

Lead Rare-Earth Oxyhalides: Syntheses and Characterization of  $\text{Pb}_6\text{LaO}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ )Oleg I. Siidra,<sup>†</sup> Sergey V. Krivovichev,<sup>\*,†</sup> Thomas Armbruster,<sup>‡</sup> and Wulf Depmeier<sup>§</sup>

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Yellowish elongated crystals of the two new compounds  $\text{Pb}_6\text{LaO}_7\text{Br}$  (**1**) and  $\text{Pb}_6\text{LaO}_7\text{Cl}$  (**2**) have been obtained by the method of solid-state reactions. Both structures can be described in the terms of oxo-centered tetrahedra. The structures of **1** and **2** consist of  $[\text{O}_7\text{Pb}_6\text{La}]^+$  chains that are built from oxocentered  $\text{OA}_4$  ( $\text{A} = \text{Pb}, \text{La}$ ) tetrahedra. The halogen ions connect the chains through weak  $\text{Pb}-\text{X}$  bonds. An arrangement of eight  $\text{OA}_4$  tetrahedra that all share the same central La atom forms a  $[\text{O}_8\text{Pb}_{10}\text{La}_3]^{13+}$  cluster. The clusters are linked into chains, and additional  $\text{OPb}_4$  tetrahedra are attached to the chains. Incorporation of Cl atoms instead of Br atoms into the structure causes a lowering of the symmetry from  $\text{Cmcm}$  to  $\text{C2/m}$ .

Lead oxyhalides can form a variety of unusual structures because of the presence of a stereochemically active lone pair and represent a class of inorganic materials with possible applications as ionic conductors<sup>1</sup> and highly anisotropic nanomaterials.<sup>2</sup> They are also of great interest from the viewpoint of environmental chemistry<sup>3</sup> and mineralogy.<sup>4</sup> The formation and precipitation of lead oxide and hydroxide

chlorides play an important role in the transport of lead from mines and mill tailings to the biosphere. To date, detailed chemical and structural information is available for pure oxychloride,<sup>4a,f,5</sup> oxybromide,<sup>6</sup> mixed oxyhalides,<sup>7</sup> and oxyiodide<sup>8</sup> systems. The incorporation of rare-earth elements into structures of lead oxyhalides may lead to new structural topologies and is also of interest from the viewpoint of interesting physical properties because rare-earth metal halides are important to the development, fabrication, and application of electronic materials.<sup>9</sup> Here we report on the syntheses and structures of the new compounds  $\text{Pb}_6\text{LaO}_7\text{X}$  [ $\text{X} = \text{Br}$  (**1**),  $\text{Cl}$  (**2**); Figure 1], high-temperature phases in the  $\text{PbO}-\text{PbCl}_2-\text{PbBr}_2-\text{La}_2\text{O}_3$  system that have been obtained by the solid-state reaction method.

Single crystals of **1** were grown by mixing  $\text{PbO}$ ,  $\text{PbBr}_2$ , and  $\text{La}(\text{NO}_3)_3$  in the ratio of 1:1:2. The produced mixture was loaded into a platinum crucible and kept at 910 °C for 1 h in air, followed by cooling to 685 °C with a cooling rate of 1 °C  $\text{min}^{-1}$  and then cooling down to room temperature over 8.5 h. The product consisted of yellowish needles of **1**, white transparent crystals of  $\text{Pb}_3\text{O}_2\text{Br}_2$ <sup>10</sup> in the mass of reddish-yellow isometric crystals of  $\text{La}_2\text{O}_3$ .<sup>11</sup> The crystals of **2** were produced by the same procedure, and  $\text{PbCl}_2$  was used instead of  $\text{PbBr}_2$ .

The structure of **1**<sup>12</sup> contains three symmetrically independent Pb sites, one La site, one Br site, and three O positions. In contrast, the structure of **2**<sup>12</sup> contains five symmetrically independent Pb sites, one La site, one Br site,

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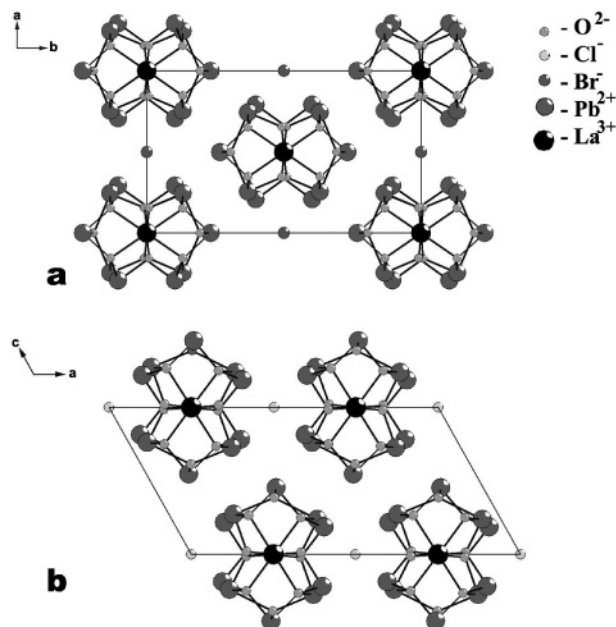
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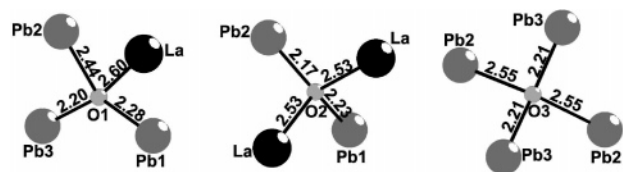
- (1) Matsumoto, H.; Miyake, T.; Iwahara, H. *Mater. Res. Bull.* **2001**, *36*, 1177–1184.
- (2) Sigman, M. B., Jr.; Korgel, B. A. *J. Am. Chem. Soc.* **2005**, *127*, 10089–10095.
- (3) (a) Ter Haar, G. L.; Bayard, M. A. *Nature* **1971**, *232*, 553–554. (b) Post, J.; Buseck, P. R. *Environ. Sci. Technol.* **1985**, *19*, 682–685. (c) Thomas, V. M.; Socolow, R. H.; Fanelli, J. J.; Spiro, T. G. *Environ. Sci. Technol.* **1999**, *33*, 3942–3948. (d) Harrison, R. M.; Whelan, M. *Environ. Sci. Technol.* **2000**, *34*, 4252–4253.
- (4) (a) Humphreys, D. A.; Thomas, J. H.; Williams, P. A.; Symes, R. F. *Mineral. Mag.* **1980**, *43*, 901–904. (b) Edwards, R.; Gillard, R. D.; Williams, P. A.; Pollard, A. M. *Mineral. Mag.* **1992**, *56*, 53–65. (c) Cooper, M. A.; Hawthorne, F. C. *Am. Mineral.* **1994**, *79*, 550–554. (d) Welch, M. D.; Criddle, A. J.; Symes, R. F. *Mineral. Mag.* **1998**, *62*, 387–393. (e) Welch, M. D.; Cooper, M. A.; Hawthorne, F. C.; Criddle, A. J. *Am. Mineral.* **2000**, *85*, 1526–1533. (f) Krivovichev, S. V.; Burns, P. C. *Eur. J. Mineral.* **2001**, *13*, 801–809. (g) Krivovichev, S. V.; Burns, P. C. *Eur. J. Mineral.* **2002**, *14*, 135–140. (h) Bonaccorsi, E.; Pasero, M. *Mineral. Mag.* **2003**, *67*, 15–21.

- (5) Vincent, H.; Perrault, G. *Bull. Soc. Fr. Miner. Cristallogr.* **1971**, *94*, 323–331.
- (6) (a) Keller, H. L. *Angew. Chem.* **1983**, *95*, 318–319. (b) Riebe, H.-J.; Keller, H. L. *Z. Anorg. Allg. Chem.* **1989**, *571*, 139–147.
- (7) Krivovichev, S. V.; Siidra, O. I.; Nazarchuk, E. V.; Burns, P. C.; Depmeier, W. *Inorg. Chem.* **2006**, *45*, 3846–3848.
- (8) Kramer, V.; Post, E. *Mater. Res. Bull.* **1985**, *20*, 407–412.
- (9) (a) Rao, C. N. R.; Cheetham, A. K. *Science* **1996**, *272*, 369. (b) Chuang, Y.-D.; Gromko, A. D.; Dessau, D. S.; Kimura, T.; Tokura, Y. *Science* **2001**, *292*, 1509. (c) Orenstein, J.; Millis, A. J. *Science* **2000**, *288*, 468.
- (10) Berdonosov, P. S.; Dolgikh, V. A.; Popovkin, B. A. *Mater. Res. Bull.* **1996**, *31*, 717–722.
- (11) Aldebert, P.; Traverse, J. P. *Mater. Res. Bull.* **1979**, *14*, 303–323.



**Figure 1.** Crystal structures of **1** (a) and **2** (b) projected along the extension of the metal oxide chains.

and five O positions. In the structure of **1**, the  $\text{Pb}^{2+}$  cations are coordinated by three  $\text{O}^{2-}$  anions (Pb3), four  $\text{O}^{2-}$  anions (Pb2), and three  $\text{O}^{2-}$  + two  $\text{Br}^-$  anions (Pb1). In the structure of **2**, the  $\text{Pb}^{2+}$  cations are coordinated by three  $\text{O}^{2-}$  + two  $\text{Cl}^-$  anions (Pb1 and Pb2), four  $\text{O}^{2-}$  anions (Pb3), four  $\text{O}^{2-}$  +  $\text{Cl}^-$  anions (Pb4), and three  $\text{O}^{2-}$  anions (Pb5) (Table 1). The coordination of  $\text{Pb}^{2+}$  cations is strongly distorted because of the stereoactivity of the  $6s^2$  lone electron pairs.<sup>14,16</sup> The  $\text{La}^{3+}$  cation has a slightly distorted cubic coordination, with the  $\text{La}-\text{O}$  bond lengths nearly 2.55 Å. Bond valence sums<sup>15</sup> for the Pb atoms range from 1.72 to 1.96 valence units (vu) in the structure of **1** and from 1.79 to 1.93 vu in the structure of **2**. Bond valence sums for the La sites are 2.68 vu in **1**



**Figure 2.** Oxo-centered tetrahedra in the structure of **1**.

**Table 1.** Selected Bond Distances (Å) in the Structures of **1** and **2**

Compound 1			
Pb1–O2	2.230(15)	Pb3–O1	2.193(11) (2×)
Pb1–O1	2.277(10) (2×)	Pb3–O3	2.211(7)
Pb1–Br	3.3096(9) (2×)		
		La–O2	2.526(9) (4×)
Pb2–O2	2.171(15)	La–O1	2.602(11) (4×)
Pb2–O1	2.436(10) (2×)		
Pb2–O3	2.543(10)		
Compound 2			
Pb1–O1	2.26(3)	Pb4–O4	2.437(18) (2×)
Pb1–O2	2.322(18) (2×)	Pb4–O5	2.69(3)
Pb1–Cl	3.202(7) (2×)	Pb4–Cl	3.473(7) (2×)
Pb2–O3	2.20(3)	Pb5–O2	2.16(2)
Pb2–O4	2.317(19) (2×)	Pb5–O4	2.17(2)
Pb2–Cl	3.187(8) (2×)	Pb5–O5	2.209(8)
Pb3–O3	2.21(3)	La–O3	2.521(16) (2×)
Pb3–O2	2.391(18) (2×)	La–O1	2.543(14) (2×)
Pb3–O5	2.45(3)	La–O4	2.57(2) (2×)
		La–O2	2.60(2) (2×)
Pb4–O1	2.09(3)		

and 2.66 vu in **2** and are notably lower than the expected value of 3 vu. Because of the variability of coordination polyhedra around cations and the high strength of metal–oxygen bonds in comparison to metal–halogen bonds, it is convenient to describe the structures of **1** and **2** in terms of metal oxide units separated by the halogen  $\text{X}^-$  ions. The structures contain three  $\text{O}^{2-}$  (**1**) and five  $\text{O}^{2-}$  (**2**) anions, which are tetrahedrally coordinated by  $\text{Pb}^{2+}$  and  $\text{La}^{3+}$  cations. Thus, each  $\text{O}^{2-}$  anion can be considered as being central for an oxocentered tetrahedron  $\text{OA}_4$  ( $\text{A} = \text{Pb}, \text{La}$ ). In the structure of **1**, the O1 and O2 atoms form mixed-metal  $\text{O1Pb}_3\text{La}$  and  $\text{O2Pb}_2\text{La}_2$  tetrahedra, respectively, whereas O3 is exclusively coordinated by Pb atoms, thus forming an oxo-centered  $\text{O3Pb}_4$  tetrahedron (**1**; Figure 2). Because of the lower symmetry, the number of mixed  $\text{OA}_4$  tetrahedra in the structure of **2** is doubled: O1 and O3 form  $\text{OPb}_2\text{La}_2$  tetrahedra, and O2 and O4 form  $\text{OPb}_3\text{La}$  tetrahedra. The O5 atom forms  $\text{OPb}_4$  (Figure 3). The average  $\langle \text{O}-\text{Pb} \rangle$  and  $\langle \text{O}-\text{La} \rangle$  bond lengths (Å) in the  $\text{OA}_4$  tetrahedra are as follows: O1–Pb 2.31, O2–Pb 2.20, O3–Pb 2.38, O1–La 2.60, O2–La 2.53 (**1**); O1–Pb 2.18, O2–Pb 2.29, O3–Pb 2.21, O4–Pb 2.31, O5–Pb 2.39, O1–La 2.54, O2–La 2.60, O3–La 2.52, O2–La 2.57 (**2**). Average distances between metal atoms within the  $\text{OA}_4$  tetrahedra ( $\langle \text{Pb}\cdots\text{La} \rangle$ ,  $\langle \text{Pb}\cdots\text{Pb} \rangle$ , and  $\langle \text{La}\cdots\text{La} \rangle$ ) in the structures of **1** and **2** are 3.79, 3.86, and 4.07 Å and 3.77, 3.86, and 4.05 Å, respectively. The  $\text{OA}_4$  tetrahedra link together to form one-dimensional  $[\text{O}_7\text{Pb}_6\text{La}]^+$  polycationic chains. The topology of the chains can be described as being based upon an arrangement of eight  $\text{OA}_4$  tetrahedra that all share the same central La atom. This complex has the  $[\text{O}_8\text{Pb}_{10}\text{La}_3]^{13+}$  composition (Figure 4) and represents a fragment of the fluorite ( $\text{CaF}_2$ ) structure, where each Ca atom is shared between eight  $\text{FCA}_4$  tetrahedra. In

(12) Crystallographic data for  $\text{Pb}_6\text{LaBrO}_7$  (**1**): orthorhombic,  $Cmcm$ ,  $a = 9.5896(17)$  Å,  $b = 16.146(3)$  Å,  $c = 8.1459(15)$  Å,  $V = 1261.2(4)$  Å<sup>3</sup>,  $Z = 4$ , crystal dims  $0.32 \times 0.05 \times 0.03$ ;  $\rho_{\text{calcd}} = 8.29$  g cm<sup>-3</sup>,  $\mu = 86.27$  mm<sup>-1</sup>. Data collection: Siemens Bruker CCD diffractometer, 3537 total reflections, 810 unique reflections, 569 unique reflections,  $|F_o| \geq 4\sigma F_o$ . The structure was solved by direct methods and refined to  $R1 = 0.0402$ ,  $wR2 = 0.067$ , and  $S = 0.983$ . Quantitative electron microprobe analysis provided the chemical formula  $\text{Pb}_{5.99}\text{La}_{1.03}\text{O}_7\text{Br}_{0.91}$ . Crystallographic data for  $\text{Pb}_6\text{LaClO}_7$  (**2**): monoclinic,  $C2/m$ ,  $a = 18.504(6)$  Å,  $b = 8.090(3)$  Å,  $c = 9.490(15)$  Å,  $\beta = 119.058(4)^\circ$ ,  $V = 1241.8(7)$  Å<sup>3</sup>,  $Z = 4$ , crystal dims  $0.28 \times 0.03 \times 0.02$ ,  $\rho_{\text{calcd}} = 8.18$  g cm<sup>-3</sup>,  $\mu = 84.62$  mm<sup>-1</sup>. Data collection: Siemens Bruker CCD diffractometer, 3480 unique reflections, 2279 unique reflections,  $|F_o| \geq 4\sigma F_o$ . The structure was solved by direct methods and refined to  $R1 = 0.0663$ ,  $wR2 = 0.1037$ , and  $S = 0.941$ . The crystal studied was pseudomerohedrally twinned, and the twinning matrix  $[1\ 0\ 0, 0\ -1\ 0, -0.5\ 0\ -1]$  was employed during the crystal structure refinement. The *HKLF5* program was used.<sup>13</sup> Electron microprobe analysis allowed the determination of Pb, La, and Cl. However, we were unable to get the correct chemical composition because of the overlapping of the  $\text{M}\alpha$  line for Pb and the  $\text{K}\alpha$  line for Cl.

(13) Bolte, M. *J. Appl. Crystallogr.* **2004**, *37*, 162–165.

(14) Shimoni-Livny, L.; Glusker, J. P.; Bock, C. V. *Inorg. Chem.* **1998**, *37*, 1853–1867.

(15) Krivovichev, S. V.; Brown, I. D. *Z. Kristallogr.* **2001**, *5*, 245–247. Brese, N. E.; O’Keeffe, M. *Acta Crystallogr.* **1991**, *47*, 192–197.

(16) Krivovichev, S. V.; Filatov, S. K. *Crystal chemistry of minerals and inorganic compounds with complexes of anion-centered tetrahedra*; St. Petersburg, 2001 (in Russian).

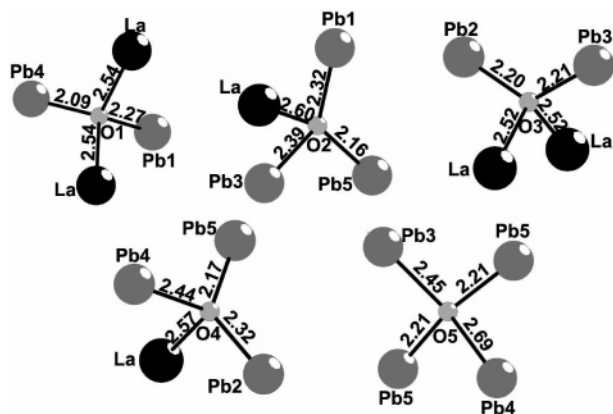


Figure 3. Oxo-centered tetrahedra in the structure of **2**.

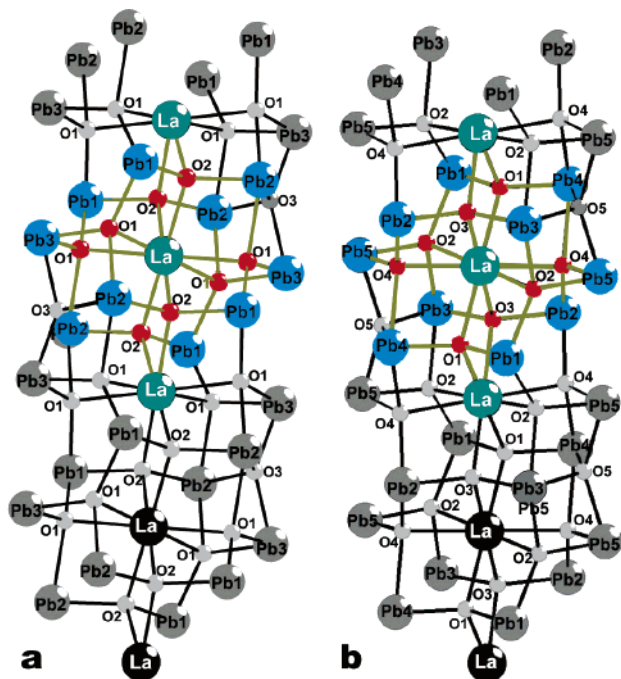


Figure 4. Metal oxide chains in the structures of **1** (a) and **2** (b). The  $[\text{O}_8\text{Pb}_{10}\text{La}_3]^{13+}$  clusters are marked in color.

general, the number of oxocentered tetrahedra sharing a common corner is no more than eight.<sup>16</sup> In Pb compounds, such kinds of complexes have been previously observed in  $\text{Pb}_{13}\text{O}_8(\text{OH})_6(\text{NO}_3)_4$ <sup>17</sup> and  $\text{Pb}_3\text{Te}_2\text{O}_6\text{Cl}_2$ .<sup>18</sup> It is important to note that the La-free  $\text{OPb}_4$  tetrahedra [ $\text{O}3\text{Pb}_4$  in **1** and  $\text{O}5\text{Pb}_4$  in **2**] do not participate in the  $[\text{O}_8\text{Pb}_{10}\text{La}_3]^{13+}$  clusters but are attached to them, providing their linkage into an one-

(17) Li, Y.; Krivovichev, S. V.; Burns, P. C. *J. Solid State Chem.* **2000**, *153*, 365–370.

(18) Porter, Y.; Halasyamani, P. S. *Inorg. Chem.* **2003**, *42*, 205–209.

dimensional chain. This makes the structure of compounds **1** and **2** even more complex.

Despite the number of symmetrically independent atoms, the metal oxide chains in **1** and **2** are topologically and geometrically identical. The halogen ions connect the chains through the weak Pb–X bonds. The shortest distance between the Pb atoms of two adjacent chains is 3.83 Å. The chains are extended along the *c* axis in the structure of **1** and along the *b* axis in **2**. It is of interest that incorporation of Cl atoms instead of Br atoms into the structure causes a lowering of the symmetry from *Cmcm* to *C2/m*. For all known lead oxyhalides that have chlorine and bromine analogues,<sup>4f,6b,11,19</sup> this effect has never been reported. As far as we know, this is the first example of lead oxyhalides with such a dramatic influence of halogen atoms on the symmetry.

In conclusion, we reported on the synthesis and structure of the first mixed-metal lead rare-earth oxyhalides of  $\text{Pb}_6\text{LaO}_7\text{X}$  (X = Cl, Br). Its structure is conveniently described on the basis of oxocentered  $\text{OA}_4$  tetrahedra. This approach is becoming more and more popular in the description of complex structural architectures in inorganic compounds with “additional”  $\text{O}^{2-}$  and  $\text{N}^{3-}$  anions.<sup>20</sup> In particular, it has been applied to pure  $\text{Pb}^{4f,g,6}$  and Ln compounds.<sup>21</sup> The compounds  $\text{Pb}_6\text{LaO}_7\text{X}$  (X = Cl, Br) reported here are the first for which the presence of mixed  $\text{OPb}_n\text{Ln}_{4-n}$  tetrahedra has been clearly recognized.

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**Supporting Information Available:** Files of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Siidra, O. I.; Krivovichev, S. V.; Depmeier, W. *Proc. Russ. Mineral. Soc.* **2007**, submitted for publication.

(20) (a) Ryazanov, M.; Hoch, C.; Mattausch, H.; Simon, A. *Z. Anorg. Allg. Chem.* **2006**, *632*, 2385–2388. (b) Mentré, O.; Ketatni, E. M.; Colmont, M.; Huvé, M.; Abraham, F.; Petricek, V. *J. Am. Chem. Soc.* **2006**, *128*, 10857–10867. (c) Huvé, M.; Colmont, M.; Mentré, O. *Inorg. Chem.* **2006**, *45*, 6604–6611. (d) Colmont, M.; Huvé, M.; Mentré, O. *Inorg. Chem.* **2006**, *45*, 6612–6621.

(21) (a) Lissner, F.; Schleid, Th. *Z. Anorg. Allg. Chem.* **2005**, *631*, 427–432. (b) Wontcheu, J.; Schleid, Th. *Z. Anorg. Allg. Chem.* **2005**, *631*, 309–315.