

Lanthanum tetrazinc, LaZn_4

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The structure of lanthanum tetrazinc, LaZn_4 , has been determined from single-crystal X-ray diffraction data for the first time, approximately 70 years after its discovery. The compound exhibits a new structure type in the space group $Cmcm$, with one La atom and two Zn atoms occupying sites with $m2m$ symmetry, and one Zn atom occupying a site with 2.. symmetry. The structure is closely related to the BaAl_4 , $\text{La}_3\text{Al}_{11}$, BaNi_2Si_2 and CaCu_5 structure types, which can be presented as close-packed arrangements of 18-vertex clusters, in this case LaZn_{18} . The kindred structure types contain related 18-vertex clusters around atoms of the rare earth or alkaline earth metal.

Comment

Lanthanum tetrazinc, LaZn_4 , was discovered approximately 70 years ago (Rolla & Iandelli, 1941). We detected the compound during a systematic study of La–Zn and La–Zn–Sn alloys with a high Zn content. Previous data by Bruzzone *et al.* (1970) included determination of the unit-cell parameters for the compound and a proposal for its space group. Those results were obtained from both Gandolfi photographs of the single-crystal and powder X-ray diffraction data, but a complete description of the crystal structure was not given. Bruzzone *et al.* also proposed a relationship between the structure of LaZn_4 and the BaAl_4 structure type (Alberti & Andress, 1935).

The single-crystal X-ray data reported here show that the title compound crystallizes in a new structure type in the orthorhombic space group $Cmcm$ (Fig. 1). The structure has four crystallographically distinct atoms, all of which occupy special equivalent positions. The La atoms (Wyckoff position 4c, site symmetry $m2m$) are surrounded by 18 Zn atoms. The coordination polyhedra of atoms Zn1 and Zn2 (Fig. 2) (also Wyckoff position 4c) are a $[\text{ZnLa}_4\text{Zn}_5]$ monocapped tetragonal antiprism [coordination number (CN) = 9] and a

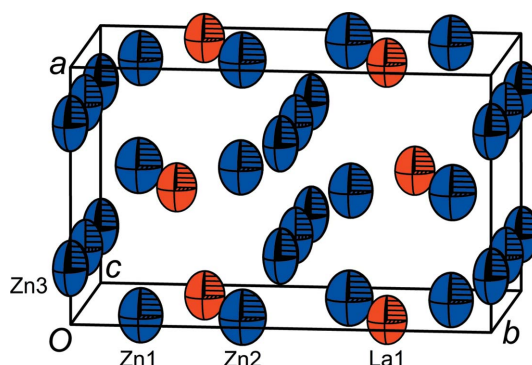


Figure 1
The unit cell of LaZn_4 , with displacement ellipsoids drawn at the 99.9% probability level.

$[\text{ZnLa}_5\text{Zn}_5]$ bicapped tetragonal antiprism (CN = 10), respectively. Atom Zn3 (Wyckoff position 8e, site symmetry 2..) is enclosed in a $[\text{ZnLa}_4\text{Zn}_8]$ deformed cuboctahedron (CN = 12).

The title compound has no isostructural intermetallic compounds. Amongst other inorganic compounds, PbSbClO_2 has a related crystal structure with the same symmetry, Pearson symbol and Wyckoff sequence (Giuseppetti & Tadini, 1973). In spite of this relationship, however, it has a significantly different b/c unit-cell parameter ratio (2.231 in PbSbClO_2 compared with 1.684 in the title compound).

The coordination polyhedron of atom La1 (Fig. 2) is the principal building block of the LaZn_4 structure. The $[\text{LaZn}_{18}]$ polyhedra share their vertices and faces. The kindred structure types BaAl_4 , $\text{La}_3\text{Al}_{11}$ (Gomes de Mesquita & Buschow, 1967), BaNi_2Si_2 (Dörrscheidt & Schäfer, 1980) and CaCu_5 (Nowotny, 1942) contain related 18-vertex clusters around atoms of the rare earth or alkaline earth metal (Fig. 3). All of these structures, including LaZn_4 , have hexagonal channels occupied by the rare earth or alkaline earth metal. Deformation of the 18-vertex cluster in the BaAl_4 structure leads to the LaZn_4

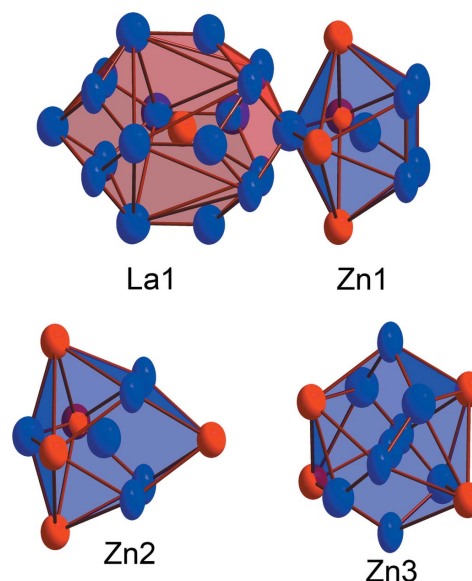


Figure 2
The coordination polyhedra for the four independent atoms.

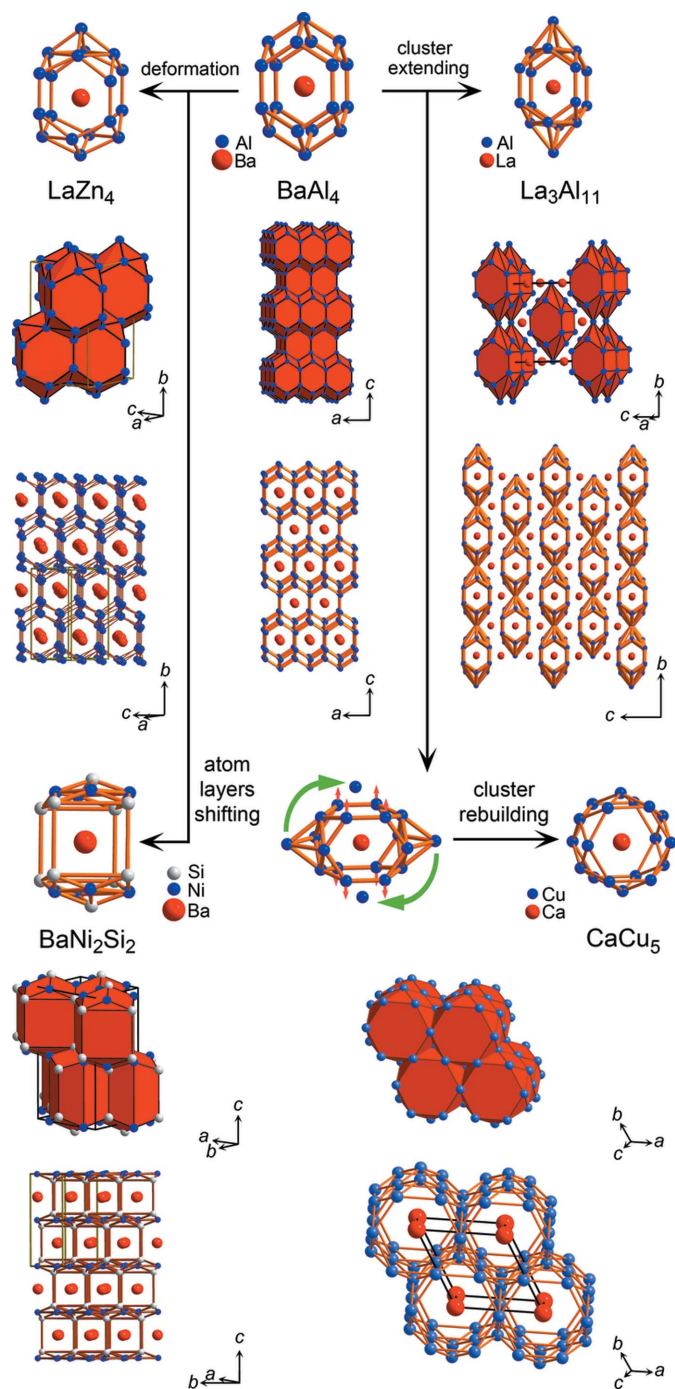


Figure 3
The relationship between the LaZn_4 , BaAl_4 , $\text{La}_3\text{Al}_{11}$, BaNi_2Si_2 and CaCu_5 structure types.

structure, with a reduction in symmetry from $I4/mmm$ to $Cmcm$ (Fig. 3). Shifting of the atomic layers in the BaAl_4 structure along the a and b unit vectors leads to the BaNi_2Si_2 structure type, again with a symmetry reduction from $I4/mmm$ to $Cmcm$. The structure of $\text{La}_3\text{Al}_{11}$ is built from two types of fragments: (i) layers of $[\text{LaAl}_{18}]$ clusters extending along b , sharing their faces and vertices; (ii) the remaining La atoms filling voids with 16 vertices between these layers. In this case, the symmetry is reduced from $I4/mmm$ to $Immm$. Finally,

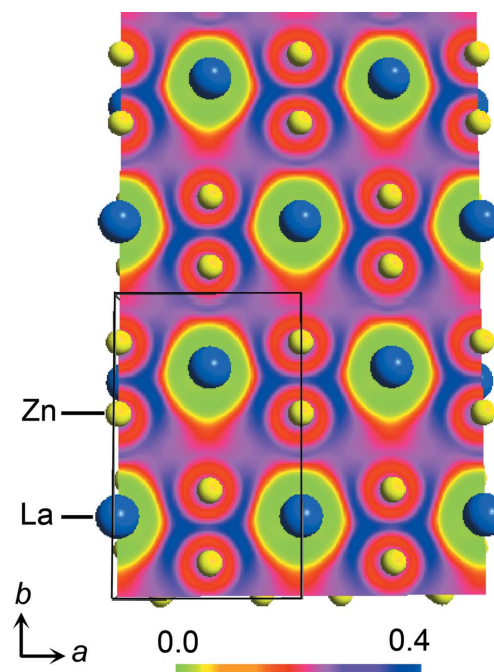


Figure 4
A section of the electron localization function (ELF), drawn parallel to the (001) plane at $z = \frac{3}{4}$.

rearrangement of the atoms in the fragment of the $\text{La}_3\text{Al}_{11}$ structure type leads to the main building block of the CaCu_5 structure type.

The electronic structure of LaZn_4 was calculated by means of the *TB-LMTO-ASA* program package (Andersen *et al.*, 1986). The electron localization function (ELF) and density of states (DOS) plots show a metallic-type conductivity (Figs. 4 and 5). Amongst other La–Zn compounds, $\text{LaZn}_{12.37}$ (Oshchapovsky, Pavlyuk, Dmytriv & White, 2011) and LaZn_5 (Oshchapovsky *et al.*, 2012) also display metallic behaviour and similar DOS plots. The main reason for such similarity is that the La atoms in $\text{LaZn}_{12.37}$, LaZn_5 and LaZn_4 have large first coordination spheres consisting of Zn atoms only. In these compounds, and also in $\text{La}_5\text{Zn}_2\text{Sn}$ (Oshchapovsky, Pavlyuk, Dmytriv, Chumak & Ehrenberg, 2011), the less electronegative La atoms donate their electron density to the more electronegative Zn and Sn atoms. Therefore, bonds between La and Zn/Sn atoms are mostly metallic but with some ionic component. Besides the dominant metallic component, the Zn–Zn bonds in LaZn_4 also reveal a weak covalent component with an ELF density up to 0.4 (see Fig. 4 and Table 1). In particular, the Zn1–Zn2 distances show a significant contraction [2.497 (3) Å compared with 2.66 Å for twice the metallic radius (Gibbs *et al.*, 1997)] and there are unusually weak La1–Zn3($x, y + 1, -z + \frac{1}{2}$) bonds with moderate bond lengths [3.4278 (12) Å]. The chemical bonding (COHP curve) exhibits strongly stabilizing $\text{Zn} \cdots \text{Zn}$ interactions between -8 and -7 eV, arising mostly from Zn d -orbitals (Fig. 5). These interactions are between atoms Zn1 and Zn2 ($-\text{iCOHP} = 1.069$ eV). The interactions observed between the La and Zn atoms are almost equal (Table 1) and their integrated crystal

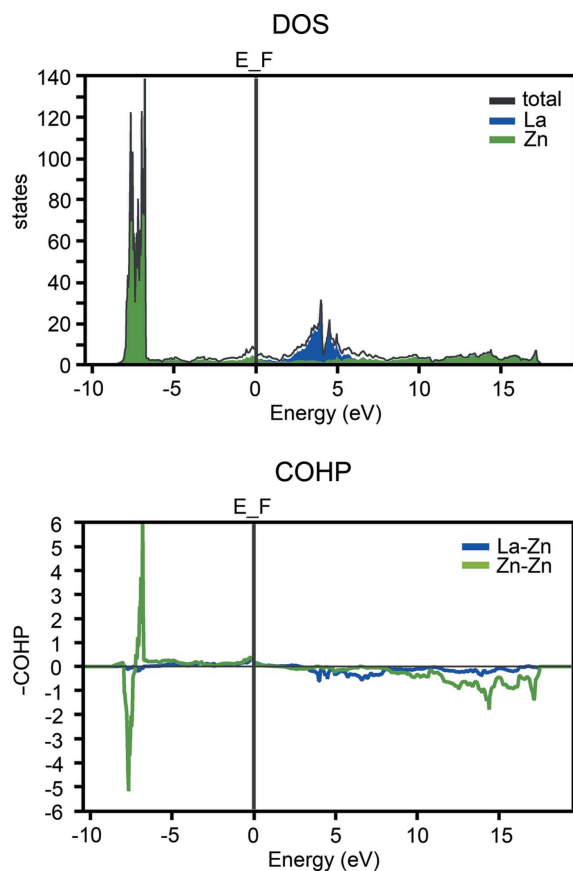


Figure 5
Density of states (DOS) plot and chemical bonding (COHP) curves.

orbital Hamilton populations are about 50% weaker than corresponding interactions between atoms Zn1 and Zn2.

Experimental

A small irregularly shaped single crystal was selected from an inhomogeneous La–Zn–Sn ternary alloy. The sample was prepared by melting stoichiometric amounts of the pure metals in an evacuated silica ampoule with subsequent annealing in a resistance furnace at 873 K for 30 d, followed by quenching in cold water. To establish that the structure of the LaZn₄ compound is not stabilized by the addition of Sn, the compound was re-synthesized by mixing stoichiometric amounts of Zn and LaZn powders with subsequent pressing into a pellet and with the same thermal treatment as described previously. Reaction between the alloy and the silica container was not observed. The resulting product contained mainly the LaZn₄ compound, together with small amounts of the compounds La₂Zn₁₇, La₃Zn₂₂, LaZn₅ and LaZn₂. This can be explained by slow flow of the chain of peritectic reactions which transform the congruent melting La₂Zn₁₇ compound into LaZn₄ (see Berche *et al.*, 2011, 2012).

Crystal data

LaZn ₄	$V = 400.2(2) \text{ \AA}^3$
$M_r = 400.47$	$Z = 4$
Orthorhombic, <i>Cmcm</i>	Mo $K\alpha$ radiation
$a = 6.340(2) \text{ \AA}$	$\mu = 33.82 \text{ mm}^{-1}$
$b = 10.312(3) \text{ \AA}$	$T = 296 \text{ K}$
$c = 6.122(2) \text{ \AA}$	$0.12 \times 0.10 \times 0.003 \text{ mm}$

Table 1

Selected bond lengths and associated bond energies.

Atoms	Distance (\AA)	iCOHP (eV per cell)
La1–Zn1 ⁱ	3.2885 (12)	–0.549
La1–Zn1 ⁱⁱ	3.2912 (12)	–0.547
La1–Zn2 ⁱ	3.3238 (13)	–0.521
Zn2–La1	3.545 (3)	–0.359
Zn2–La1 ^{vi}	3.5558 (14)	–0.438
La1–Zn3 ⁱⁱⁱ	3.3734 (12)	–0.485
La1–Zn3 ⁱⁱⁱ	3.4278 (12)	–0.033
Zn1–Zn2	2.497 (3)	–1.069
Zn1–Zn3	2.5725 (15)	–0.537
Zn2–Zn3 ⁱⁱ	2.6055 (14)	–0.725
Zn3–Zn3 ^{iv}	2.772 (3)	–0.495
Zn3–Zn3 ^v	3.0610 (11)	–0.381

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $x, y + 1, -z + \frac{1}{2}$; (iv) $-x, -y, -z$; (v) $x, y, -z + \frac{1}{2}$; (vi) $x + \frac{1}{2}, y - \frac{1}{2}, z$.

Data collection

Agilent SuperNova Dual (Cu at zero) diffractometer with an Atlas detector	1354 measured reflections 271 independent reflections 249 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2011)	$R_{\text{int}} = 0.055$
$T_{\text{min}} = 0.028, T_{\text{max}} = 1.000$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	18 parameters
$wR(F^2) = 0.112$	$\Delta\rho_{\text{max}} = 2.53 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -2.15 \text{ e \AA}^{-3}$
270 reflections	

Structure solution with direct methods in the space group *Cmcm* succeeded without problems. Initial refinement identified the La and Zn atoms clearly. In order to test for possible mixed site occupation involving Sn, refinements were made in which the site-occupation factors for the Zn atoms were refined, but the resulting values did not differ significantly from unity.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3038). Services for accessing these data are described at the back of the journal.

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