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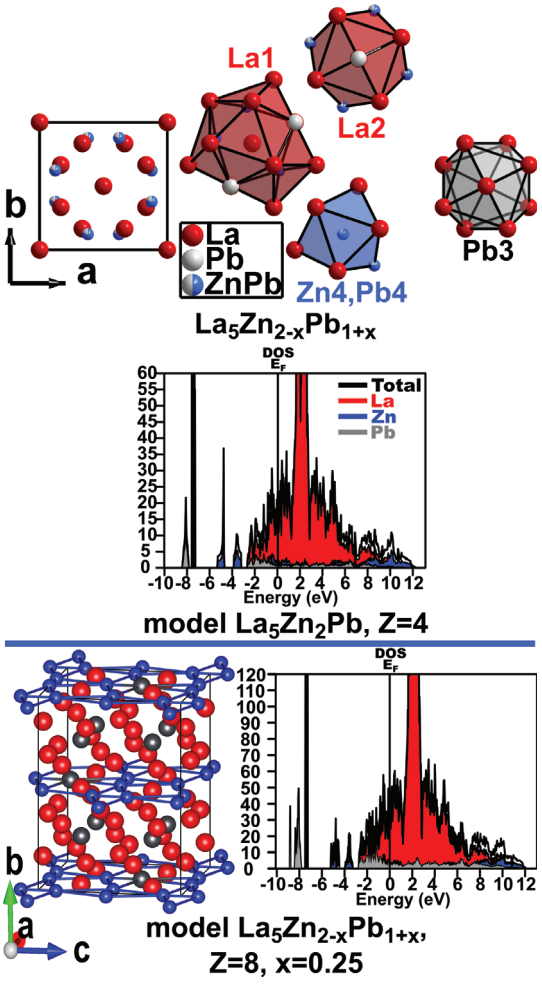
Investigation of the compound $La_5Zn_{2-x}Pb_{1+x}$ ($x = 0.20–0.32$)



https://doi.org/10.1515/ncrs-2017-0173
Received June 22, 2017; accepted October 10, 2017; available online November 8, 2017

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Abstract

$La_5Zn_{2-x}Pb_{1+x}$ ($x = 0.20–0.32$), tetragonal, $I4/mcm$ (no. 140), $a = 8.1673(12)$ Å, $c = 15.367(3)$ Å, $V = 1025.1(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0261$, $wR_{ref}(F^2) = 0.0441$, $T = 293$ K.

CCDC no.: 1578718

Projection of the unit cell and coordination environment of the atoms are shown in the Figure. DOS, calculated using models La_5Zn_2Pb, $La_5Zn_{2-x}Pb_{1+x}$ ($x = 0.25$, $Z = 8$), together with a structure of model $La_5Zn_{2-x}Pb_{1+x}$ are also shown in the Figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Single crystals of appropriate quality were selected from a La_7Zn_2Pb sample prepared by stepwise melting at max. 880 °C of the pure metals (>99.9% wt.) in an evacuated quartz ampoule in a resistance furnace and finally annealed at 600 °C.

Table 1: Data collection and handling.

Crystal:	Irregular platelet, metallic grey
Size:	0.08 × 0.06 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	43.99 mm^{-1}
Diffractometer, scan mode:	X-AREA, ω-scans
$2\theta_{max}$, completeness:	27.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4243, 332, 0.077
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 321
$N(param)_{refined}$:	582
Programs:	X-SHAPE & X-RED [1], SUPERFLIP [2], Jana2006 [3], DIAMOND [4], VESTA [5], publCIF [6], enCIFer [7]

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

Atom	x	y	z	U_{iso}*/U_{eq}
La1	0.66534(6)	0.16534(6)	0.14953(5)	0.0143(3)
La2	0	0	0	0.0251(4)
Pb3	0	0	0.25	0.0098(3)
Zn4[a]	0.12450(15)	0.62450(15)	0	0.0146(4)
Pb4[b]	0.12450(15)	0.62450(15)	0	0.0146(4)

[a]Occupancy: 0.901(5), [b]Occupancy: 0.099(5).

Experimental details

Reflections with $I < 3\,\sigma(I)$ were treated as unobserved. Reflections with $|I\text{-}avg(I)| > 20\,\sigma(I)$ were culled.

Discussion

$La_5Zn_{2-x}Pb_{1+x}$ with a small homogeneity range ($x = 0.20$–0.32) was found for the first time during a systematic investigation of the La-rich part of the ternary system La–Zn–Pb. Two single crystals were selected from a La_7Zn_2Pb sample and their crystal structures were determined by X-ray diffraction ($a = 8.133(2)$ Å, $c = 15.635(4)$ Å for the crystal with $x = 0.32$, and $a = 8.167(1)$ Å, $c = 15.367(3)$ Å for $x = 0.20$). The title compound is isostructural with La_5Zn_2Sn [8] and adopts the Mo_5SiB_2 type [9]. On the basis of the results of the structure refinement we suggest that $La_5Zn_{2-x}Pb_{1+x}$ has a homogeneity range: $x = 0.20$–0.32. Increasing Pb content slightly increases the cell volume ($V = 1034.2(4)$ Å^3 at $x = 0.32$, $V = 1025.1(3)$ Å^3 at $x = 0.20$).

A projection of the unit cell and the coordination environment are shown in the Figure. Three of the four crystallographically independent positions are completely ordered and only one is occupied by a statistical mixture of Zn4 and Pb4 atoms.

Coordination polyhedra of the atoms La1 and La2 are 15-vertex polyhedra (CN = 15) and a trigon-tetrahexahedron (CN = 14) respectively (Figure).

The closest coordination environment of the Pb3 atoms forms a bicapped tetragonal antiprism (CN = 10).

Atoms in positions, occupied by the statistical mixture Zn4 and Pb4, are enclosed into tricapped trigonal prisms (CN = 9), consisting of eight lanthanum atoms and one atom Zn4/Pb4.

Coordination polyhedra of the Pb3 atoms share their edges forming layers, which, in turn, are connected by shared vertices of building blocks. Voids between the layers are occupied by a statistical mixture Zn4 and Pb4.

Calculations of the electronic structure were performed using TB-LMTO-ASA v. 4.7 [10]. These calculations were performed for two fully ordered models:

1. La_5Zn_2Pb, mixed Zn/Pb site solely occupied by Zn (symmetry preserved);
2. $La_{40}Zn_{14}Pb_{10}$($La_5Zn_{2-x}Pb_{1+x}$, $x = 0.25$, Z = 8) mixed Zn/Pb site split into several sites, fully occupied by Zn or Pb each, with altered symmetry and double cell volume.

The second model, avoiding direct Pb-Pb contacts due to strong length contraction, was obtained by a series of group-subgroup transformations, in order to transform the Zn4/Pb4 position into several ones and to obtain the desired composition with a minimal volume (see details in Appendix).

DOS calculated for both structure models, have similar shapes (Figure) and show metallic bonding. Higher values of ELF around Zn and Pb in comparison to La atoms, and local minima at the DOS plots near Fermi level can indicate partial electron transfer from the La atoms to Zn, Pb and weak ionic bonding, which is typical for other related compounds [8, 11–14].

Acknowledgements: Funding for this research was provided by: Ministry of Education and Science of Ukraine (award No. 0115U003257) and National Science Centre, Poland (award No. 2014/15/B/ST8/00101).

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