Crystal Structure of $La_3OBr[AsO_3]_2$

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Colorless needles of the arsenite bromide $La_3OBr[AsO_3]_2$ were synthesized from ammonium dihydrogen arsenate, ammonium bromide and lanthanum oxide in an NaBr/KBr flux at 900 °C. $La_3OBr[AsO_3]_2$ crystallizes with the centrosymmetric tetragonal $La_3OCl[AsO_3]_2$ type, space group $P4_2/mnm$. The structure was refined from single-crystal diffractometer data: $a = 13.0431(15)$, $c = 5.6127(7)$ Å, $wR2 = 0.0454$, 945 F^2 values, and 39 variables. It consists of chains of *trans*-edge-sharing $OLa_{4/2}$ tetrahedra which are coordinated by $[AsO_3]^{3-}$ units *via* the oxygen atoms.

Key words: Oxoarsenite, Rare Earth Compound, Crystal Structure

Introduction

During diverse NaCl/KCl salt flux syntheses of rare-earth metal(III) (*RE*) pnictide (*Pn*) oxides *RETPn*O (*T* = late transition metal) [1 – 3] we observed incorporation of the halide flux into the reaction products, leading to well-shaped single-crystals of $Eu_5[PO_4]_3Cl$ [4], $Ce_3OCl[AsO_3]_2$ [5] and $Pr_5O_4Cl[AsO_3]_2$ [6]. Furthermore we obtained a new structure type realized for the series $RE_4O_4Cl[XO_4]$ (*RE* = La, Pr, Nd, Sm, Eu, Gd; *X* = P, As), $RE_4O_4Br[PO_4]$ (*RE* = La, Pr, Nd, Sm) and $RE_4O_4Br[AsO_4]$ (*RE* = La, Pr) [7]. Optimization of the $La_4O_4Br[AsO_4]$ synthesis yielded a new arsenite bromide as by-product. The synthesis and structure refinement of $La_3OBr[AsO_3]_2$ are reported herein.

Experimental Section

Synthesis

The title compound was prepared by a solid-state reaction from a mixture of ammonium dihydrogen arsenate ($NH_4H_2AsO_4$), ammonium bromide (NH_4Br) and lanthanum oxide (La_2O_3) in an NaBr/KBr salt flux (1 : 1 molar ratio). $NH_4H_2AsO_4$, NH_4Br, and La_2O_3 were first mixed in a 1 : 1 : 2 molar ratio, heated in an open platinum crucible in air at 500 °C for 6 h and at 850 °C for 60 h. The product was then mixed with 20 equivalents of the salt flux and put in a silica tube which was sealed under vacuum. The tube was heated at 900 °C for 72 h. By decreasing the temperature at a rate of 10 °C/h to r. t. we obtained colorless, needle-shaped crystals of $La_3OBr[AsO_3]_2$ besides $La_4O_4Br[AsO_4]$ [7] in polycrystalline form.

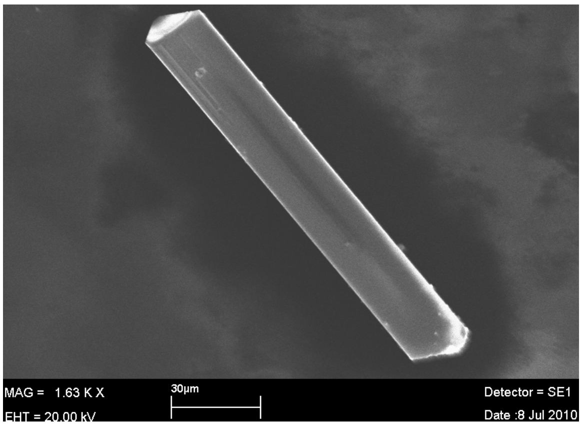

Fig. 1. SEM image of the $La_3OBr[AsO_3]_2$ single crystal used for the XR data collection.

EDX data

Semiquantitative EDX analyses of different needle-shaped single-crystals including the one investigated on the diffractometer (Fig. 1) were carried out with a Leica 420i scanning electron microscope using LaB_6, InAs and KBr as standards. The experimentally observed compositions were close to the ideal one. No impurity elements were observed.

X-Ray diffraction

The polycrystalline bulk sample and bunches of needles were characterized by a Guinier pattern (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha1}$ radiation and α-quartz ($a = 4.9130$, $c = 5.4046$ Å) as an internal standard. The powder pattern of the needle fraction (Fig. 2) could be indexed with the reflections of $La_3OBr[AsO_3]_2$ and a small contribution of $La_4O_4[AsO_4]Br$ (asterisks in Fig. 2). The correct indexing of both phases was ensured through intensity calculations [8].

A needle of $La_3OBr[AsO_3]_2$ suitable for single-crystal X-ray diffraction was selected on the basis of the size and the sharpness of the diffraction spots on Laue photographs

Table 1. Crystal data and structure refinement for $La_3OBr[AsO_3]_2$.

Composition	$La_3OBr[AsO_3]_2$
Description	colorless needle
Crystal size, μm^3	$14 \times 34 \times 116$
Molar mass, g mol^{-1}	758.5
Space group	$P4_2/mnm$
Unit cell dimensions	
a, pm	13.0431(15)
c, pm	5.6127(7)
Cell volume V, nm^3	0.9548(2)
Formula units Z	4
$F(000)$, e	1312
Calculated density, g cm^{-3}	5.27
Absorption coefficient, mm^{-1}	24.2
θ range, deg	2–32
Range in hkl	±19, ±19, ±8
Total no. of reflections	11182
R_{int}	0.1198
Transm. ratio (max / min)	0.701 / 0.261
Independent reflections	945
Reflections with $I \geq 3\,\sigma(I)$	625
Data / ref. parameters	945 / 39
$R1$ / $wR2$ for $I \geq 3\sigma(I)$	0.0260 / 0.0379
$R1$ / $wR2$ for all data	0.0633 / 0.0454
Goodness-of-fit on F^2	0.80
Weighting scheme	$w = 1/(\sigma^2(I) + 0.000004I^2)$
Extinction coefficient	3720(90)
Largest diff. peak / hole, e Å^{-3}	2.40 / −2.91

Table 2. Atom positions and equivalent isotropic displacement parameters (Å^2) for $La_3OBr[AsO_3]_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Site	x	y	z	U_{eq}
La1	4f	0.26254(3)	x	0	0.00712(12)
La2	8i	0.13755(3)	0.54694(3)	0	0.00962(11)
As	8i	0.97253(6)	0.21224(6)	0	0.00844(19)
Br	4g	0.35251(7)	0.64749(7)	0	0.0218(3)
O1	4d	0	1/2	1/4	0.0109(17)
O2	8i	0.0808(5)	0.2921(5)	0	0.0191(18)
O3	16k	0.9080(3)	0.2794(3)	0.2345(8)	0.0127(11)

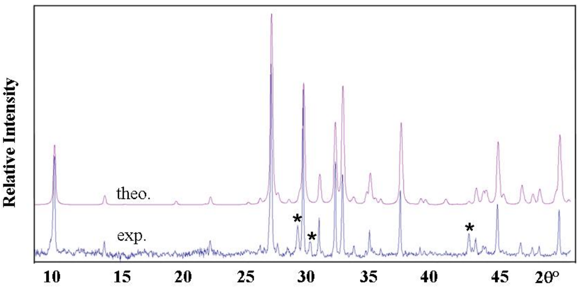

Fig. 2 (color online). Theoretical and experimental X-ray powder pattern (Cu$K_{\alpha 1}$ radiation) of $La_3OBr[AsO_3]_2$. Asterisks mark the impurity phase $La_4O_4Br[AsO_4]$.

obtained on a Buerger camera (using white Mo radiation). The data collection was carried out on a Stoe IPDS II diffractometer using MoK_α radiation. Data processing and refinements were performed with the JANA2006 program package [9]. A Gaussian-type absorption correction was applied, and the shape of the crystal was determined with the video microscope of the Stoe CCD. Details about data collection and refinement are summarized in Table 1.

Structure refinement

The $La_3O[AsO_3]_2Br$ data set showed a primitive tetragonal unit cell with high Laue symmetry. The systematic extinctions ($00l$ only observed for $l = 2n$, $h00$ only for $h = 2n$) led to the space groups $P4_2/mnm$ and $P4_2nm$, of which the centrosymmetric group was found to be correct during structure refinement. The atomic parameters of isotypic $La_3OCl[AsO_3]_2$ [10] were taken as starting values, and the structure was refined with the JANA2006 package [9] with anisotropic atomic displacement parameters (APDs) for all atoms The reliability factors coverged to the values listed in Table 1. The refined atomic positions and the ADPs are listed in Tables 2 and 3, respectively.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421948.

Discussion

The arsenite bromide $La_3OBr[AsO_3]_2$ is isotypic with $La_3OCl[AsO_3]_2$ [10]. Both lanthanum com-

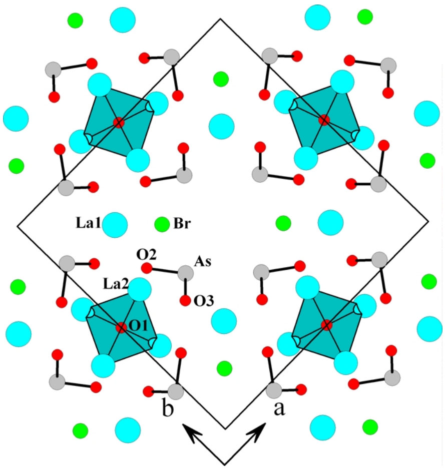

Fig. 3 (color online). Projection of the $La_3OBr[AsO_3]_2$ structure along the short unit cell axis. The chains of *trans*-edge-sharing $OLa_{4/2}$ tetrahedra and the $[AsO_3]^{3-}$ units are emphasized.

Table 3. Anisotropic displacement parameters (Å^2) for $La_3OBr[AsO_3]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La1	0.00737(16)	0.00737(16)	0.0066(3)	0.0020(2)	0	0
La2	0.00759(19)	0.00863(19)	0.0126(2)	−0.00061(15)	0	0
Br	0.0175(3)	0.0175(3)	0.0304(8)	−0.0075(5)	0	0
As	0.0090(3)	0.0083(3)	0.0081(4)	−0.0003(3)	0	0
O1	0.007(2)	0.007(2)	0.019(4)	0	0	0
O2	0.012(2)	0.018(3)	0.027(4)	−0.004(2)	0	0
O3	0.0142(17)	0.017(2)	0.007(2)	−0.0014(16)	0.0036(15)	−0.0014(15)

Table 4. Interatomic distances (Å), angles (deg) and bond valence sums (BVSs with coordination numbers in brackets) for $La_3OBr[AsO_3]_2$.

	Distance	BV[a]
La1–O2 (2×)	2.402(6)	0.537
La1–O3 (4×)	2.474(4)	0.442
	⟨2.45⟩	BVS [6] = 2.842
La1–Br (2×)	3.5184(9)	0.112
		BVS [8] = 3.066
La2–O1 (2×)	2.3585(5)	0.604
La2–O3 (2×)	2.584(4)	0.328
La2–O3 (2×)	2.686(4)	0.249
La2–O2 (2×)	2.985(2)	0.111
	<2.65>	BVS [8] = 2.584
La2–Br	3.0953(12)	0.353
		BVS [9] = 2.937
As–O2	1.754(6)	1.099
As–O3 (2×)	1.791(4)	0.995
	<1.78>	BVS [3] = 3.089

[a] BV = $e^{(r0-r)/b}$ with the following parameters: $b = 0.37$, r_0 (La–O) = 2.172, r_0 (As^{III}–O) = 1.789, and r_0 (La–Br) = 2.72 Å [12, 13].

pounds crystallize with the centrosymmetric space group $P4_2/mnm$. Small distortions (puckering effects) occur in the structures of $Ce_3OCl[AsO_3]_2$ [5] and $Gd_3OCl[AsO_3]_2$ [11]. The smaller rare earth cations cause a displacement of the chloride anions off the mirror plane, leading to non-centrosymmetric structures in space group $P4_2nm$.

A projection of the $La_3OBr[AsO_3]_2$ structure along the short unit cell axis is presented in Fig. 3, emphasizing the chains of *trans*-edge-sharing $OLa_{4/2}$ tetrahedra and the surrounding Ψ^1-tetrahedral $[AsO_3]^{3-}$ units. The bromine atoms are located in the centers of di-capped trigonal prisms formed by the lanthanum and arsenic atoms (Fig. 4). The interatomic distances and coordination numbers lead to the bond valence sums [12, 13] listed in Table 4, in good agreement with the salt-like formulation $(3La^{3+})O^{2-}Br^-(2AsO_3{}^{3-})$. For a more detailed crystal chemical discussion we refer to the previous work on isotypic $La_3OCl[AsO_3]_2$ [10] and $Ce_3OCl[AsO_3]_2$ [5].

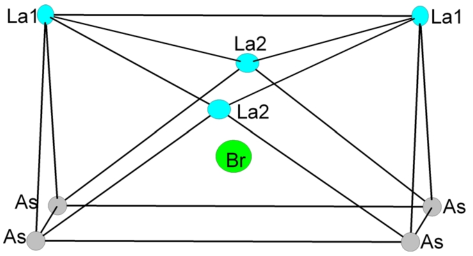

Fig. 4 (color online). Coordination of the bromine atoms in the centrosymmetric structure of $La_3OBr[AsO_3]_2$.

Acknowledgements

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