

La_{4.27}Mg_{2.89}Zn₃₀, a new structure type with strong positional disorder

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Received 28 November 2010

Accepted 13 January 2011

Online 4 February 2011

Ternary tetralanthanum trimagnesium tricontazinc, La_{4.27}Mg_{2.89}Zn₃₀, crystallizes as a new structure type. It belongs to the structural family that may be derived from the hexagonal CaCu₅ and Th₂Ni₁₇ structure types by combination of internal deformation and multiple substitution. The triangular 3₆ and hexagonal 6₃ nets are alternately stacked with Kagomé 3636 nets. The atoms with the largest radius (La) are enclosed in 18-vertex polyhedra (distorted pseudo-Frank–Kasper polyhedra). The coordination polyhedra of the two Mg atoms are bicapped and monocapped hexagonal antiprisms, with coordination numbers of 14 and 13, respectively. For all the Zn atoms, the typical icosahedral coordination is observed. In the direction of the six- and threefold axes, strong positional disorder is observed as a result of partial substitutions of La atoms by pairs of Mg atoms.

Comment

Recently, intermetallic compounds containing rare earths, transition metals and magnesium have been of particular interest to researchers because of their useful properties as modern lightweight alloys and hydrogen-storage materials. The crystal structures, physical properties and hydrogenation behaviour of these materials have been reviewed by Rodewald *et al.* (2007). The most heavily studied of these intermetallic compounds have been those with metals such as nickel and copper. Only two ternary compounds, *i.e.* La₂Mg₃Zn₃ (cubic, $a = 7.145$ Å; Melnik *et al.*, 1978) and La₃(Zn_{0.874}Mg_{0.126})₁₁ (Pavlyuk *et al.*, 2010), were investigated from the La–Mg–Zn ternary system. The results of our crystallographic studies of a new intermetallic compound, La_{4.27}Mg_{2.89}Zn₃₀, are presented here.

During the systematic study of the ternary alloys of La–Mg–Zn from the concentration region with a high content of zinc a new ternary phase was detected. The powder diffraction pattern of this compound is similar to the powder pattern of the RE₂Zn₁₇ (RE = rare earth metal) binary phase, but has

some differences. It was decided to investigate this phase further using single-crystal methods. The single-crystal data showed that the title compound crystallized in the hexagonal crystal system in the space group $P6_3/mmc$. The projection of the unit cell and coordination polyhedra are shown in Fig. 1. The number of neighbouring atoms correlates well with the dimensions of the central atoms. The largest atoms, La, are enclosed in 18-vertex polyhedra which can be treated as distorted pseudo-Frank–Kasper polyhedra. The coordination polyhedra of the Mg1 and Mg2 atoms are bicapped and monocapped hexagonal antiprisms, with coordination numbers (CN) of 14 and 13, respectively. All the Zn atoms are surrounded by 12 nearest neighbours in the form of icosahedra (CN = 12). The shortest interatomic distances in La_{4.27}Mg_{2.89}Zn₃₀ are in the ranges typical for intermetallic compounds containing La, Mg and Zn, and indicate metallic-type bonding.

A detailed crystal chemical analysis shows that the title structure is an intergrowth of fragments of the CaCu₅ and Th₂Ni₁₇ types. It should be noted that the La–Zn binary system forms LaZn₅ (Pavlyuk *et al.*, 1997) and La₂Zn₁₇ (Iandelli & Palenzona, 1967) with the CaCu₅ and Th₂Ni₁₇ structure types, respectively. In the Th₂Ni₁₇ structure (Florio *et al.*, 1956), which also crystallizes in $P6_3/mmc$, the Ni atoms occupy the 12*k*, 12*j*, 6*g* and 4*f* positions, and the Th atoms are located on the 2*b* and 2*c* sites. In the La_{4.27}Mg_{2.89}Zn₃₀ structure, the Zn atoms occupy 12*k*, 12*j* and 6*g* sites, but the 4*f* site is partially occupied by the Mg2 atom. The Mg1 atom partially occupies the 4*e* site, which is not occupied in Th₂Ni₁₇. The La1 atom partially occupies the 2*b* site and the 2*c* site is fully occupied by the La3 atom. The La2 atom partially occupies the 2*d* site, which is also not occupied in Th₂Ni₁₇. In the structure of the title compound, so-called split atoms are observed. Atoms are distributed over some sites, which are located close to each other. The split positions of La1–Mg1, Mg1–Mg1 and La2–Mg2 are observed in the direction of the

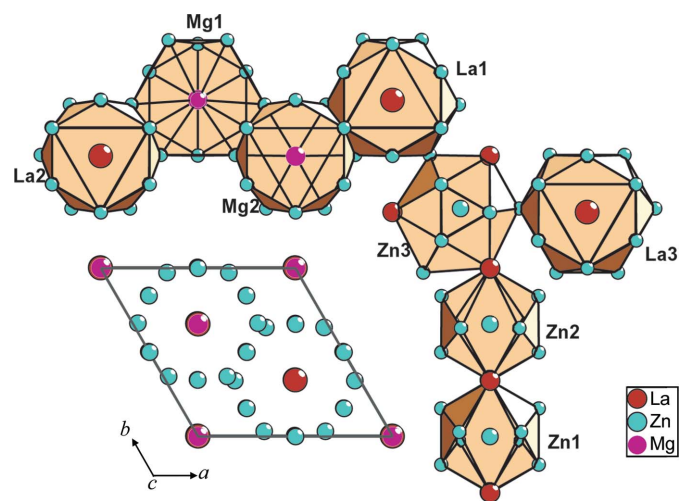


Figure 1

A clinographic projection of the La_{4.27}Mg_{2.89}Zn₃₀ unit-cell contents and the coordination polyhedra of atoms.

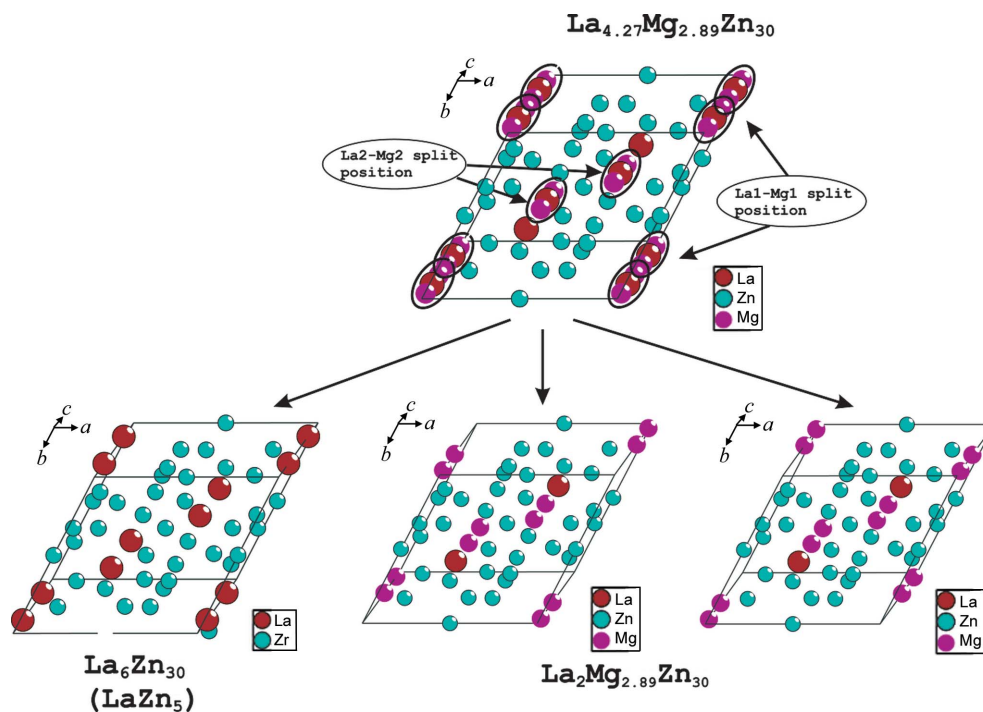


Figure 2
The $\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$ structure as a combination of $\text{La}_6\text{Zn}_{30}$ and $\text{La}_2\text{Mg}_{2.89}\text{Zn}_{30}$ sub-cells.

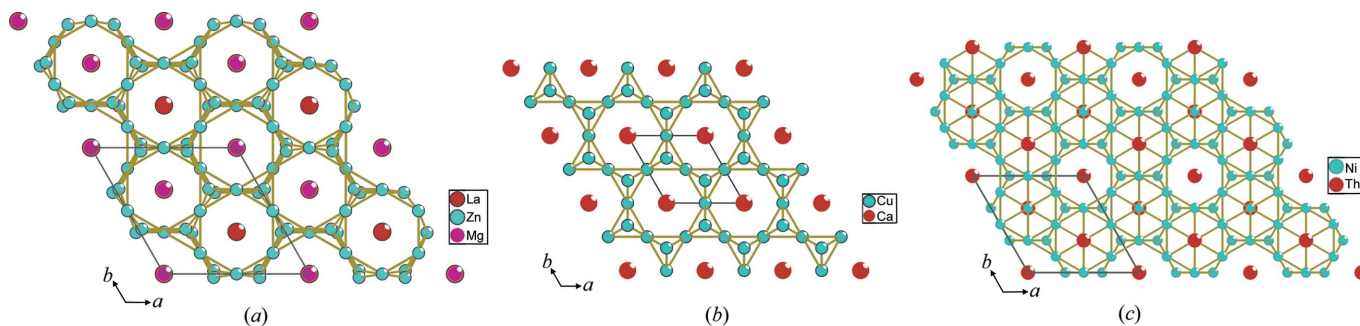


Figure 3
The triangular 3_6 and hexagonal 6_3 atomic nets in the (a) $\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$, (b) CaCu_5 and (c) $\text{Th}_2\text{Ni}_{17}$ structure types.

six- and threefold axes, respectively (Fig. 2). Thus, in the $\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$ structure, sub-cells with compositions of $\text{La}_6\text{Zn}_{30}$ and $\text{La}_2\text{Mg}_{2.89}\text{Zn}_{30}$ (Fig. 2) can be selected. The $\text{La}_6\text{Zn}_{30}$ sub-cell corresponds to the sixfold unit cell of LaZn_5 which has the CaCu_5 structure type. CaCu_5 belongs to the family of structures with large coordination polyhedra (CN = 20 for Ca atom) and in which triangular 3_6 and hexagonal 6_3 nets are alternately stacked with Kagomé 3636 nets. The same type of net is observed in the title compound (Fig. 3). It should be noted that La1–Mg1, Mg1–Mg1 and La2–Mg2 split atoms are located in the channels of these nets.

Known derivatives of the CaCu_5 type can be formed by partial or complete substitution of larger (R) atoms by various proportions of smaller-sized atoms (M) or by the shift of layers perpendicular to the sixfold axis (Krypyakevich, 1977). In the first case, if one third of the R atoms are replaced by pairs of M atoms, structures of the R_2M_{17} composition (structural types hexagonal $\text{Th}_2\text{Ni}_{17}$ and rhombohedral $\text{Th}_2\text{Zn}_{17}$) are obtained.

The substitution of half the R atoms by pairs of M atoms results in tetragonal cells of ThMn_{12} . In the case of shifted layers, the change in symmetry from hexagonal to orthorhombic was observed and the structures of BaZn_5 and SrZn_5 (Baenziger & Conant, 1956) were realized. The title structure is an intergrowth of fragments of both CaCu_5 and $\text{Th}_2\text{Ni}_{17}$ types and belongs to the first group of derivatives, where one-third of the R atoms are replaced by pairs of M atoms. The scheme of the relationship CaCu_5 – $\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$ – $\text{Th}_2\text{Ni}_{17}$ is shown in Fig. 4. The title compound is an example of a class whose representative members may be derived from the hexagonal CaCu_5 and $\text{Th}_2\text{Ni}_{17}$ structure types by a combination of internal deformation and multiple substitution.

The formation of ternary intermetallic magnesium structures which are related to the structure of binary phases has been observed previously. Typically, these structures are formed by ordered or partial substitution of rare earth metal atoms by Mg atoms. For example, REMg_2Cu_9 (Solokha *et al.*,

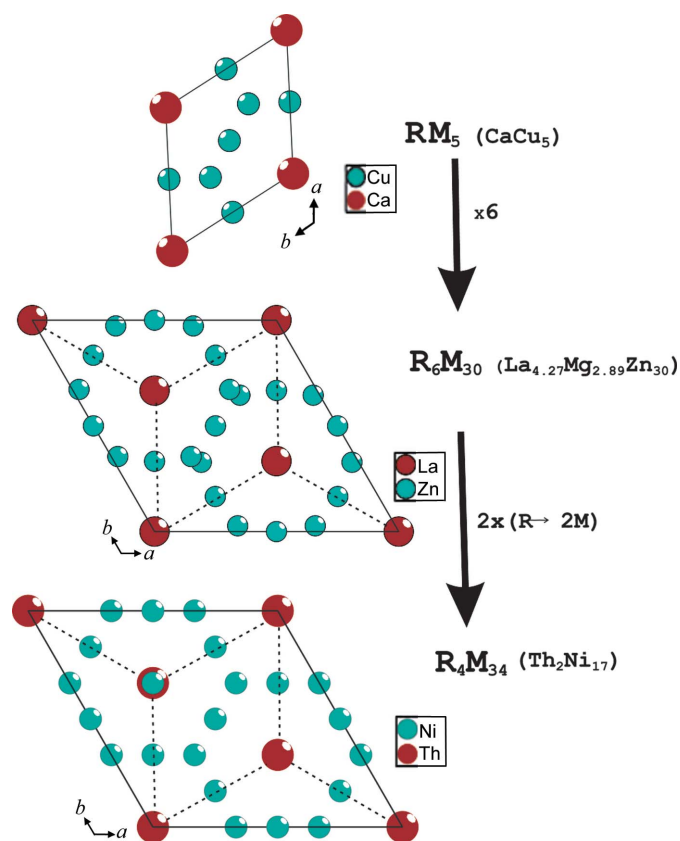


Figure 4
A scheme showing the relationship between the CaCu_5 , $\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$ and $\text{Th}_2\text{Ni}_{17}$ structure types.

2006) is a hexagonal ordered superstructure of the CeNi_3 type and REMg_2Ni_9 (Kadir *et al.*, 1997) is a rhombohedral ordered superstructure of the PuNi_3 type. Such substitution is possible because in these cases steric factors have a decisive role. The atomic radius of magnesium is only 9–11% smaller than that of atoms of the rare earth metals. On the other hand, magnesium has a different electronic structure, and this is apparently the reason why in the title compound Mg atoms cannot substitute for La atoms. Thus, they can displace lanthanum atoms out of the occupied sites very close to them and form split positions. In general, this mechanism is a multiple substitution, in which a pair of smaller atoms replaces one atom of larger size. In the title structure, this substitution is incomplete.

Experimental

Lanthanum, magnesium and zinc, all with a nominal purity better than 99.9 wt%, were used as starting elements. First, the powders of the pure metals with a stoichiometry $\text{La}_{10}\text{Mg}_{10}\text{Zn}_{80}$ were pressed into pellets, enclosed in an evacuated silica ampoule (internal pressure 10^{-5} – 10^{-6} Pa) and placed in a resistance furnace with a thermocouple controller. The heating rate from room temperature to 670 K was 5 K min^{-1} . This temperature was maintained over a period of 3 d and then the temperature was increased from 670 to 1070 K over a period of 4 d. The alloy was annealed at this temperature for 3 h and cooled slowly to room temperature. After the melting and annealing

procedures, the total weight loss was less than 2%. The brittle sample was stable in air and showed a metallic lustre. Wavelength dispersive spectrometry and electron-probe microanalysis (CAMECA SX100 analyser) were used to control the number of phases and their content in the sample. Various point analyses on this phase were in good agreement with the ideal composition determined from the single-crystal X-ray data (an average result for the title compound is 11.6–11.5 at.% La, 8.8–7.8 at.% Mg and 79.6–80.8 at.% Zn). A tabular-shaped single crystal, exhibiting a metallic lustre, was isolated by mechanical fragmentation of the reaction product.

Crystal data

$\text{La}_{4.27}\text{Mg}_{2.89}\text{Zn}_{30}$	$Z = 1$
$M_r = 2625.71$	Mo $K\alpha$ radiation
Hexagonal, $P6_3/mmc$	$\mu = 31.10 \text{ mm}^{-1}$
$a = 9.4415 (4) \text{ \AA}$	$T = 293 \text{ K}$
$c = 9.1937 (8) \text{ \AA}$	$0.09 \times 0.07 \times 0.05 \text{ mm}$
$V = 709.75 (7) \text{ \AA}^3$	

Data collection

Oxford Diffraction Xcalibur diffractometer	3083 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	342 independent reflections
$T_{\min} = 0.089$, $T_{\max} = 0.198$	299 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.013$	31 parameters
$wR(F^2) = 0.048$	$\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$
$S = 1.12$	$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$
342 reflections	

The systematic absences indicated five possible space groups, *viz.* $P31c$ (No. 159), $P\bar{3}1c$ (No. 163), $P6_3mc$ (No. 186), $P6_3c$ (No. 190) and $P6_3/mmc$ (No. 194). A statistical test of the distribution of the E values using the program *E-STATS* from the *WinGX* system (Farrugia, 1999) suggested that the structure is centrosymmetric and that the space group is $P6_3/mmc$ (No. 194), which was confirmed by the following structure refinement. The structure was solved by direct methods. The Zn atoms fully occupied the $12k$, $12j$ and $6g$ sites. The $2c$ site was fully occupied by the La3 atom. During the refinement of the atomic parameters of other atoms, two features were found: first, the La1 and La2 atoms partially occupy the $2b$ and $2c$ sites, respectively; second, two peaks of different heights on the Fourier map of the residual electron density with a very short distance to the La1 and La2 atoms. Therefore, this structure is positionally disordered. The refinement of the structure model with La1–Mg1, Mg1–Mg1 and La2–Mg2 split atoms leads to a sharp reduction in the value of the conventional R index from 0.052 to 0.013. The final refined chemical composition of the title compound is very well correlated with the results of electron-probe microanalysis.

In the final refinement cycles, all atoms were successfully refined with anisotropic displacement parameters. The atomic coordinates were standardized using the *STRUCTURE_TIDY* program (Gelato & Parthé, 1987).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

Financial support from the Polish Ministry of Science and Higher Education (project No. N507 378035) is acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3072). Services for accessing these data are described at the back of the journal.

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