ABiO₂X (A = Cd, Ca, Sr, Ba, Pb; X = halogen) *Sillen* X1 Series: Polymorphism Versus Optical Properties

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ABSTRACT: The *Sillen* X1 series of Bi³⁺A²⁺O₂X (A = Cd, Ca, Sr, Ba, Pb; X = Cl, Br, I) compounds is composed of three main crystallographic types, namely, the tetragonal form (space group (S.G.) *I4/mmm*), the orthorhombic form (S.G. *Cmcm*), and the monoclinic form (S.G. *P2₁/m*). Because of Bi³⁺/A²⁺ disorder the Bi³⁺ based photoluminescence (PL) of the tetragonal polytypes is quenched at room temperature (RT). In the two other ordered forms, the Bi–O–Bi connectivity is different but limited, such that bluish/greenish emission occurs at RT in the monoclinic CdBiO₂Cl and CaBiO₂Cl and orthorhombic SrBiO₂Cl and BaBiO₂Cl phases. The crystal structure of BaBiO₂Br was refined in the orthorhombic *Cmcm* space group and also shows RT emission. Focusing on the RT luminescent activity as a key parameter, the PL active compounds were investigated by means of density functional theory calculations and UV–visible reflectance spectroscopy. The influence of A and X ions on the excitation energy is discussed by analyzing the A–O–Bi and Bi–X bonding schemes and gives some insights for rational tuning of both the excitation and emission energies.

■ INTRODUCTION

Nowadays, the development of new phosphors is a hot topic in view of energy saving activities. In this context, ions with ns² configuration (Tl⁺, Pb²⁺, Bi³⁺) offer great benefit since they may lead to extremely bright emission and efficient excitation processes due to parity allowed, fast s² ↔ sp electronic transitions.¹ Bi³⁺ emerges due to its rather low toxicity, large availability and stability^{2,3} and is therefore an ideal candidate for applications in, for example, LEDs. In addition, not only Bi³⁺ generates bright emissions when incorporate as a dopant, but also when part of the structural framework and present in stoichiometric. Intense emission happens even at room temperature due to a low thermal quenching.⁴ Moreover, a recent report about the optical properties of undoped and lanthanide doped BiMg₂(XO₆) (X = P, V) phases revealed efficient room temperature luminescence of Bi³⁺ emitters, although the possibility for defect centers were argued.⁵ Besides, control of the luminescence properties can be achieved by incorporation of heterotypic anions (O²⁻ and X⁻ halogen ions) in pertinent bismuth oxide halides. In this context the luminescence of LaOCl:Bi was undoubtedly ascribed to Bi³⁺ emitters.⁶ Dealing with Bi rich phases and, despite significant thermal quenching, the *Sillen* phases ABiO₂Cl (A = Sr, Ba) and BaBiO₂Br show room temperature luminescence with a remarkably effect of the A and X ionic nature on the optical properties.⁷ For these three materials, no correlation between the electronic structure and the optical properties was analyzed yet, therefore the effect of A and X on the excitation and emission energies remains unexplored. In

addition, due to the existence of photocatalytic activities for BiOCl,⁸ CdBiO₂Cl and PbBiO₂Cl/Br,^{9–11} the rationalization of their optical properties (presence of radiative recombination) under UV illumination in the extended ABiO₂X series appears relevant.^{12–17} This aspect is of fundamental interest due to the duality between the needs for efficient electron–hole pairs separation upon photoexcitation for photocatalysis (PC), while enhanced radiative recombination is desired for light emission.

In this paper, we reinvestigated the ABiO₂X optical properties with the aim to establish correlations between the topology of the [ABiO₂] layers and intensity of the room temperature luminescence. Depending on the A and X sizes, three distinct crystal structures are adopted with various Bi/A ordering which is found to be a key parameter for Bi³⁺ concentration quenching. For active materials, the luminescent properties are discussed on the basis of first principle calculations presented in this paper and intrinsic bond features.

■ EXPERIMENTAL SECTION

Synthesis. Polycrystalline powder sample of all investigated compounds were prepared by conventional solid state reaction between BiOX (X = Cl, Br, I), CdO, PbO, SrCO₃, CaCO₃ or BaCO₃, respectively, in stoichiometric amounts. After the reactants were ground with a small amount of acetone, BaBiO₂Cl and CdBiO₂Cl were obtained as single phase materials after heating the mixture at 700 °C during 24h in an

Table 1. Symmetry and Lattice Parameters for All ABiO₂X Compounds from the Literature with Various A²⁺ Divalent Cations and X[−] Halides

S.G.	samples	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	RT ^a lumin
I4/mmm	CaBiO ₂ Br ¹²	3.9617(5)	3.9617(5)	12.584(3)		no
	CaBiO ₂ I ¹²	4.01943(4)	4.01943(4)	13.2144(1)		no
	CdBiO ₂ Br ¹⁴	3.943	3.943	12.620		-
	CdBiO ₂ I ¹⁵	3.9582(3)	3.9582(3)	13.970(2)		-
	PbBiO ₂ Cl ¹⁶	3.9562(5)	3.9562(5)	12.629(2)		no
	PbBiO ₂ Br ¹⁶	3.9818(4)	3.9818(4)	12.766(2)		no
	PbBiO ₂ I ¹⁶	4.0533(4)	4.0533(4)	13.520(2)		no
	BaBiO ₂ Cl ¹³	5.880(4)	12.945(18)	5.677(3)		yes
Cmcm	BaBiO ₂ Br ^b	5.9485(7)	13.375(2)	5.7414(6)		yes
	BaBiO ₂ I ¹²	6.0492(1)	14.0224(2)	5.8212(1)		-
	SrBiO ₂ Cl ¹¹	5.7109(2)	12.4081(5)	5.5888(2)		yes
	SrBiO ₂ Br ¹²	5.6460(1)	12.8246(4)	5.7676(1)		-
	SrBiO ₂ I ¹²	5.776(3)	13.509(8)	5.863(2)		no
	PbBiO ₂ Cl ¹²	5.627(5)	12.425(9)	5.575(2)		no
	CaBiO ₂ Cl ¹¹	7.7311(1)	4.1234(1)	6.3979(2)	105.215	yes
		7.5878(7)	4.1397(4)	6.0594(6)	101.529(1)	yes
P2 ₁ /m						

^aThese compounds could not be synthesized as pure powder in our study and were not checked. ^bThis work.

alumina crucible. For CaBiO₂Cl, SrBiO₂Cl and BaBiO₂Br, the reaction was completed after a further annealing stage at 800 °C during 48h. Several intermediate grindings were necessary to obtain single crystalline phases as checked by XRD patterns (see Supporting Information S1). CaBiO₂X (X = Br, I) were prepared according to ref 13. Namely, stoichiometric amounts of BiOX (X = Br, I) and CaO (preliminary decarbonated at 1100 °C) were grounded and placed in an alumina crucible sealed into evacuated quartz ampule and heated at 750 °C during 5 days. Finally, the respective lead compound was synthesized following the preparation method of ref 17. In this case a stoichiometric well mingled mixture of PbO and BiOCl calcined at 700 °C in an alumina crucible during 10h gives single phases of PbBiO₂Cl.

Single-Crystal Growth of BaBiO₂Br. Polycrystalline samples of BaBiO₂Br were melted at 1050 °C, cooled to 600 °C with a rate of 3 °C/h and then cooled to room temperature with a rate of 15 °C/h leading to agglomerated single crystals. One single crystal was carefully isolated by hand and mounted on a glass rod. Data for structure analysis were collected using a Bruker Apex Duo diffractometer with a Mo- μ S microfocus tube (λ = 0.710 73 Å). The intensity data have been extracted from the collected frames using the program SAINT Plus 6.02.¹⁸ Lattice parameters have been defined from the complete data set. Absorption corrections have been performed using multiscan methods in SADABS.¹⁹ Atomic parameters of BaBiO₂Br are depicted in Supporting Information Table S1.

Optical Measurements. UV/vis reflectance spectra have been collected at room temperature with a PerkinElmer Lambda 650 spectrophotometer in the 240–800 nm range using an integration sphere designed for the characterization of solids. A spectrum of the blank was recorded before each sample measurement to calibrate the device.

Photoluminescence excitation and emission spectra were collected on a FluoroLog HORIBA fluorescence spectrometer within the spectral range of 250–800 nm. The emission spectra were corrected for the photomultiplier sensitivity, and the excitation spectra were corrected for the lamp intensity.

Calculations. Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP).²⁰ The calculations were carried out within the generalized gradient approximation (GGA) for the electron exchange and correlation corrections using the Perdew–Wang (PW91) functional and the frozen core projected wave vector method.^{21,22} The full geometry optimizations were performed using a plane wave energy cutoff of 550 eV and 10 *k* points in the irreducible Brillouin zone for all compounds. All structural optimizations converged with residual Hellman Feynman forces on the atoms smaller than 0.03 eV/Å and led to reasonable structures regarding the distances and the local geometries (Supporting

Information Table S2). The experimental structures match well the optimized one, i.e. within a reasonable error expected for the GGA method. The relaxed structures were used for calculations of the electronic structure. For the later, we used a plane wave energy cutoff of 400 eV, an energy convergence criterion of 10^{−6} eV and 20 *k* points in the irreducible Brillouin zone.

■ RESULTS AND DISCUSSIONS

Polymorphism of the Sillen X1 Phases and Preliminary Photoluminescence Activity. The richness of the crystal chemistry of bismuth oxides and oxy salts is governed not only by the labile distorted geometry of the coordination spheres of Bi³⁺ ions due to its stereoactive 6s² lone pair,²³ but also by its ability for creating building units of oxo centered OBi_n polyhedra.²⁴ Typically, fluorite type [Bi₂O₂]²⁺ layers are formed by edge sharing OBi₄ tetrahedra. The easy replacement of Bi³⁺ in these units of aliovalent Aⁿ⁺ cations offers even broader opportunities for original structural topologies based on O(Bi,A)₄ units.²⁴ For instance, dealing with mixed Bi³⁺/Pb²⁺ oxide halides, we have recently designed the [Pb_nBi_{10−n}O₁₃][Bi₂O₂]_nCl_{4+n} (*n* = 1, 2, 3, and 4) series with 2D crenel like oxo centered units isolated by chloride layers.²⁵ After incorporation of other but compatible structural blocks, a diversity of ordered modular structures have been isolated and reported. Their sequences give rise to ideal tetragonal structures with *a* ≈ 3.9 Å (i.e., $\sqrt{2}/2a(\text{fluorite})$) and *c* varying from 6 to 50 Å depending on the structural complexity.^{26–32} The title Sillen phases^{15,33} consist of [(A,Bi)₂O₂] layers intergrown with single [X₁], double [X₂] or triple [M'_xX₃] halide layers, where X represents halide atoms. It produces the rather simple structures of ABiO₂Cl (X1 type) (A²⁺ = Cd, Ca, Pb, etc.),¹³ BiOCl (X2 type)³⁴ and Ca_{1.25}Bi_{1.5}O₂Cl₃ or LiCa₂Bi₃O₄Cl₆ (X3 type).³⁵

Dealing with luminescence properties, the Sillen phases are particularly relevant due to the variable topologies between the Bi³⁺ ions in the oxo centered layers, a major parameter avoiding the thermal quenching. Indeed, although there is no direct correlation between the crystal structure and quenching of the luminescence in Bi rich phases, one can intuitively propose that the nonradiative transitions are favored with high concentration of Bi³⁺. Bi rich luminescent compounds are rather rare,⁴ and the luminescence is either of semiconducting type (Bi₁₂TiO₂₀) or

Figure 1. (a) Structure of ABiO_2Cl (S.G. $I4/mmm$) projected along the b axis and (b) projected along c axis. (c) Bismuth anion coordination and the lone pair (LP) position. (d) Structure of ABiO_2X (S.G. $Cmcm$) and (e) projected along b axis. (f) Bismuth anion coordination for ABiO_2X ($A = \text{Sr}$ and Ba , $X = \text{Cl}$ or Br) and the lone pair (LP) position. (g) Structure of ABiO_2Cl ($A = \text{Ca}$ and Cd , S.G. $P2_1/m$) projected along the monoclinic b axis and (h) projected along c axis. (i) Bismuth anion coordination for ABiO_2Cl ($A = \text{Ca}$ and Cd) and the lone pair (LP) position.

due to localized Bi states ($\text{Bi}_2\text{Ge}_3\text{O}_9$, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$), but in the latter case, they involve rather long Bi–Bi distances. For instance, although surprising $\alpha\text{-Bi}_2\text{O}_3$ shows luminescence at room temperature but restricting the Bi–Bi distances below 3.6 Å, the Bi–Bi connectivity is three only, and the PL was attributed a band to band transition.³⁶

(i) BiOCl (the X2 prototype) possesses undoped $[\text{Bi}_2\text{O}_2]^{2+}$ layers with high Bi–O–Bi connectivity and Bi–Bi distances that are plausibly responsible for quenching of photoemission at room temperature; that is, the photoluminescence of BiOCl (each Bi atom has eight Bi neighbors via Bi–O–Bi bridges with Bi–Bi distances between 3.73 and 3.88 Å) is quenched above 100 K.³⁷ (ii) In the more rare X3 series, the stabilization of triple $[\text{M}'_x\text{X}_3]$ layers involves multiple non stoichiometric substitution in the $[\text{Bi}_2\text{O}_2]^{2+}$ layers, resulting in disordered character with similar quenching effects. (iii) Contrarily, the ABiO_2Cl X1 series is more relevant due to possibilities for ordered A/Bi phases with limited Bi–O–Bi connectivity. The symmetry and disorder in the phases depend on the relative size of Bi, A, and X.

Typically for similar $r\text{Bi}^{3+}$ and $r\text{A}^{2+}$ ionic radii and large X anions the phase is disordered with respect to the tetragonal $I4/mmm$ symmetry; see Table 1 and Figure 1a–c. It results in the layers to Bi–O–Bi connectivities up to eight Bi neighbors per Bi ions. During this work, we checked that the tetragonal compounds PbBiO_2Br and PbBiO_2Cl with mixed $\text{Bi}^{3+}/\text{Pb}^{2+}$ sites do not show luminescence at room temperature due to the presence of Pb^{2+} activators resulting in a too high concentration of

ns^2 ions causing photoluminescence quenching. For another disordered tetragonal phase, CaBiO_2Br , we detected luminescence only below 190 K, which will be presented in a future work. Some other tetragonal phases are dark colored such as iodine based phases, which led to fully luminescence quenching. Finally, CdBiO_2Br and CdBiO_2I cannot be prepared as single phase materials using standard methods.¹³ Our attempts also failed.

For larger A^{2+} cations, for example, $A = \text{Sr}^{2+}$, Ba^{2+} , the structure is fully rearranged with respect to the orthorhombic $Cmcm$ symmetry, independently of the X^- halide ionic radius (Table 1). An ambiguity remains concerning BaBiO_2Br first assigned to the $I4/mmm$ symmetry according to a statistic Bi/Ba disorder.³⁸ It was later announced as a fully ordered $Cmcm$ polytype from powder XRD patterns, but to the best of our knowledge, no crystal structure has been deposited.¹³ Using single crystal XRD data, we confirmed this latter hypothesis leading to good agreement factors ($R = 3.98\%$ and $wR = 4.09\%$). We note a significant difference on the b cell parameter (13.375(2) Å compared to previous report 13.162(6) Å¹³), while our powder and single crystal XRD data are in perfect agreement. Details on the refined crystal structure are given in the Supporting Information. The data collection and refinement parameters are given in the Table 2. We checked the homogeneity of the polycrystal line sample after refining the cell parameters of BaBiO_2Br using FullProf.³⁸ It confirms a single phased fully ordered $Cmcm$ polytype.

Table 2. Crystal Data, Measurement, and Structural Refinement Parameters for BaBiO₂Br

crystal symmetry	orthorhombic
space group	<i>Cmcm</i>
<i>a</i> (Å)	5.9485(7)
<i>b</i> (Å)	13.375(2)
<i>c</i> (Å)	5.7414(6)
<i>V</i> (Å ³)	456.81(9)
<i>Z</i>	4
<i>D_x</i> (g/cm ³)	6.6606
<i>μ</i> (mm ⁻¹) (0.7107 Å)	55.614
appearance	colorless platelet
crystal size (mm)	0.24 × 0.12 × 0.03
data collection	
<i>λ</i> (Mo Kα), (Å)	0.710 73
scan mode	<i>ω</i> and <i>φ</i>
<i>θ</i> (min max), (deg)	3.75 46.69
<i>R</i> (int), (%)	5.5
reciprocal space recording	10 ≤ <i>h</i> ≤ 12 27 ≤ <i>k</i> ≤ 26 11 ≤ <i>l</i> ≤ 11
refinement	
meas, obs, indep all (obs = <i>I</i> > 3σ(<i>I</i>))	5084, 889/1154
no. of refined parameters	18
refinement method	minimization on <i>F</i>
<i>R</i> 1(<i>F</i> ²) (obs)/ <i>R</i> 1(<i>F</i> ²) (all) (%)	3.98/5.57
<i>wR</i> 2(<i>F</i> ²) (obs)/ <i>wR</i> 2(<i>F</i> ²) (all) (%)	4.09/4.27
GOF(obs)/GOF(all)	1.49/1.37
<i>Δρ</i> _{max} / <i>Δρ</i> _{max} (e Å ⁻³)	6.22/ 5.98

In this crystallographic form, [BiAO₂]⁺ layers consist of stripes of Bi³⁺ along the *c* axis alternating with A²⁺ stripes (Figure 1d). Each Bi³⁺ ion is connected only to two other ones by Bi–O–Bi bridges, in favor of possible radiative emission even at room temperature (Figure 1e) despite rather short Bi–Bi distances, for example, Bi–Bi = 3.45 Å in BaBiO₂Cl. In the layers, Bi³⁺ is eight coordinated with four short Bi–O bonds and four much longer Bi–Cl/Br bonds, while the Bi³⁺ lone pair points toward the [Cl[−]] interleave. Here, the reported iodine isomorphs BaBiO₂I and SrBiO₂I are dark colored, which favors strong absorption, so their optical properties were not investigated.

Finally the third possible *Sillen* X1 subgroup concerns the calcium and cadmium bismuth oxide chlorides with

comparable sizes of *r*Bi³⁺ and *r*A²⁺ and relatively small X[−] anions. These compounds crystallize in the monoclinic space group *P*2₁/*m* but conserved a layered topology (Figure 1g). However, the Bi/A organization is such that double Bi³⁺ stripes and Ca²⁺/Cd²⁺ stripes growing along the *b* axis alternate in the layers (Figure 1h,i). It leads to a low Bi–O–Bi connectivity with four Bi³⁺ neighbors connected to each Bi³⁺ via Bi–O–Bi bridges, favorable for unquenched luminescence at room temperature. The Bi³⁺ and A²⁺ ions show a sevenfold coordination, four Bi/A–O bonds at one side and three Bi/A–Cl bonds at the other side. Bond distances *d*(Bi–Cl) are in the range of 3.32–3.41 Å for CdBiO₂Cl and 3.43–3.47 Å for CaBiO₂Cl. Once again the Bi³⁺ electron lone pair points toward the [Cl[−]] interleave; see Figure 1i.

Finally, the room temperature PL activity after our tests for all available samples is listed in the Table 1. As expected the disordered compounds adopting the space group *I*4/*mmm* do not show photoluminescence, whereas the two other forms (*Cmcm* and *P*2₁/*m*) show room temperature luminescence as already reported for three of them and announced above.⁷ In this work, the electronic structure, optical activity, and photoluminescence properties of ABiO₂Cl (A = Ca, Cd, Sr, Ba) and BaBiO₂Br phases will be discussed with respect to their respective crystal structure. All structural data used for the electronic structure calculations are listed in the Table 3.

Electronic Structures. The projected density of states (DOS) are reported in Figures 2 and 3 for the three orthorhombic and two monoclinic phases, respectively. The energy region between −5 and 7 eV is shown to emphasize the top of the valence band (VB) and the bottom of the conduction band (CB).

For post transition lone pair metal oxides (Tl⁺, Pb²⁺, Bi³⁺)^{39,40} it is known that (i) strong interactions between the cation *s* and gen *p* orbitals result in antibonding states with a great degree of cation *s* character at the top of the VB. (ii) The interactions between nominally empty cation *p* states (Bi³⁺: 6s² 6p⁰) and the antibonding orbitals results in the familiar lone pair asymmetric electron density within distorted coordination. For all X1 investigated compounds, this behavior is consistent with the presence in the same energy region of mixed O 2p, Bi 6s, and Bi 6p states in the vicinity of the Fermi level indicating strong gen bismuth electronic transfer and lone pair activity. In details, for the orthorhombic phases (Figure 2) the highest VB part (for SrBiO₂Cl, BaBiO₂Cl, and BaBiO₂Br, respectively, from −4.28, −4.20, and −4.18 to 0 eV) is essentially dominated by O 2p, Cl

Table 3. Selected Bi–O and Bi–X Bonds for the Five Compounds Photoluminescence Active at Room Temperature

	CdBiO ₂ Cl	CaBiO ₂ Cl	SrBiO ₂ Cl	BaBiO ₂ Cl	BaBiO ₂ Br
space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>Cmcm</i>	<i>Cmcm</i>	<i>Cmcm</i>
<i>a</i> (Å)	7.5878(7)	7.7311(1)	5.7109(2)	5.880(4)	5.9485(7)
<i>b</i> (Å)	4.1397(4)	4.1234(1)	12.4081(5)	12.945(18)	13.3754(15)
<i>c</i> (Å)	6.0594(6)	6.3979(2)	5.5888(2)	5.677(3)	5.7414(6)
<i>β</i> (deg)	101.529(11)	105.21(1)			
Bi–O (Å)	2.1596 2.2231 × 2 2.2978	2.0603 2.1958 2.2627 × 2	2.2117 × 4	2.1778 × 4	2.1952 × 4
Bi–O average (Å)	2.2259	2.1954	2.2117	2.1778	2.1952
Bi–X (Å)	3.3201 × 2 3.4083	3.4299 × 2 3.4700	3.4906 × 2 3.5267 × 2	3.6528 × 2 3.6739 × 2	3.7388 × 2 3.7652 × 2
Bi–X average (Å)	3.3495	3.4433	3.5086	3.6633	3.7520

Figure 2. Projected DOS and total DOS for the orthorhombic Sillen X1 series. (a) SrBiO_2Cl , (b) BaBiO_2Cl , and (c) BaBiO_2Br . The black arrows show the idealized Bi: $s^2 \rightarrow sp$ excitation transitions. The Fermi level was set to 0 eV.

3p/Br 4p, and Bi 6p states, while a small contribution of Bi 6s states is present just below the Fermi level. The 3p (Cl) or 4p (Br) states of the halide ions show significant mixing with Bi. Similarly, gen 2p states show hybridization with Bi states. This is indicative of a certain degree of covalency of the Bi–X and Bi–O bonds. A certain degree of covalency for both Pb–O and Pb–Br bonds have also been recently reported in the lead oxide halide $\text{Pb}_7\text{O}_6\text{Br}_2$.⁴¹

In contrast, the main ionic character of the Ba^{2+} and Sr^{2+} cations is shown by their minor contribution in top of the VB. The lower part of the CB is represented by Bi 6p, Bi 6s, O 2p, Sr 4d/Ba 5d as well as negligible contribution of Cl 3p/Br 4p. The Bi and O states are located at the bottom of the CB, whereas Sr/Ba states are mainly localized at higher energy.

For the two monoclinic phases, the highest energy part of the VB is situated from -4.45 and -4.33 to 0 eV, respectively, for CdBiO_2Cl and CaBiO_2Cl . As for the orthorhombic phases, it is mainly composed of O 2p, Cl 3p, and Bi 6p 6s states. In addition, we notice a more significant Ca 3d state at the top of VB for CaBiO_2Cl , although it can still be considered with rather ionic character, the Ca state being mostly located ca. -16 eV, much lower in the VB. For CdBiO_2Cl , however, the Cd states 4d 5s 5p show strong contributions. The Cl 3p states show a significant hybridization with Bi 6p 6s and, in the case of CdBiO_2Cl , with Cd 4d 5s states. It indicates a certain covalent character of Bi–Cl and Cd–Cl bonds. The main difference between these two compounds resides on the bottom of the VB: for CdBiO_2Cl , Cd

5s 5p states are present as well as Bi 6s 6p, O 2p, and Cl 3p states, whereas for CaBiO_2Cl , only the Bi 6s 6p, O 2p, and Cl 3p states are present. The Ca valence states are mostly situated around -16 eV in the VB. Then, it can be concluded that there is a significant mixing between Cd 5s 5p with O 2p leading to a certain degree of covalency of Cd–O bonds, whereas the DOS reveal a more ionic character for Ca–O bonds.

From the analysis of the band structure diagrams, all five compounds present an indirect bandgap (Supporting Information S2) with calculated values between 2.85 and 3.59 eV. The respective results are given in Table 4.

These calculated values are in reasonable agreement with the experimental ones deduced from our diffuse reflectance spectra (DRS) using the Kubelka–Munk representation (Figure 4), considering the known underestimation of band gaps using GGA.⁴² The latter is given by $F(R) = (1 - R)^2/2R$, where R is the reflectance and $F(R)$ is the Kubelka–Munk function. For bandgap determination, Tauc plots (i.e., $(F(R)h\nu)^{1/2}$ vs $h\nu$) were used. Dealing with indirect bandgaps, the line drawn on the linear part of $[F(R)h\nu]^{1/2}$ intersection at $y = 0$ gives the values of the optical bandgap. The results are reported in Table 4 and compared to the calculated ones. The difference between calculated and experimental bandgaps is at maximum 6.6%, for CdBiO_2Cl , while the deviations are much smaller in most of the cases. Along the X1 series, we observe an important variation of the gap depending on A and X elements ($\Delta U \approx 0.7$ eV), which comforts their sizable electronic and optical properties.

Figure 3. Projected DOS and total DOS for the monoclinic X1 Sillen series. (a) CdBiO_2Cl (b) CaBiO_2Cl . The black arrows show the idealized Bi: $s^2 \rightarrow sp$ excitation transitions, and the Fermi level was set to 0 eV.

Table 4. Comparison of the Bandgap Value Obtained by DFT and by UV (Kubelka Munk), Optical Properties of the Five Titled Compounds (ABiO_2Cl with $A = \text{Ca, Cd, Ba, Sr, and BaBiO}_2\text{Br}$), the Ionic Radii Size of A^{2+} and Its Polarizing Power

	CdBiO_2Cl	CaBiO_2Cl	SrBiO_2Cl	BaBiO_2Cl	BaBiO_2Br
DFT BG	2.85 eV	3.59 eV	3.32 eV	3.18 eV	3.11 eV
UV-KM BG	3.05 eV	3.52 eV	3.53 eV	3.28 eV	3.15 eV
error	6.6%	2%	5.9%	3%	1.3%
DOS $s^2 \rightarrow sp$ transition	4.10 eV 33 070 cm^{-1}	3.98 eV 32 100 cm^{-1}	4.12 eV 33 230 cm^{-1}	3.86 eV 31 130 cm^{-1}	3.76 eV 30 320 cm^{-1}
max excitation	34 720 cm^{-1} (4.30 eV)	36 100 cm^{-1} (4.48 eV)	37 450 cm^{-1} (4.64 eV)	33 450 cm^{-1} (4.15 eV)	35 090 cm^{-1} (4.35 eV)
ref 7			35 710 cm^{-1} (4.43 eV)	33 330 cm^{-1} (4.13 eV)	32 787 cm^{-1} (4.07 eV)
excitation edge	33 000 cm^{-1} (4.09 eV)	32 100 cm^{-1} (3.98 eV)	30 870 cm^{-1} (3.87 eV)	28 900 cm^{-1} (3.58 eV)	28 300 cm^{-1} (3.51 eV)
max emission/	21 010 cm^{-1} (2.60 eV)	20 120 cm^{-1} (2.50 eV)	21 840 cm^{-1} (2.71 eV)	19 420 cm^{-1} (2.41 eV)	18 760 cm^{-1} (2.33 eV)
ref 7			23 260 cm^{-1} (2.88 eV)	20 410 cm^{-1} (2.53 eV)	20 000 cm^{-1} (2.48 eV)
Stokes shift/	13 710 cm^{-1} (1.70 eV)	15 980 cm^{-1} (1.98 eV)	15 610 cm^{-1} (1.94 eV)	14 030 cm^{-1} (1.74 eV)	16 330 cm^{-1} (2.02 eV)
ref 7			12 450 cm^{-1} (1.54 eV)	12 920 cm^{-1} (1.60 eV)	12 790 cm^{-1} (1.59 eV)
ionic radii A^{2+}	1.03 Å (7)	1.06 Å (7)	1.26 Å (8)	1.42 Å (8)	1.42 Å (8)
polar pow A^{2+}	1.94	1.89	1.59	1.41	1.41
CIE coord	0.2192/	0.2672/	0.2026/	0.2904/	0.3076/
(x/y)	0.2705	0.3222	0.2231	0.3786	0.4320

Photoluminescence. The Bi^{3+} cation (ns^2 group) is a promising activator for optical applications.^{43,44} Its photo

luminescence properties generated by the electronic transition $6s^2 \leftrightarrow 6s6p$ situated on its outer valence shell strongly depend on

Figure 4. Reflection spectra and Kubelka–Munk plots with extrapolation of the bandgaps for the five compounds.

the Bi atom's environment. It allows tuning the position of excitation and emission bands according to the nature of the host lattice.^{45,46} For Bi^{3+} ions, the ground state $6s^2$ is represented by the singlet 1S_0 , while excited states $6s6p$ give rise in order of increasing energy to a triplet level (3P_0 , 3P_1 , 3P_2) and a singlet state 1P_1 . Usually, the forbidden transition $^1S_0 \rightarrow ^3P_1$ (A band) gains intensity due to a spin–orbit coupling between 3P_1 and 1P_1 states, so that the respective excitation can be observed. The transitions from the ground states to 3P_0 and 3P_2 states are spin and parity forbidden, whereas the transition $^1S_0 \rightarrow ^1P_1$ (C band), which is an allowed electronic dipole transition, is situated at high energy and rarely observed due to the limits of the spectrophotometers. The influence of bismuth coordination for the three orthorhombic (SrBiO_2Cl , BaBiO_2Cl , and BaBiO_2Br) and the two monoclinic (CaBiO_2Cl , CdBiO_2Cl) compounds on the luminescence properties was investigated by means of the electronic structure and intrinsic bond features.

All five compounds show broad emission bands in the visible range at room temperature after UV excitation. They are all linked by a large Stokes shift (between 13 710 and 16 330 cm^{-1} ; see Figure 5). This is related to a large Bi^{3+} lone pair (s^2) stereoactivity, leading to a strong relaxation during excitation processes. In detail, the excited $6s6p$ state shows a much higher centrosymmetric symmetry than the $6s^2$ state in this case, leading to a large shift of the excited state potential relative to this of the ground state, as schematized in Figure 6a. Therefore, the amount of the Stokes Shift is an indicator of the stereoactivity of the $6s^2$ configuration. The maxima of excitation and emission bands as well as the coordinates representing their emission color on the chromaticity diagram (CIE 1931) are shown Figure 6b and listed Table 4, as well as the edge of the excitation band. The two Ba containing phosphors emit a greenish white emission, and the Cd and Sr compounds exhibit a bluish luminescence, whereas for the Ca one cyan white light was observed. The emission spectra for the entire series depicted broad bands typical for ns^2 ions and can be attributed to the Bi^{3+} : $^3P_1 \rightarrow ^1S_0$ transitions, whereas the excitations are assigned to the A bands ($^1S_0 \rightarrow ^3P_1$).

Compared to the energies reported by Porter Chapman et al.⁷ for the three orthorhombic phases, SrBiO_2Cl , BaBiO_2Cl , and BaBiO_2Br , we found sensitively different results as highlighted in Table 4. In our study, the emission maxima are systematically red shifted compared to the previously reported ones, except for BaBiO_2Cl , while the excitation maxima are blue shifted leading

Figure 5. (a) RT excitation (left) and emission (right) spectra of ABiO_2X ($A = \text{Sr}, \text{Ba}$ and $X = \text{Cl}, \text{Br}$), for BaBiO_2Br $\lambda_{\text{ex}} = 285 \text{ nm}$ and $\lambda_{\text{em}} = 535 \text{ nm}$, red line, BaBiO_2Cl $\lambda_{\text{ex}} = 299 \text{ nm}$ and $\lambda_{\text{em}} = 515 \text{ nm}$, black line, SrBiO_2Cl $\lambda_{\text{ex}} = 267 \text{ nm}$ and $\lambda_{\text{em}} = 458 \text{ nm}$, blue line, and (b) room temperature excitation (left) and emission (right) spectra of ABiO_2Cl ($A = \text{Ca}, \text{Cd}$) for CdBiO_2Cl $\lambda_{\text{ex}} = 288 \text{ nm}$ and $\lambda_{\text{em}} = 476 \text{ nm}$, blue line, CaBiO_2Cl $\lambda_{\text{ex}} = 277 \text{ nm}$ and $\lambda_{\text{em}} = 497 \text{ nm}$, red line.

to higher Stokes shifts in our work. This difference is hard to explain in other ways than by the different experimental setups (namely, spectral corrections) or improbable significant difference of microstructure between the two studies. Strikingly, the three orthorhombic compounds display multiple excitation maxima, not mentioned in the previous work.⁷ It is very uncommon to find an experimental doublet structure for the A band, although theoretically possible.⁴⁷ This may be a result from a splitting of the excited state due to the interaction with lattice vibrations (dynamical Jahn–Teller effect).⁴⁸ This effect is expected rather pronounced in alkaline earth halide hosts and has no consequences on the emission: exciting at all submaxima energies leads to the same emission band.⁴⁷

Excitation Process. The energetic position of Bi^{3+} excitation bands strongly depends on antagonist bonds effects, which interact in its coordination sphere but *in fine* mainly depend on the degree of covalence of the bands mediated by the nephelauxetic effect.^{49,50} It is given by the interelectronic repulsion of the bismuth valence electrons due to Bi anion covalence and polarizability in comparison with the free ion. Increasing this effect leads to a red spectral shift of the excitation transitions. In the series of *Sillen* X1 phases, this effect can be

Figure 6. (a) Configurational coordinate diagram showing the stereoactivity of the lone pair of electrons, a low stereoactivity faintly shifts the excited state Δr , and results on a small Stokes shift (full line). A high stereoactivity induces a larger shift $\Delta r'$ and hence induces a bigger Stokes shift (dashed line). (b) Representation of color emission of all the compounds in the CIE 1931 diagram.

considered taking the cationic polarizing power (expressed as z/r , where z is the charge, and r is the cationic radii) and the anion size according to the Fajan's rules into account.^{51,52}

Influence of X^- . The comparison between the photoexcitation spectra of BaBiO_2Cl (onset at $28\,900\text{ cm}^{-1}$) and BaBiO_2Br (onset at $28\,300\text{ cm}^{-1}$, Figure 5a) can be used as a direct probe of the minor X influence, and was already discussed in ref 7 on the basis of the Stoke shifts, despite the slightly different results mentioned above. Inspection of the DOS for these compounds validates the mixing of bismuth and halide states, with some degree of covalence. In this context the size of the anions is an important parameter. The largest Br^- anions and close Bi/Br electronegativities play in favor of more covalent character compared to Bi–Cl bonds (Figure 7a). It involves the

effects due to A–O–Bi bridges should be considered, see Figure 1.

Typically, increasing the A^{2+} polarizing power induces more covalent A–O bonds, which decreases the gen partial charge,⁵⁰ and also the Bi^{3+} –O covalent characters by inductive effects, such that the excitation of the barium compound is red shifted by “indirect” nephelauxetic effects (Figure 7b).

The inspection of SrBiO_2Cl and BaBiO_2X ($X = \text{Cl}, \text{Br}$) excitation energies shows the expected behavior. According to the ionic radii, the low Ba^{2+} polarizing power increases the Bi–O covalency, leading to a considerable red shift of $\Delta\nu_{\text{ex}} \approx 2000\text{ cm}^{-1}$, much larger compared to SrBiO_2Cl . However, dealing with large Ba^{2+} and Sr^{2+} cations with a low electronegative character, the contrasted Ba/Sr–O bond natures cannot be detected in the DOS (Figure 2a), which highlights their main ionic character with no significant mixing between O and A states.

Concerning the monoclinic compounds, CdBiO_2Cl and CaBiO_2Cl show very comparable excitation band onsets. In detail, the excitation process starts at lower energy for the calcium compared to the cadmium compound ($32\,100$ against $33\,000\text{ cm}^{-1}$), even though its maximum is slightly blue shifted. Again, the difference of polarizing power calculated for Cd^{2+} (1.94) and Ca^{2+} (1.89) leads to a stronger nephelauxetic effect for Bi^{3+} in the calcium compound, which coincides with the difference in the onsets of the excitation bands. However, the bismuth first coordination sphere is largely changed in these two monoclinic phases, which may compensate the inductive effect.

One common and particular feature in these series of phases is highlighted in Figure 8, which shows that the bandgap values received from reflectivity measurements (and also from DFT calculations) are much lower in energy than those obtained from excitation measurements, for example, the difference is $\sim 0.8\text{ eV}$ for CaBiO_2Cl . This particularly differs from typical excitation spectra of Ln doped materials for which the excitation band is usually at lower or at same energy than the lowest absorption band. However, the examination of the literature shows similar behaviors for other stoichiometric $6s^2$ ionic compounds, for example, $\text{Bi}_2\text{Al}_4\text{O}_9$,⁵³ BiM_2PO_6 ($M = \text{Mg}, \text{Zn}, \text{Cd}$),⁵ and KPb_2Cl_5 .^{54,55} The reasons for this behavior are twofold. First, the radiative transition from the ground $6s^2$ state to the lowest Bi

Figure 7. Sketch of the influence of the nature of (a) the halide (b) the cation. A small cation strongly polarizes the A–O bond, and by inductive effect the Bi–O covalence will be lowered. A bigger halide increases Bi–X covalent character.

experimentally verified excitation red shift (Figure 5a). However, this effect is very weak ($\Delta\nu_{\text{ex}} = 600\text{ cm}^{-1}$) but remains respected in the emission spectra. It is probable that the longer Bi–O bonds in the bromide (2.195 Å) compared to the chloride ones (2.178 Å) attenuate this effect by increasing the Bi–O covalent character in BaBiO_2Cl .

Influence of A^{2+} . In the oxo centered layers of the *Sillen* X1 phases, the influence on the excitation spectra in terms of indirect

Figure 8. Comparison between the absorbance and excitation spectra.

6s6p state (3P_0) is fully forbidden; that is, it is not observed in the excitation spectra. Second, dealing with lone pair active ions, the shift of the excited state potentials along the M–L axis should shift the PL excitation bands to higher energies (Figure 9)

Figure 9. Sketch representing energy differences between absorption (bandgap) and excitation (bismuth predominant levels) spectra. Both forbidden transitions and M–L shift push the $s^2 \rightarrow sp$ excitation toward higher energies.

compared to most of the $VB \rightarrow CB$ transitions. Dealing with $s^2 \rightarrow sp$ transitions, it is convenient to consider the PL excitation transition starting from the Fermi level (with strong Bi 6s contribution) to the lowest empty Bi 6s 6p mixed states in the CB; see arrows in Figure 2. From the DOS, these “ideal” calculated excitation energies match rather well with the experimental values of the onset of the respective excitation bands; see Table 4.

Emission Process. The emission spectra of all materials consist of broad bands covering a large range of the visible spectrum (Figure 5). Although the comparison between the different compounds should be performed for similar Bi^{3+} point symmetries and coordination spheres (which is not the case for the two active polymorphs, namely, C_{2v} for orthorhombic and C_s for monoclinic compounds), the Stokes shift remains of the same

order of magnitude in a rough approximation for all phases (between 13 700 and 16 300 cm^{-1}). This suggests similar relaxation processes for all compounds. Indeed, the DOS show similar Bi s and p contributions to the CB. However, the lone pair stereoactivities can give a more detailed vision of the relative position of emission energies bands.

Monoclinic Form. In $CaBiO_2Cl$ and $CdBiO_2Cl$ the c cell parameter can be considered as a good indicator of the Bi^{3+} electron lone pair stereoactivity (Figure 1i). As discussed above, the lone pair stereoactive effect takes place perpendicularly to the $[BiO_2]^+$ layers, toward the three halide ligands. In a rough approximation, increasing the c parameter from 6.05 Å (Cd case) to 6.39 Å (Ca case), while the mean Bi–Cl distances are increased only by 0.1 Å (see Table 3), suggests a more pronounced lone pair stereoactivity for Ca compound. This leads to a more important structural reorganization during excitation and to a shift of the emission bands toward lower energies (higher Stokes shift). The higher Stokes shift (SS) and lower energy emission position for $CaBiO_2Cl$ (SS: 15 980 cm^{-1} , ν_{em} : 20 120 cm^{-1}) compared to $CdBiO_2Cl$ (SS: 13 710 cm^{-1} , ν_{em} : 21 010 cm^{-1}) fits well with our assumptions caused by structural reasons. In other words, the higher lone pair stereoactivity induces the higher Stokes shift.

Orthorhombic Form. For the other series, namely, $SrBiO_2Cl$, $BaBiO_2Cl$, and $BaBiO_2Br$, the red shift of the emission bands could be rationalized in the same way, following the evolution of the b cell parameter in this case (lone pair stereoactivity perpendicular to the layers, see Figure 1f). For the two oxide chloride phases, the greatest stereoactivity of the barium phase is shown by the longest b value ($b = 12.94$ Å for Ba against 12.41 Å for Sr) and also by the mean Bi–Cl distances (3.66 Å for Ba against 3.51 Å for Sr). It matches well with the red shift of the emission maxima. We also expect an increase of the Stokes shift, hard to estimate due to the multiplet structure of the excitation bands. From a sterical point of view, the estimation of the lone pair activity after substitution of Cl^- for Br^- is difficult in this case, due to differences in the anionic radii.

■ CONCLUSIONS

The Sillen X1 series with the formulas ABiO_2X is composed of three main crystallographic types, namely, the tetragonal form (S.G. $I4/mmm$), the orthorhombic form (S.G. $Cmcm$), and monoclinic form (S.G. $P2_1/m$). The A/Bi statistics distribution in the $[\text{ABiO}_2]^+$ layers leads to a full quenching of the luminescence of Bi^{3+} emitters at room temperature due to Bi rich domains. Only the two latter forms of this series show fully ordered Bi/A topologies with a limited Bi–O–Bi connectivity favorable for unquenched photoluminescence at room temperature. It was checked that the monoclinic compounds CdBiO_2Cl and CaBiO_2Cl and orthorhombic ones SrBiO_2Cl , BaBiO_2Cl , and BaBiO_2Br show luminescence at room temperature originated by Bi^{3+} activators. The influence of the chemical nature of X on the energy of the excitation band is rather weak, but cannot be fully deconvoluted of the antagonist effect of the lattice Bi–O bonds contraction/dilatation changing Cl^- for Br^- . On the one hand, at least a slight redshift of the excitation bands is observed for BaBiO_2Br compared to BaBiO_2Cl as expected from Fajan's rules in the context of more covalent Bi–Br bonds. On the other hand, the tuning of the excitation energies playing on the A^{2+} chemical nature through the A–O–Bi bonding scheme is much significant and mediated by inductive effects. The shift of the emitting radiation from bluish to greenish white color comforts sizable optical properties in possible relation with the degree of lone pair stereoactivity. In general, we observed specific electronic features typical of Bi^{3+} phosphors concerning the excitation energy well above the bandgap but giving rise to radiative emission. This feature is related to the specificity of the $6s^2 \rightarrow 6s6p$ excitation process of ns^2 ions and may be favored by indirect bandgaps observed for the five active samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01024.

XRD patterns, crystallographic data, atomic parameters, bond distances, and electronic band diagrams. (PDF)

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