Crystal structure and powder X-ray diffraction data for new $Tb_3CuAl_3Ge_2$ compound

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The crystal structure of new $Tb_3CuAl_3Ge_2$ quaternary compound was studied by the Rietveld method from powder X-ray diffraction (XRD) data. The $Tb_3CuAl_3Ge_2$ compound crystallized in the hexagonal $Y_3NiAl_3Ge_2$-type structure with space group P-62m (no. 189) and lattice parameters $a = 7.0041$ (2) Å, $c = 4.1775(1)$ Å, $V = 177.48$ Å^3. There is only one formula in each unit cell, $Z = 1$, and the density of $Tb_3CuAl_3Ge_2$ is $\rho_x = 7.1696$ g cm^{-3}. The reliability factors characterizing the Rietveld refinement results are $R_p = 6.43\%$, $R_{wp} = 8.65\%$, $R_B = 4.81\%$, and $R_F = 4.09\%$, respectively. The powder XRD data of $Tb_3CuAl_3Ge_2$ were presented and the reliability of indexation is $F_{30} = 120.9(0.0073, 34)$.
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Key words: crystal structure, $Tb_3CuAl_3Ge_2$, powder X-ray diffraction

I. INTRODUCTION

It is well known that there are many novel functional materials containing rare-earth elements. Abundant inermetallic compounds with excellent properties were found during the past few decades. Searching for novel compounds, especially rare-earth compounds, with excellent properties is very important for developing new potential function materials. A new quaternary compound of $Tb_3CuAl_3Ge_2$ was found during our investigation on the phase relationship of the Al–Cu–Ge–Tb system. The crystal structure and powder X-ray diffraction (XRD) data of new compounds are very important for the phase identification in the materials research and applications. In this paper, the crystal structure and powder XRD data of the $Tb_3CuAl_3Ge_2$ compound are reported.

II. EXPERIMENTAL

The sample of $Tb_3CuAl_3Ge_2$ was prepared by arc melting of Al (99.8%), Cu (99.99%), Tb (99.5%), and Ge (99.99%) in a water-cooled copper hearth with a non-consumable tungsten electrode under argon atmosphere. The sample of $Tb_3CuAl_3Ge_2$ was turned over and remelted three times to ensure sample homogeneity. The weight loss of the sample was less than 1 wt%. The obtained ingot of $Tb_3CuAl_3Ge_2$ was annealed in an evacuated quartz tube at 800 °C for 480 h, and then cooled down slowly at a rate of 10 °C h^{-1} to room temperature. The specimen of $Tb_3CuAl_3Ge_2$ for XRD measurements was ground in an agate mortar and pestle to a particle size of less than 10 μm. Powder sample of $Tb_3CuAl_3Ge_2$ was loaded to an Al-holder and gently pressed. Two sets of the powder XRD patterns, with or without Si (99.9999%) added as an internal standard, were collected at room temperature on a Rigaku D/Max 2500 V diffractometer (with Cu$K\alpha$ radiation and a graphite monochromator). The scan ranged from 10° to 110°2θ with a step size of 0.02° and a counting time of 2 s per step. The Jade 6 software package (Materials Data, Inc., 2002) was used to analyze the data. The XRD pattern of the $Tb_3CuAl_3Ge_2$ specimen with high-purity Si internal standard was used to obtain the observed peak positions $2\theta_{obs}$ for indexing, whereas the XRD pattern without Si internal standard was used to pick out the observed intensity of each peak, I_{obs}. The $2\theta_{obs}$ values of the peaks were determined by the Savitzky–Golay second derivative method after background subtracting, $K\alpha_2$ stripping and Si internal standard calibration using PDF 027-1402 (ICDD, 2011) with $\lambda = 1.540\,56$ Å.

III. RESULTS AND DISCUSSION

A. Crystal structure

The powder XRD pattern of $Tb_3CuAl_3Ge_2$, shown in Figure 1, was successfully indexed using the Jade 6 program

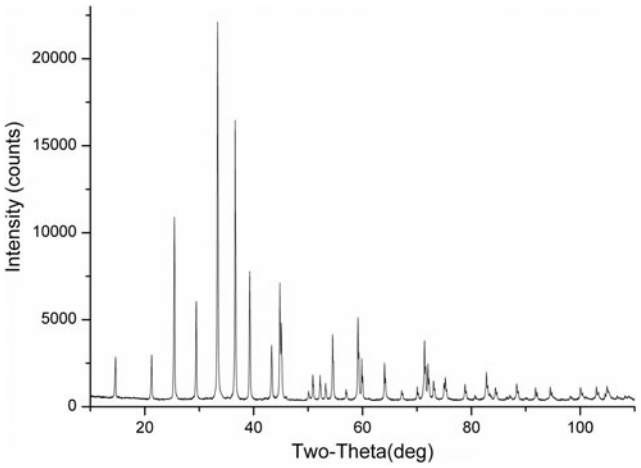


Figure 1. Powder XRD pattern of $Al_3CuGe_2Tb_3$.

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TABLE I. Rietveld refinement data of $Tb_3CuAl_3Ge_2$.

Formula	$Tb_3CuAl_3Ge_2$
Space group	*P*-62*m* (no. 189)
Radiation wavelength Cu$K\alpha_1$ (Å)	1.540 56
Unit-cell parameters (Å)	$a = 7.0040(1)$, $c = 4.1771(1)$
Unit-cell volume (Å^3)	177.48
Calculated density (g cm^{-3})	7.1696
Formula units per unit cell	$Z = 1$
Scan range	$10° \le 2\theta \le 110°$
Residual values	
R_p	0.0643
R_{wp}	0.0865
R_B	0.0481
R_F	0.0409

$$R_P = \frac{\sum |Y_i(\text{obs}) - Y_i(\text{calc})|}{\sum Y_i(\text{obs})}, R_{WP} = \left\{ \frac{\sum \omega_i [Y_i(\text{obs}) - Y_i(\text{calc})]^2}{\sum \omega_i [Y_i(\text{obs})]^2} \right\}^{1/2}$$

$$R_B = \frac{\sum |I_H(\text{obs}) - I_H(\text{calc})|}{\sum I_H(\text{obs})}, R_F = \frac{\sum \left| [I_H(\text{obs})]^{1/2} - [I_H(\text{calc})]^{1/2} \right|}{\sum (I_H(\text{obs}))^{1/2}}$$

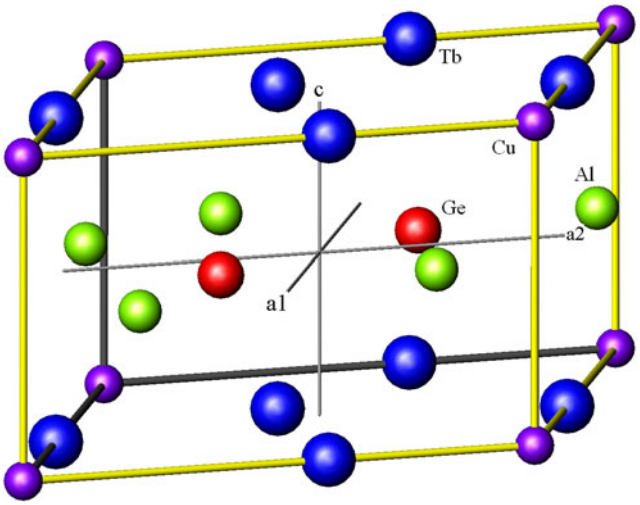


Figure 3. (Color online) The crystal structure of $Tb_3CuAl_3Ge_2$.

TABLE III. Selected interatomic distances (nm) for $Tb_3CuAl_3Ge_2$.

Bond distance
Tb–Ge 0.2985(2)
Tb–Cu 0.2823(1)
Tb–Al 0.3327(3)
Tb–Tb 0.3694(2)
Al–Tb 0.3221(2)
Al–Al 0.2755(1)

in a hexagonal unit cell with the lattice parameters $a = 7.0041$ (2) Å and $c = 4.1775(1)$ Å. No conditions for reflections of the $Tb_3CuAl_3Ge_2$ pattern pointed to five possible space groups: *P*6/*mmm* (no. 191), *P*-62*m* (no.189), *P*-6*m*2 (no. 187), *P*6*mmm* (no. 183), and *P*622 (no. 177) (Hahn, 1992). By comparing the crystallographic characteristics of the $Tb_3CuAl_3Ge_2$ compound with those presented in the structural type database it was found that $Tb_3CuAl_3Ge_2$ and $Y_3NiAl_3Ge_2$ (Zhao and Parthe, 1990) have the same structure type. So the space group *P*-62*m* (no. 189) and the atomic position parameters of $Y_3NiAl_3Ge_2$ were taken as the starting values to refine the structural parameters of $Tb_3CuAl_3Ge_2$. The Tb sites correspond to the Y sites and the Cu to the Ni sites in $Y_3NiAl_3Ge_2$. The structural refinement of $Tb_3CuAl_3Ge_2$ was then performed using the DBWS9807a program (Young

TABLE II. Atomic coordinates and thermal parameters for $Tb_3CuAl_3Ge_2$.

Atom	Wyckoff Position	*x*	*y*	*z*	Occupancy	B_{iso} (Å^2)
Tb	3f	0.5969(1)	0	0	1	0.040(3)
Cu	1a	0	0	0	1	0.073(9)
Ge	2d	1/3	2/3	0.5	1	0.024(6)
Al	3 g	0.2279(7)	0	0.5	1	0.025(10)

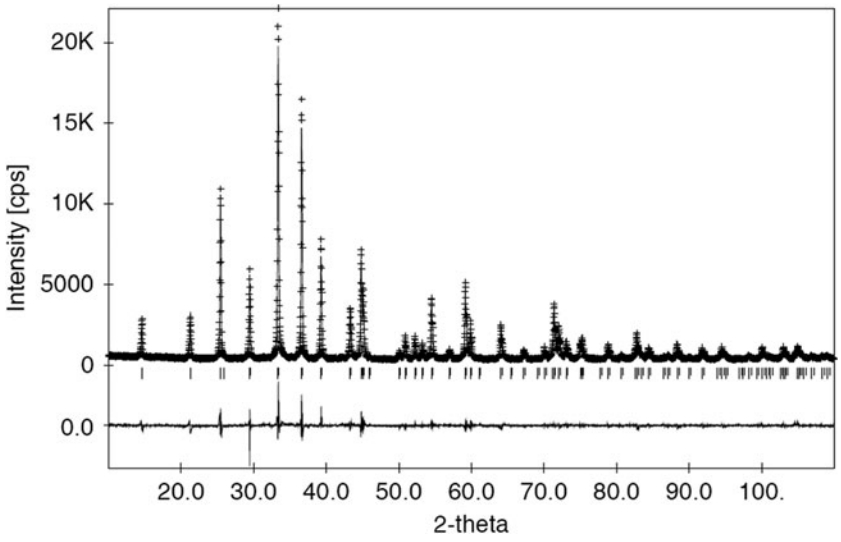


Figure 2. The observed, calculated, and residuals powder XRD patterns of $Tb_3CuAl_3Ge_2$.

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et al., 2000). The pseudo-Voigt function was used for the simulation of the peak shapes. The indexing results for $Tb_3CuAl_3Ge_2$ were taken as the starting lattice parameters. A total of 23 parameters of the $Tb_3CuAl_3Ge_2$ compound were refined, including peak shape parameters, scale factor, cell parameters, atomic coordinates, isotropic displacement parameters, full-width at half-maximum (FWHM) parameters, and preferred orientation parameter. The background of the XRD data of $Tb_3CuAl_3Ge_2$ was refined with a polynomial. The final Rietveld refinement led to agreement factors of: $R_p = 6.43\%$, $R_{wp} = 8.65\%$, and $R_B = 4.81\%$, and $R_F = 4.09\%$, respectively. The details of the Rietveld Refinement of $Tb_3CuAl_3Ge_2$ are summarized in Table I, and the atomic positions and thermal displacement factors for $Tb_3CuAl_3Ge_2$ are presented in Table II. The observed, calculated, and residual powder XRD patterns of $Tb_3CuAl_3Ge_2$ are shown in

TABLE IV. Powder diffraction data for $Tb_3CuAl_3Ge_2$ ($CuK\alpha_1$,with $\lambda = 1.540\,56$ Å).

Sl. no	$2\theta_{obs}$	h	k	l	$2\theta_{calc}$	$\Delta 2\theta$	I/I_o	d_{obs}	d_{calc}
1	14.595	1	0	0	14.591	0.004	9	6.0642	6.0658
2	21.243	0	0	1	21.251	−0.008	10	4.1790	4.1775
3	25.403	1	1	0	25.412	−0.009	44	3.5033	3.5021
4	25.871	1	0	1	25.875	−0.004	0.8	3.4410	3.4405
5	29.438	2	0	0	29.426	0.012	26	3.0317	3.0329
6	33.364	1	1	1	33.358	0.006	100	2.6833	2.6838
7	36.597	2	0	1	36.583	0.014	77	2.4534	2.4543
8	39.278	2	1	0	39.264	0.014	36	2.2919	2.2926
9	43.278	0	0	2	43.280	−0.002	15	2.0889	2.0888
10	44.800	3	0	0	44.787	0.013	34	2.0214	2.0219
11	45.081	2	1	1	45.070	0.011	21	2.0094	2.0099
12	45.925	1	0	2	45.912	0.013	0.7	1.9744	1.9750
13	50.093	3	0	1	50.079	0.014	2	1.8195	1.8200
14	50.863	1	1	2	50.857	0.006	7	1.7937	1.7939
15	52.201	2	2	0	52.195	0.006	7	1.7508	1.7510
16	53.213	2	0	2	53.201	0.012	5	1.7199	1.7203
17	54.497	3	1	0	54.499	−0.002	20	1.6824	1.6823
18	56.982	2	2	1	56.977	0.005	3	1.6148	1.6149
19	59.160	3	1	1	59.154	0.006	25	1.5604	1.5605
20	59.861	2	1	2	59.851	0.010	12	1.5438	1.5440
21	64.041	3	0	2	64.040	0.001	12	1.4527	1.4528
22	67.218	3	2	0	67.219	−0.001	3	1.3916	1.3916
23	70.058	2	2	2	70.063	−0.005	4	1.3420	1.3419
24	71.173	4	1	0	71.173	0	4	1.3237	1.3237
25	71.380	3	2	1	71.385	−0.005	17	1.3203	1.3203
26	72.019	3	1	2	72.017	0.002	10	1.3102	1.3102
27	73.059	1	1	3	73.066	−0.007	5	1.2941	1.2940
28	74.983	2	0	3	74.988	−0.005	5	1.2656	1.2655
29	75.239	4	1	1	75.244	−0.005	5	1.2619	1.2618
30	78.821	5	0	0	78.831	−0.010	5	1.2133	1.2132
31	80.676	2	1	3	80.661	0.015	1	1.1900	1.1902
32	82.586	3	3	0	82.577	0.009	3	1.1673	1.1674
33	82.764	5	0	1	82.779	−0.015	8	1.1652	1.1650
34	83.378	3	2	2	83.383	−0.005	2	1.1582	1.1581
35	84.398	3	0	3	84.390	0.008	4	1.1467	1.1468
36	84.438	4	2	0	84.437	0.001	1	1.1463	1.1463
37	86.497	3	3	1	86.491	0.006	5	1.1242	1.1243
38	87.085	4	1	2	87.093	−0.008	0.8	1.1181	1.1181
39	88.321	4	2	1	88.341	−0.020	4	1.1057	1.1055
40	89.939	2	2	3	89.942	−0.003	0.5	1.0899	1.0899
41	91.781	3	1	3	91.790	−0.009	4	1.0728	1.0727
42	94.498	5	0	2	94.490	0.008	0.8	1.0490	1.0491
43	95.038	0	0	4	95.045	−0.007	0.5	1.0444	1.0444
44	98.209	3	3	2	98.209	0	0.5	1.0190	1.0190
45	100.078	4	2	2	100.081	−0.003	1	1.0050	1.0049
46	100.651	1	1	4	100.644	0.007	4	1.0008	1.0008
47	101.155	4	3	0	101.147	0.008	0.6	0.9971	0.9972
48	102.521	2	0	4	102.530	−0.009	0.6	0.9875	0.9875
49	102.980	3	2	3	102.989	−0.009	4	0.9844	0.9843
50	103.239	6	0	1	103.242	−0.003	2	0.9826	0.9826
51	104.937	5	2	0	104.941	−0.004	3	0.9713	0.9713
52	105.158	4	3	1	105.149	0.009	2	0.9699	0.9700
53	106.800	4	1	3	106.814	−0.014	1	0.9595	0.9594
54	108.277	2	1	4	108.283	−0.006	1	0.9505	0.9504
55	109.018	5	2	1	109.016	0.002	0.9	0.9460	0.9461

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Figure 2 and the crystal structure of $Tb_3CuAl_3Ge_2$ is given in Figure 3. The selected atomic distances are listed in Table III.

B. X-ray powder diffraction data

The $Tb_3CuAl_3Ge_2$ compound is in a hexagonal unit cell with parameters $a = 7.0041(2)$ Å, $c = 4.1775(1)$ Å, and unit-cell volume $V = 177.48$ Å^3. The figure of merit for the indexing F_N (Smith and Snyder, 1979) is $F_{30} = 120.9$ (0.0073, 34). The powder XRD data for $Tb_3CuAl_3Ge_2$ are listed in Table IV.

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SUPPLEMENTARY MATERIALS AND METHODS

The supplementary material refered to in this paper can be found online at http://www.journals.cambridge.org/PDJ

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