Journal of Alloys and Compounds 367 (2004) 132–136

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure of the "La_5Al_4" compound

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Abstract

The crystal structure of the "La_5Al_4" compound, probably stabilized by some metallic admixtures, has been studied by X-ray powder diffraction. It was shown that "La_5Al_4" crystallizes in a new structure type (hexagonal symmetry, $a = 9.1628(7)$ Å, $c = 11.2309(7)$ Å).

Keywords: Lanthanum–aluminum system; Crystal structure; Intermetallic compound; X-ray powder diffraction

1. Introduction

The La–Al phase diagram first presented in [1] exhibited the existence of four intermetallic compounds: La_3Al_2, LaAl, $LaAl_2$ and $LaAl_4$. Further investigations, carried out using high-purity metals by Buschow [2], resulted in a variant of the La–Al phase diagram with six intermetallic compounds: La_3Al, LaAl, $LaAl_2$, $LaAl_{2+x}$, $LaAl_3$ and La_3Al_{11} (the existence of the La_3Al_2 compound was not confirmed). According to Buschow [2], and Gschneidner and Calderwood [3], two of them form in the La-rich region (50 at.% La and more) and crystallize in the Ni_3Sn (La_3Al, $a = 7.228$ Å, $c = 5.517$ Å) and CeAl (LaAl, $a = 9.531$ Å, $b = 7.734$ Å, $c = 5.809$ Å) structure types, respectively.

The existence of the La_3Al_2 compound in the La-rich region of the La–Al phase diagram was confirmed by Chaban and Kuz'ma [4] during their study of an isothermal section of the La–Al–B system. A single crystal investigation of La_3Al_2 [4] displayed hexagonal symmetry with $a = 9.26$ Å, $c = 11.20$ Å.

2. Experimental details

Alloys of the binary La–Al system (35–50 at.% Al) were prepared by arc melting of lanthanum (97.67 wt.% purity) and electrolytic aluminum (99.99 wt.%) under purified argon atmosphere. The ingots were remelted several times in order to ensure perfect homogeneity. The chemical composition of the alloys was checked via the weight losses of the ingot. After arc melting the samples were wrapped in molybdenum foil, sealed in an evacuated quartz tube and annealed at 400 °C for 1200 h, with subsequent quenching in cold water.

The X-ray powder diffraction data were collected with a DRON-3 automatic diffractometer (Cu Kα radiation). The phase composition of the as-cast and annealed alloys and the crystal structure of the compounds were determined from the X-ray diffraction patterns. These patterns were obtained in a discrete mode using the following scanning parameters: step scan 0.05°, counting time per step (3–5 s). The peak positions and integral intensities of the observed reflections were determined using full-profile analyses. After removal of the Cu $K\alpha_2$ component, the diffraction profiles were fitted using Lorentz functions.

For the phase composition of the alloys and the crystal structure determinations we used our own software program packages with special databases for the X-ray diffraction data and for the structure types of intermetallic and inorganic compounds (more than 10,000 information units). The Ito method [5] was used to determine the symmetry and unit cells of the compounds. Unit cell refinements were carried out by a least-square method. By using the original software complex [6], tests of the structure models and refinements of the structural parameters were carried out.

3. Results and discussion

Since the previous investigations carried out using high-purity metals (La 99.9 wt.% and Al 99.99 wt.%) [2] led to the conclusion that the La_3Al_2 compound does not exist, first of all the raw lanthanum was tested with a "Philips"

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doi:10.1016/j.jallcom.2003.08.024

Table 1
Crystallographic data for the "La_5Al_4" compound

Atom	Site	*x*	*y*	*z*
La(1)	6I	0.3891(6)	0	0.336(1)
La(2)	3g	0.7399(9)	0	0.5
La(3)	3f	0.237(1)	0	0
La(4)	4h	0.333	0.667	0.1572(9)
Al(1)	6i	0.714(3)	0	0.206(2)
Al(2)	2e	0	0	0.732(4)
Me(1)	2d	0.333	0.667	0.5
Me(2)	3f	0.572(3)	0	0
Space group			$P\bar{6}2m$ (#189)	
Independent reflections			150	
Total *B* factor (Å^2)			1.56(3)	
Reliability factor			$R_W = 0.042$	
Me = 0.95 Al + 0.05 La				

X-ray spectrometer. The microprobe analysis showed the presence (wt.%) of Pr (0.30), Nd (0.10), Gd (1.12) and Al (0.16) as main impurities (the content of other impurities was less than 0.05 wt.%). The percentage of lanthanum was equal to 97.67 and the total percentage of lanthanum and other RE metals was about 99.3.

Five alloys of the La–Al system with compositions near La_3Al_2 were checked by X-ray powder and microprobe analysis. The diffraction patterns display the single-phase state at ∼44 at.% Al, rather than at 40 at.% Al. It should also be noted that the lattice constants of the binary phases, coexisting with the "La_3Al_2" compound (LaAl, for example) differ from those reported in [2,3]. Moreover, the lattice constants of LaAl annealed at 750 °C (a = 9.465(7) Å, b = 7.754(5) Å, c = 5.801(8) Å) and LaAl annealed at 400 °C (a = 9.388(9) Å, b = 7.745(9) Å, c = 5.773(6) Å), in turn, differ from each other. Certainly, the large difference in the lattice constants observed for the La-rich compounds cannot be caused only by the observed amount of impurities in the raw lanthanum. Due to these facts, the studied compound will hereinafter be denoted as "La_5Al_4".

The indexing of the diffraction pattern of the alloy with 44 at.% Al ("La_5Al_4") indicated a hexagonal symmetry. It should be noted that the symmetry and the refined values of the lattice constants of the "La_5Al_4" compound (a = 9.1628(7) Å, c = 11.2309(7) Å) are in a satisfactory agreement with those obtained earlier for the La_3Al_2 compound by single crystal investigation [4]. Because of the absence of systematic extinctions, the possible space groups are: *P*6/*mmm*, *P*622, $P\bar{6}2m$, $P\bar{6}m2$ and *P*6*mm*.

Comparing the X-ray powder diffraction pattern for the "La_5Al_4" compound, as well as its crystallographic characteristics, with those presented in the structure type database did not reveal any probable structural analogues. Therefore, the crystal structure determination was carried out by the trial-and-error method. The calculations of several possible structure models led to an atomic arrangement (space group $P\bar{6}m2$) that gave a good agreement between observed and calculated intensities (Table 1, Fig. 1). It should be noted that the statistical occupations of the 2d and 3f positions (Me = 0.95 Al + 0.05 La) were used in this model to provide the observed composition (44 at.% Al) of "La_5Al_4". The rest of the lanthanum and aluminum atoms were assumed to completely fill their positions in the structure.

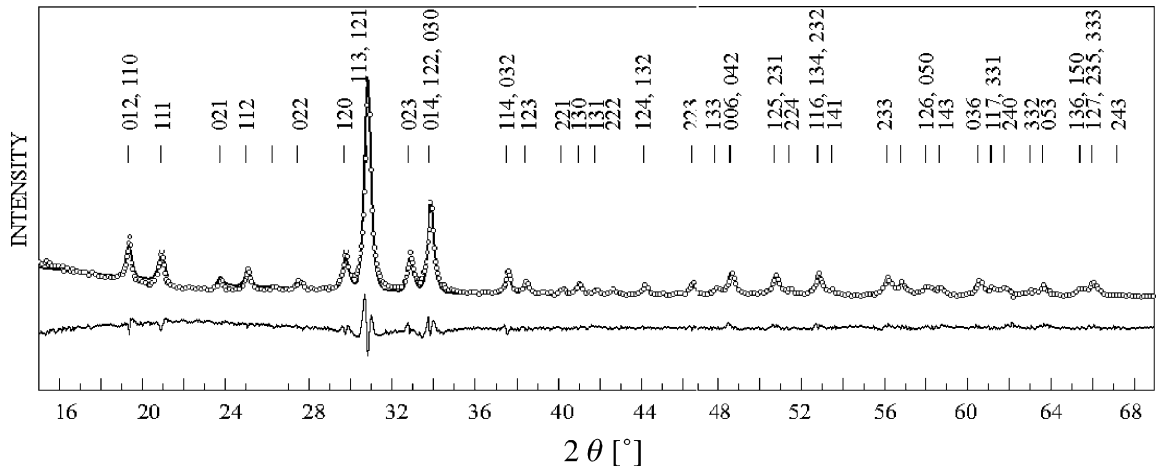

Fig. 1. Part of the observed X-ray diffraction powder pattern (points) and calculated pattern (solid line) for "La_5Al_4" (Cu Kα radiation).

Table 2
Part of the X-ray diffraction pattern for "La_5Al_4", Cu Kα radiation

d_{cal} (Å)	d_{obs} (Å)	I_{cal}	I_{obs}	hkl	d_{cal} (Å)	d_{obs} (Å)	I_{cal}	I_{obs}	hkl
4.584	4.583	85	157	0 1 2	2.161	2.159	0	16	0 1 5
4.581		71		1 1 0	2.160		7		0 3 3
4.242	4.244	119	118	1 1 1	2.160		25		1 3 1
3.968	3.961	4	4	0 2 0	2.121	2.121	21	22	2 2 2
3.744	3.743	4	33	0 0 3	2.050	2.050	13	41	1 2 4
3.741		30		0 2 1	2.049		30		1 3 2
3.550	3.550	74	73	1 1 2	2.017	–	2	1	1 1 5
3.386	3.377	12	12	0 1 3	1.984	1.984	9	10	0 4 0
3.240	3.236	37	34	0 2 2	1.955	1.954	3	61	0 2 5
2.999	2.999	151	150	1 2 0	1.954		57		2 2 3
2.899	2.898	660	1000	1 1 3	1.954		0		0 4 1
2.898		339		1 2 1	1.925	1.930	4	5	0 3 4
2.808	2.808	4	4	0 0 4	1.897	1.897	30	34	1 3 3
2.723	2.721	162	163	0 2 3	1.872	1.870	63	111	0 0 6
2.647	2.649	66	432	0 1 4	1.871		50		0 4 2
2.646		69		1 2 2	1.822	1.819	3	8	0 1 6
2.645		297		0 3 0	1.820		4		2 3 0
2.575	–	3	1	0 3 1	1.798	1.797	57	99	1 2 5
2.394	2.392	71	78	1 1 4	1.979		41		2 3 1
2.393		13		0 3 2	1.775	1.775	23	30	2 2 4
2.341	2.340	53	43	1 2 3	1.753	–	0	1	0 4 3
2.292	2.290	6	10	0 2 4	1.733	1.732	15	103	1 1 6
2.291		5		2 2 0	1.732		48		1 3 4
2.246	2.242	0	20	0 0 5	1.732		15		2 3 2
2.244		27		2 2 1	1.732		25		1 4 0
2.201	2.201	48	46	1 3 0					

The results of the refinement of the structure model for the "La_5Al_4" compound (reliability factor $R_W = 0.042$), as well as the diffraction data, are summarized in Tables 1 and 2, and are shown in Fig. 1.

The projections of these crystal structures on the *xy*-plane and the typical polyhedrons of the aluminum atoms are shown in Fig. 2. The main fragments of the "La_5Al_4" structure are: atomic grids ($z = 0$) similar to those in the

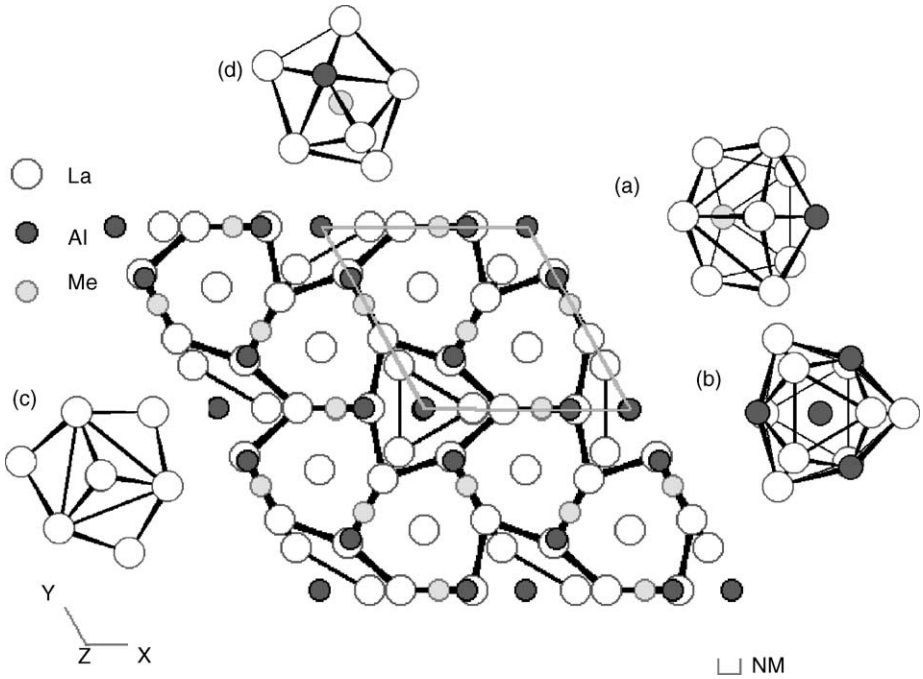

Fig. 2. Projection of the "La_5Al_4" structure on the *xy*-plane and coordination polyhedrons of the (a) Al(1), (b) Al(2), (c) Me(1) and (d) Me(2) atoms.

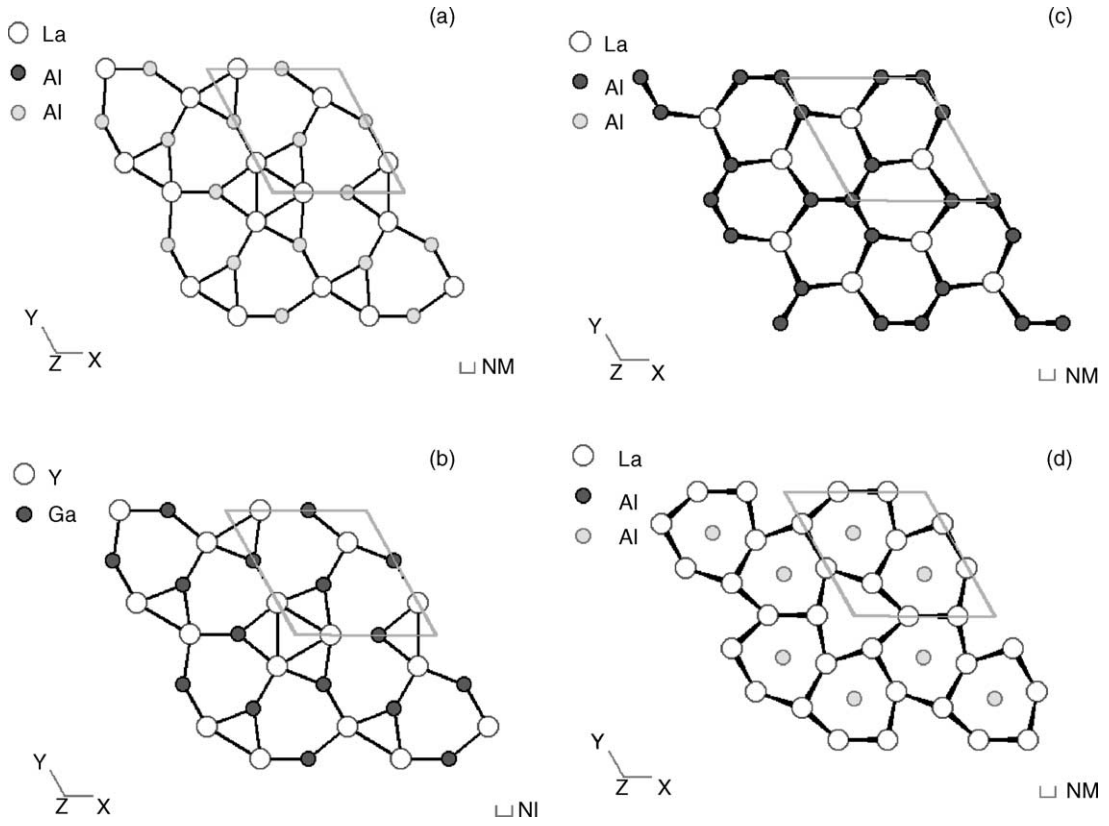

Fig. 3. Atomic grids in the "La_5Al_4" structure at (a) $z = 0$, (c) $z \approx 0.3$, (d) $z \approx 0.5$ and (b) in Y_5Ga_3 (Mn_5Si_3-type structure) at $z = 0.25$.

Mn_5Si_3-type structure (Fig. 3a and b), crimped graphite-like grids ($z \approx 0.3$, 0.7) (Fig. 3c) and other slabs ($z \approx 0.5$) (Fig. 3d).

A set of interatomic distances is given in Table 3. The shortest bond lengths ($d_{La-Al} = 3.1$ Å and $d_{Al-Al} = 2.7$ Å) are comparable with the sum of the La + Al and Al + Al atomic radii, respectively.

A comparison of the crystallographic characteristics of the "La_5Al_4" compound with those contained in the database of structure types of intermetallic and inorganic compounds

Table 3
Interatomic distances in the crystal structure of "La_5Al_4"

Atom–atom	d (Å)	Atom–atom	d (Å)	Atom–atom	d (Å)
La(1)–1Al(1)	3.317(2)	La(3)–2Al(2)	3.711(2)	Al(1)–1La(1)	3.317(2)
La(1)–1Me(1)	3.376(3)	La(3)–2La(3)	3.761(2)	Al(1)–1La(4)	3.334(2)
La(1)–1Me(1)	3.379(3)	La(3)–2La(4)	3.985(2)	Al(1)–1La(4)	3.339(2)
La(1)–1La(4)	3.471(2)	La(3)–2La(4)	3.990(2)	Al(1)–2La(3)	3.353(2)
La(1)–1La(4)	3.474(1)	La(3)–2La(1)	4.022(2)	Al(1)–2La(1)	3.516(2)
La(1)–2Al(1)	3.516(2)	La(4)–1Me(2)	3.244(2)	Al(2)–3Al(1)	2.711(2)
La(1)–2La(2)	3.644(3)	La(4)–1Me(2)	3.245(2)	Al(2)–3La(2)	3.531(2)
La(1)–1Al(2)	3.645(3)	La(4)–1Me(2)	3.251(2)	Al(2)–3La(1)	3.645(2)
La(1)–1La(1)	3.684(2)	La(4)–1Al(1)	3.334(2)	Al(2)–3La(3)	3.711(2)
La(1)–1La(2)	3.706(1)	La(4)–1Al(1)	3.339(2)	Me(1)–2La(1)	3.376(2)
La(1)–1La(3)	4.022(2)	La(4)–1Al(1)	3.342(2)	Me(1)–2La(1)	3.379(2)
La(1)–1Me(2)	4.129(3)	La(4)–1La(1)	3.471(2)	Me(1)–2La(1)	3.384(2)
La(2)–2Al(1)	3.310(3)	La(4)–1La(1)	3.474(2)	Me(1)–1La(2)	3.435(2)
La(2)–1Me(1)	3.435(2)	La(4)–1La(1)	3.479(2)	Me(1)–1La(2)	3.441(2)
La(2)–1Me(1)	3.441(1)	La(4)–1La(4)	3.526(2)	Me(1)–1La(2)	3.444(2)
La(2)–2Al(2)	3.531(2)	La(4)–1Me(1)	3.852(2)	Me(1)–2La(4)	3.852(2)
La(2)–4La(1)	3.644(3)	La(4)–1La(3)	3.985(2)	Me(2)–2Al(1)	2.654(2)
La(2)–2La(1)	3.706(2)	La(4)–1La(3)	3.990(2)	Me(2)–1La(3)	3.070(2)
La(2)–2La(2)	4.126(3)	La(4)–1La(3)	3.993(2)	Me(2)–2La(4)	3.244(2)
La(3)–1Me(2)	3.070(2)	Al(1)–1Me(2)	2.654(2)	Me(2)–2La(4)	3.245(2)
La(3)–4Al(1)	3.353(2)	Al(1)–1Al(2)	2.711(2)	Me(2)–2La(3)	3.403(2)
La(3)–2Me(2)	3.403(1)	Al(1)–1La(2)	3.310(2)	Me(2)–2La(1)	4.129(2)

(more than 10,000 U) permits us to conclude that it crystallizes in a new structure type.

4. Conclusions

The obtained data did not give conclusive evidence for the existence of an intermetallic compound containing ∼44 at.% Al in the La-rich part of the La–Al system. Even a small amount of metallic impurities (such as Pr, Nd, Gd) leads to the formation of the "La_5Al_4" compound (earlier La_3Al_2). This compound was also revealed in ternary systems. An extended solid solution based on the "La_5Al_4" compound was detected, for example, in the La–Al–Ga system.

A structure model for "La_5Al_4" in the $P\bar{6}m2$ space group was proposed and refined.

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