Experimental synthesis and crystal structure refinement of a new ternary intermetallic compound Al_3GaCu_9

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A new ternary intermetallic compound Al_3GaCu_9 was synthesized experimentally. A high-quality powder diffraction pattern of the compound was collected by an X-ray diffractometer, and its crystal structure was determined using the Rietveld refinement method. Results show that the compound has a cubic cell with the Al_4Cu_9 structure type (space group $P\bar{4}3m$ and Pearson symbol $cP52$). The lattice parameter $a = 8.7132(3)$ Å, unit-cell volume $V = 661.52$ Å^3, calculated density $D_{calc} = 7.26$ g/cm^3, and $Z = 4$. The residual factors converge to $R_p = 2.96\%$, $R_{wp} = 4.06\%$, and $R_{exp} = 2.57\%$. The experimentally obtained reference intensity ratio value is 7.04.

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Key words: Al_3GaCu_9, intermetallic compound, powder X-ray diffraction, Rietveld refinement

I. INTRODUCTION

Al–Cu alloys are widely used in aerospace, transportation, and other fields due to their good comprehensive mechanical properties (Cheng et al., 2022). And since the properties of materials are closely related to their crystal structure, it is necessary to study the crystal structure of Al–Cu alloy compounds. Al_4Cu_9 is an intermetallic compound in the Al–Cu binary system, it crystallizes in a cubic crystal structure, and its space group and Pearson symbol are $P\bar{4}3m$ and $cP52$, respectively (Westman, 1965). In recent decades, few investigations have been conducted on intermetallic compound with the Al_4Cu_9 structure type. In addition, these studies have focused mainly on compounds of binary systems. For instance, binary compounds $Cu_{7.8}Ga_{5.2}$, $Cu_{8.45}Ga_{4.55}$, and $Cu_{8.06}Ga_{4.94}$ were reported in a study of structural changes during the solidification of copper–gallium alloys by Tikhomirova et al. (1969). The structure of Cu_9Ga_4 compound was refined from single-crystal diffractometer data by Stokhuyzen et al. (1974). A high-temperature phase Cu_9In_4 was synthesized by Che and Ellner (1992), who reported the powder crystal data. The crystal structure data of these binary compounds are included in the ICSD database (2015). As far as we know, only few studies and reports on Al–Cu–Ga ternary intermetallic compounds. According to the ICSD database, simultaneously review the Powder Diffraction File (PDF) of the current International Center for Diffraction Data (ICDD), no ternary intermetallic compounds of Al–Cu–Ga system have been reported in these databases, but an intermetallic compound $Al_2Cu_9In_2$ was discovered in a similar system Al–Cu–In, and has Al_4Cu_9 (Westman, 1965) crystal structure.

In this paper, a new ternary intermetallic compound Al_3GaCu_9 in the Al–Cu–Ga system was synthesized experimentally, and the results of crystal structure refinement, powder diffraction data, and experimental value of the reference intensity ratio (RIR) of the intermetallic compound Al_3GaCu_9 are reported.

II. EXPERIMENTAL

A. Alloy sample preparation of Al_3GaCu_9

The alloy ingot of Al_3GaCu_9 intermetallic compound was prepared by arc melting with the total mass was 1.5 g. The initial materials such as Al, Cu, and Ga elements in the alloy ingot were small pieces and the purity was more than 3 N. To obtain a uniform composition, the alloy ingot was remelted many times, and the melting losses were less than 0.5%. After melting, the alloy ingot was annealed in a high-temperature furnace at 823 K for 720 h, and cooled to room temperature in the furnace.

B. Powder diffraction patterns collection

Alloy ingot of Al_3GaCu_9 was ground in an agate mortar and pestle to particle sizes of less than 30 μm. The powder X-ray diffraction (PXRD) patterns of the Al_3GaCu_9 intermetallic compound were collected at ambient temperature by a powder X-ray diffractometer (Smart Lab 9 kW, Rigaku Corporation). The X-ray goniometer optics had a goniometer radius of 300 mm and was equipped with an X-ray source of Cu K(alpha) radiation (lambda −1.54060 Å) and a graphite monochromator. The step scanning collection method was adopted, and the collection conditions were as follows: step

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TABLE I. Powder X-ray diffraction (PXRD) data of Al_3GaCu_9.

No.	$2\theta_{obs}$	h	k	l	$2\theta_{cal}$	$\Delta 2\theta^a$	$I\%$	d_{cal}	d_{obs}
1	14.383	1	1	0	14.364	−0.019	1	6.1614	6.153
2	22.801	2	1	0	22.802	0.000	2	3.8968	3.897
3	25.019	2	1	1	25.011	−0.007	6	3.5573	3.556
4	30.743	2	2	1	30.758	0.015	3	2.9045	2.906
5	35.662	2	2	2	35.664	0.003	4	2.5154	2.516
6	38.619	3	2	1	38.631	0.011	3	2.3288	2.329
7	44.060	4	1	1	44.055	−0.005	100	2.0538	2.054
8	46.575	4	2	0	46.574	−0.001	1	1.9484	1.948
9	48.982	3	3	2	48.993	0.011	4	1.8577	1.858
10	51.340	4	2	2	51.326	−0.015	4	1.7786	1.778
11	53.581	4	3	1	53.585	0.004	2	1.7089	1.709
12	57.900	5	2	1	57.919	0.019	1	1.5909	1.591
13	64.060	6	0	0	64.066	0.005	7	1.4522	1.452
14	66.061	6	1	1	66.041	−0.020	1	1.4135	1.413
15	73.677	6	3	1	73.677	0.001	1	1.2847	1.285
16	75.540	4	4	4	75.535	−0.005	2	1.2577	1.258
17	77.378	5	5	0	77.377	0.000	1	1.2323	1.232
18	81.021	6	3	3	81.025	0.003	9	1.1858	1.186
19	91.802	7	4	1	91.808	0.006	4	1.0726	1.073
20	97.190	8	2	2	97.199	0.010	1	1.0269	1.027
21	106.358	8	3	3	106.357	−0.002	1	0.9622	0.962
22	114.007	8	5	1	113.995	−0.013	1	0.9185	0.918
23	122.120	9	4	1	122.119	−0.001	1	0.8802	0.880
24	126.448	7	7	2	126.456	0.008	1	0.8628	0.863

[a]$\Delta 2\theta = 2\theta_{obs} - 2\theta_{cal}$.

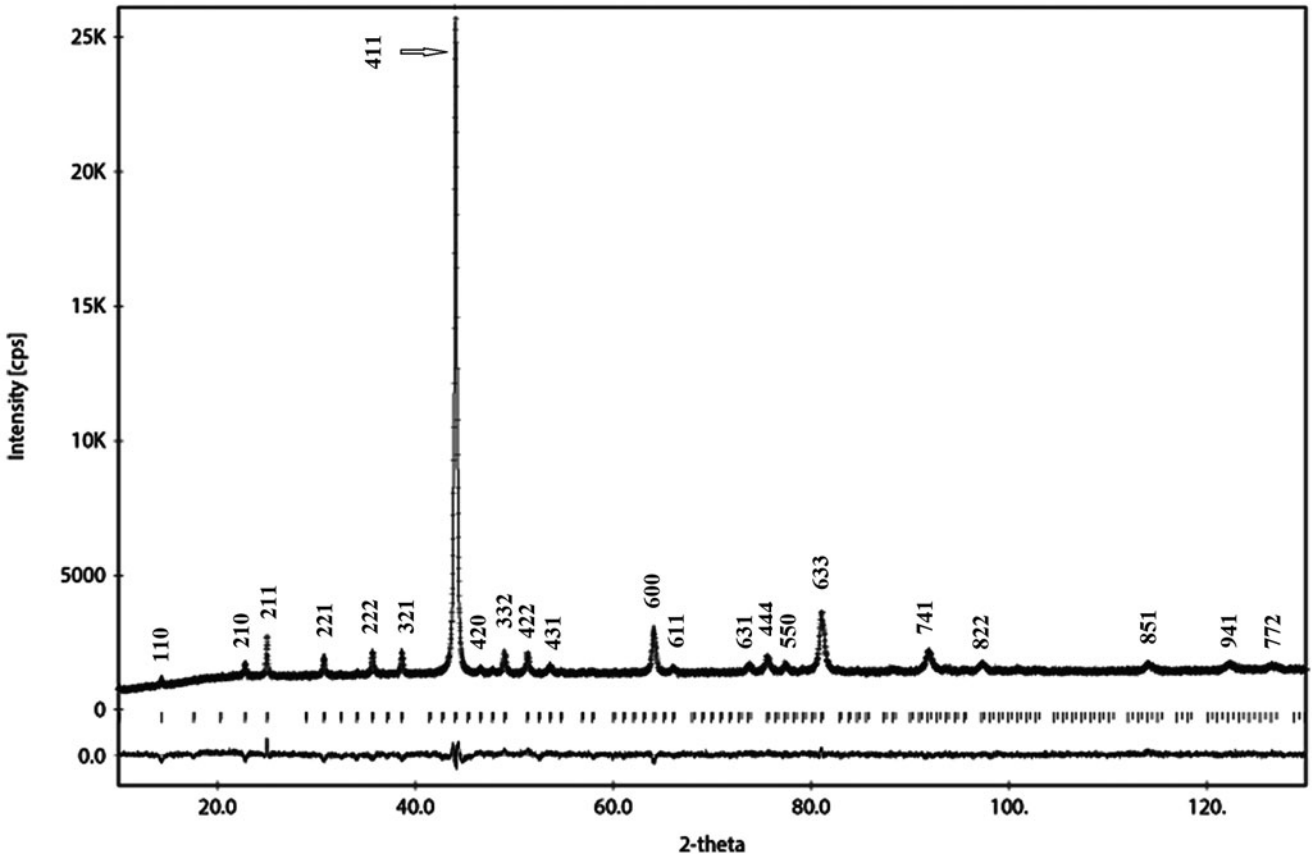

Figure 1. Peak shape fitting of the PXRD patterns of Al_3GaCu_9. "+" and "|" symbols represent the observed patterns and the possible positions of Bragg reflections, respectively. The solid line represents the calculated patterns, and the bottom curve represents the residual between the observed and calculated patterns.

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TABLE II. Rietveld refinement results of Al_3GaCu_9.

Formula	Al_3GaCu_9
Space group	$P\bar{4}3m$ (No. 215)
Radiation wavelength Cu $K\alpha_1$ (Å)	1.5405981
Unit cell parameter (Å)	$a = 8.7132(3)$ Å
Unit-cell volume (Å^3)	661.52
Calculated density (g/cm^3)	7.26
Formula units per unit cell	$Z = 4$
Scan range	$10° \le 2\theta \le 130°$
Residual values	
R_p	2.96%
R_{wp}	4.06%
R_{exp}	2.57%
S	1.57

size 0.02°, a count time 2 s per step, two-theta scan range 10° to 130°, operating voltage 40 kV, and current 150 mA. To reduce the displacement systematic error, high-purity silicon was added as the internal standard during the testing. Finally, 50 wt.% Al_2O_3 was added to the Al_3GaCu_9 compound; the PXRD pattern was collected and used to obtain the experimental value of *RIR* (Walter and Schreiner, 1995).

III. RESULTS AND DISCUSSION

After collecting the PXRD patterns of the Al_3GaCu_9 intermetallic compound, the program JADE 6.5 (Materials Data Inc., 2002) was used for indexing. The results show that the compound crystallized in a cubic crystal structure. Comparing the crystallographic characteristics of Al_3GaCu_9 with the structural types in the database revealed that the Al_3GaCu_9 intermetallic compound has an Al_4Cu_9 structure type, where the space group and Pearson symbol are $P\bar{4}3m$ (No. 215) and $cP52$, respectively. The Al_4Cu_9 structure type has eight atomic positions of the elements, the occupancy of elements in all positions is 1, the number of atoms and formula units per unit cell are 52 and 4, respectively. Therefore, these parameters of Al_4Cu_9 structure and the indexed lattice parameter of Al_3GaCu_9 were used as the initial parameters for Rietveld refinement using the DBWS9807a program (Young et al., 2000).

To obtain the lattice parameter as accurately as possible and reduce the systematic error, a high-purity silicon internal standard for two-theta correction was used. After correction, the lattice parameter was found to $a = 8.7134(2)$ Å. The PXRD data for Al_3GaCu_9 are listed in Table I. During the refinement, the pseudo-Voigt function was used to simulate the peak shapes. The peak shape fitting of the PXRD patterns for Al_3GaCu_9 is shown in Figure 1. After the refinement of 32 parameters, including the lattice parameter, atomic positions, thermal parameters, and occupancy and mix parameters, the refinement results were shown via the DMPLOT program (Marciniak and Diduszko, 1997) and are summarized in Table II. As listed in Table II, lattice parameter $a = 8.7132$ (3) Å, unit-cell volume $V = 661.52$ Å^3, and calculated density $D_{calc} = 7.26$ g/cm^3. The residual factors converge to $R_p = 2.96\%$, $R_{wp} = 4.06\%$, $R_{exp} = 2.57\%$, and $S = 1.57$. These results combined with the results of peak shape fitting, clearly show that the refinement is reliable. Table III summarizes the final results of atomic positional parameters of Al_3GaCu_9. As presented in Table III, Ga atom replaces the 4e position of Al in Al_4Cu_9 structure and the occupancy is 1, whereas the other atoms remain unchanged. Table IV lists the bond lengths (<3.0 Å) and nearest neighbors of each atom for Al_3GaCu_9. The number of nearest neighbor atoms of Ga(4e), Al(12i), Cu1(4e), Cu2(4e), Cu3(4e), Cu4(6f), Cu5(6g), and Cu6(12i) are 10, 11, 12, 12, 13, 13, 13, and 11, respectively. The structure, *a*-axis projection, and the coordination environment of

TABLE IV. The bond lengths (<3.0 Å) and nearest neighbors of each atom for Al_3GaCu_9.

Atom	Neighbor atoms and numbers	Distance (Å)	Atom	Neighbor atoms and numbers	Distance (Å)
Ga	Cu1 × 3	2.612(1)	Cu4	Al × 2	2.414(7)
	Cu4 × 3	2.569(1)		Al × 2	2.681(1)
	Cu6 × 3	2.501(3)		Ga × 2	2.569(1)
	Cu3× 1	2.994(7)		Cu1 × 2	2.664(9)
Al	Cu1 × 1	2.622(1)		Cu4 × 1	2.426(2)
	Cu2 × 1	2.634(7)		Cu6 × 4	2.790(3)
	Cu3 × 1	2.533(3)	Cu5	Al × 4	2.817(6)
	Cu4 × 1	2.414(7)		Cu2 × 2	2.553(3)
	Cu4 × 1	2.681(1)		Cu3 × 2	2.686(4)
	Cu5 × 2	2.817(6)		Cu5 × 1	2.464(5)
	Cu6 × 2	2.517(4)		Cu6 × 2	2.485(3)
	Cu6 × 2	2.606(1)		Cu6 × 2	2.687(9)
Cu1	Al × 3	2.622(1)	Cu6	Al × 2	2.571(4)
	Ga × 3	2.612(1)		Al × 2	2.606(1)
	Cu4 × 3	2.664(9)		Ga × 1	2.501(3)
	Cu6 × 3	2.479(8)		Cu1 × 1	2.479(8)
Cu2	Al × 3	2.634(7)		Cu3 × 1	2.620(1)
	Cu2 × 3	2.795(2)		Cu4 × 2	2.790(3)
	Cu3 × 3	2.627(9)		Cu5 × 1	2.485(3)
	Cu5 × 3	2.553(3)		Cu5 × 1	2.687(9)
Cu3	Al × 3	2.533(3)			
	Cu2 × 3	2.627(9)			
	Cu5 × 3	2.686(4)			
	Cu6 × 3	2.620(1)			
	Ga × 1	2.994(7)			

TABLE III. Atomic positional parameters of Al_3GaCu_9.

Atom	Position	X	Y	Z	Occ.	B(Å^2)
Ga	4e	0.1264(6)	0.1264	0.1264	1	1.15(4)
Al	12i	0.8193(12)	0.8193	0.5321(15)	1	0.06(3)
Cu1	4e	0.8324(18)	0.8324	0.8324	1	1.19(3)
Cu2	4e	0.6134(6)	0.6134	0.6134	1	0.63(2)
Cu3	4e	0.3248(8)	0.3248	0.3248	1	0.42(1)
Cu4	6f	0.3608(11)	0	0	1	0.31(1)
Cu5	6g	0.8586(12)	0.5	0.5	1	0.07(1)
Cu6	12i	0.3161(5)	0.3161	0.3161	1	1.18(2)

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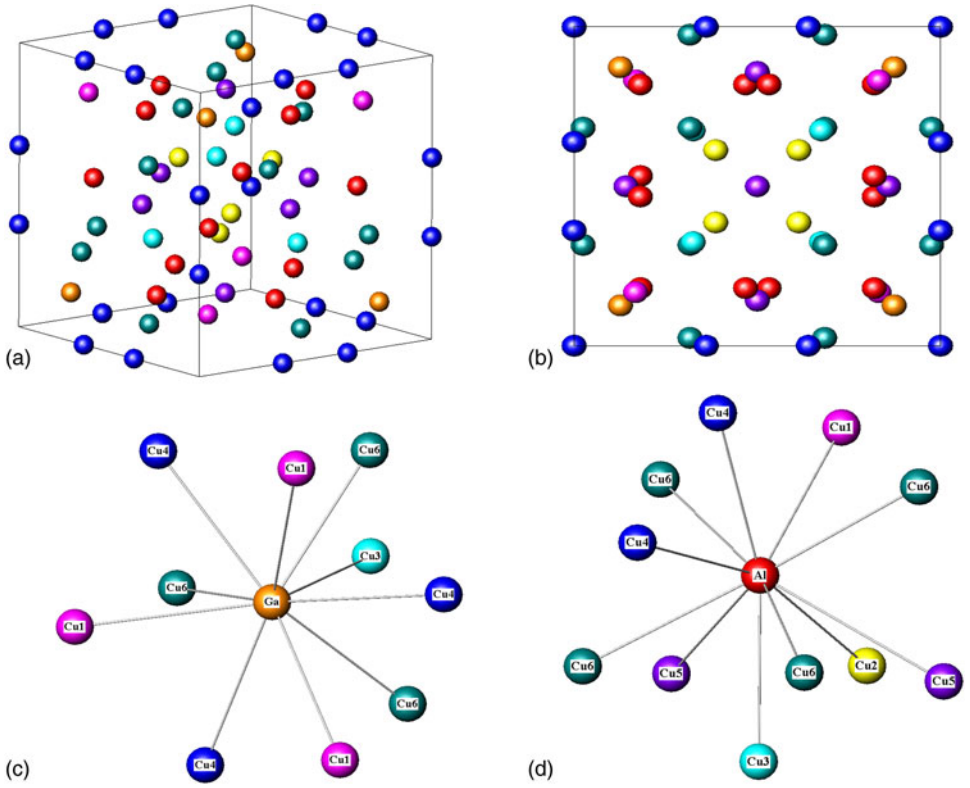

Figure 2. Structure, *a*-axis projection, and the coordination environment of some atoms for Al_3GaCu_9. (a) Al_3GaCu_9 structure, (b) Al_3GaCu_9 *a*-axis projection, (c) Ga atom, and (d) Al atom.

some atoms in Al_3GaCu_9 are shown in Figure 2(a)–(d), respectively. Finally, The *RIR* experimental value of 7.04 was obtained by analyzing the strongest line ratio of Al_3GaCu_9 and corundum when in a 50:50 mixture by weight (Hubbard et al., 1976; Snyder, 1992).

IV. CONCLUSION

The new ternary intermetallic compound Al_3GaCu_9 was successfully synthesized. The crystal structure was determined by the Rietveld refinement method based on the PXRD pattern, The results show that the compound has a cubic cell with the Al_4Cu_9 structure type (space group $P\bar{4}3m$ and Pearson symbol $cP52$). The lattice parameter $a = 8.7132$ (3) Å, unit-cell volume $V = 661.52$ Å^3, calculated density $D_{calc} = 7.26$ g/cm^3, and $Z = 4$. The residual factors converge to $R_p = 2.96\%$, $R_{wp} = 4.06\%$, and $R_{exp} = 2.57\%$. The experimentally obtained *RIR* value is 7.04.

V. DEPOSITED DATA

CIF and/or RAW data files were deposited with ICDD. You may request this data from ICDD at pdj@icdd.com.

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CONFLICT OF INTEREST

The author has no conflicts of interest to declare.

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