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Structure of $TbAg_{0.46}In_{1.54}$ from single crystal data

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The $TbAg_{0.46}In_{1.54}$ compound was prepared by arc-melting of pure metal ingots under an argon atmosphere. The crystal structure of $TbAg_{0.46(16)}In_{1.54(16)}$ was refined from X-ray single crystal diffraction data: space group $P6_3/mmc$, Pearson code $hP6$, Z = 2, a = 4.798(2), c = 7.341(2) Å, $R1$ = 1.79%, $wR2$ = 4.40%. The title compound crystallizes in the $CaIn_2$ structure type with the 4*f* site occupied by a statistical mixture of Ag and In atoms.

Terbium / Silver / Indium / Crystal structure / X-ray single crystal diffraction

Introduction

The compounds of rare-earth metals with transition metals and indium are an important group of intermetallics with very interesting physical properties [1,2]. Whereas the interaction of the components in systems that contain rare earth (*RE*) metals, 3*d*-metals, particularly Co, Ni, Cu, and indium are well studied, the systems containing Ag, Au and platinum group metals have not been systematically investigated and only the formation of several compounds has been established.

Most indides are characterized by complex stoichiometry and structures. However, sometimes binary structure types are realized in ternary systems, for example $CaIn_2$, AlB_2, Laves phases, *etc*. Compounds with the $CaIn_2$ structure type are widespread in the ternary systems *RE*–Zn–In [3] and *RE*–Cd–In [4]. The crystal structure of the *RE*(Ag,In)$_2$ compounds (*RE* = Y-Lu) has been well described [5]. Neutron diffraction and magnetic susceptibility measurements performed on Tb_2AgIn_3, which belongs to the $CaIn_2$-type structure, revealed antiferromagnetic ordering below T_N = 42(1) K [6]. The crystal structure and magnetic properties of the ternary copper indides RE_2CuIn_3 (*RE* = Ce, Pr, Nd, Sm, Gd) with the $CaIn_2$ structure type were described by Tyvanchuk *et al.* [7]. The crystal and magnetic structures of the Tb_2CuIn_3 intermetallic compound ($CaIn_2$-type) have been studied by neutron diffraction in the temperature range 3.8 to 293 K [8].

Preliminary investigations of the *RE*–Ag–In systems showed that compounds with $CaIn_2$ structure type exist in the systems with *RE* = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu [9]. The formation of phases with $CaIn_2$ structure type in the ternary systems {Tb,Dy}–Ag–In was reported in [10]. The structures were determined by X-ray powder diffraction and the homogeneity ranges were established. The phases are characterized by variable compositions, $TbAg_{0.95\text{-}0.30}In_{1.05\text{-}1.70}$ and $DyAg_{0.83\text{-}0.53}In_{1.17\text{-}1.47}$, assuming Ag/In atom substitution. Single crystals suitable for structure refinement were later synthesized in the Tb–Ag–In system at a temperature of 870 K.

In this paper we present results on the synthesis and crystal structure investigation of $TbAg_{0.46}In_{1.54}$ by X-ray single crystal diffraction and EDX analysis.

Experimental

A sample of composition $Tb_{33.3}Ag_{16.7}In_{50}$ was prepared by arc melting under an argon atmosphere (purified with a titanium getter) from metal ingots of high purity: Tb 99.8 wt.%, Ag 99.98 wt.%, and In 99.999 wt.%. The ingot was annealed at 600°C under vacuum in a quartz ampoule for one month and subsequently quenched in cold water. The weight loss during the preparation of the sample was less than 1% of the total mass, which was 1 g.

On the surface of the specimen irregularly shaped single crystals had formed. Single crystals were isolated by mechanical fragmentation and investigated by Laue photographs and the rotation method (Mo $K\alpha$ radiation) in order to check their quality for the intensity data collection, symmetry and lattice parameters. Intensity data were collected on a Bruker SMART X-ray diffractometer, equipped with an APEX-CCD area detector and using graphite-monochromatic Mo $K\alpha$ (λ = 0.71073 Å) radiation at room temperature. An absorption correction was applied to the data using the SADABS program [11]. The structure was solved with direct methods and refined on F^2 with the full-matrix least-squares method, using SHELXS-97 and SHELXL-97 [12] programs, respectively. After the data collection the single crystal was analyzed by EDX with a JEOL SEM 5900LV scanning electron microscope equipped with an Oxford Instruments INCA energy dispersive X-ray microanalysis system. No impurity elements heavier than sodium were observed. The obtained composition within the standard deviations agrees well with the nominal composition of the synthesized alloy (Table 1).

Results

The results of the single crystal structure studies showed that $Tb(Ag,In)_2$ belongs to the hexagonal symmetry. As predicted, the compound crystallizes in the $CaIn_2$ structure type. The final refinement was performed in the anisotropic approximation and led to the composition $TbAg_{0.46(16)}In_{1.54(16)}$, which agrees well with the nominal composition of the alloy and the results of the EDX analysis of a single crystal. The Tb atoms occupy the positions of the calcium atoms (2*b*) of the $CaIn_2$ type, whereas the Ag and In atoms statistically occupy the positions of the indium atoms (4*f*). Experimental details and results of the crystal structure determination are listed in Table 2. The refined atomic coordinates and displacement parameters of $TbAg_{0.46(16)}In_{1.54(16)}$ are listed in Table 3.

Table 1 Results of the EDX analysis of the single crystal $TbAg_{0.46}In_{1.54}$.

Element	Content, at.%	Accuracy of analysis, at.%
Tb	29.84	±3.20
Ag	19.15	±2.00
In	51.01	±3.20

Table 2 Experimental details and crystallographic data for $TbAg_{0.46}In_{1.54}$.

Refined composition		$TbAg_{0.46(16)}In_{1.54(16)}$
Formula weight M_r		385.09
Structure type		$CaIn_2$
Pearson symbol		*hP*6
Space group, *Z*		$P6_3/mmc$, 2
Unit-cell parameters:	*a*, Å	4.798(2)
	c, Å	7.341(2)
Cell volume *V*, $Å^3$		146.157(4)
Density D_x, g/cm^3		8.800
Diffractometer		Bruker APEX, CCD detector
Radiation; wavelength λ, Å		Mo $K\alpha$; 0.710730
Absorption coefficient μ, mm^{-1}		19.014
Crystal shape		plate
Crystal size, µm^3		0.020×0.074×0.116
Color		metallic grey
Number of reflections:	measured	12922
	independent	113
	with $I > 2\sigma(I)$	104
Range of *hkl*		±6, ±6, ±10
Range of θ, °		4.91–31.12
Number of refined parameters		7
Residual electron density:	$\Delta\rho_{max}$, e/Å^3	2.612
	$\Delta\rho_{min}$, e/Å^3	-0.338
Reliability factors [$I > 2\sigma(I)$]:	*R*1	0.0179
	*wR*2	0.0440

A projection of the structure of $TbAg_{0.46}In_{1.54}$ onto the *xy* plane is shown in Fig. 1 and interatomic distances within the first coordination sphere are listed in Table 4. The coordination polyhedra of the Tb atoms are base-capped hexagonal prisms (CN = 14) and those of the Ag/In atoms are trigonal prisms with capped lateral faces (CN = 9). Considering the structure of the $TbAg_{0.46}In_{1.54}$ compound as corrugated nets formed by the smaller atoms (Fig. 2), it should be noted that the shortest distance is between the Ag/In atoms (2.824(3) Å). The voids between the nets are occupied by terbium atoms with the shortest distance to the nearest neighbors within the sum of their atomic radii [13].

Ternary compounds with the $CaIn_2$ structure type exist in *RE*–*T*–In systems with larger size *d*-metals (*T* = Zn, Pd, Ag, Cd) [1] for the majority of the rare-earth metals. A survey of structure types of $RE(T,In)_2$ compounds in *RE*–*T*–In systems is presented in Table 5. In the *RE*–{Zn,Cd}–In systems (*RE* = La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb) only the existence of compounds with equiatomic composition *RE*Zn(Cd)In has been reported. In the *RE*–Ag–In systems compounds with the $CaIn_2$ structure type are formed at the stoichiometric composition RE_2AgIn_3 for a series of rare-earth metals (Y, La-Nd, Sm, Gd-Tm, Lu).

Table 3 Atomic coordinates and displacement parameters ($Å^2$) for $TbAg_{0.46(16)}In_{1.54(16)}$ (*hP*6, $P6_3/mmc$, $a = 4.798(2)$, $c = 7.341(2)$ Å).

Atom	Wyckoff position	Occupancy, %	x	y	z	$U_{11} = U_{22}$	U_{33}	U_{12}	$U_{eq.}$
Tb	2*b*	100	0	0	¼	0.0129(3)	0.0110(3)	0.00646(14)	0.0123(2)
Ag/In	4*f*	23(8)/77(8)	⅓	⅔	0.46212(10)	0.0107(3)	0.0206(4)	0.00537(14)	0.0140(2)

$U_{13} = U_{23} = 0$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $U_{ij} = -2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

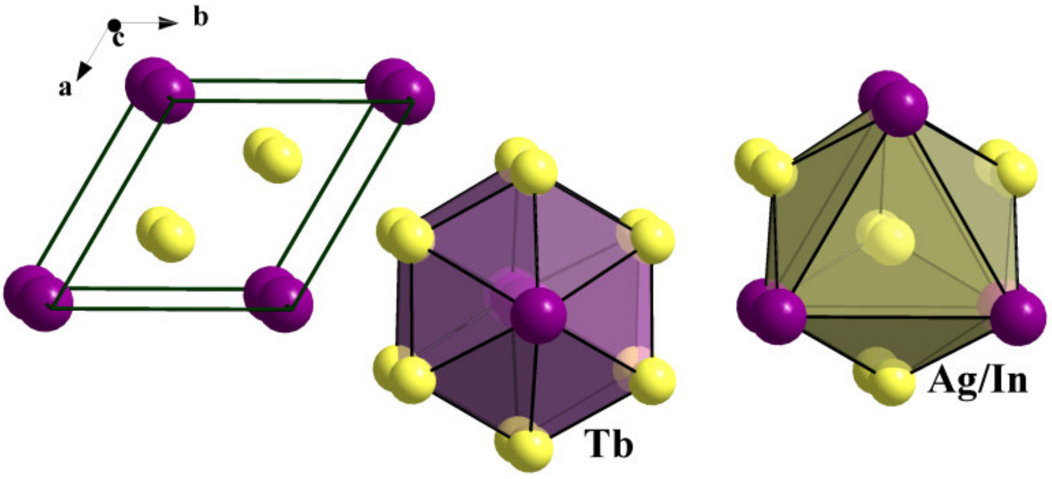

Fig. 1 Unit-cell content and coordination polyhedra of the atoms in the structure of $TbAg_{0.46}In_{1.54}$.

Table 4 Interatomic distances and coordination numbers (CN) of the atoms in the structure of $TbAg_{0.46}In_{1.54}$ (*hP*6, $P6_3/mmc$, $a = 4.798(2)$, $c = 7.341(2)$ Å).

Atoms		δ, Å	CN
Tb	6 Ag/In	3.176(4)	14
	6 Ag/In	3.483(4)	
	2 Tb	3.672(4)	
Ag/In	3 Ag/In	2.824(3)	9
	3 Tb	3.176(4)	
	3 Tb	3.483(4)	

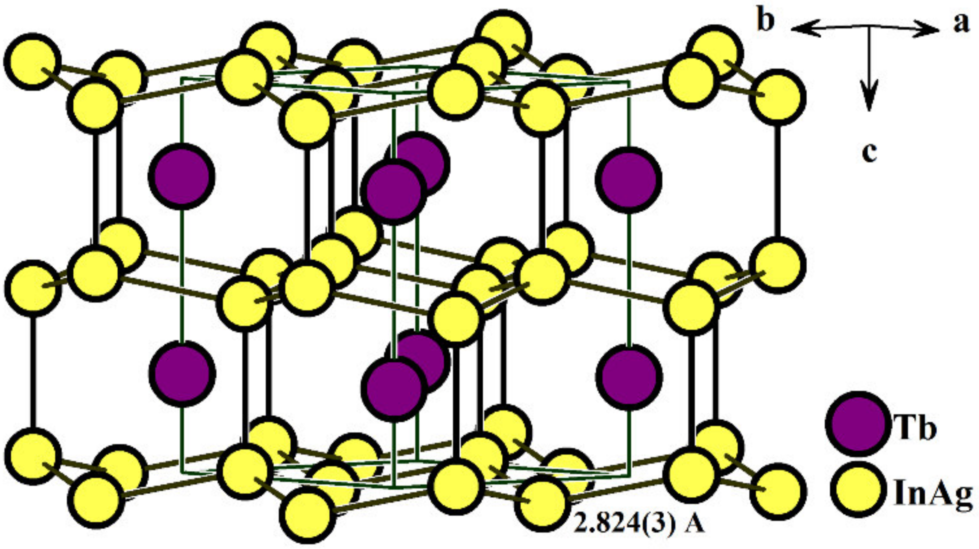

Fig. 2 View of the $TbAg_{0.46}In_{1.54}$ structure approximately along the [110] direction. Arrangement of the hexagonal Ag/In nets is indicated.

Table 5 Survey of structure types of $RE(T,In)_2$ compounds in selected *RE*–*T*–In systems: Δ $CaIn_2$-type, ▲ AlB_2-type, – no compound with these structure types was found, … no information available.

RE *d*-metal	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ref.
Mn	…	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	…	▲	[14]
Fe	…	…	…	…	…	…	…	…	…	–	–	…	–	…	…	…	[15,16]
Co	–	–	–	–	–	–	–	…	–	–	–	–	–	–	–	–	[17]
Ni	–	–	▲	▲	▲	▲	▲	▲	–	–	–	–	–	–	–	–	[18,19]
Cu	–			Δ	Δ	Δ	Δ		Δ						–	–	[7]
		▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲			[8,20]
Zn	…	…	Δ	Δ	Δ	Δ	Δ	–	Δ	…	Δ	Δ	Δ	…	Δ	…	[3,21]
Ru	…	…	…	–	…	…	…	…	…	…	…	…	…	…	…	…	
Rh	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	
Pd	–	Δ	Δ	Δ	Δ	Δ	–	–	–	–	Δ	–	–	–	–	–	[22,23]
Ag	–	Δ	Δ	Δ	Δ	Δ	Δ	–	Δ	Δ	Δ	Δ	Δ	Δ	–	Δ	[9,10]
Cd	…	…	Δ	Δ	Δ	Δ	Δ	…	Δ	…	Δ	Δ	Δ	…	Δ	…	[4]

It is interesting to note that there is an electronic reason: in all the cases the valence electron concentration (VEC) of the compounds is eight per formula unit (or close to this value, taking into account the homogeneity region of some compounds), which is similar to that of $CaIn_2$. Among the lanthanides, only Eu and Yb [24] form $CaIn_2$-type binary $REIn_2$ compounds, having most probably the *RE* cation in oxidation state +2, whereas with other rare-earth metals this structure type can be realized only in ternary systems containing transition metals with filled outer *d*-orbitals (0, 1, 2 valence electrons).

Another large group of ternary indides with the $RE(T,In)_2$ composition in the *RE*–*T*–In systems (*T* = Mn, Ni, Cu) adopt the AlB_2-type structure, which is the aristotype of $CaIn_2$. The systems *RE*–Cu–In are transitional: in some of them both structure types are realized, *i.e.* the AlB_2-type at 870 K and the $CaIn_2$-type (*RE* = Ce-Sm, Gd) at 900 K. A transformation $AlB_2 \leftrightarrow CaIn_2$ should not be difficult from an energetic point of view. The AlB_2-type structure contains flat honeycomb nets of *T*/In atoms instead of puckered nets as in the $CaIn_2$-type (Fig. 2).

Conclusions

The crystal structure of the ternary compound $TbAg_{0.46}In_{1.54}$ has been studied by X-ray single crystal diffraction. It is a representative of the well known $CaIn_2$ structure type, space group $P6_3/mmc$. The rare-earth atoms occupy the positions of the calcium atoms and a mixture of silver and indium atoms occupies the indium positions. This fact can be explained by the closeness of the atomic radii of the silver and indium atoms, which form a statistical mixture in the 4*f* position, as well as by electronic factors.

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