one can see from Table 2, the atomic coordinates differ slightly from the theoretical values $z_{Tb} = 1/3$, $z_{T_3} = 1/2$ and $z_{T_4} = 2/3$. As a result, the CNs of the atoms have changed too. The CN for terbium atoms is 19 (in the Th_2Zn_{17} structure, CN = 20). The distance from the twentieth atom (Tb) is 4.087 Å, which is considerably larger than from all the others. The other change is observed for the T_4 atoms, which have CN = 12 instead of CN = 13 for the theoretical atomic coordinates. The thirteenth atom (T_4) lies at 3.633 Å from the central T_4 atom, and it is unrealistic to include it in the nearest coordination sphere of the T_4 atoms. Thus, we can see, that a change of the atomic coordination takes place in real structures because of internal deformations. The crystal structure of Tb_2Zn_{17} ($6R6X^I9X^{II}18X^{III}18X^{IV}$) may be described theoretically by the following set of CNs: R-20, X^I-14, X^{II}-12, X^{III}-12 and X^{IV}-13, while in the $Tb_2(Cu_{0.47}Al_{0.53})_{17}$-structure the CNs of the atoms are to some extent different: R-19, X^I-14, X^{II}-12, X^{III}-12 and X^{IV}-12.

Taking the CN values of the X atoms in the $Tb_2(Cu_{0.47}Al_{0.53})_{17}$ structure into consideration, one can analyse the atomic distribution of copper and aluminium atoms in all statistically occupied positions. The position 6(c) with CN = 14 contains more aluminium atoms than those in the other occupied positions. This is in good agreement with atomic radii of aluminium and copper atoms ($r_{Al} = 1.43$ Å, $r_{Cu} = 1.27$ Å).

The crystal structure of $Tb(Cu_{0.58}Al_{0.42})_{11}$ (Fig. 2) is closely related to the tetragonal $BaCd_{11}$-structure (space group $I4_1/amd$). This is also indicated by the lattice dimensions of both structures: $a' = b' = 2a''$,

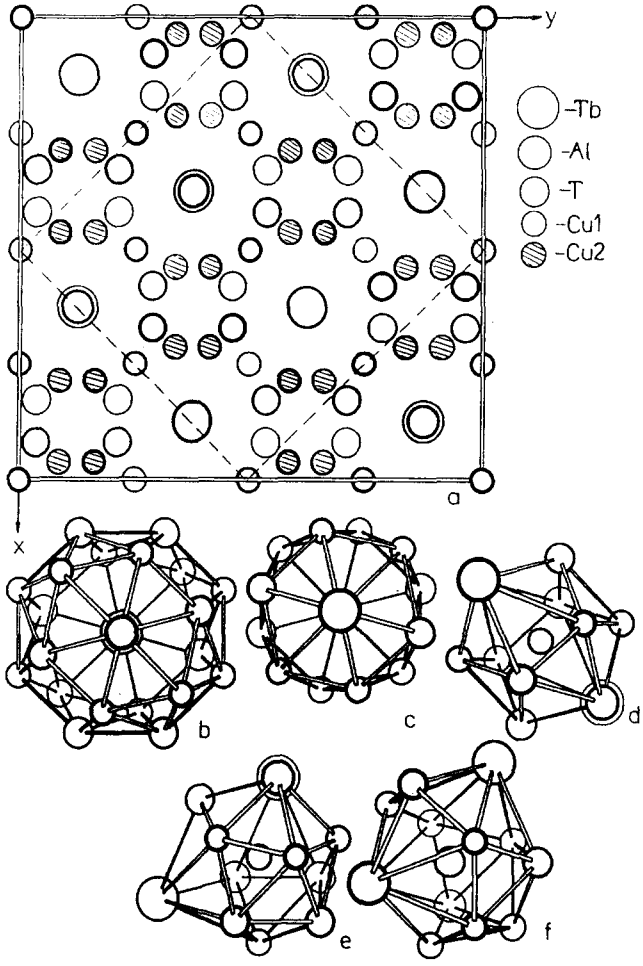

Fig. 2. (a) *XY* projection of the $Tb(Cu_{0.58}Al_{0.42})_{11}$ structure, and coordination polyhedra of atoms: (b) $[TbX_{19}]$; (c) $[AlTb_2X_{13}]$; (d) $[Cu1Tb_2X_{10}]$; (e) $[Cu2Tb_2X_{10}]$; (f) $[TTb_2X_{10}]$.

$c' = c''$, where a', b', c' and a'', c'' are the lattice parameters of the $Tb(Cu_{0.58}Al_{0.42})_{11}$ and $BaCd_{11}$ structures respectively. The coordination polyhedra in both structures are similar, Cu1, Cu_2 and X atoms having distorted icosahedral environments (see Fig. 2).

The structures investigated belong to a structure group with an icosahedral coordination of the smallest atoms [4]. Structure types with such coordination are characteristic of RE–Cu–Al systems at relatively low RE content (up to 0.25 mole fraction of RE). In earlier investigated RE–Cu–Al systems [1,3] the other known structure types which belong to this structure group, namely $NaZn_{13}$, $BaCd_{11}$, $ThMn_{12}$, Th_2Zn_{17}, $CaCu_5$, Th_6Mn_{23}, $PuNi_3$, etc., are realized.

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