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Preparation and Crystal Structure of the Intermetallics $La_4Mo_7Al_{51}$ and $La_4W_7Al_{51}$

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The title compounds have been prepared by reaction of the elemental components in alumina crucibles. Their crystal structure was determined from single-crystal X-ray data of $La_4Mo_7Al_{51}$: $P\bar{3}m1$, $a = 1042.4(3)$ pm, $c = 1174.3(3)$ pm, $Z = 1$, $R = 0.023$ for 892 structure factors and 62 variables. The lattice constants of the isotypic compound $La_4W_7Al_{51}$ are $a = 1041.3(4)$ pm, $c = 1173.3(4)$ pm. The structure is closely related to that reported for $Ca_4Cr_7Al_{48}$. The atoms occupy 12 atomic positions, of which four show significant deviations from the full occupancy, resulting in the formula $La_{3.662(4)}Mo_7Al_{50.26(8)}$. All atoms have high coordination numbers. The two different lanthanum atoms are coordinated by 1 lanthanum and 15 aluminum atoms, the two molydenum sites by 12 and 11 aluminum atoms, respectively, in the form of bi- and monocapped pentagonal antiprisms. The eight different aluminum atoms have between 11 and 14 neighbors with between 2 and 4 lanthanum and/or molybdenum atoms. All coordination polyhedra of the aluminum atoms have at least some rectangular or nearly rectangular faces.

INTRODUCTION

A large number of ternary intermetallic compounds of the rare earth elements (*Ln*) with the early transition metals (*T*) and a high content of aluminum have been prepared in recent years. More than 70 compounds have been reported with the composition $Ln_6T_4Al_{43}$ (1–7) and almost 60 with the composition LnT_2Al_{20} (7–13). The compounds with the relatively low aluminum content $Ln_6T_4Al_{43}$ were predominantly found with the late (heavy) lanthanoids, including the series $Ln_6Mo_4Al_{43}$ and $Ln_6W_4Al_{43}$ (Ln = Nd, Sm, Gd–Lu) (2). In samples containing the early lanthanoids we found compounds with a very high aluminum content, again also with molybdenum and tungsten, e.g., the series $LnMo_2Al_{20}$ and LnW_2Al_{20} (Ln = La–Nd) (12). The presently reported compounds have a lower aluminum content and we have found them up to now only with lanthanum as the rare earth component.

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

The compounds $La_4Mo_7Al_{51}$ and $La_4W_7Al_{51}$ were synthesized by reaction of the elemental components (all with nominal purities ≥ 99.9%) in alumina crucibles, which were sealed in silica tubes under an argon atmosphere. Filings of lanthanum were prepared from ingots and stored under dry (sodium) paraffin oil. This was washed away by dry hexane prior to the reactions, and the hexane was evaporated under high vacuum. Aluminum was used in the form of turnings, and molybdenum and tungsten were already purchased in the form of powders. The starting compositions were in the atomic ratio La:Mo(W):Al = 6:4:48. The samples were heated to 850°C at a rate of 50°C/h, held at that temperature for 2 weeks, and subsequently cooled to room temperature at a rate of 6°C/h. The aluminum-rich matrix was dissolved in diluted hydrochloric acid.

Both compounds were obtained in well-crystallized form. The crystallites have a silvery color with metallic luster. They are easily ground to fine black powders, which are stable in air for long periods of time. The compounds do not dissolve in hydrochloric acid or in solutions of sodium hydroxide. The energy dispersive X-ray fluorescence analyses of the crystals in a scanning electron microscope showed no impurities of elements with atomic numbers equal to or greater than sodium.

The samples were characterized by their Guinier powder patterns using $CuK\alpha_1$ radiation with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The lattice constants were obtained by least-squares fits. Those of $La_4Mo_7Al_{51}$ are given in Table 1. For $La_4W_7Al_{51}$ they are $a = 1041.3(4)$ pm, $c = 1173.3(4)$ pm, $V = 1.102(1)$ nm^3. The isotypism of the two compounds was proven by the excellent agreement of the observed powder patterns with those calculated using the program LAZY PULVERIX (14) and the positional parameters of $La_4Mo_7Al_{51}$ obtained from the single-crystal structure determination.

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TABLE 1
Crystal Data of $La_{4-x}Mo_7Al_{51-y}$

Composition	$La_{3.662(4)}Mo_7Al_{50.26(8)}$
Space group	$P\bar{3}m1$ (No. 164)
a (pm)	1042.4(3)
c (pm)	1174.3(3)
V (nm^3)	1.1050(9)
Formula units per cell	$Z = 1$
Formula mass	2536.3
Calculated density (g cm^{-3})	3.81
Crystal dimensions (μm^3)	22 × 22 × 55
$\theta/2\theta$ scans up to	$2\theta = 70°$
Range in h, k, l	± 16, ± 16, 0–18
Total number of reflections	10084
Absorption correction	From psi scans
Transmission ratio (highest/lowest)	1.22
Unique reflections	1843
Inner residual	$R_i = 0.041$
Reflections with $I_0 > 3\sigma(I_o)$	892
Number of variables	62
Highest residual electron density (e/Å^3)	1.43
Conventional residual	$R = 0.023$
Weighted residual	$R_W = 0.025$

STRUCTURE DETERMINATION

Single crystals of $La_4Mo_7Al_{51}$ were investigated with a four-circle diffractometer (Enraf–Nonius). The trigonal lattice constants of $a = 1042.4(2)$ pm and $c = 1174.1(2)$ pm were in excellent agreement with those obtained from the powder data (Table 1). The intensities were recorded with graphite-monochromated Mo$K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The background was determined at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were made from psi-scan data.

The structure of $La_4Mo_7Al_{51}$ was solved using the program package SHELXTL PLUS (15). The positions of the two lanthanum and the two molybdenum atoms were obtained from a Patterson function. The eight aluminum positions were found by difference Fourier syntheses. For the full-matrix least-squares refinements we used the atomic scattering factors as supplied by the SDP program package (16). The weighting scheme included a term, which accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was optimized as a least-squares parameter. To check for deviations from the ideal compositions, occupancy parameters were varied in one series of least-squares cycles together with variable thermal parameters and a fixed scale factor. Most atomic positions were found to be practically fully occupied. The occupancy values for these positions varied between 0.995(4) and 1.014(2) for the Mo(2) and La(1) positions, respectively. These positions were refined with ideal (100%) occupancy in the final least-squares cycles. The exceptions were the positions of the La(2), Al(2), Al(4), and Al(7) atoms. These atomic positions were allowed variable occupancy in the final least-squares cycles resulting in occupancy values of 83.1(1), 95.4(6), 97.4(6), and 94.9(6)%, respectively. Thus, they all showed less scattering power than what would be expected for a full occupancy. Since the aluminum atoms are the lightest atomic species of the compound, there is only the possibility that these positions are not fully occupied. This is different for the La(2) position, which also could have a mixed La/Mo or La/Al occupancy. However, since this position has the same coordination number (of 16) as the La(1) position, and since the interatomic distances for this site are even slightly larger than those for La(1), we preferred to refine this position with the sole occupancy of lanthanum. The exact formula of the compound resulting from this refinement is $La_{3.662(4)}Mo_7Al_{50.26(8)}$; however, for simplicity we use the ideal formula $La_4Mo_7Al_{51}$ for most purposes. The corresponding Pearson formula is $hP62$–1.08 (17, 18). The positional parameters of the structure were standardized using the program STRUCTURE TIDY (19). The final residuals, atomic parameters and interatomic distances are listed in Tables 1–3. A stereoplot of the structure and the coordination polyhedra are shown in Figs. 1 and 2.

DISCUSSION

At first sight the two new compounds $La_4Mo_7Al_{51}$ and $La_4W_7Al_{51}$ appeared to crystallize with a new structure type; however, when we looked up the compounds listed in Pearson's Handbook (17) under the Pearson symbol $hP62$ we found the structure of "$Ca_4Cr_7Al_{48}$" to crystallize with the same atomic positions (listed with the ideal occupancies) as found by us for $La_4Mo_7Al_{51}$. Thus, the empirical formula of the calcium chromium compound characterized in

TABLE 2
Atom Parameters of $La_{3.662(4)}Mo_7Al_{50.26(8)}$[a]

Atom	$P\bar{3}m1$	Occupancy	x	y	z	B
La(1)	$2d$	1	1/3	2/3	0.09186(6)	0.455(8)
La(2)	$2d$	0.831(2)	1/3	2/3	0.42031(7)	0.72(1)
Mo(1)	$6i$	1	0.83087(3)	$-x$	0.34355(4)	0.299(6)
Mo(2)	$1a$	1	0	0	0	0.28(2)
Al(1)	$12j$	1	0.0700(2)	0.4008(2)	0.2450(1)	0.77(3)
Al(2)	$6i$	0.954(6)	0.0917(1)	$-x$	0.4002(2)	1.08(3)
Al(3)	$6i$	1	0.1554(1)	$-x$	0.0447(1)	0.79(3)
Al(4)	$6i$	0.974(6)	0.5773(1)	$-x$	0.3449(1)	0.62(3)
Al(5)	$6i$	1	0.7578(1)	$-x$	0.1415(1)	0.80(3)
Al(6)	$6i$	1	0.9087(1)	$-x$	0.1697(1)	0.76(3)
Al(7)	$6h$	0.949(6)	0.3651(2)	0	1/2	1.89(6)
Al(8)	$3e$	1	1/2	0	0	1.79(8)

[a] The structure was refined with ellipsoidal displacement parameters; the last column contains the equivalent isotropic displacement parameters (× 10^4 in pm^2 units).

TABLE 3
Interatomic Distances in $La_{3.662(4)}Mo_7Al_{50.26(8)}$[a]

La(1):	3Al(5)	319.6	Al(2):	2Mo(1)	273.0	Al(6):	1Mo(1)	247.9
	3Al(8)	319.6		2Al(7)	277.3		1Mo(2)	258.6
	3Al(3)	326.0		2Al(2)	286.7		1Al(5)	274.5
	6Al(1)	329.3		2Al(2)	286.9		1Al(3)	277.1
	1La(2)	385.7		2Al(1)	300.4		2Al(3)	284.9
La(2):	3Al(4)	319.4		2Al(6)	317.1		2Al(6)	285.4
	6Al(1)	344.2		1Mo(1)	331.8		2Al(1)	293.2
	6Al(7)	345.1	Al(3):	1Al(5)	269.0		2Al(2)	317.1
	1La(1)	385.7		1Al(6)	277.1	Al(7):	2Mo(1)	265.6
Mo(1):	1Al(6)	247.9		2Al(1)	283.6		2Al(4)	269.2
	2Al(4)	257.1		2Al(6)	284.9		2Al(2)	277.3
	2Al(7)	265.6		1Mo(2)	285.4		1Al(7)	281.2
	2Al(1)	271.4		2Al(3)	299.5		2Al(1)	306.1
	1Al(5)	271.6		2Al(8)	316.0		2La(2)	345.1
	2Al(2)	273.0		1La(1)	326.0		2Al(7)	380.6
	1Al(2)	331.8	Al(4):	2Mo(1)	257.1	Al(8):	4Al(5)	309.4
Mo(2):	6Al(6)	258.6		2Al(7)	269.2		4Al(3)	316.0
	6Al(3)	285.4		2Al(1)	272.9		2La(1)	319.6
Al(1):	1Mo(1)	271.4		2Al(4)	279.2		4Al(1)	326.1
	1Al(1)	271.9		2Al(5)	289.2			
	1Al(4)	272.9		1La(2)	319.4			
	1Al(1)	279.8	Al(5):	1Al(3)	269.0			
	1Al(3)	283.6		1Mo(1)	271.6			
	1Al(6)	293.2		1Al(6)	274.5			
	1Al(2)	300.4		2Al(5)	285.0			
	1Al(7)	306.1		2Al(4)	289.2			
	1Al(5)	307.0		2Al(1)	307.0			
	1Al(8)	326.1		2Al(8)	309.4			
	1La(1)	329.3		1La(1)	319.6			
	1La(2)	344.2						

[a] All distances shorter than 400 pm are listed. The standard deviations are all 0.2 pm or less.

the original publication (20) is $Ca_4Cr_7Al_{51}$, and not "$Ca_4Cr_7Al_{48}$." Nevertheless, like the presently reported compound $La_{3.662(4)}Mo_7Al_{50.26(8)}$, the calcium chromium compound might be nonstoichiometric. However, this had not been investigated at that time (20). We have successfully refined our data in the centrosymmetric group $P\bar{3}m1$ (No. 164), while the structure of $Ca_4Cr_7Al_{51}$ has been refined in the corresponding acentric group $P3m1$ (No. 156). The fact that the structure of $Ca_4Cr_7Al_{51}$ could possibly also be refined in the centrosymmetric group $P\bar{3}m1$ has already been noticed by Parthé *et al.* (18). Up to now no other isotypic compounds have been reported with this structure type.

The lanthanum atoms of $La_4Mo_7Al_{51}$ occupy two crystallographic sites both with 1 lanthanum and 15 aluminum neighbors. The average La(1)–Al distance of 324.8 pm is somewhat smaller than the average La(2)–Al distance of 339.6 pm. This difference may possibly be due to the fact that the coordination polyhedron of the La(1) atom is similar to that of the Franck-Kasper polyhedron (21) with the coordination number (CN) 16, while the coordination polyhedron of the La(2) atom is less regular (although formally of the same point symmetry 3m) and several of its faces are close to rectangular (Fig. 2).

The Mo(2) atom has 12 aluminum neighbors in slightly distorted icosahedral arrangement. Icosahedral aluminum coordination (CN 12) is frequently found for the transition elements in compounds with high aluminum content; e. g., in $Ho_6Mo_4Al_{43}$ one of the two molybdenum sites has (slightly distorted) icosahedral aluminum coordination with an average Mo–Al distance of 276.1 pm (1), and in $CeMo_2Al_{20}$ the only molybdenum site has distorted icosahedral aluminum coordination with an average Mo–Al distance of 270.5 pm (11). These distances are similar to the average Mo(2)–Al distance of 272.0 pm in $La_4Mo_7Al_{51}$. The coordination of the Mo(1) atom in this structure is also similar to that of an icosahedron, except that one corner is missing (CN 11). However, the average Mo(1)–Al distance of 271.4 pm is only slightly smaller than the average Mo(2)–Al distance of 272.0 pm. The twelfth coordination site of the Mo(1) "icosahedron" is occupied with a La(2) atom at the

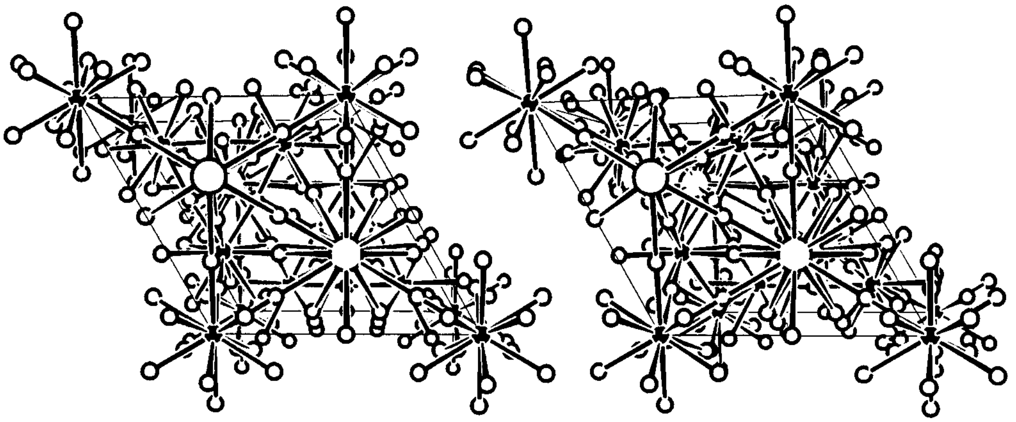
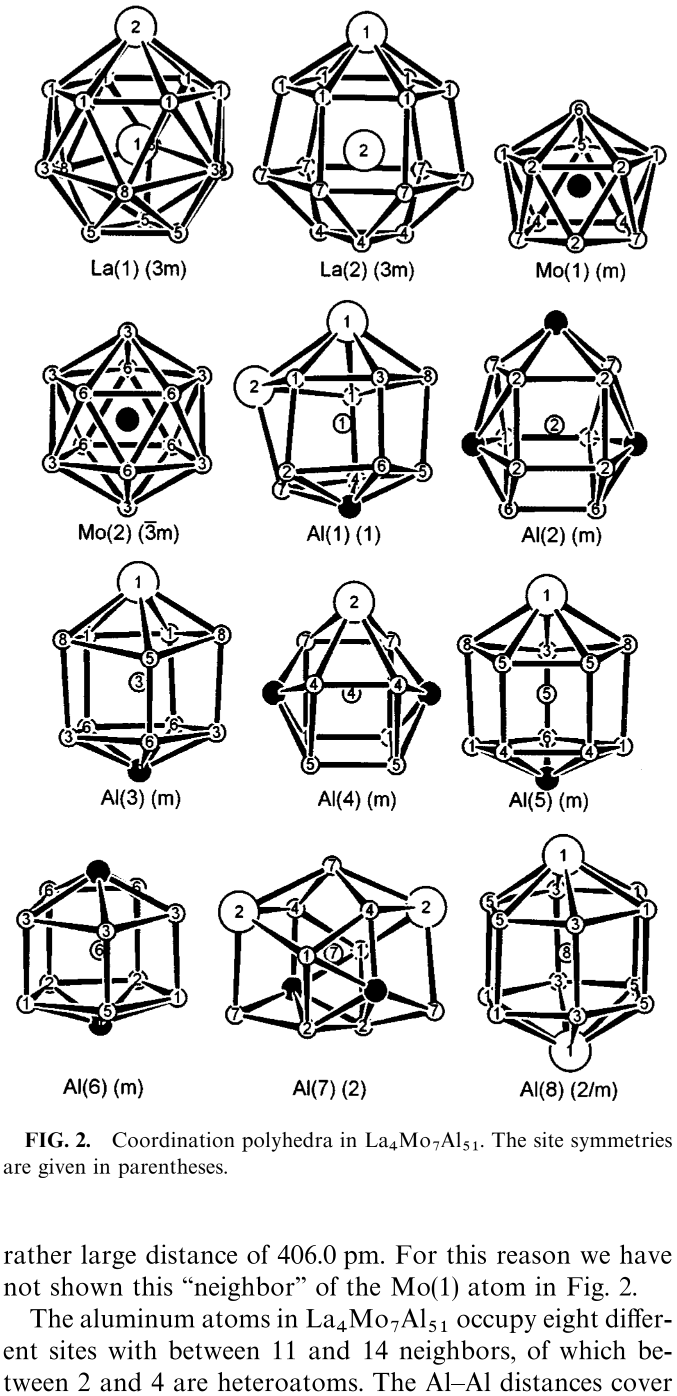


FIG. 1. Stereoplot of the structure of $La_4Mo_7Al_{51}$. The molybdenum atoms are represented by black spheres. Only the Mo–Al and La–Al bonds are shown.



La(1) (3m) La(2) (3m) Mo(1) (m)

Mo(2) ($\bar{3}$m) Al(1) (1) Al(2) (m)

Al(3) (m) Al(4) (m) Al(5) (m)

Al(6) (m) Al(7) (2) Al(8) (2/m)

FIG. 2. Coordination polyhedra in $La_4Mo_7Al_{51}$. The site symmetries are given in parentheses.

rather large distance of 406.0 pm. For this reason we have not shown this "neighbor" of the Mo(1) atom in Fig. 2.

The aluminum atoms in $La_4Mo_7Al_{51}$ occupy eight different sites with between 11 and 14 neighbors, of which between 2 and 4 are heteroatoms. The Al–Al distances cover the wide range from 269.0 to 380.6 pm, and these distances may be compared with the Al–Al distance of 286.3 pm in elemental aluminum (22). It is remarkable that all of the coordination polyhedra of the aluminum atoms in $La_4Mo_7Al_{51}$ have at least some rectangular or nearly rectangular faces. The coordination polyhedra of the Al(1), Al(3), Al(5), and Al(6) atoms may be considered as bicapped pentagonal prisms (CN 12), which are also found in the structures of $CeCr_2Al_{20}$ (7) and $Ho_6Mo_4Al_{43}$ (1). The coordination polyhedron of the Al(8) atom is a slightly distorted bicapped hexagonal prism, which also occurs in the structure of $CeCr_2Al_{20}$ (7). And also the coordination polyhedra of the remaining aluminum atoms of $La_4Mo_7Al_{51}$ have several nearly rectangular faces (Fig. 2). All of the just mentioned structures have very high aluminum contents. The coordination polyhedron of elemental aluminum (fcc) has CN 12 with eight triangular and again six rectangular faces.

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