The new ternary phases of La$_3$(Zn$_{0.874}$Mg$_{0.126}$)$_{11}$ and Ce$_3$(Zn$_{0.863}$Mg$_{0.137}$)$_{11}$

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The new ternary intermetallic title compounds, namely trilanthanum undeca(zinc/magnesium), La$_3$(Zn$_{0.874}$Mg$_{0.126}$)$_{11}$, (I), and tricerium undeca(zinc/magnesium), Ce$_3$(Zn$_{0.863}$Mg$_{0.137}$)$_{11}$, (II), are isostructural and crystallize in the orthorhombic La$_3$Al$_{11}$ structure type. These three phases belong to the same structural family, the representative members of which may be derived from the tetragonal BaAl$_4$ structure type by a combination of internal deformation and multiple substitution. Compared to the structure of La$_3$Al$_{11}$, in (I), a significant decrease of 11.9% in the unit-cell b axis and an increase in the other two directions, of 3.6% along a and 5.2% along c, are observed. Such an atypical deformation is caused by the closer packing of atoms in the unit cell due to atom shifts that reflect strengthening of metallic-type bonding. This structural change is also manifested in a significant difference in the coordination around the smaller atoms at the 8l Wyckoff position (site symmetry m). The Al atom in La$_3$Al$_{11}$ is in a tricapped trigonal prismatic environment (coordination number 9), while the Zn atoms in (I) and (II) are situated in a tetragonal antiprism with two added atoms (coordination number 10).

Comment

Recently, intermetallic compounds containing rare earths, transition metals and magnesium have been of particular interest to researchers in relation to 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). Until now, the most heavily studied intermetallic compounds in this class have been those with transition metals such as Ni and Cu. Only one ternary compound, *i.e.* La$_2$Mg$_3$Zn$_3$ (cubic, a = 7.145 Å), was investigated from the La–Mg–Zn ternary system (Melnik, Kinzhibalo *et al.*, 1978). The Ce–Mg–Zn ternary system was first reported by Melnik, Kostina *et al.* (1978), and the isothermal section of the phase diagram was constructed partially up to 60 at.% of Zn and 50 at.% of Ce at 573 K. Four new ternary compounds with preliminary compositions ~CeMg$_7$Zn$_{12}$, ~Ce(Mg$_{0.5-0.85}$Zn$_{0.5-0.15}$)$_9$, ~CeMg$_3$Zn$_5$ and ~Ce$_2$Mg$_3$Zn$_3$ were reported in this region. The last compound was found to crystallize with a cubic unit cell (a = 7.064 Å), whereas the crystal structures of the first three compounds remain unknown. We decided to explore the rest of the phase diagram starting from the Zn-rich region. During the investigation of the Ce–Mg–Zn phase diagram in the Zn-rich concentration range, several ternary phases were found. In our previous papers, the crystal structures of CeMgZn$_2$ (Pavlyuk *et al.*, 2007) and Ce$_{20}$Mg$_{19}$Zn$_{81}$ (Pavlyuk *et al.*, 2008) were reported, and it was found that the CeMgZn$_2$ ternary phase [MnCu$_2$Al structure type, cubic, cF16, a = 7.0358 (4) Å] belongs to a numerous family of Heusler-type structures, which are an ordered variant of the BiF$_3$ cubic structure type, while the ternary compound Ce$_{20}$Mg$_{19}$Zn$_{81}$ crystallizes with a large cubic unit cell [space group $F\bar{4}3m$, a = 21.1979 (8) Å] and represents a new type of structure. The results of crystallographic studies of two further intermetallic compounds, *i.e.* La$_3$(Zn$_{0.874}$Mg$_{0.126}$)$_{11}$, (I), and Ce$_3$(Zn$_{0.863}$Mg$_{0.137}$)$_{11}$, (II), are presented here.

The title compounds crystallize with the orthorhombic La$_3$Al$_{11}$ structure type (space group $Immm$), with 28 atoms per unit cell. The formation of compounds with this structure type is typical for the R_3Al$_{11}$ (Buschow & Van Vucht, 1967) and R_3Zn$_{11}$ (Bruzzone *et al.*, 1970) binary intermetallics (R = rare earth), and for the ternary compounds in the following systems: R–Ag–Al, R–Cu–Al (Stel'makhovych *et al.*, 2000), R–T–Ga (T = Cu, Ag, Au, Pd, Pt, Rh, Ir; Grin *et al.*, 1993) and Yb–Zn–Al (Fornasini *et al.*, 2005). The shortest interatomic distances in (I) and (II) are in the ranges typical for intermetallic compounds containing La (or Ce), Mg and Zn, and indicate metallic-type bonding. The projection of the unit cell and coordination polyhedra of the atoms are shown in Fig. 1. The number of neighbour atoms correlates well with the dimensions of the central atoms. The largest La or Ce atoms are enclosed in 17- and 18-vertex polyhedra that can be treated as distorted pseudo-Frank–Kasper polyhedra. The statistical mixture of (Zn/Mg)6 is characterized by the monocapped cuboctahedron polyhedra having the coordination number (CN) of 13. The statistical mixture of (Zn/Mg)5 and the Zn3 atom are surrounded by 12 neighbours in the form of distorted cuboctahedra (CN = 12), while the atomic environment of the Zn4 atom is a bicapped tetragonal antiprism (CN 8 + 2).

Although the isostructural compounds (I) and (II) are very similar to the La$_3$Al$_{11}$ structure type in terms of having the same space group, the same Wyckoff positions and similar lattice parameters, these two compounds cannot be treated as being isostructural with it. Comparing the structure of (I) with that of La$_3$Al$_{11}$ (Gomes de Mesquita & Buschow, 1967) we observe a significant decrease in the unit-cell dimension along the b axis of 11.9% [b = 10.132 (7) Å for La$_3$Al$_{11}$ and b = 9.0514 (8) Å for (I)], while the dimensions of the other two

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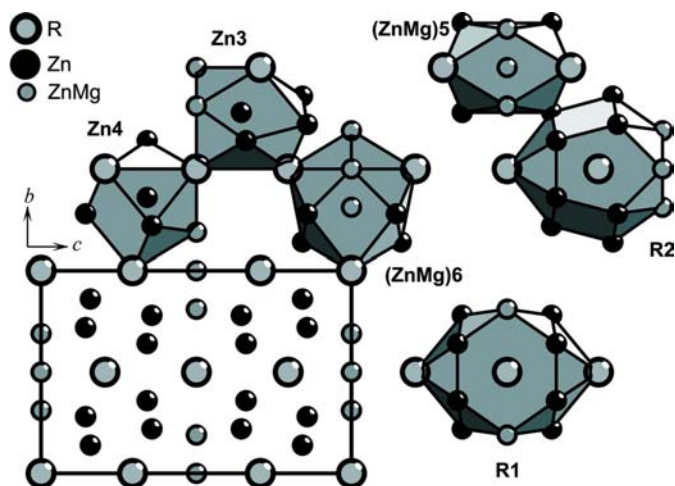
Figure 1
The clinographic projection of the $R_3(ZnMg)_{11}$ (R = La or Ce) unit-cell contents and the coordination polyhedra of atoms.

directions increase by 3.6% [a = 4.431 (5) Å for La_3Al_{11} and a = 4.5992 (4) Å for (I)] and 5.2% [c = 13.142 (10) Å for La_3Al_{11} and c = 13.8635 (11) Å for (I)]. This atypical deformation of the unit cell at the transition from the structure type La_3Al_{11} to (I) cannot be associated only with the geometric factor of the difference in atomic radius of Al (r = 1.43 Å) and Zn (r = 1.38 Å) (Slater, 1964). The relative reduction of the radius in this case is only 3.5%. Rather, the reason for this atypical deformation is closer packing of atoms in the unit cell of (I) caused by shifts in atomic positions resulting from the strengthening of metallic-type bonding. The last assertion is based on the fact that Zn and Mg are still common metal atoms (d- and s-block elements, respectively), while Al has electronic nature as a p-block element, though with metal properties. Thus, bonding between the d electrons of the La atom and d electrons of the Zn atom (or bonding between the d electrons of the La atom and s electrons of the Mg atom) in structure (I) is stronger than bonding between the d electrons of the La atom and p electrons of the Al atom in the La_3Al_{11} structure type.
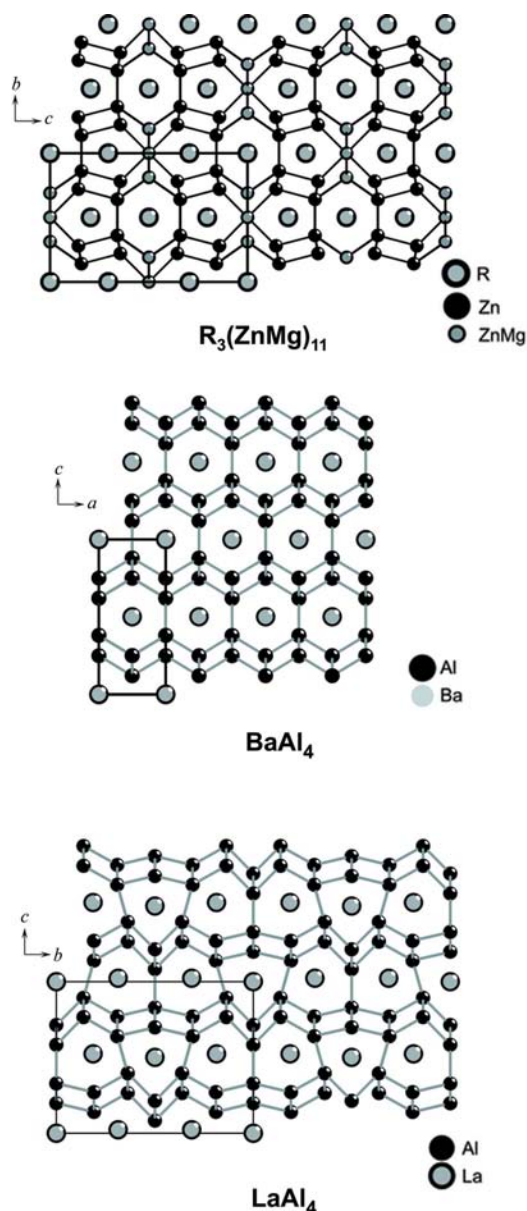
A detailed crystal chemical analysis shows that, in the case of the La_3Al_{11} structure, the Al2 atom has a trigonal prismatic coordination polyhedron with three additional capping atoms (CN = 9), while in structures (I) and (II) the Zn4 atom (which occupies the same $8l$ Wyckoff position as Al2 in La_3Al_{11}) has a tetragonal antiprismatic coordination polyhedron with two added atoms (CN = 10) (Fig. 2). Significant deformation in the direction of the b-cell axis and shifts of atoms in the same direction cause the observed changes in the coordination polyhedra. In fact, there is a close relationship between the tetragonal antiprism (CN = 8), in the ideal case, and the trigonal prism with two additional atoms (CN = 6 + 2) (Fig. 2a). Transformation of the tetragonal antiprism to a trigonal prism with two additional capping atoms is due only to the shifts of two atoms of a square face, which is bent forming two triangular faces. The same method of transformation of the $8l$ coordination polyhedron occurs at the transition between (I)

(Fig. 2b) and La_3Al_{11} (Fig. 2c). The Al2—La2 distance in the La_3Al_{11} structure is large (3.7382 Å), and thus the La2 atom does not belong to the Al2 polyhedron. By contrast, in the structure of (I) [and also in the Ce analogue, (II)], the distance between the corresponding atoms, *i.e.* betwen Zn4 and La2, is much smaller [3.3198 (10) Å] causing atom La2 to belong to the Zn4 polyhedron. As a result of these differences the title compounds and La_3Al_{11} belong to different structural classes in the classification scheme of Krypyakevich (1977). (I) and (II) belong to class 9 (tetragonal antiprism as a coordination polyhedron), while La_3Al_{11} belongs to class 10 (trigonal prism as a coordination polyhedron).

If we compare the known Al-containing compounds from systems R–Ag–Al and R–Cu–Al (Stel'makhovych *et al.*, 2000) with the structure of La_3Al_{11}, we do not observe this atypical deformation. For these ternary compounds, it is observed that the decrease in the unit-cell dimension along the b axis is in the range 1.19–3.21% for $R_3(CuAl)_{11}$ and 0.51–1.58% for $R_3(AgAl)_{11}$ depending on the rare earth element (R). By contrast, in the binary compounds R_3Zn_{11} (Bruzzone *et al.*, 1970), the decrease in the unit-cell dimension along the b axis is in the range 11.61–12.90% depending on R. Solid evidence that this anomaly is characteristic only for compounds containing Zn is obtained by comparing our results with data for compounds that contain Ga instead of Al (*i.e.* from systems R–T–Ga where T = Cu, Ag, Au, Pd, Pt, Rh, Ir; Grin *et al.*,
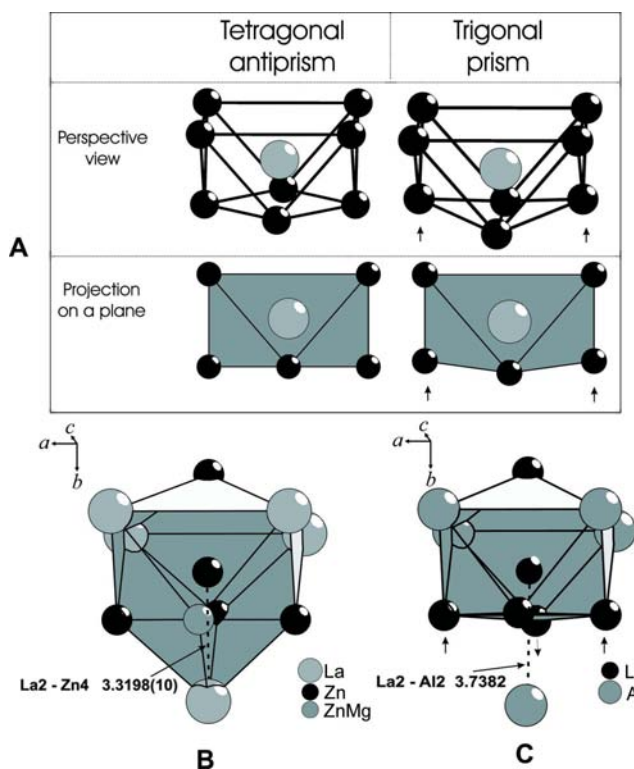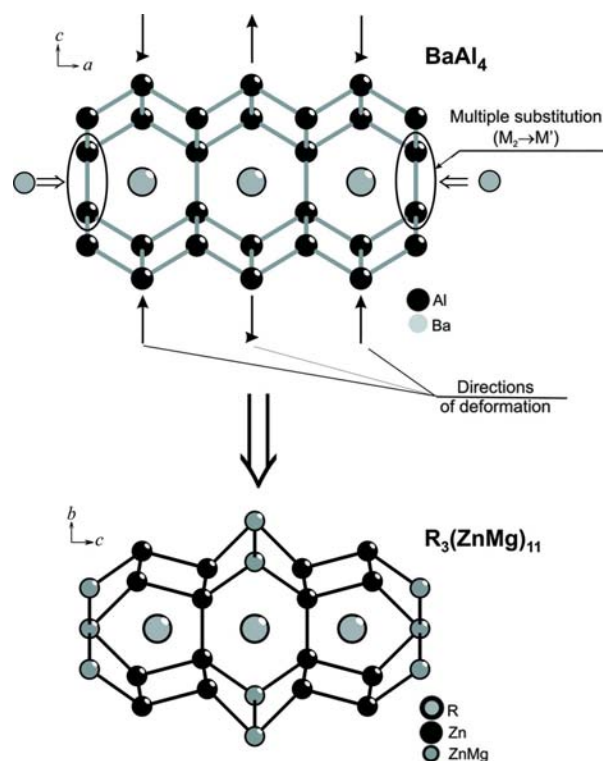

Figure 2
(a) Scheme of the transformation of the tetragonal antiprism to the trigonal prism with two added atoms. (b) Coordination polyhedra for atom Zn4 in $La_3(Zn_{0.874}Mg_{0.126})_{11}$ and (c) for Al2 in La_3Al_{11}. The La—Al2 and La—Zn4 distances are denoted by dashed lines. The atom shifts are denoted by arrows.

Figure 3
Crystallographic relations between the $R_3(ZnMg)_{11}$ (R = La or Ce), BaAl$_4$ and LaAl$_4$ structures.

Figure 4
The transformation of the BaAl$_4$ tetragonal structure to the $R_3(ZnMg)_{11}$ (R = La or Ce) orthorhombic structure by means of deformation and multiple substitutions.

atoms are embedded in the three-dimensional networks, which are formed by the smaller metal atoms (Fig. 3). The primary fragment of such networks has the composition $[RM_{18}]$. For example, in the BaAl$_4$ structure, each Ba atom is surrounded by 18 Al atoms. Further, the structural $[RM_{18}]$ fragment is connected to six other identical fragments. The structures of (I) and (II) also contain the analogous $[RM_{18}]$ fragments and each of them is connected to six fragments containing 16 smaller atoms $[RM_{16}]$. The $[RM_{16}]$ fragment type can be derived from the $[RM_{18}]$ fragment by internal deformation and multiple substitutions (Fig. 4).

Experimental

La, Ce, Mg and Zn, all with a nominal purity greater than 99.9 wt%, were used as the starting elements. First, the powders of the pure metals with a stoichiometry La(or Ce):Mg:Zn = 2:1:7 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}. The alloys were kept at this temperature over a period of 2 d and then the temperature was increased from 670 to 1073 K over a period of 6 d. The alloys were then annealed at this temperature for 4 h and cooled slowly to room temperature. In the second step, the pellets were remelted in an arc furnace under an argon atmosphere at least three times in order to ensure homogeneity. After the melting procedures, the total weight loss was less than 2%. The brittle samples were stable in air, showing a metallic lustre. Wavelength dispersive spectrometry and electron-probe microanalysis (CAMECA SX100 analyser) were used to control the

1993). The atomic radius of Ga (r = 1.35 Å) (Slater, 1964) is very close to the radius of Zn (r = 1.38 Å), but the b axis in the Ga-containing compounds is larger than that in the Zn-containing compounds by an average of 5%. This is entirely inconsistent with the geometric factor (radius) and supports our assumption that the structural deformation is driven by closer packing in the Zn-containing structure caused by strengthening of metallic-type bonding as a consequence of changes in the electronic nature of the element.

The crystal structures of the title compounds are also closely related to the tetragonal BaAl$_4$ (space group $I4/mmm$; Andress & Alberti, 1935) and orthorhombic LaAl$_4$ (space group $Imm2$; Zalutskii & Krypyakevych, 1967) structural types, $i.e.$ types adopted by the binary rare earth compounds RAl$_4$ (R = La, Ce, Pr, Nd). In these structures, the rare earth

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number of phases and their content in the samples. Various point analyses on this phase were in good agreement with the ideal composition determined by the single-crystal X-ray data [an average result for the title compounds is 21.4 at.% La, 9.9 at.% Mg and 68.7 at.% Zn for (I), and 21.3 at.% Ce, 10.1 at.% Mg and 68.6 at.% Zn for (II)]. Tabular-shaped single crystals, exhibiting a metallic lustre, were isolated by mechanical fragmentation from the alloys.

Compound (I)

Crystal data

$La_3(Zn_{0.874}Mg_{0.126})_{11}$	$V = 577.13 (8)$ Å^3
$M_r = 2158.41$	$Z = 1$
Orthorhombic, $Immm$	Mo $K\alpha$ radiation
$a = 4.5992 (4)$ Å	$\mu = 30.42$ mm^{-1}
$b = 9.0514 (8)$ Å	$T = 293$ K
$c = 13.8635 (11)$ Å	$0.14 \times 0.11 \times 0.04$ mm

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	1821 measured reflections
	372 independent reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)	336 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$
$T_{min} = 0.031$, $T_{max} = 0.288$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	26 parameters
$wR(F^2) = 0.051$	$\Delta\rho_{max} = 1.32$ e Å^{-3}
$S = 1.11$	$\Delta\rho_{min} = -1.08$ e Å^{-3}
372 reflections	

Compound (II)

Crystal data

$Ce_3(Zn_{0.863}Mg_{0.137})_{11}$	$V = 560.96 (14)$ Å^3
$M_r = 2155.40$	$Z = 1$
Orthorhombic, $Immm$	Mo $K\alpha$ radiation
$a = 4.5641 (6)$ Å	$\mu = 31.79$ mm^{-1}
$b = 8.9542 (14)$ Å	$T = 293$ K
$c = 13.7261 (18)$ Å	$0.11 \times 0.10 \times 0.03$ mm

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	1896 measured reflections
	395 independent reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)	349 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.032$
$T_{min} = 0.046$, $T_{max} = 0.379$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	27 parameters
$wR(F^2) = 0.051$	$\Delta\rho_{max} = 1.71$ e Å^{-3}
$S = 1.00$	$\Delta\rho_{min} = -1.41$ e Å^{-3}
395 reflections	

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. The analysis of systematic extinctions yielded the space group $Immm$ (No. 71), and this was confirmed by the following structure refinement. The structure was solved by direct methods. The rare earth atoms were located in the Wyckoff sites $2a$ and $4i$. The Zn3 and Zn4 atoms were

localized in the two $8l$ Wyckoff sites. The Zn5 and Zn6 atoms in the $4h$ and $2d$ Wyckoff sites, respectively, showed displacement parameters which differ considerably from those of the Zn atoms in the other sites. This suggested that, in addition to Zn, these positions are partially occupied by the Mg atoms. In (I), the $2d$ site is occupied by 0.393 (15) Mg and 0.607 (15) Zn, and the $4h$ site is occupied by 0.495 (10) Mg and 0.505 (10) Zn. In (II), the $2d$ site is occupied by 0.378 (13) Mg and 0.622 (13) Zn, and the $4h$ site is occupied by 0.484 (10) Mg and 0.516 (10) Zn. In the final refinement cycles, the isotropic displacement parameters for the (ZnMg) statistical mixtures in the $4h$ and $2d$ Wyckoff sites were refined. All other atoms were successfully refined with anisotropic displacement parameters. The positional and U_{iso} parameters for the (ZnMg) statistical mixtures were equated using the EXYZ and EADP constraints. The atomic coordinates were standardized using the *STRUCTURE_TIDY* program (Gelato & Parthé, 1987).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; 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*.

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