Syntheses and Crystal Structures of the Solid Solution $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and the Elusive Ba_2OBr_2

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Transparent and colorless single crystals of the compounds $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and Ba_2OBr_2 were obtained by solid-state reactions of $SrCl_2$, $SrBr_2$ and SrO (3 : 3 : 2 molar ratio) or by using an excess of BaO together with $BaBr_2$ and Ba as a flux with the molar ratio 3 : 2 : 2, respectively. Ba_2OBr_2 crystals are isopointal to K_2ZnO_2 adopting the orthorhombic space group *Ibam* (no. 72, $Z = 4$) with the cell parameters $a = 7247.44(10)$, $b = 1297.76(20)$ and $c = 657.43(10)$ pm. $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ is isotypic to Ba_4OCl_6 (or isopointal to K_6ZnO_4) and crystallizes in the hexagonal space group $P6_3mc$ (no. 186, $Z = 2$) with the cell parameters $a = 982.20(4)$ and $c = 750.41(7)$ pm.

Key words: Alkaline Earth Metal, Strontium, Barium, Oxide, Chloride, Bromide, Solid Solution, Structure Elucidation

Introduction

Alkaline earth metal oxide halides were studied intensively in the 1960s [1, 2]. Before they were crystallographically characterized, in many cases as unwanted by-products of attempts to synthesize alkaline earth metals halides, hydrides and/or nitrides [3 – 5] due to oxygen contamination of the starting materials.

We recently noticed that the compounds reported as '$Ba_9O_5X_8$' (X = Br or I) [1] and two years later as '$Sr_9O_5I_8$' [2] were indeed Ba_2OI_2 [6] and Sr_2OI_2 [7], respectively. But we were not able to verify the existence of the compound reported as $Ba_9O_5Br_8$ [1] which still puzzled us. Another claim made in the early papers was that solid solutions such as $Sr_4OCl_{6-x}Br_x$ ($0 \leq x \leq 6$) can be prepared [2], rather than an ordered variant. This also seemed worth reexamining by single-crystal X-ray methods, since the coordination environment of the two halide positions is quite different in the respective parent compounds ($x = 0$ and 6).

In this paper we present the syntheses and the structural characterization of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and Ba_2OBr_2.

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless otherwise stated. To obtain $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$, a 3 : 3 : 2 molar mixture of $SrCl_2$, $SrBr_2$ (both Alfa Aesar, powder, ultra dry, 99.995 %) and SrO (Alfa Aesar, powder, 99.5 %) were intimately ground and arc-welded into a clean Ta container. Ba_2OBr_2 was synthesized by employing a 2 : 2 : 3 molar mixture of Ba, $BaBr_2$ (Alfa Aesar, powder, ultra dry, 99.995 %) and BaO (Alfa Aesar, powder, 99.5 %) where the Ba metal was added to explore its potential role as a flux for crystal growth. These reactants were arc-welded into a clean Ta container in an argon atmosphere with minimal exposure to air. In both cases, the welded metal container was subsequently sealed into an evacuated silica tube. The reaction containers were placed upright in a box furnace and heated to 1300 K within 12 h. This temperature was held for another 12 h. The furnace was then cooled to 1200 K and held at that temperature for 3 d before it was switched off and allowed to cool to r. t.

No solid solutions such as $Sr_4OCl_{6-x}I_x$ were found, but only a mixture of Sr_4OCl_6 [3] and Sr_4OI_6 [8] – as reported before by Frit *et al.* [2].

$Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ was obtained as the main product (> 80 % judging from the powder X-ray diffraction diagram along with some unreacted $SrBr_2$ and SrO) in the form of single crystalline colorless and transparent needles, while Ba_2OBr_2 formed colorless, transparent rectangular plates (> 50 %) next to red transparent BaO spheres and some leftover Ba metal.

Crystallographic studies

Samples of the product mixtures were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobuty-

Table 1. Details of the single-crystal structure determinations of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and Ba_2OBr_2.

Compound	$Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$	Ba_2OBr_2
M_r	708.11	450.5
Crystal color	transparent colorless	
Crystal shape	needle	rectangular plate
Crystal size, mm^3	$0.08 \times 0.02 \times 0.01$	$0.10 \times 0.05 \times 0.01$
Crystal system	hexagonal	orthorhombic
Space group (no.), Z	$P6_3mc$ (186), 2	*Ibma* (72), 4
a, pm	969.3(2)	724.4(1)
b, pm	a	1297.8(2)
c, pm	731.6(2)	657.4(1)
V, Å^3	595.3(2)	618.1(2)
D_{calcd}, g cm^{-3}	3.95	4.84
$F(000)$, e$^-$	628	760
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	28.2	25.5
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD	
Radiation ; λ, pm	MoK_α; 71.073	
Monochromator	graphite	
Scan mode; T, K	ϕ- and ω-scans; 173(2)	
Range $2\theta_{\max}$, deg	62.99°	62.29°
h, k, l	$-12 \rightarrow 11$, $-13 \rightarrow 14$, $-10 \rightarrow 19$	± 10, $-15 \rightarrow 18$, ± 9
Data correction	Lp, SADABS	
Transmission: min. / max.	0.5165 / 0.7462	0.4022 / 0.7462
Reflections: measd / unique	4600 / 735	2057 / 539
Unique reflections with $F_o \geq 4\sigma(F_o)$	577	494
R_{int} / R_σ	0.079 / 0.069	0.027 / 0.024
Refined parameters	27	16
Flack's x parameter	0.01(2)	–
$R1^a$ / $wR2^b$	0.0547 / 0.0456	0.0205 / 0.0384
GoF^c (all refl.)	0.976	1.059
Factors x / y (weighting scheme)^b	0 / 0	0.0167 / 0.2745
Max. shift / esd, last ref. cycle	< 0.00005	< 0.00005
$\Delta\rho_{\text{fin}}$ (max, min), e$^-$ Å^{-3}	0.99 (104 pm to Sr1) -0.85 (226 pm to X1)	0.89 (92 pm to Ba) -0.85 (80 pm to Br)
CSD number	423480	423479

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o{}^2,0) + 2F_c{}^2)/3$ and x and y are constants adjusted by the program; [c] $\text{GoF} = S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

lene > 90 %) for single-crystal selection. Suitable single crystals of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and Ba_2OBr_2 were selected 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 protecting it from oxygen and moisture in the air. Single-crystal X-ray diffraction data were collected 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 intensity data were manipulated with the program package [9] that came with the diffractometer. An empirical absorption correction was applied using SADABS [10]. The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared by XPREP [11]. The atomic coordinates of Sr_4OBr_6 [6] and Sr_2OI_2 [7], respectively, were used as starting models which were refined by full-matrix least-squares techniques with the use of SHELXL-97 [12] including Flack's x parameter [13] for $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$. The refinement for Ba_2OBr_2 converged after a few cycles, but for $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$, both halide positions showed displacement parameters about four times larger than those of the other atomic positions. Therefore, Br1 and Cl1 as well as Br2 and Cl2 occupancy were refined together on their respective crystallographic positions but were constrained to full occupancy. After introducing this mixed occupancy, the refinement converged as well. Refinements of the intensity data in the only t (*'translationengleiche'*) subgroup ($P3m1$, no. 156) of the space group typically found for M_4OX_6 compounds ($P6_3mc$, no. 186), where a splitting of the halide positions can be observed and refined, yielded the same structural results as the previous refinement. Attempts to find superstructure reflections by tripling the exposure time yielded no additional results. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2.

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-karlsruhe.de/request_for_deposited_data.html), on quoting the depository number shown in Table 1.

Results and Discussion

Crystal structures

Metal oxyhalides of the M_4OX_6 type have been known for a long time whereas M_2OX_2 compounds were only recently identified [6, 7, 14] in terms of their unit cell parameters, structure and correct composition (Table 3). The previously reported lattice parameters are somewhat larger than those obtained by us probably due to the fact that the powder data were obtained at r. t. while our measurements were carried out at 170 K. The title compounds are isopointal to K_2ZnO_2 [15] and to K_6ZnO_4 [16]. Most of the atomic distances are in the expected range set by the sums of the pertinent ionic radii [17], but the M–O distances are shorter than expected by this concept and the Sr–X distances for the solid solution $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ are nearly in the middle of the range set by Sr_4OCl_6 and

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}[a] (pm^2) of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ ($P6_3mc$, no. 186) and Ba_2OBr_2 (*Ibma*, no. 72).

Atom	Wyckoff site	Site Occupation Factor	x	y	z	U_{eq}
Sr1	6*c*	1	0.19922(4)	$-x$	0.00363(8)	147(2)
Sr2	2*b*	1	1/3	2/3	0.4318(2)	163(3)
Br1 / Cl1	6*c*	0.332(2) / 0.668(2)	0.53381(6)	$-x$	0.2144(2)	134(3)
Br2 / Cl1	6*c*	0.632(2) / 0.368(2)	0.13747(6)	$-x$	0.3967(1)	169(3)
O	2*b*	1	1/3	2/3	0.1083(12)	112(18)
Ba	8*j*	1	0.18796(3)	0.59841(2)	0	127(1)
Br	8*j*	1	0.15100(6)	0.85261(4)	0	166(1)
O	4*b*	1	1/2	0	1/4	126(8)

[a] U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Table 2a. Anisotropic displacement parameters U_{ij}[a] (pm^2) of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ and Ba_2OBr_2.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr1	146(3)	U_{11}	179(3)	3(2)	−3(2)	94(3)
Sr2	179(4)	U_{11}	129(6)	0	0	89(2)
Br1 / Cl1	134(5)	U_{11}	140(5)	0(3)	0(3)	71(6)
Br2 / Cl2	130(4)	U_{11}	192(5)	−11(2)	11(2)	23(4)
O	119(30)	U_{11}	99(40)	0	0	59(15)
Ba	158(1)	123(1)	100(1)	0	0	−33(1)
Br	196(2)	148(2)	153(2)	0	0	−19(2)
O	139(18)	149(22)	90(18)	0	0	0

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

Table 3. Synopsis of the refinement results[a] of the literature powder diffractograms of '$AE_9O_5X_8$' (assuming a body-centered orthorhombic unit cell) with single-crystal data for Ba_2OBr_2, Sr_2OI_2 and Ba_2OI_2.

Compound	Lines indexed / lines reported	Refined lattice parameters (pm) T = 293 K	Experimental lattice parameters (pm) T = 173 K	Compound
'$Sr_9O_5I_8$' [2]		745.2(5)	741.23(11)	Sr_2OI_2
(PDF No. 21-1185)	22 / 23	1298.3(7)	1295.5(3)	[7]
		649.2(3)	647.5(1)	
'$Ba_9O_5Br_8$' [1]		726.9(5)	724.4(1)	Ba_2OBr_2
(PDF No. 19-118)	22 / 25	1300.4(10)	1297.8(2)	this work
		658.6(5)	657.4(1)	
'$Ba_9O_5I_8$' [1]		749.2(8)	747.20(9)	Ba_2OI_2
(PDF No. 19-119)	22 / 22	1390.9(14)	1392.0(2)	[6]
		674.7(7)	678.12(9)	

[a] All lines not indexed had $I \leq 5\,\%\ I_{max}$.

Table 4. Selected atomic distances (in pm) of Sr_4OX_6-type and M_2OX_2-type compounds (M = Sr, Ba and X = Cl, Br or I).

	Range d(O–M)	Ionic radii sum [17]	Range d(X–M)	Ionic radii sum [17]	Ref.
Sr_4OCl_6	234.9 – 236.6	256	296.0 – 363.9	299	[3]
$Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$	236.7 – 237.8	256	304.1 – 372.3	299 / 314	this work
Sr_4OBr_6	236.8 – 238.9	256	308.9 – 375.8	314	[6]
Sr_2OI_2	236.9	256	336.1 – 361.5	338	[7]
Ba_2OBr_2	248.7	273	331.0 – 354.6	331	this work
Ba_2OI_2	250.9	273	356.6 – 369.6	355	[6]

Sr_4OBr_6 (Table 4). Both crystal structures adopted by the title compounds (Figs. 1 and 2) have already been described in detail [6, 14 – 16], therefore, we leave this out here and concentrate on the reaction conditions which led to the synthesis of Ba_2OBr_2 and on the discussion of ordered compound versus solid solution.

Solid solutions of M_4OX_6 compounds

Early on, Frit *et al.* reported solid solutions such as $Sr_{4-x}Ba_xOX_6$, $M_4OCl_{6-x}Br_x$, $M_4OBr_{6-x}I_x$, and $Sr_{4-x}Ba_xOBr_{6-x}I_x$ and their width of existence [1, 2]. Later on, doping experiments for luminescence measurements led to $Eu_{3.92}Sc_{0.08}OBr_6$ and $Eu_{1.63}Ba_{2.37}OBr_6$ [18], but also to Eu^{2+}- and Pb^{2+}-activated M_4OX_6 (M = Ca, Sr, Ba; X = Cl, Br) [19]. Since there is only one crystallographic position for M in M_4OX_6 compounds, the solid solution seemed to be without real alternative to us, whereas two crystallographic halide positions for X (Fig. 3) which are different in terms of their coordination environment make an

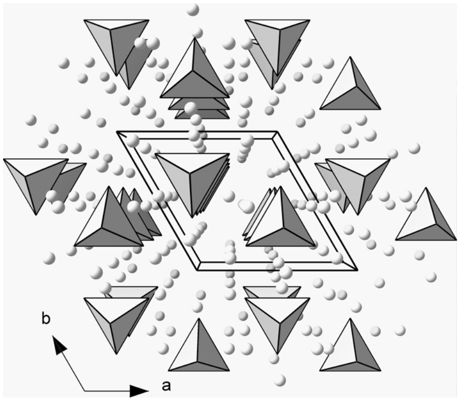

Fig. 1. Perspective view at the unit cell of $Sr_4OCl_{4-x}Br_x$ along the crystallographic *c* axis. The coordination tetrahedra about O^{2-} are drawn as white to grey polyhedra, X^- are displayed as light-grey shaded circles.

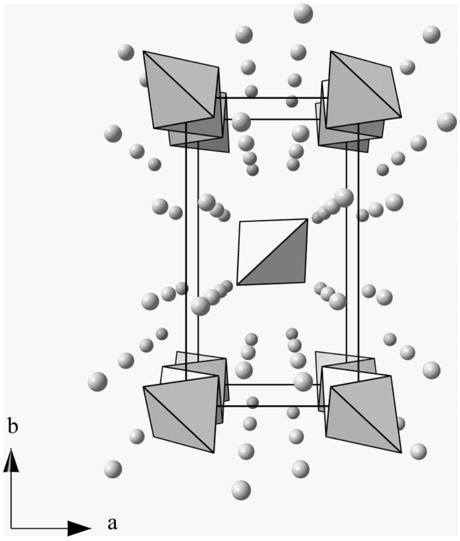

Fig. 2. Perspective view at the unit cell of Ba_2OBr_2 along the *c* axis. The coordination tetrahedra about O^{2-} are drawn as white to grey polyhedra, Br^- are displayed as light-grey shaded circles.

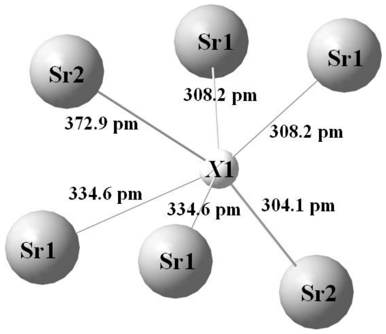

Fig. 3a. The coordination environment of $X1$ by Sr in $Sr_4OCl_{4-x}Br_x$. X are displayed as light-grey, Sr as white shaded circles.

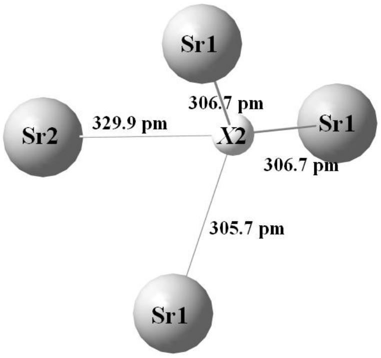

Fig. 3b. The coordination environment of $X2$ by Sr in $Sr_4OCl_{4-x}Br_x$. X are displayed as light-grey, Sr as white shaded circles.

ordered variant easily possible. Our synthesis attempts therefore targeted the composition '$Sr_4OBr_3Cl_3$', but with single-crystal X-ray methods neither a superstructure nor an ordering was observed. The refined composition of $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ is close to the targeted one and close to the calculated composition $Sr_4OBr_{2.8}Cl_{3.2}$ obtained using the experimentally determined cell volume under the assumption of a continuous volume increase for $Sr_4OCl_{6-x}Br_x$ ($0 \leq x \leq 6$). These results basically show the correctness of the claims made by Frit *et al.* [2]. It was reasoned that the solid solutions are formed because of the small difference of the ionic radii of the pair Cl^-/Br^- (15 pm) and Br^-/I^- (25 pm), respectively [16]. The large difference of the ionic radii (40 pm) of Cl^- and I^- must be the reason that no solid solutions such as $Sr_4OCl_{6-x}I_x$ are formed, but only a mixture of Sr_4OCl_6 and Sr_4OI_6 can be observed – as we observed and as reported before by Frit *et al.* [2].

Reaction conditions for the synthesis of Ba_2OBr_2

Previous attempts to synthesize Ba_2OBr_2 under metal-rich conditions with oxygen as the limiting reagent were unsuccessful [6]. Frit *et al.* reported the use of stoichiometric mixtures of $BaBr_2$ and BaO, but only powders were obtained [1]. According to our experience, either powders are formed or Ba_4OBr_6 is formed, if the halide is present in at least stoichiometric amounts [6]. Since we have experience growing single crystals from low-melting metal fluxes, we just changed the limiting reagent from BaO to $BaBr_2$

– which was found to push the chemical equilibrium to the side of Ba_2OBr_2. The Ba melt also seems to be necessary for single-crystal formation, probably due to the fact that BaO is a refractory compound.

Conclusion

The compound previously described as '$Ba_9O_5Br_8$' and predicted to be Ba_2OBr_2 [6] was synthesized using an excess of BaO and Ba metal as a flux. $Sr_4OBr_{2.89(2)}Cl_{3.11(2)}$ has been synthesized and characterized. No ordering of the halide anions was observed. With our synthetic strategies, no solid-solution compounds such as $Sr_4OCl_{6-x}I_x$ were found but only the compounds Sr_4OCl_6 [3] and Sr_4OI_6 [8] were obtained due to phase separation.

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[1] B. Frit, B. Tanguy, P. Hagenmuller, *Bull. Soc. Chim. France* **1966**, 2190.

[2] B. Frit, M. Moakil-Chbany, B. Tanguy, P. Hagenmuller, *Bull. Soc. Chim. France* **1968**, 127.

[3] H. Hagemann, F. Kubel, H. Bill, *Eur. J. Inorg. Chem.* **1996**, *33*, 1101; O. Reckeweg, H.-J. Meyer, *Z. Kristallogr.* **1997**, *212*, 235.

[4] H.-J. Meyer, O. Reckeweg, *private Communication*, **2004**; CSD 408175.

[5] O. Reckeweg, F. J. DiSalvo, *Solid State Sci.* **2002**, *4*, 575.

[6] O. Reckeweg, F. J. DiSalvo, *Z. Naturforsch.* **2008**, *63b*, 519.

[7] O. Reckeweg, F. J. DiSalvo, *Z. Kristallogr. (NCS)* **2006**, *221*, 271.

[8] M. G. Barker, M. G. Francesconi, T. H. Shutt, C. Wilson, *Acta Crystallogr.* **2001**, *E57*, i44.

[9] APEX2 (version 1.22) and SAINT PLUS, Software for the CCD system, Bruker Analytical X-ray Systems, Madison, Wisconsin (USA) **2004**.

[10] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.

[11] XPREP (version 6.14), Bruker Analytical X-ray Systems, Madison, Wisconsin (USA) **2003**.

[12] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**; see also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[13] H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876; H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, *A55*, 908.

[14] S. Hammerich, G. Meyer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1244.

[15] R. Hoppe, E. Vielhaber, *Naturwissenschaften* **1964**, *51*, 103.

[16] P. Kastner, R. Hoppe, *Z. Anorg. Allg. Chem.* **1974**, *409*, 69

[17] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751.

[18] S. Hammerich, Dissertation, Universität zu Köln, Cologne (Germany) **2006**.

[19] W. J. Schipper, Z. A. E. P. Vroon, G. Blasse, T. Schleid, G. Meyer, *Chem. Mater.* **1992**, *4*, 688.