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Crystal structure of the hydrogen storage active phase $\text{La}_{12}\text{Mg}_{46}\text{LiMn}$

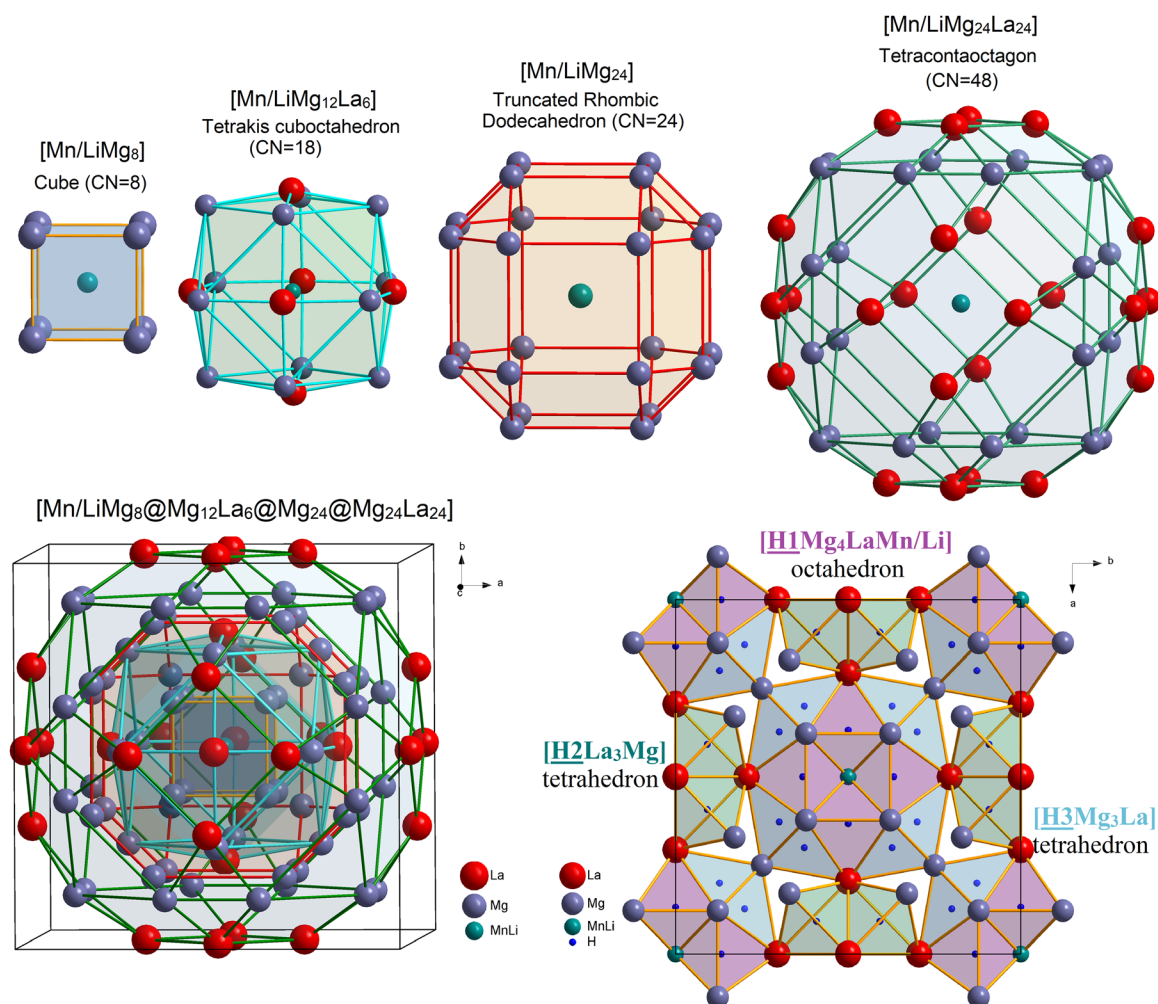


Figure 1: Atomic structure of a four-shell cluster $[\text{Mn}/\text{LiMg}_8@\text{Mg}_{12}\text{La}_6@\text{Mg}_{24}@\text{Mg}_{24}\text{La}_{24}]$. Packing of $[\text{H1Mg}_4\text{LaMn/Li}]$ octahedra (violet) and $[\text{H2La}_3\text{Mg}]$ (green), $[\text{H3Mg}_3\text{La}]$ (grey) tetrahedrons.

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Abstract

$\text{La}_{12}\text{Mg}_{46}\text{LiMn}$, cubic, $Fm\bar{3}m$ (no 225), $a = 14.7119(3) \text{ \AA}$, $V = 3184.24(19) \text{ \AA}^3$, $Z = 2$, $R_{gt}(F) = 0.0330$, $wR_{ref}(F^2) = 0.0601$, $T = 293(2) \text{ K}$.

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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 1: Data collection and handling.

Crystal:	Grey prism
Size:	0.06 × 0.05 × 0.03 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	8.51 mm ⁻¹
Diffractometer, scan mode:	Oxford diffraction Xcalibur3, ω
$\theta_{\max}$, completeness:	26.3°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5052, 205, 0.079
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 180
$N(\text{param})_{\text{refined}}$:	17
Programs:	SHELX [1, 2], publCIF [3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
La1	0.20542 (9)	0.0000	0.0000	0.0159 (3)
Mg1	0.0000	0.2500	0.2500	0.0164 (14)
Mg2	0.3781 (3)	0.3781 (3)	0.3781 (3)	0.0210 (13)
Mg3	0.1703 (2)	0.1703 (2)	0.1703 (2)	0.0179 (13)
Mg4	0.0000	0.0000	0.0000	0.009 (3)
Mn1 ^a	0.5000	0.5000	0.5000	0.042 (5)*
Li1 ^b	0.5000	0.5000	0.5000	0.042 (5)*

^aOccupancy: 0.4996, ^bOccupancy: 0.5002.

1 Source of material

The La₁₂Mg₄₆LiMn sample was prepared in Ta-crucibles which were placed in a resistance furnace with a thermocouple controller. The heating rate from room temperature to 670 K was equal to 5 K per minute. The purity of constituent elements was more than 99.98 wt%. At this temperature, the alloy was kept for over 2 days and then the temperature was increased from 670 K to 1170 K for over 4 h. Then, the alloy was annealed at this temperature for 12 h and slowly cooled to room temperature. After the mechanical defragmentation of the alloy, the small prismatic single crystals were isolated for X-ray investigations. The density of the alloy was determined using the volumetric method. For the ternary phase of La₁₂Mg₄₆LiMn, the measured density is 2.98(2) g/cm³, which is less than 2 % different from the density calculated from X-ray data.

2 Experimental details

The crystal structure of the La₁₂Mg₄₆LiMn was studied by single crystal X-ray 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 the structure solution, the positions of La and Mg atoms were obtained correctly by Direct Methods. The statistical mixture of Li and Mn atoms occupies one site 4b. The refinement of the structure model with a statistical mixture of Li and Mn atoms leads to a significant reduction in the value of the conventional *R* index. Crystal data and details of the structure refinement for La₁₂Mg₄₆LiMn are given in Table 1.

3 Comment

Previous studies have shown that magnesium is capable to forming ternary intermetallic compounds and solid solutions at the interaction with rare-earth elements and 3-*d* metals [5–8], as well as *p*-elements [9–13]. Some of these ternary phases exhibit hydrogen sorption activity.

La₁₂Mg₄₆LiMn compound crystallizes in the cubic Zr₆Zn₂₃Si structure type [14] which is as “filled” variant of Th₆Mn₂₃-type [15] structure. The quaternary intermetallic compound La₁₂Mg₄₆LiMn can be described as four-shell clusters of cluster [Mn/LiMg₈@Mg₁₂La₆@Mg₂₄@Mg₂₄La₂₄] (see Figure 1). The [Mn/LiMg₈] cube is encapsulated in the tetrakis cuboctahedron [Mg₁₂La₆] cluster and both together are encapsulated in a truncated rhombic dodecahedron [Mg₂₄]. The fourth core-shell is a tetracontaoctagon [Mg₂₄La₂₄] cluster. Our study of hydrogen sorption properties shows a hydrogen sorption capacity of up to 1.8 wt% H₂, which corresponds to the formula of the hydride La₁₂Mg₄₆LiMnH₅₂. The theoretical basics of the analysis of voids in crystal structures by means of a crystallo-chemical approach give three types of voids between the shells of clusters, namely octahedral (site 24e: $x = 0.368$, $y = 1/2$, $z = 1/2$) and two tetrahedral (32f: $x = 0.092$, $y = 0.092$, $z = 0.092$ and 96j: $x = 0.373$, $y = 1/2$, $z = 0.300$). The void in site 96j can be occupied by half because of hydrogen atoms in the split position. The mutual stacking of hydrogen-filled octahedra and tetrahedra is shown in Figure 1. For the hydrogenated phase the unit cell dimension increases up to $a = 14.793$ Å.

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Conflict of interest: The authors declare no conflicts of interest regarding this article.

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