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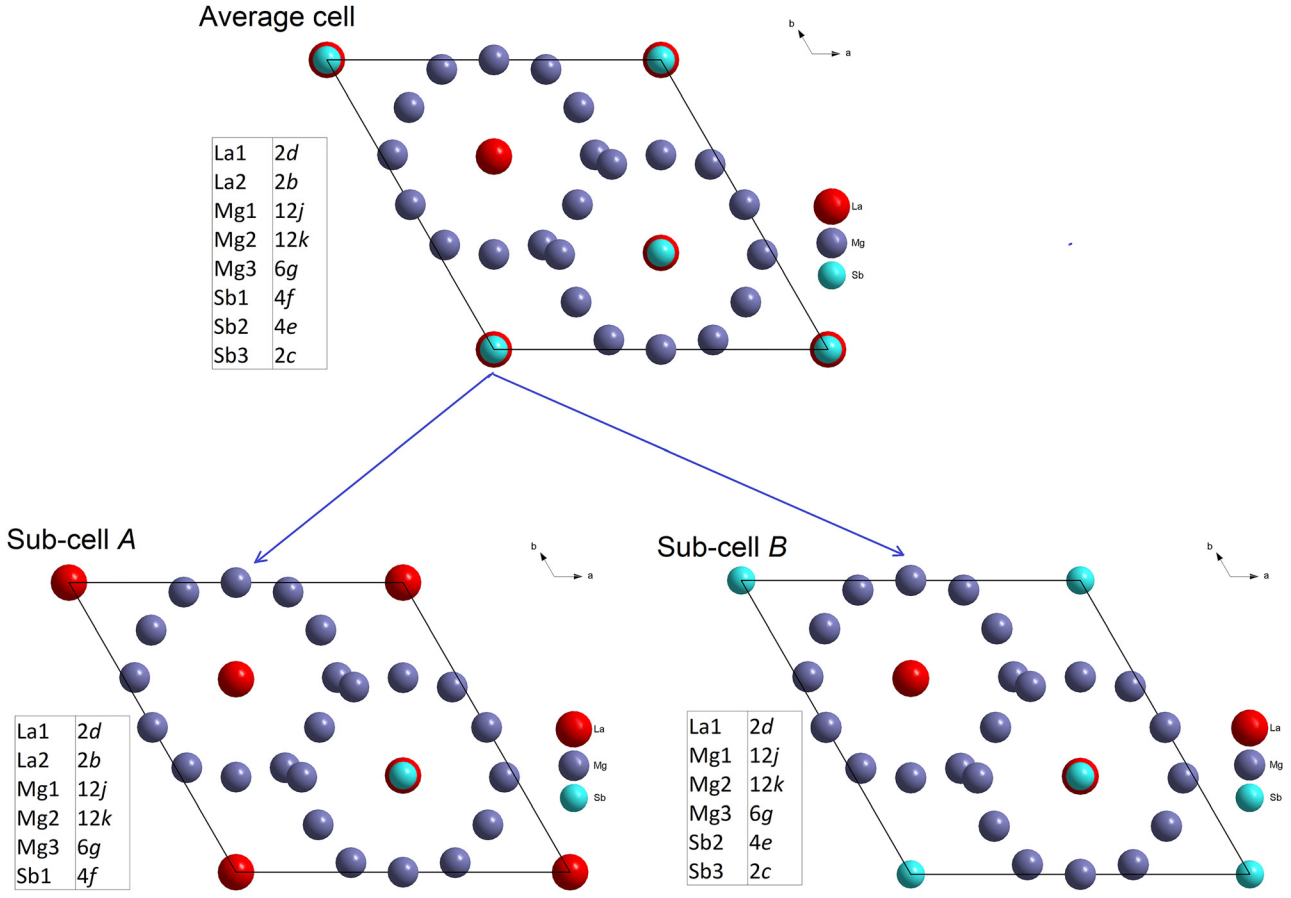
$La_{3.65}Mg_{30}Sb_{1.07}$ as a disordered derivative of Th_2Ni_{17}-type structure



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Abstract

$La_{3.65}Mg_{30}Sb_{1.07}$, hexagonal, $P6_3/mmc$ (no. 194), a = 10.3895(2) Å, c = 10.2547(3) Å, V = 958.61(5) Å^3, Z = 1, $R_{gt}(F)$ = 0.0166, $wR_{ref}(F^2)$ = 0.0429, T = 293(2) K.

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Table 1: Data collection and handling.

Crystal:	Plate, metallic dark grey
Size:	0.07 × 0.05 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.5 mm^{-1}
Diffractometer, scan mode:	Xcalibur3, ω-scans
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5875, 407, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 339
$N(param)_{refined}$:	28
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], *publ*CIF [4], DIAMOND [5]

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
La1	0.3333	0.6667	0.7500	0.0154 (2)
La2[a]	0.0000	0.0000	0.7500	0.0186 (2)
Mg1	0.32751 (13)	0.96714 (16)	0.2500	0.0249 (3)
Mg2	0.16403 (7)	0.32807 (14)	0.52028 (12)	0.0223 (3)
Mg3	0.5000	1.0000	0.5000	0.0197 (4)
Sb1[b]	0.6667	0.3333	0.6018 (2)	0.025*
Sb2[c]	0.0000	0.0000	0.8984 (12)	0.027*
Sb3[d]	0.6667	0.3333	0.7500	0.027*

Occupancies: [a] = 0.825(3), [b] = 0.2111(15), [c] = 0.0395(12), [d] = 0.034(2).

Source of material

The $La_{10}Mg_{85}Sb_5$ (in at.%) sample was prepared in Ta-crucibles which were placed in a resistance furnace with a thermocouple controller. Heating rate from room temperature to 670 K was equal 5 K per minute. The purity of constituent elements was more than 99.98 wt%. At this temperature the alloy was kept for over two days and then the temperature was increased to 1170 K for over 4 h. The alloy was annealed at this temperature for 12 h and slowly cooled down to room temperature. After mechanical defragmentation of alloy the small prismatic single crystals were isolated for X-ray investigations. The density of alloy was determined using the volumetric method. For ternary phase of $La_{10}Mg_{85}Sb_5$ the measured density is 2.40(5) g/cm^3 and this value is less than 2% different from the density calculated from X-ray data.

Experimental details

The crystal structure of the $La_{3.65}Mg_{30}Sb_{1.07}$ solid solution was studied by single crystal X-ray diffraction (diffractometer Xcalibur Oxford Diffraction). Absorption correction was performed by analytical method. The solution of the crystal structure was carried out by direct methods. In the first stage of structure solution, the positions of La, Mg, and Sb atoms were obtained correctly by direct methods. All Sb atoms partially occupy three sites 4*f*, 4*e* and 2*c*. The refinement of the structure model with La2—Sb2 and Sb1—Sb3 split atoms leads to sharp reduction in the value of conventional *R* index.

Discussion

In our previous work [6] we investigated $La_{3.65}Mg_{30}Sn_{1.10}$. In this work we studied the Sb-containing phase with a similar crystal structure. The solubility of antimony and tin in the binary La_2Mg_{17} intermetallic compound, studied by XRD and EDX-analysis, reaches 4–5 at.%, because similar atomic radii (r_{Sb} = 1.59 Å, r_{Sn} = 1.62 Å). Both phases are related to the Th_2Ni_{17} and parental $CaCu_5$-type structure and demonstrate hydrogen sorption ability [6]. Mg-based intermetallics as hydrogen sorption material and negative electrodes in Ni–MH batteries are described in refs. [7, 8]. $La_{3.65}Mg_{30}Sb_{1.07}$ is strongly disordered due to the presence of mutually excluding atoms and split positions. Therefore, in the average structure two sub-cells (*A* and *B*) can be selected. In the average structure the fraction ratio of sub-cells *A* to sub-cells *B* is 4:1 (Figure). Sub-cell *A*, which contains La1, La2, Mg1, Mg2, Mg3 and Sb1 has the composition $La_4Mg_{30}Sb_4$ or $La_2Mg_{15}Sb_2$ (for Z = 2) corresponding to the structure type $Ce_2Mg_{15}Fe_2$ [9], which is an ordered superstructure to Th_2Ni_{17}-type. Sub-cell *B* contains the La1, Mg1, Mg2, Mg3, Sb2 and Sb3 atoms. The La2–Sb2 and Sb1–Sb3 atoms mutually exclude each other. The projection of the *A* and *B* unit cells are shown in the figure. Detailed crystal chemical analysis shows that La1 and La2 atoms are enclosed in pseudo–Frank–Kasper polyhedra [La1$Mg_{18}Sb_{20}$] and [La2Mg_{18}], respectively. For all Mg and Sb3 atoms typical is icosahedral coordination. The Sb1 and Sb2 atoms formed the 14-vertex polyhedra [Sb1Mg_{12}SbLa] and [Sb2$Mg_{12}Sb_2$]. These type of polyhedra and values of interatomic distances are similar to other known Mg-based intermetallics [10–12].

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