

Crystal structure of $\text{La}_6\text{Mg}_{23+x}\text{Sn}_{1-x}$ compound

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Magnesium-rich materials for hydrogen storage, particularly in the form of alloys, intermetallic compounds or composites, are considered highly promising due to their favourable performance characteristics. Many of the intermetallic compounds with high magnesium content exhibit cluster-shell structures. One representative example is $\text{La}_6\text{Mg}_{23}\text{Sn}_x$ ($x = 1$), which was first examined by powder X-ray diffraction in [1]. In this study, we present the crystal structure of the $\text{La}_6\text{Mg}_{23+x}\text{Sn}_{1-x}$ refined from single-crystal X-ray diffraction data and first results of electrochemical hydrogenation of this compound.

The $\text{La}_6\text{Mg}_{23}\text{Sn}_{0.5}$ alloy was synthesised by arc melting high-purity elemental metals (≥ 99.98 wt.%) in tantalum crucibles placed inside a resistance furnace. The heating schedule involved increasing the temperature from room temperature to 670 K at a rate of $300 \text{ K}\cdot\text{h}^{-1}$, followed by isothermal annealing at 670 K for over 7 days. The temperature was then raised to 1170 K over 4 hours, maintained at that level for 12 hours, and subsequently cooled to room temperature at a rate of $30 \text{ K}\cdot\text{h}^{-1}$. After solidification, block-like single crystals were extracted from the alloy by mechanical grinding for further structural investigation. The chemical composition of the alloy was verified using scanning electron microscopy and energy-dispersive X-ray spectroscopy, performed on a Tescan Vega 3 LMU microscope equipped with an Oxford Instruments Aztec ONE system. The measured elemental ratios were found to be in good agreement with the nominal stoichiometry. Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Xcalibur3 diffractometer with $\text{Mo } K\alpha_1$ radiation (graphite-monochromator, ω -scan, analytical absorption correction). The crystal structure was solved using direct methods and full-matrix least-squares refinement on F^2 [2].

The $\text{La}_6\text{Mg}_{23+x}\text{Sn}_{1-x}$ phase crystallises in the cubic $\text{Zr}_6\text{Zn}_{23}\text{Si}$ -type structure, which represents a “filled” variant of the $\text{Th}_6\text{Mn}_{23}$ -type structure (Table 1). Structurally, this phase can be described in terms of a four-shell cluster model: $[\text{Sn}/\text{MgMg}_8@[\text{La}_6\text{Mg}_{12}@[\text{Mg}_{24}@[\text{La}_4\text{Mg}_{24}]]]]$. The innermost $[\text{Sn}/\text{MgMg}_8]$ cube is encapsulated by a tetrakis cuboctahedron formed by a $[\text{La}_6\text{Mg}_{12}]$ cluster. These two inner shells are enclosed within a truncated rhombic dodecahedron composed of 24 Mg atoms, and the entire assembly is surrounded by an outer shell comprising 24 La and 24 Mg atoms. A similar cluster-coordination geometry has been reported for the $\text{La}_{12}\text{Mg}_{46}\text{LiMn}$ compound [3], which also exhibits hydrogen storage properties analogous to those observed in the present system.

Electrochemical hydrogenation of the compound, which served as a negative electrode, was conducted in galvanostatic mode using a two-electrode Swagelok-type cell. $\text{Ni}(\text{OH})_2$ powder with graphite served as a positive electrode, and 6 M KOH aqueous solution was used as an electrolyte. An electrode material based on the studied compound demonstrated good stability in an alkaline environment and reversible hydrogen-sorption ability.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for $\text{La}_6\text{Mg}_{23+x}\text{Sn}_{1-x}$, $x = 0.96$
($a = 14.7131(2) \text{ \AA}$, $V = 3185.02(7) \text{ \AA}^3$, $Z = 4$, structure type $\text{Zr}_6\text{Zn}_{23}\text{Si}$, space group $Fm\text{-}3m$, Pearson code $cF120$,
 $R_1 = 0.0313$, $wR_2 = 0.0553$)

Atom	Site	Atom coordinates			$U_{eq}, \text{ \AA}^2$
		x/a	y/b	z/c	
La	24e	0.20543(8)	0	0	0.0170(4)
Mg1	24d	0	1/4	1/4	0.0174(14)
Mg2	32f	0.3781(2)	0.3781(2)	0.3781(2)	0.0219(13)
Mg3	32f	0.1703(2)	0.1703(2)	0.1703(2)	0.0190(13)
Mg4	4a	0	0	0	0.010(3)
M (0.96Mg + 0.04Sn)	4b	1/2	1/2	1/2	0.040(5)

[1] De Negri, S., Solokha, P., Minetti, R., Skrobańska, M., Saccone, A. (2017). *J. Solid State Chem.*, **248**, 32.

[2] Sheldrick, G.M. (2008). *Acta Crystallogr.*, **A64**, 112.

[3] Pavlyuk, N., Nytko, V., Kordan, V., Pavlyuk, V. (2023). *Z. Kristallogr. - New Cryst. Struct.*, **238(6)**, 1223