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Syntheses and Crystal Structures of $PbSbO_2Br$, $PbSbO_2I$, and $PbBiO_2Br$

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Dedicated to Professor Gerd Meyer on the Occasion of His 60th Birthday

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Abstract. Transparent single crystals of $PbSbO_2Br$ (green), $PbSbO_2I$, and $PbBiO_2Br$ (yellow) were obtained by solid state reactions of stoichiometric amounts of PbO, Pn_2O_3 (Pn = Sb, Bi) and PnX_3 (X = Br, I). The crystal structures were determined from single-crystal X-ray data. The title compounds crystallize tetragonally in the space group $I4/mmm$ (No. 139): Lattice constants and refinement values are: $PbSbO_2Br$: a = 3.9463(3), c = 12.849(1) Å, V = 200.10(3) Å^3, and Z = 2, R_1 = 0.0236, and wR_2 = 0.0513. $PbSbO_2I$: a = 4.0074(3), c = 13.627(2) Å, V = 218.84(3) Å^3, and Z = 2, R_1 = 0.0244, and wR_2 = 0.0538. $PbBiO_2Br$: a = 3.9818(2), c = 12.766(2) Å, V = 202.39(4) Å^3, and Z = 2, R_1 = 0.0276, and wR_2 = 0.0715. The compounds are isotypic and crystallize in the *anti*-$ThCr_2Si_2$ structure type with lead and Pn statistically disordered on one common position. In case of Pn = Sb a slight separation of the positions of the cations becomes obvious. Optical bandgaps were determined by UV/Vis spectroscopy. They are 2.67 eV ($PbSbO_2Br$), 2.48 eV ($PbSbO_2I$), and 2.47 eV ($PbBiO_2Br$).

Introduction

The minerals *Nadorite* $PbSbO_2Cl$ and *Perite* $PbBiO_2Cl$ and their homologous bromide and iodide compounds have been in focus of research since many years. *Perite* was first found in Langban, Sweden in 1960. The crystal structure of *Perite* was first solved by *Gillberg* in 1960 [1]. He determined orthorhombic symmetry for *Perite*. However, in 1976 a *Perite* with tetragonal symmetry was found in Australia [2]. *Nadorite* was first described in 1941 by *Sillén* with orthorhombic symmetry [3], the crystal structure is described in [4]. The first report of a synthetic analogue of *Nadorite* was not until 2002 [5]. It was tried to synthesize the homologues compounds with bromine and iodine since the first discovery of *Perite* and *Nadorite*. The first characterization of these synthetic compounds from X-ray powder data was reported in 1970 [6]. In 1985 the single-crystal X-ray structure of $PbBiO_2I$ was determined [7]. Very recently $PbBiO_2Br$ was described as a catalyst for photocatalytic degradation of organic dyes [8]. Surprisingly, there are no single crystal structure data of this compound available in literature. However, it is desirable to have a good knowledge of structural data in case of compounds, which are discussed as promising heterogeneous catalysts in order to get some idea about the catalytic processes. In addition, the question arises for a structural differentiation of Pb^{2+} and Sb^{3+} located on one crystallographic position. As observed earlier one finds a clear tendency of Sb^{3+} to prefer a small number of short contacts to counterions and in addition to have a greater number of long distances to further counterions. The gap between such short and long distances differs significantly in case of isotypic Bi^{3+} compounds, i.e., the distances vary in a much smaller range, see [9–11] for a discussion. Herein, we report on the synthesis and single-crystal X-ray structure determination of $PbBiO_2Br$ and its homologues compounds $PbSbO_2Br$ and $PbSbO_2I$.

Results and Discussion

$PbSbO_2Br$, $PbSbO_2I$, and $PbBiO_2Br$ are isotypic and crystallize tetragonally in the space group $I4/mmm$ (No. 139) with two formula units per unit cell in the *anti*-$ThCr_2Si_2$ structure [12]. Crystallographic data and experimental details of the data collection are listed in Table 1.

Figure 1 shows the crystal structure of $PbPnO_2X$ along [010]. The structures consist of metal oxide layers perpendicular to [001] separated by halide ions. This matches with a Sillén X1-phase [13]. In the metal-oxide layer the metal position seems to be statistically occupied by lead and antimony, respectively and bismuth, in the ratio 1:1, which was confirmed by free refinement of the occupancies. This agrees with the model for cation ordering in Sillén X1-phases [14]. However, the assumption of a statistical distribution of lead and antimony on one single position leads to a non-balanced electron density in the final difference-Fourier synthesis, i.e., the most negative residues are about 4 e$^-$Å^{-3} located close to the Pb/Sb position. An independent refinement of lead and antimony, respectively and bismuth, showed a displacement of the Pn atom along the z-axis towards the oxygen layer for the antimony-bearing compounds. The displacement is significant for the antimony compounds ($PbSbO_2Br$: 0.311 Å; $PbSbO_2I$: 0.371 Å) but in the range of error for $PbBiO_2Br$. This matches with the findings

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Table 1. Crystallographic data for $PbSbO_2Br$, $PbSbO_2I$ and $PbBiO_2Br$ [23].

Empirical formula	$PbSbO_2Br$	$PbSbO_2I$	$PbBiO_2Br$
Crystal system	tetragonal		
Space group	$I4/mmm$		
Lattice constants a, c /Å (powder refinement)	3.9463(3), 12.849(1)	4.0074(3), 13.627(2)	3.9818(4), 12.766(2)
V /Å^3, Z	200.10(3), 2	218.84(3), 2	202.39(4), 2
$\rho_{X\text{-ray}}$ /g·cm^{-3}	7.317	7.456	8.665
Diffractometer	STOE IPDS I		
2θ-range /°	$3.2 \leq 2\theta \leq 53.12$	$3.0 \leq 2\theta \leq 49.7$	$3.2 \leq 2\theta \leq 53.12$
μ(Mo-K_α) /mm^{-1}	58.557	51.467	94.632
T /K	293		
Crystal size /mm^3	0.2 × 0.17 × 0.03	0.23 × 0.05 × 0.08	0.12 × 0.14 × 0.04
Reflections (measured/unique)	1467, 84	1385, 80	1541, 86
R_{int}	0.0889	0.0658	0.1148
R_σ	0.0304	0.0247	0.0311
Structure solution	SIR2004 [18]		
Structure refinement	SHELXL [19]		
R_1 ($I > 2\sigma_I$)	0.0236	0.0244	0.0276
R_1 (all)	0.0236	0.0244	0.0291
wR_2 ($I > 2\sigma_I$)	0.0513	0.0538	0.0715
wR_2 (all)	0.0513	0.0538	0.0724
Parameters	12	12	9
GooF	1.291	1.277	1.397
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e·Å^{-3}	+1.288, –1.440	+0.808, –1.735	+2.144, –1.390

described in [9]. It seems quite reasonable to find a slightly different coordination for Sb^{3+} as compared to Pb^{2+}, whereas Bi^{3+} and Pb^{2+} can be described on one position with a mixed occupancy.

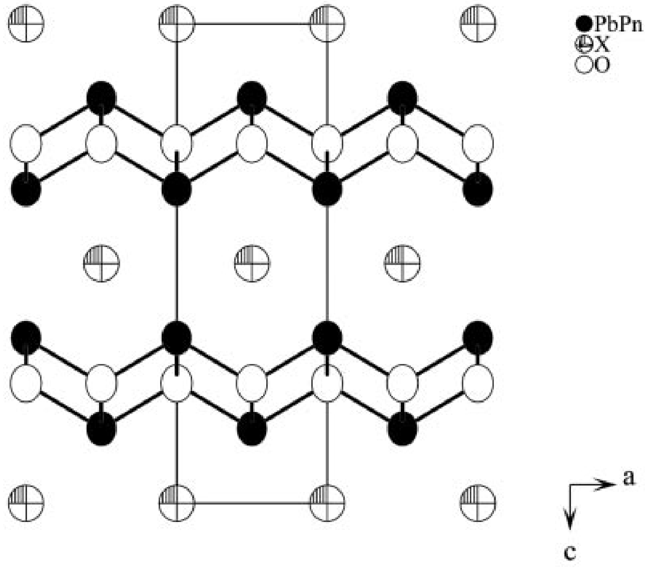

Figure 1. Crystal structure of $PbPnO_2X$ (Pn = Sb, Bi; X = Br, I) along [010]. The separation of the metal positions for $Pn = Sb^{3+}$ is not displayed. Ellipsoids correspond to a probability of 90 %.

Each oxygen atom is coordinated by four metal atoms with bond lengths d(Pb–O) = 2.400(1) Å / d(Sb–O) = 2.237(2) Å ($PbSbO_2Br$), d(Pb–O) = 2.428(8) Å / d(Sb–O) = 2.240(1) Å ($PbSbO_2I$), and d(Pb/Bi–O) = 2.3281(1) Å ($PbBiO_2Br$). The resulting OM_4-tetrahedra (M = metal) are edge-sharing and form MO-layers perpendicular to [001], separated by halide ions. Each metal atom is surrounded by four oxygen and four halogen atoms in a longer distance forming the motif of a distorted tetragonal antiprism. The halogen atoms have a slightly distorted cubic environment of eight metal atoms. The degree of distortion is more significant in case of the antimony compounds. The compounds are isotypic to $PbBiO_2I$ [7], Bi_2O_2Se [15], a series of compounds with the composition $(M, Bi)_2O_2X$ (M = alkaline earths, X = Cl, Br, I) [16], and $MPbF_2X$ (M = Li, Na, K) [17] (Table 2).

Table 2. Atom positions[a)] and equivalent displacement parameters[b)] for $PbSbO_2Br$, $PbSbO_2I$, and $PbBiO_2Br$.

Atom	Wyck.	Occ.	x	y	z	U_{eq} /Å^2
$PbSbO_2Br$						
Pb	4e	0.5	0	0	0.3563(1)	0.027(1)
Sb	4e	0.5	0	0	0.3321(3)	0.031(1)
Br	2a	1	0	0	0	0.033(1)
O	4d	1	0	1/2	1/4	0.047(2)
$PbSbO_2I$						
Pb	4e	0.5	0	0	0.3507(1)	0.023(1)
Sb	4e	0.5	0	0	0.3235(2)	0.019(1)
Br	2a	1	0	0	0	0.027(1)
O	4d	1	0	1/2	1/4	0.048(2)
$PbBiO_2Br$[c)]						
Pb/Bi	4e	0.5/0.5	0	0	0.3445(1)	0.029(1)
Br	2a	1	0	0	0	0.039(1)
O	4d	1	0	1/2	1/4	0.035(3)

a) Estimated standard deviations of the last significant digits in parantheses. b) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. c) Lead and bismuth are statistically disordered on one position in the ratio 1:1.

Optical bandgaps of 2.67 eV ($PbSbO_2Br$), 2.48 eV ($PbSbO_2I$), and 2.47 eV ($PbBiO_2Br$) were calculated from UV/Vis absorption spectra by extrapolation of the absorption edge to the base line. Figure 2 shows the absorption spectra of the title compounds.

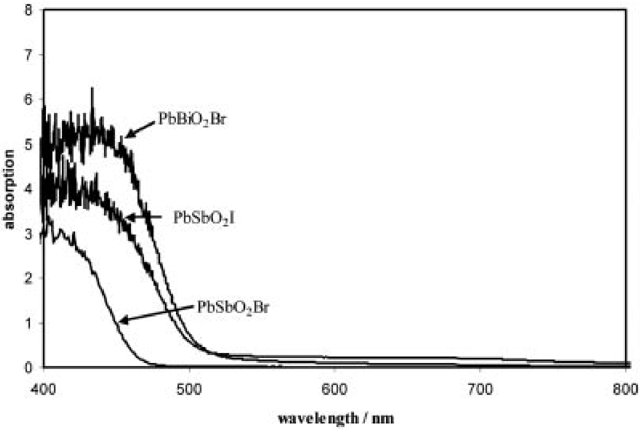

Figure 2. UV/Vis spectra of $PbSbO_2Br$, $PbSbO_2I$, and $PbBiO_2Br$.

Conclusions

A closer inspection of the structural data of $PbSbO_2Br$ and $PbSbO_2I$ with the heavier homologues $PbBiO_2Br$ and $PbBiO_2I$ shows a slightly increasing unit cell volume as expected. However, the ratio $c : a$ systematically decreases for about 2 % in both cases. This compression of the crystal structures in case of the bismuth compounds might be caused by the different site occupation behaviour of Pb^{2+} and Pn^{3+} for $Pn = Sb^{3+}$ as compared to $Pn = Bi^{3+}$. It is certainly due to the preference of Sb^{3+} to form shorter bonds to the oxide ions and to further increase the distances to the halide ions as a consequence. For Bi^{3+} a different trend is observed, namely the formation of a greater number of contacts. This leads to an elongation of the shorter contacts. However, this seems to be crucial for the $c : a$ ratio since the bonding interactions along [001] are increased by this behavior.

Experimental Section

$PbPnO_2X$ with Pn = Sb, Bi and X = Br, I were synthesized directly from PbO, Pn_2O_3 and PnX_3 in evacuated silica ampoules by annealing the corresponding 3:1:1 mixtures at 500 °C for 4 months ($PbSbO_2Br$), 550 °C for 12 days ($PbSbO_2I$), and 650 °C for 34 days ($PbBiO_2Br$). The product consists of pale green powder and pale greenish transparent crystals ($PbSbO_2Br$), yellow powder and yellow transparent crystals ($PbSbO_2I$ and $PbBiO_2Br$). The purity of the products was confirmed by X-ray powder diffraction. All compounds are air stable. Single crystal diffraction data of the title compounds were collected with a STOE IPDS I diffractometer equipped with a graphite monochromator and Mo-K_α radiation at room temperature. Numerical absorption corrections were performed with optimized crystal shapes using the X-SHAPE and X-RED programs [20, 21]. The structures were solved by direct methods (SIR2004 [18]) and refined by full-matrix least-squares using SHELXL [19]. The final cycles included anisotropic displacement parameters for all atoms and an extinction parameter for the antimony compounds. The lattice constants were refined from X-ray powder diffraction data and used in the structure refinements.

Diffuse UV/Vis reflectance spectra were recorded with a Bruins Instruments Omega 20 spectrometer. Data were transferred to absorption spectra by the Kubelka-Munk method [22].

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