

Alkaline Earth Metal Oxyhalides Revisited – Syntheses and Crystal Structures of Sr_4OBr_6 , Ba_4OBr_6 and Ba_2OI_2

Olaf Reckeweg and Francis J. DiSalvo

Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA

Reprint requests to Dr. Olaf Reckeweg. Fax: +1-607-255-4137. E-mail: or22@cornell.edu

Z. Naturforsch. **2008**, *63b*, 519–524; received December 28, 2007

Single crystals of the compounds Ca_4OCl_6 , Sr_4OBr_6 , Ba_4OBr_6 , and Ba_2OI_2 were obtained by solid-state reactions. The crystals of Ba_2OI_2 are transparent and colorless and isopointal to K_2ZnO_2 adopting the orthorhombic space group *Ibam* (no. 72, $Z = 4$) with the cell parameters $a = 747.20(9)$, $b = 1392.02(18)$, and $c = 678.12(9)$ pm. Sr_4OBr_6 and Ba_4OBr_6 are isotypic to Ba_4OCl_6 (or isopointal to K_6ZnO_4) and crystallize in the hexagonal space group *P6₃mc* (no. 186, $Z = 2$) exhibiting the cell parameters $a = 982.20(4)$ and $c = 750.41(7)$ pm for Sr_4OBr_6 and $a = 1030.10(2)$ and $c = 785.92(4)$ pm for Ba_4OBr_6 . In the ternary systems Ca-O-X ($X = \text{Cl, Br or I}$) the only compound found other than the starting materials was the already known Ca_4OCl_6 which is also isotypic to Ba_4OCl_6 crystallizing in the hexagonal space group *P6₃mc* (no. 186, $Z = 2$) with the cell parameters $a = 903.30(6)$ and $c = 683.27(8)$ pm.

Key words: Alkaline Earth Metal, Strontium, Barium, Oxide, Bromide, Iodide, Oxyhalide, Oxybromide, Oxyiodide

Introduction

Recently the ‘pseudo’ alkaline earth metal oxyhalide Eu_2OI_2 [1] was synthesized and found to adopt the antitype of the well-known oxide K_2ZnO_2 [2]. A few weeks later we found by serendipity Sr_2OI_2 [3] which is – not too surprisingly – isotypic to Eu_2OI_2 .

Since the ternary oxyhalide compounds of ‘real’ and ‘pseudo’ alkaline earth metals such as Ca, Sr and Ba or Eu, Sm and Yb [4–19], respectively, have been explored intensively, it seemed surprising to us that nobody had ever encountered oxyhalides such as Eu_2OI_2 or Sr_2OI_2 before, and that only the well-known oxyhalides with the stoichiometry $M_4\text{OX}_6$ ($M = \text{Ca, Sr, Ba, Eu, Sm or Yb}$ and $X = \text{Cl, Br or I}$) [4–19] had been found.

Reading the papers of Frit *et al.* [8, 12], it seemed probable to us that the compounds reported next to Ba_4OX_6 as ‘ $\text{Ba}_9\text{O}_5\text{X}_8$ ’ ($X = \text{Br or I}$) [12] and two years later additionally ‘ $\text{Sr}_9\text{O}_5\text{I}_8$ ’ [8] are quite close in stoichiometry to $M_2\text{OX}_2$. We were able to index the powder diffractograms given for ‘ $\text{Sr}_9\text{O}_5\text{I}_8$ ’, ‘ $\text{Ba}_9\text{O}_5\text{Br}_8$ ’ and ‘ $\text{Ba}_9\text{O}_5\text{I}_8$ ’ isotypically to Sr_2OI_2 and to refine the cell parameters to results which compared well to Sr_2OI_2 (Table 1). Thus, we decided to revisit the ternary *AE-O-X* systems (*AE* = Ca, Sr, and Ba; *X* = Cl,

Br, and I). In this paper we present the syntheses and the structural characterization of Sr_4OBr_6 , Ba_4OBr_6 , and Ba_2OI_2 .

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless stated otherwise. The compounds were synthesized in two ways using slightly differing starting materials. The easiest way seemed to be the straightforward use of a 1 : 1 molar mixture of SrO or BaO (both Alfa Aesar, powder, 99.5 %) with SrBr_2 (Alfa Aesar, powder, ultra dry, 99.995 %), BaBr_2 (Alfa Aesar, powder, ultra dry, 99.998 %) or BaI_2 (Alfa Aesar, powder, ultra dry, 99.995 %), respectively. Unfortunately, this method led exclusively to powders of either Sr_4OBr_6 and SrO, Ba_4OBr_6 and BaO or Ba_2OI_2 .

The best results in terms of single crystals were achieved alternatively by a 1 : 1 molar mixture of the oxide coating scraped off from either a Sr ingot (Aldrich, ingot, 99 %) or a Ba rod (Aldrich, rod, ≥ 99 %) with the respective Sr or Ba halide. The intimately ground starting materials were arc-welded into a clean Ta container. The metal container was sealed into an evacuated silica tube. The tube was placed upright in a box furnace and heated to 1200 K within 12 h. After 3 d the furnace was switched off and allowed to cool to r. t. This method yielded colorless to red plates and nee-

Compound	Lines indexed / lines reported: ref. [8, 12]	Refined lattice parameters (pm) based on literature data: refs. [8, 12]	Experimental lattice parameters (pm) based on ref. [3] and this work	Compound	Table 1. Synopsis of the refinement results ^a of the literature powder diffractograms of 'AE ₉ O ₅ X ₈ ' (assuming a body-centered orthorhombic unit cell) with experimental data for Sr ₂ OI ₂ and Ba ₂ OI ₂ .
'Sr ₉ O ₅ I ₈ ' [8] (PDF 21-1185)	22 / 23	745.2(5) 1298.3(7) 649.2(3)	741.23(11) 1295.5(3) 647.5(1)	Sr ₂ OI ₂ [3]	
'Ba ₉ O ₅ Br ₈ ' [12] (PDF 19-118)	22 / 25	726.9(5) 1300.4(10) 658.6(5)	?	?	
'Ba ₉ O ₅ I ₈ ' [12] (PDF 19-119)	22 / 22	749.2(8) 1390.9(14) 674.7(7)	747.20(9) 1392.0(2) 678.12(9)	Ba ₂ OI ₂ This work	

Table 2. Details of the X-ray single crystal structure determination on Ca₄OCl₆, Sr₄OBr₆, Ba₄OBr₆ and Ba₂OI₂.

Compound	Ca ₄ OCl ₆	Sr ₄ OBr ₆	Ba ₄ OBr ₆	Ba ₂ OI ₂
Space group (no.), Z	<i>P</i> 6 ₃ <i>mc</i> , (186), 2	<i>P</i> 6 ₃ <i>mc</i> , (186), 2	<i>P</i> 6 ₃ <i>mc</i> , (186), 2	<i>I</i> bm \bar{a} , (72), 4
CSD number	418946	418452	391435	391434
Lattice parameters: <i>a</i> , pm	903.30(6)	982.20(4)	1030.10(2)	747.20(9)
<i>b</i> , pm	<i>a</i>	<i>a</i>	<i>a</i>	1392.02(18)
<i>c</i> , pm	683.27(8)	750.41(7)	785.92(4)	678.12(9)
Calculated density, g cm ⁻³	2.68	4.48	4.81	5.13
Crystal color	transparent colorless	transparent colorless	transparent light blue	transparent colorless
Crystal shape	needle	rectangular lath	elongated block	rectangular lath
Crystal size, mm ³	0.14 × 0.02 × 0.02	0.14 × 0.03 × 0.03	0.12 × 0.10 × 0.03	0.16 × 0.04 × 0.02
Diffractometer		Bruker X8 Apex II equipped with a 4 K CCD		
Radiation; monochromator; temperature, K		MoK α ($\lambda = 71.073$ pm); graphite: 173(2)		
Ranges, 2 θ_{\max} ; <i>h</i> , <i>k</i> , <i>l</i>	59.22°; -10 → 11, -8 → 12, ± 9	60.29°; -11 → 13, ± 13 , ± 10	70.13°; ± 16 , -11 → 16, ± 12	66.38°; -10 → 7, -17 → 21, -8 → 9
Distance detector-crystal, mm	40	40	40	40
Number of frames	782	840	951	2004
Exposure time, sec	10	30	10	15
Data correction	LP	LP, SADABS [22]	LP, SADABS [22]	LP, SADABS [22]
μ , mm ⁻¹	3.84	35.99	27.31	19.73
Measured reflections	3813	5685	8548	2624
Unique reflections	532	722	1214	625
Unique reflections with $F_0 \geq 4\sigma(F_0)$	472	605	1151	584
R_{int}	0.063	0.091	0.057	0.042
Refined parameters	26	25	25	17
Flack parameter <i>x</i> [25]	0.27(13)	0.04(4)	0.003(19)	–
Weight factors <i>x</i> / <i>y</i>	0.0144/0.170800	0.0065/0	0.0228/0	0.0204/11.0555
$R1^a/wR2^b/\text{GooF}^c$ (all refls.)	0.036/0.052/1.140	0.042/0.050/1.040	0.031/0.061/1.155	0.028/0.075/1.287
Max. shift/esd, last refinement cycle	< 0.00005	< 0.00005	< 0.00005	0.0001
Res. electron density: max./min., e Å ⁻³	0.42 (186 pm to Cl2) / -0.57 (238 pm to Cl2)	0.83 (60 pm to Sr1) / -0.88 (240 pm to Br2)	1.03 (118 pm to Ba2) / -2.01 (308 pm to Br2)	1.46 (122 pm to Ba) / -1.72 (183 pm to I)

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2] / 3$; ^c GooF: $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, with *n* being the number of reflections and *p* being the number of parameters.

dles of Sr₄OBr₆, colorless, transparent hexagonal needles of Ba₄OBr₆, or colorless, transparent lath-shaped crystals of Ba₂OI₂ as main products. The rest of the reaction mass consisted of excess alkaline earth metal and material encrusted into it.

We also tried to synthesize the corresponding Ca₄OBr₆, Ca₄OI₆, Ca₂OBr₂ and Ca₂OI₂. These attempts resulted in the recovery of recrystallized educts, whereas reactions aim-

ing at Ca₂OCl₂ yielded single crystals of Ca₄OCl₆ next to remaining starting materials.

Crystallographic studies

Samples of the reaction mixtures were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90 %) for single-crystal selection. Suitable single crystals of Sr₄OBr₆, Ba₄OBr₆ and Ba₂OI₂ were selected

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (pm²) of Ca₄OCl₆, Sr₄OBr₆, Ba₄OBr₆, (all *P*6₃*mc*, no. 186), Sr₂OI₂ [3] (for comparison), and Ba₂OI₂. (The latter two adopt the space group *Ibma*, no. 72).

Atom	W.-Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ca1	2 <i>b</i>	1/3	2/3	0.42790(20)	117(4)
Ca2	6 <i>c</i>	0.19804(5)	− <i>x</i>	−0.00022(10)	85(2)
Cl1	6 <i>c</i>	0.46371(6)	− <i>x</i>	0.70802(16)	97(2)
Cl2	6 <i>c</i>	0.13667(7)	− <i>x</i>	0.38453(15)	113(2)
O	2 <i>b</i>	1/3	2/3	0.1066(7)	49(11)
Sr1	2 <i>b</i>	2/3	1/3	0.5833(2)	100(3)
Sr2	6 <i>c</i>	0.80003(5)	− <i>x</i>	0.99841(9)	80(2)
Br1	6 <i>c</i>	0.53372(5)	− <i>x</i>	0.29416(10)	103(2)
Br2	6 <i>c</i>	0.86245(5)	− <i>x</i>	0.61183(11)	113(2)
O	2 <i>b</i>	2/3	1/3	0.8988(12)	67(22)
Ba1	2 <i>b</i>	1/3	2/3	0.41868(9)	89(1)
Ba2	6 <i>c</i>	0.19868(2)	− <i>x</i>	0.00016(5)	71(1)
Br1	6 <i>c</i>	0.46992(4)	− <i>x</i>	0.70781(9)	94(1)
Br2	6 <i>c</i>	0.14167(4)	− <i>x</i>	0.39436(10)	120(1)
O	2 <i>b</i>	1/3	2/3	0.0999(11)	43(13)
Sr	8 <i>j</i>	0.17227(5)	0.59013(3)	0	116(1)
I	8 <i>j</i>	0.14836(3)	0.84922(2)	0	148(1)
O	4 <i>b</i>	1/2	0	1/4	108(8)
Ba	8 <i>j</i>	0.17507(6)	0.59392(3)	0	100(2)
I	8 <i>j</i>	0.15813(7)	0.84990(3)	0	128(2)
O	4 <i>b</i>	1/2	0	1/4	121(15)

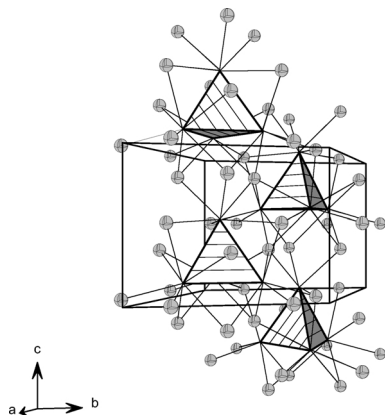


Fig. 1. Perspective view of the unit cell of AE₄OX₆ along the *c* axis. The coordination tetrahedra about O^{2−} are drawn as white hatched, O^{2−} and X[−] are displayed as crossed black and light grey circles, respectively. AE atoms are omitted for clarity. Displacement ellipsoids are drawn at the 95 % probability level.

under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen (*T* = 173(2) K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture from the air. Preliminary examination and subsequent data collection were per-

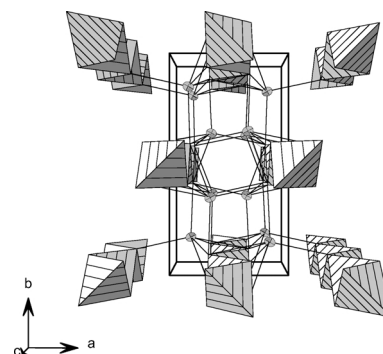


Fig. 2. Perspective view of the unit cell of Ba₂OI₂ along the *c* axis. The coordination tetrahedra about O^{2−} are drawn as white hatched, O^{2−} and I[−] are displayed as crossed black and light grey circles, respectively. Displacement ellipsoids are drawn at the 95 % probability level.

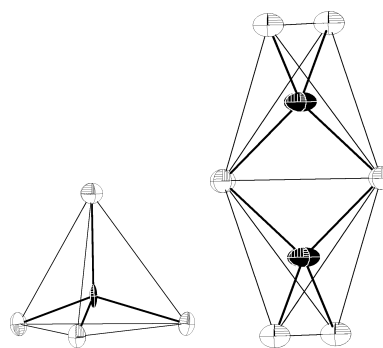


Fig. 3. Synopsis of an isolated tetrahedron taken from Ba₄OBr₆ (left) and two tetrahedra taken from Ba₂OI₂ (right). Ba²⁺ is displayed as crossed white circles, otherwise the same color code is applied as in Figs. 1 and 2.

formed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the respective lattice parameters were obtained by using APEX2 [20]. The program SAINT [21] was used to integrate the data. An empirical absorption correction was applied using SADABS [22]. The initial input file for solving the crystal structures was prepared by XPREP [23]. The atomic coordinates of Ca₄OCl₆ [4] or Sr₂OI₂ [3], respectively, were used as starting models which were refined by full-matrix least-squares techniques with SHELXL-97 [24]. The refinements converged and resulted in stable models for the crystal structures of Ba₄OBr₆ and Ba₂OI₂. For Ca₄OCl₆, a twin option had to be introduced since the crystal was found to be an inversion twin with a twin ratio of approximately 3 : 1. Sr₄OBr₆ had the other absolute structure as indicated by the Flack parameter *x* [25] and was inverted. After refining the inverted structure, the final Flack parameter *x* of 0.04(4) indicated the correct absolute structure

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	139(6)	U_{11}	72(6)	0	0	70(3)
Ca2	90(4)	U_{11}	85(4)	1(2)	-1(2)	53(4)
Cl1	99(4)	U_{11}	103(4)	2(2)	-2(2)	58(5)
Cl2	96(4)	U_{11}	118(4)	-5(2)	5(2)	27(5)
O	44(18)	U_{11}	61(20)	0	0	22(9)
Sr1	119(5)	U_{11}	63(6)	0	0	59(2)
Sr2	81(3)	U_{11}	84(3)	7(2)	-7(2)	45(4)
Br1	104(3)	U_{11}	98(4)	1(2)	-1(2)	50(4)
Br2	92(3)	U_{11}	130(4)	-12(2)	12(2)	27(4)
O	86(37)	U_{11}	31(42)	0	0	43(18)
Ba1	93(2)	U_{11}	81(3)	0	0	47(9)
Ba2	57(1)	U_{11}	104(2)	4(2)	-4(1)	31(1)
Br1	89(2)	U_{11}	101(3)	-6(1)	6(1)	44(3)
Br2	83(2)	U_{11}	155(3)	-16(1)	16(1)	14(2)
O	10(20)	U_{11}	107(35)	0	0	5(10)
Ba	126(3)	91(2)	84(3)	0	0	-30(1)
I	147(3)	117(3)	119(3)	0	0	-22(2)
O	169(38)	135(34)	58(36)	0	0	0

Table 4. Anisotropic displacement parameters U_{ij}^a (pm²) of Ca₄OCl₆, Sr₄OBr₆, Ba₄OBr₆, and Ba₂OI₂.

^a The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

model. Additional crystallographic details are summarized in Table 2.

Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 3, and Table 4 displays the anisotropic displacement parameters.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the deposition number CSD-418946 for Ca₄OCl₆, CSD-418452 for Sr₄OBr₆, CSD-391435 for Ba₄OBr₆ and CSD-391434 for Ba₂OI₂.

Results and Discussion

Crystal structures

Metal oxyhalides of the M_4OX_6 type have been well-known for a long time whereas M_2OI_2 compounds were only recently identified. The title compounds are isopointal to K₆ZnO₄ [26] and to K₂ZnO₂ [2], respectively. While the structure types have been described in great detail [4–19], we focus here on the description as a close-packed arrangement of the metal atoms. In the M_4OX_6 structures, the M atoms form a hexagonal close packing in which half of the halide atoms occupy three quarters of the octahedral voids while the remaining halogen and the oxygen atoms are located in 50 % of the tetrahedral voids. This can be expressed in short as $M_4(\square X_3)^0(\square X_3 \square_3 O)^t$. Therefore, the $[M_4O]^{6+}$ tetrahedra are strictly separated from each other and held together by the halide anions.

The M_2OI_2 type can be regarded as a stuffed variation of the SiS₂ structure which itself is derived from

the CaF₂ structure [27]. The metal atoms are in a cubic close packed arrangement in which one quarter of the tetrahedral voids is occupied by oxygen atoms to form 1D chains of *trans*-edge sharing, oxygen centered tetrahedra which can be expressed as ${}^\infty[M_{4/2}O]^{4+}$. This can be described as $M_2(\square_3O)^t(I_2)^0$, since the iodine atoms occupy the octahedral voids and hold together the chains of cationic tetrahedra.

Table 5 gives an overview of compounds containing $[M_4O]$ tetrahedra as a prominent structural motif including the title compounds, isotypic compounds and the suboxide NaBa₂O [28]. In the case of the M_4OX_6 -type compounds, the M–O–M angles in the isolated $[M_4O]$ tetrahedra are close to the ideal tetrahedral angle of 109.5°, deviating maximally by ±2°, but for the M_2OI_2 compounds and for NaBa₂O as well, the deviation ranges from 6 to 12°. This ‘squashing’ of the tetrahedra is a consequence of the *trans*-edge sharing connectivity pattern.

All distances are approximately in the expected range set by the sums of the pertinent ionic radii [29], but the M–O distances are shorter than expected by this concept (Table 5).

Conclusion

The compounds previously described as ‘Sr₉O₅I₈’ and ‘Ba₉O₅I₈’ were found to be Sr₂OI₂ [3] and Ba₂OI₂, respectively, as expected after the indexing and refinement of the reported X-ray powder diffractograms (Table 1). Neither ‘Sr₂OBr₂’ nor ‘Ba₂OBr₂’ could be obtained, of which we had expected to find at least the latter one (Table 1). Instead, Sr₄OBr₆ and

Table 5. Selected atomic distances (pm) and angles (deg) of M₄OX₆-type compounds, of M₂OI₂-type compounds (M = Ca, Sr, Ba, Eu, Sm or Yb and X = Cl, Br or I) and of NaBa₂O.

	Range of <i>d</i> (O–M)	Ionic radii sum: ref. [29]	Range of tetrahedral angles	Range of <i>d</i> (X–M)	Ionic radii sum: ref. [29]	Ref.
Ca ₄ OCl ₆	220.1–224.8	238	109.0–110.0	281.3–352.8	281	[4]
Ca ₄ OBr ₆	219.6–223.9	238	109.0–109.9	279.9–351.3	281	This work
Sr ₄ OCl ₆	234.9–236.6	256	108.6–110.4	296.0–363.9	299	[5]
Ba ₄ OCl ₆	250.1–251.0	273	107.6–111.3	311.6–376.0	316	[11]
Sr ₄ OBr ₆	236.8–238.9	256	108.2–110.7	308.9–375.8	314	This work
Ba ₄ OBr ₆	250.5–252.7	273	108.1–110.8	326.1–388.2	331	This work
Sr ₄ OI ₆	236.6–239.4	256	108.8–110.2	336.6–408.7	338	[9]
Ba ₄ OI ₆	254.2–255.5	273	107.6–111.3	355.6–408.6	355	[13]
Eu ₄ OCl ₆	237.5–236.2	255	107.8–111.1	295.9–361.2	298	[17]
Eu ₄ OBr ₆	236.8–239.3	255	108.8–110.8	308.1–374.9	313	[17]
Eu ₄ OI ₆	239.1–241.7	255	108.2–110.9	329.1–396.2	337	[18]
Sm ₄ OCl ₆	236.1–237.6	260	108.3–110.7	296.5–362.4	303	[14]
Sm ₄ OBr ₆	237.9–240.5	260	108.2–110.7	310.4–375.7	318	[15]
Sm ₄ OI ₆	239.3–243.6	260	108.0–110.9	330.6–396.5	332	[16]
Yb ₄ OCl ₆	224.5–228.9	240	108.9–110.0	283.5–352.7	283	[20]
Sr ₂ OI ₂	236.9	256	93.8–121.0	336.1–361.5	338	[3]
Eu ₂ OI ₂	239.0	255	94.5–120.1	338.2–363.9	337	[1]
Ba ₂ OI ₂	250.9	273	95.0–117.2	356.6–369.6	355	This work
NaBa ₂ O	252.9	273	98.6–116.3	–	–	[28]

Ba₄OBr₆ were isolated. These compounds were structurally characterized for the first time and are members of the AE₄OX₆ family (AE = Ca, Sr, Ba; X = Cl, Br, I). This family is complete except for Ca₄OX₆ (X = Br or I). The only Ca-containing compound we were able to synthesize was the well-known Ca₄OCl₆ which was the only compound other than the starting mate-

rials to be formed in the Ca-O-X (X = Cl, Br or I) system.

Acknowledgement

It is a pleasure to thank Dr. Emil B. Lobkovsky (Cornell University, Ithaca, NY, USA.) for letting us use his diffractometer.

- | | |
|---|--|
| [1] S. Hammerich, G. Meyer, <i>Z. Anorg. Allg. Chem.</i> 2006 , 632, 1244. | [12] B. Frit, B. Tanguy, P. Hagenmuller, <i>Bull. Soc. Chim. France</i> 1966 , 2190. |
| [2] R. Hoppe, E. Vielhaber, <i>Naturwiss.</i> 1964 , 51, 103. | [13] M. G. Barker, M. G. Francesconi, C. Wilson, <i>Acta Crystallogr.</i> 2001 , E57, i41. |
| [3] O. Reckeweg, F. J. DiSalvo, <i>Z. Kristallogr. (NCS)</i> 2006 , 221, 271. | [14] Th. Schleid, G. Meyer, <i>Z. Anorg. Allg. Chem.</i> 1987 , 553, 231. |
| [4] H.-J. Meyer, G. Meyer, M. Simon, <i>Z. Anorg. Allg. Chem.</i> 1991 , 596, 89. | [15] S. Hammerich, I. Pantenburg, G. Meyer, <i>Z. Anorg. Allg. Chem.</i> 2006 , 632, 2181. |
| [5] H. Hagemann, F. Kubel, H. Bill, <i>Eur. J. Inorg. Chem.</i> 1996 , 33, 1101. | [16] S. Hammerich, I. Pantenburg, G. Meyer, <i>Acta Crystallogr.</i> 2005 , E61, i234. |
| [6] O. Reckeweg, H.-J. Meyer, <i>Z. Kristallogr.</i> 1997 , 212, 235. | [17] Th. Schleid, G. Meyer, <i>Z. Anorg. Allg. Chem.</i> 1987 , 554, 118. |
| [7] O. Reckeweg, F. J. DiSalvo, <i>Sol. State Sci.</i> 2002 , 4, 575. | [18] W. Liao, R. Dronskowski, <i>Acta Crystallogr.</i> 2005 , C60, i23. |
| [8] B. Frit, M. Moakil-Chbany, B. Tanguy, P. Hagenmuller, <i>Bull. Soc. Chim. France</i> 1968 , 127. | [19] Th. Schleid, G. Meyer, <i>J. Less-Common Met.</i> 1987 , 127, 161. |
| [9] M. G. Barker, M. G. Francesconi, T. H. Shutt, C. Wilson, <i>Acta Crystallogr.</i> 2001 , E57, i44. | [20] APEX2 (version 1.22): Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) 2004 . |
| [10] B. Frit, B. Holmberg, J. Galy, <i>Acta Crystallogr.</i> 1970 , B26, 16. | |
| [11] H. J. Meyer, O. Reckeweg, private communication, 2004 , CSD 408175. | |

- [21] SAINT PLUS, Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.
- [22] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.
- [23] XPREP (version 6.14), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.
- [24] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [25] H. D. Flack, *Acta Crystallogr.* **1983**, A39, 876; H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, A55, 908.
- [26] P. Kastner, R. Hoppe, *Z. Anorg. Allg. Chem.* **1974**, 409, 69
- [27] U. Müller, *Anorganische Strukturchemie*, 2nd Edition, B. G. Teubner, Stuttgart **1992**, pp. 248.
- [28] G. V. Vajenine, A. Simon, *Angew. Chem.* **2001**, 113, 4348; *Angew. Chem. Int. Ed.* **2001**, 40, 4220.
- [29] R. D. Shannon, *Acta Crystallogr.* **1976**, A32, 751.