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Crystal structural refinement of the new compound $TmAlB_{14}$

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Abstract

Single crystals of the new phase $TmAlB_{14}$ were grown using the high-temperature solution method. The crystal structure of $TmAlB_{14}$ was refined from X-ray powder diffraction data using the Rietveld method. The structure is of $MgAlB_{14}$-type with the space group Imma and unit cell parameters $a=5.8212(3)$ Å, $b=10.3837(2)$ Å and $c=8.1762(3)$ Å. The final, conventional R-value and profile R-value are 0.031 and 0.064, respectively. The structure is characterized by a partial occupancy of both metal positions and a splitting of the thulium atomic position.

1. Introduction

Binary and ternary borides, crystallizing in the $MgAlB_{14}$-type structure, were recently reviewed and discussed by Korsukova [1]. In addition to the earlier studied phases of this type [2–7], new rare earth ternary borides $REAlB_{14}$ were prepared for RE = Y, Tb, Dy, Ho, Er, Yb, and Lu [8–11]. In the present paper we report the preparation and structure refinement of $TmAlB_{14}$ using the Rietveld method.

2. Experimental details

Single crystals of $TmAlB_{14}$ were prepared by high temperature solution growth from aluminium melts [10] under an inert gas flow. The purities of the starting materials were 99.7–99.9 wt.%, better than 99 wt.%, and 99.99 wt.% for thulium, amorphous boron and aluminium, respectively. The atomic ratio of thulium to boron is 1:14, and the concentration of boron in aluminium melt is 1.9 wt.%. A vertical, resistively heated furnace was used. The mixture was heated at 1400 °C for 4 h, then cooled to room temperature at a cooling rate of 100 $°C\ h^{-1}$. The matrix was dissolved with dilute hydrochloric acid (1:3). Crystals were obtained ranging up to more than 1 mm in size.

Phase analysis was performed by X-ray powder diffraction using a Guinier–Hägg camera with $CuK\alpha_1$ radiation ($\lambda=1.540\,598$ Å) and semiconductor-grade silicon ($a=5.431\,065$ Å) as internal calibration standard [12]. The intensity profile was measured with a computer-controlled microdensitometer [13]. The orthorhombic unit-cell parameters were determined from least-squares refinement [14].

The X-ray powder profile refinement was performed with a VAX computer using a local modification of the Rietveld program LHPM1 by Wiles and Young [15] and Hill and Howard [16]. Since the sample contained calibration Si and some agate from the mortar, used for the pulverization of the $TmAlB_{14}$ crystals, the whole refinement procedure was carried out on three phases ($TmAlB_{14}$, Si and α-SiO_2) simultaneously. The pseudo-Voigt function was used to describe the peak profile shape. The initial value for the positional parameters and the occupancy factors of both metal positions were taken from the single crystal study of $MgAlB_{14}$ [2]. Initially the scale factor, positional and temperature parameters were refined. No satisfactory convergence was, however, obtained until the occupancy factors for thulium and aluminium atoms were allowed to be refined. Even lower agreement indices were obtained, when the thulium position was split and the x value of the 8*i* position allowed to be refined.

Crystals were analyzed using an ARL electron microprobe (20 kV accelerated voltage). Five crystals were analyzed with a total of 17 testing points. There were some differences between the crystals. The standard deviations given below were estimated using the formula

$$\sigma=\sqrt{\sum_{i}^{N}\frac{(x_i-\bar{x})^2}{N-1}}$$

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TABLE 1. Final structure data for $Tm_{0.52}Al_{0.58}B_{14}$. Estimated standard deviations in parentheses. Space group Imma (No. 74)

Atom	Position	x	y	z	B_{iso} (Å^2)	Occupancy
Tm	8*i*	0.0271(7)	1/4	0.6407(2)	0.42(6)	0.262(3)[a]
Al	4*c*	1/4	1/4	1/4	1.2(3)	0.58(1)
B_1	8*h*	0	0.1738(8)	0.9569(13)	1.1(3)	1
B_2	8*h*	0	0.1510(8)	0.3718(15)	1.4(3)	1
B_3	8*h*	0	0.0857(10)	0.1697(15)	2.3(3)	1
B_4	16*j*	0.1625(11)	0.0642(8)	0.8383(11)	2.5(3)	1
B_5	16*j*	0.2350(13)	0.0810(8)	0.4501(10)	1.5(3)	1

[a] The occupancy of the hole is 0.524(6).

The microprobe instrument does not permit a quantitative analysis of the light element boron and accordingly the concentration of boron is given by difference only. The composition as obtained from microprobe analysis is $Tm_{0.57(2)}Al_{0.62(3)}B_{14}$ with standard deviations given in parentheses.

3. Results and discussion

The unit cell dimensions of crystalline $TmAlB_{14}$ are $a=5.8212(3)$ Å, $b=10.3837(2)$ Å and $c=8.1762(3)$ Å, respectively. The structure refinement was based on the recording of 3550 intensity values in the 2Θ-range 9.0°–90.1°. A total of 29 parameters were refined. The final Bragg R-value, unweighted profile R-value and weighted profile R-value were 0.031, 0.064, 0.086, respectively. The final positional, thermal and occupancy parameters are given in Table 1. A list of the observed and calculated Bragg angles and intensities for the low angle reflections ($Q<0.313$, with Q defined as $4\sin^2\Theta/\lambda^2$) is given in Table 2. Interatomic distances are listed in Table 3.

The atomic arrangement of the $MgAlB_{14}$-type structure has been described in detail in several recent publications [1–3, 11] and in the present context we only mention the most conspicuous features. The structure is built up of slightly deformed boron icosahedra (B(1), B(3)–B(5)), which are interconnected via external B–B contacts or via non-icosahedral boron atoms (B(2)). The metal atoms are accommodated in interstitial holes: aluminium at an average distance of 2.26 Å from 12 boron neighbours and thulium at an average distance of 2.72 Å from 18 boron neighbours. Both metal atoms display the shortest interatomic distance (and therefore the shortest metal–boron bond) to the non-icosahedral B(2) atom (2.04 Å for Al–B(2) and 2.44 Å for Tm–B(2), respectively). This supports the conclusion by Higashi [6] that metal atoms bond more strongly to non-icosahedral than to icosahedral boron atoms.

TABLE 2. X-ray diffraction data of $Tm_{0.52}Al_{0.58}B_{14}$ for the low angle reflections ($0.024<Q<0.313$)

h k l	Θ_{calc}	Θ_{obs}	$(I/I_1)_{calc}$	$(I/I_1)_{obs}$
0 1 1	6.887	6.894	862	700
0 2 0	8.532	8.536	521	550
1 0 1	9.348	9.353	234	214
0 0 2	10.861	–	11	0
1 2 1	12.709	12.705	769	756
0 2 2	13.876	13.886	53	86
0 3 1	13.985[a]	–	284	–
1 1 2	13.999[a]	13.994	716	1000
2 0 0	15.346	15.342	178	157
2 1 1	16.891	16.885	505	554
0 1 3	16.990	16.971	125	197
0 4 0	17.261	17.259	103	84
2 2 0	17.662	17.658	498	481
1 0 3	18.184	18.134	210	230
1 3 2	18.676	18.671	707	644
2 0 2	18.985	–	9	0
1 4 1	19.772	19.766	223	207
1 2 3	20.215	20.209	740	727
0 4 2	20.579	20.574	58	57
2 2 2	20.925	–	17	0
2 3 1	21.001	20.996	575	629
0 3 3	21.084	21.079	199	188
0 0 4	22.138	22.138	102	110
0 5 1	22.500	22.500	129	144
2 1 3	23.218	23.216	62	73
2 4 0	23.428	23.425	81	65
0 2 4	23.891	23.893	78	101
1 1 4	23.968	23.964	93	103
3 0 1	24.079	24.075	44	60
1 4 3	25.507	25.505	207	159

[a] These two diffraction lines overlap in the observed reflections.

The rigid three-dimensional boron network of the $MgAlB_{14}$-type phases is relatively independent of metal atoms accommodated in the structure. However, there are two characteristics that distinguish the phases from each other. The first is the partial occupancies of the metal positions and the second is the split 8*i* position of the RE atom. There is a good agreement between the occupancy of the aluminium position as obtained from the structure refinement, 0.58(1) (Table 1), and that obtained from microprobe analysis, 0.62(3). For $TmAlB_{14}$ this occupancy is significantly lower than the values obtained for $Er_{0.62}Al_{0.73}B_{14}$ and for $Y_{0.62}Al_{0.71}B_{14}$, respectively [11]. The Al atoms of $TmAlB_{14}$ form a

TABLE 3. Interatomic distances in $Tm_{0.52}Al_{0.58}B_{14}$. Distances listed are all M–M<3.70 Å, M–B<3.60 Å, B–B<2.10 Å

Atoms	Distances	Atoms	Distances
Tm–Tm	0.316(8)	B(1)–B(1)	1.582(17)
–2B(2)	2.443(12)	–2B(4)	1.769(11)
–2B(4)	2.637(8)	–B(3)	1.966(16)
–2B(5)	2.641(8)	–2B(5)	1.971(9)
–2B(4)	2.649(7)		
–2B(1)	2.708(11)		
–2B(4)	2.748(8)		
–2B(5)	2.799(8)	B(2)–2B(5)	1.676(9)
–2B(4)	2.873(7)	–B(3)	1.786(18)
–2B(1)	2.973(5)	–B(2)	2.058(17)
–Tm	3.151(7)		
–2B(1)	3.268(5)		
–2Tm	3.416(2)		
–Al	3.448(2)	B(3)–2B(4)	1.823(11)
–Al	3.579(2)	–2B(5)	1.828(9)
–Tm	3.688(7)		
Al–4B(2)	2.042(8)		
–4B(3)	2.337(8)		
–4B(5)	2.410(9)	B(4)–B(4)	1.767(15)
–2Al	2.911(1)	–B(5)	1.838(12)
–4B(1)	2.913(9)	–B(5)	1.861(11)
–4B(4)	3.380(7)	–B(4)	1.892(8)

straight chain with Al–Al distances of 2.91 Å (Table 3) at full occupancy.

Depending on the splitting 8*i* position, the thulium atoms form a slightly irregular zig-zag chain with Tm–Tm distances 0.32 Å, 3.15 Å, 3.416 Å and 3.69 Å. The first-mentioned distance originates from the $+x$ and $-x$ coordinates of the 8*i* position, and does not, of course, occur in the structure due to the low crystallographic occupancy of 0.26 (involving a *hole* occupancy of 0.52). The splitting means that a static positional disorder of the thulium atoms occurs with the thulium atoms randomly distributed in the different unit cells among $+x$ and $-x$ positional coordinates (+0.023 72, 0.25, 0.642 19). It is also noted that the distance 3.416 Å is close to the average of 3.15 Å and 3.69 Å. A similar splitting of the 4*e* position has been observed for $Mg_{0.78}Al_{0.75}B_{14}$ [3], $Y_{0.62}Al_{0.71}B_{14}$ and $Er_{0.62}Al_{0.73}B_{14}$ [11].

Though the reasons for this splitting are unknown as yet, it seems likely that the splitting is favoured by the partial occupancies of the metal positions in general and of the 4*e* position in particular. Thus, in the isostructural compounds $LiAlB_{14}$ [6], $NaB_{0.8}B_{14}$ [17] and Mg_2B_{14} [5], where the 4*e* position is almost completely occupied by the lithium, sodium and magnesium atoms, respectively. No splitting was found. On the other hand, in the structure of $HoAlB_{14}$ no splitting of the 4*e* position was reported either, in spite of the partial occupancies of the metal sites by holmium and aluminium atoms [8]. Structural studies on other representatives of this structure family might throw some light on this problem.

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