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# Synthesis and Structure of $CaBiO_2Cl$ and $SrBiO_2Cl$: New Distorted Variants of the Sillen X1 Structure

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**Two new layered oxyhalides, $M$BiO$_2$Cl ($M=$ Ca, Sr), have been synthesized and characterized. Both are derived from the ideal Sillen X1 structure type, being composed of fluorite-like $[M\mathrm{BiO_2}]^+$ layers separated by single $\mathrm{Cl}^-$ layers. However, deviations from the idealized tetragonal structure due to cation site ordering lead to two different superstructures being formed. The structure of $CaBiO_2Cl$ has been solved *ab initio* and refined from a combination of X-ray and neutron powder diffraction data: monoclinic, space group *P*2$_1$/*m*, $a = 7.7311(1)$ Å, $b = 4.1234(1)$ Å, $c = 6.3979(2)$ Å, $\beta = 105.21(1)^\circ$ ($a \sim 2a_{\mathrm{ideal}}$, $b \sim b_{\mathrm{ideal}}$, $c \sim c_{\mathrm{ideal}}/2$). The large distortion from the ideal structure arises due to the small size of the $Ca^{2+}$ and consequent reduction of the cation coordination numbers from 8 (4O + 4Cl) to 7 (4O+3Cl). $SrBiO_2Cl$ is shown by Rietveld refinement of powder X-ray data to adopt the $BaBiO_2Cl$ superstructure: orthorhombic, space group *Cmcm*, $a = 5.7109(2)$ Å, $b = 12.4081(5)$ Å, $c = 5.5888(2)$ Å ($a \sim \sqrt{2}\, a_{\mathrm{ideal}}$, $b \sim c_{\mathrm{ideal}}$, $c \sim \sqrt{2}\, b_{\mathrm{ideal}}$).**

## INTRODUCTION

The first members of the Sillen series of layered bismuth-based oxyhalides were reported in 1941 (1). These compounds are of interest, for example, as selective oxidation catalysts (2, 3). Despite this, little detailed crystallographic characterization of these materials has been carried out. Sillen proposed idealized structures only for his homologous series based on intergrowths of oxide and chloride-containing blocks, which may be stacked in varying sequences to produce structures of increasing complexity. The original Sillen series has bismuth oxide-based fluorite-like layers, $[M_2O_2]$, intergrown with single, double, or triple halide layers, $[X]$, $[X_2]$, or $[M'_xX_3]$, producing compositions such as $PbBiO_2Cl$ (X1), BiOCl (X2), and $Ca_{1.25}Bi_{1.5}O_2Cl_3$ (X3). More complex intergrowths such as X1X2 etc. are also possible. More recently, analogous phases containing "triple" fluorite layers, $[M_3O_4]$, have also been reported (4, 5). An excellent review of the structural chemistry of many of these materials has been given by Dolgikh *et al.* (6). Sillen's original report suggests that the "ideal" structures of these phases are tetragonal, with $a_{\mathrm{ideal}} \sim 4$ Å, and $c_{\mathrm{ideal}}$ variable, depending on the number of fluorite and halide layers. As far as we know, the only refinements of truly tetragonal X1 phases yet reported are those of $PbBiO_2Cl$ (7) and $NaBi_3O_4Cl_2$ (8); the other known example $BaBiO_2Cl$ (9) and the related $PbSbO_2Cl$ (10) both have orthorhombic superstructures $a \sim c \sim \sqrt{2}\, a_{\mathrm{ideal}}$, $b \sim c_{\mathrm{ideal}}$, due to complete ordering of the cation sublattice. Our work has also been motivated by the possibility of obtaining layered intergrowths between these Sillen phases and the well known Ruddlesden–Popper-type layered cuprates, such as $Ca_2CuO_2Cl_2$. One such phase has been recently suggested by Zhu *et al.* (11). Here we report the outcome of some of our studies in this area, *viz.* the synthesis and structural characterization of the two new cation-ordered X1 phases $CaBiO_2Cl$ and $SrBiO_2Cl$.

## EXPERIMENTAL

$CaBiO_2Cl$ was prepared by solid state reaction. Stoichiometric quantities of BiOCl, $CaCO_3$, and $CuCl_2$ corresponding to the composition "$Bi_3Ca_3CuO_6Cl_5$" were ground together and heated at 800°C for 48 h in air, with one intermediate regrinding. CuO was identified as an impurity phase by preliminary X-ray powder diffraction data; it was subsequently shown that pure $CaBiO_2Cl$ could be prepared simply by similar reaction of stoichiometric amounts of $CaCO_3$ and BiOCl. $SrBiO_2Cl$ was prepared by the reaction of stoichiometric amounts of $SrCO_3$ and BiOCl in air at 800°C for 36 h.

Powder X-ray diffraction data for both materials were collected on a Stoe STADI/P transmission system, using monochromatised Cu$K\alpha_1$ radiation. Data suitable for structure solution and refinement were collected over the range $5^\circ < 2\theta < 85^\circ$ in 0.02° steps, the entire run lasting 15 h. Appropriate absorption corrections were applied by measuring the transmission factors of the samples at $2\theta = 0^\circ$. Powder neutron diffraction data for $CaBiO_2Cl$ were collected from a 5 g sample on the Polaris instrument at the

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**TABLE 1**
**Crystal Data and Details of Structure Solution and Refinement**

| | $CaBiO_2Cl$ | $SrBiO_2Cl$ |
|---|---|---|
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/m$ | *Cmcm* |
| Cell parameters | $a = 7.7311(1)$ Å<br>$b = 4.1234(1)$ Å<br>$c = 6.3979(2)$ Å<br>$\beta = 105.215°$ | $a = 5.7109(2)$ Å<br>$b = 12.4081(5)$ Å<br>$c = 5.5888(2)$ Å |
| Absorption factor | $\mu t = 1.08$ | $\mu t = 1.32$ |
| Structure solution | | |
| $2\theta$ range | 5°–85° | |
| No. reflections | 203 | |
| Structure refinement | | |
| X-ray | | |
| $2\theta$ range | 5°–85° | 5°–85° |
| No. reflections | 203 | 93 |
| No. data points | 3988 | 3989 |
| $R_{wp}$, $R_p$ | 13.6%, 9.9% | 12.7%, 9.4% |
| Neutron | | |
| *d*-spacing range | 0.64–3.02 Å | |
| No. reflections | 1042 | |
| No. data points | 3079 | |
| $R_{wp}$, $R_p$ | 3.35%, 5.90% | |
| No. of parameters | 63 | 27 |
| Combined $\chi^2$ | 9.58 | 6.66 |

CLRC ISIS facility, Chilton, UK. Data analysis was carried out by the Rietveld method using the GSAS program suite (12) and the SIR88 direct methods package (13).

## STRUCTURE DETERMINATION

Preliminary analysis of the X-ray data for $CaBiO_2Cl$ suggested a novel phase had been formed. The powder pattern was indexed using the TREOR program (14) to give a primitive monoclinic cell with the approximate dimensions $a = 7.73$ Å, $b = 4.12$ Å, $c = 6.40$ Å, and $\beta = 105.2°$. Except for the clear CuO impurity, all the observed lines in the X-ray pattern were indexable using this cell. The only clearly resolved $0k0$ peak position (010) was absent, suggesting centrosymmetric $P2_1/m$ as the most probable space group, which was used to solve the structure. Structure solution commenced using the X-ray data only, with integrated intensities being extracted by the LeBail profile-fitting technique (15). These were used as input to the SIR88 program, from which the three strongest peaks in the best solution were identified as Bi, Cl, and Ca. Subsequent Rietveld refinement of this partial model followed by difference Fourier maps revealed the additional O atom positions and led to successful completion of the structure. Further details are given in Table 1. In order to obtain a better determination of this new structure type, neutron diffraction data were included and the model was refined against both datasets simultaneously. This improves the precision of the light atom parameters, while still allowing the discrimination of the Ca/Bi ordering (neutron scattering lengths ($\times 10^{-12}$ cm): Ca 0.490, Bi 0.853, O 0.5805, Cl 0.958). Allowing the occupancies of the metal sites to refine suggested no significant deviation from complete ordering, so these were fixed as such in the final stages. CuO was included as a second phase in the refinement of both data sets. A small amount of preferred orientation (along [001]) was also observed in both cases. The data were of sufficient quality to allow anisotropic treatment of all atoms. Final Rietveld plots for the neutron and X-ray refinements are given in Figs. 1a and 1b, respectively.

In the case of $SrBiO_2Cl$, the structure was characterized from X-ray powder data only, since these data suggested an obvious relationship to the supercell previously reported for $BaBiO_2Cl$ (9). An initial cell was refined from the positions of the first 20 peaks, before using the $BaBiO_2Cl$ model as the starting point for a Rietveld refinement. The refinement proceeded straightforwardly, which allowed anisotropic temperature factors for the metal atoms. A small amount of unidentified impurity was apparent, which does not significantly affect the refinement. The final Rietveld plot is shown in Fig. 2.

## RESULTS AND DISCUSSION

Final refined atomic parameters for $CaBiO_2Cl$ are given in Table 2, and selected bond lengths are in Table 3.

**TABLE 2**
**Final Atomic Parameters for $CaBiO_2Cl$**

| Atom | Site | *x* | *y* | *z* | $U_{11}$/ Å$^2$ | $U_{22}$/ Å$^2$ | $U_{33}$/ Å$^2$ | $U_{13}$/ Å$^2$ |
|---|---|---|---|---|---|---|---|---|
| Bi | 2*e* | 0.5914(2) | 0.25 | 0.3237(2) | 0.0103(7) | 0.0179(7) | 0.011(1) | 0.0017(6) |
| Ca | 2*e* | 0.0778(4) | 0.25 | 0.3245(5) | 0.017(2) | 0.007(1) | 0.006(2) | 0.005(1) |
| O1 | 2*e* | 0.4043(3) | 0.25 | 0.5293(5) | 0.011(1) | 0.004(1) | 0.009(2) | 0.009(1) |
| O2 | 2*e* | 0.8531(3) | 0.25 | 0.5096(6) | 0.0034(9) | 0.003(1) | 0.015(2) | 0.006(1) |
| Cl | 2*e* | 0.8197(2) | 0.75 | 0.0604(4) | 0.0151(9) | 0.0287(9) | 0.007(1) | 0.0031(8) |

*Note.* $U_{12} = U_{23} = 0$.

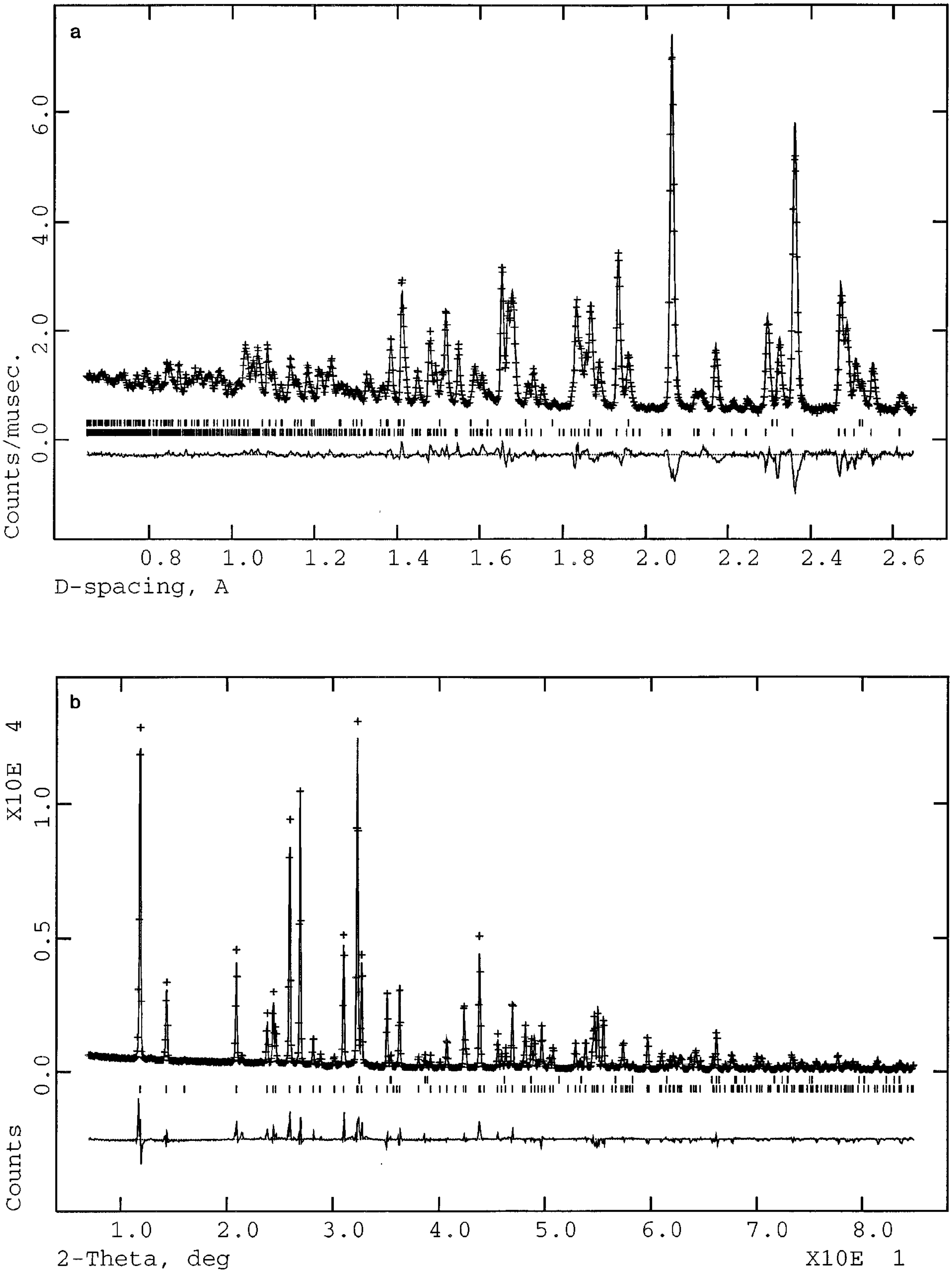

**FIG. 1.** Final Rietveld fits for CaBiO$_2$Cl (a) neutron data, (b) X-ray data. Crosses represent observed data, the solid line is the calculated pattern, and the difference profile and allowed reflection positions are shown beneath.

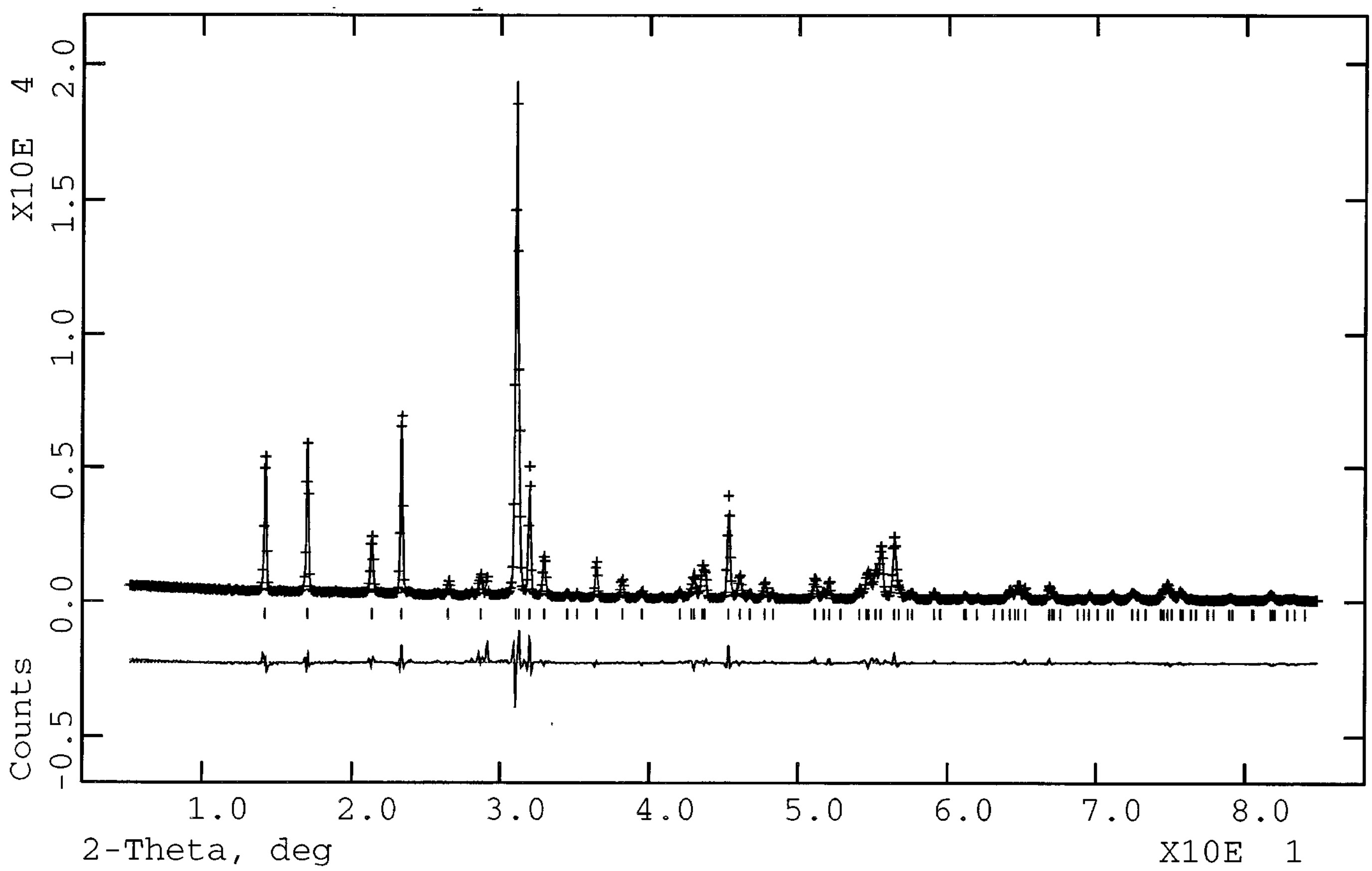

**FIG. 2.** Final Rietveld fit for $SrBiO_2Cl$, X-ray data.

Corresponding parameters for $SrBiO_2Cl$ are given in Tables 4 and 5. Both structures are derived from the idealized Sillen X1 structure type, formally represented in space group I4/*mmm* (Fig. 3). This structure has layers of fluorite-like $[M_2O_2]$ with oxygen in tetrahedral coordination to $M$, linked by chloride layers, with chloride in 8-fold coordination; this results in "square-antiprismatic" geometry around $M$, with a square of four oxygens above and a square of four chlorides below.

Although $SrBiO_2Cl$ adopts the previously known $BaBiO_2Cl$ cation-ordering scheme (Fig. 4), leading to a C-centred orthorhombic, an $\sqrt{2}\,a_{\mathrm{ideal}}$, $b \sim c_{\mathrm{ideal}}$, $c \sim \sqrt{2}\,b_{\mathrm{ideal}}$ supercell, $CaBiO_2Cl$ is found to adopt a novel cation-

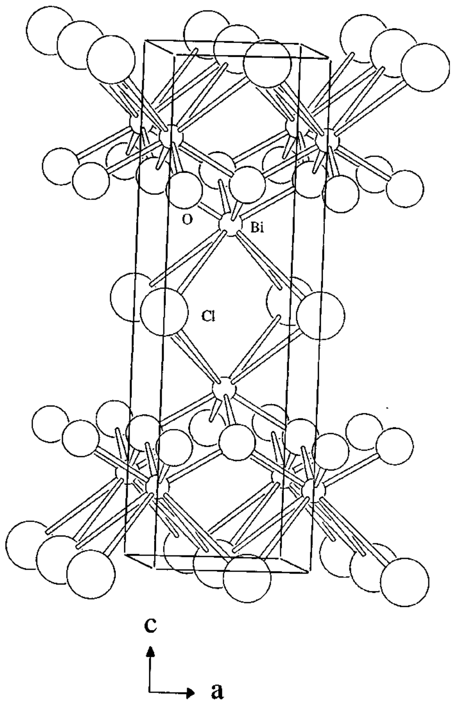

**FIG. 3.** Idealized tetragonal Sillen X1 structure with disordered cation arrangement.

**TABLE 3**
**Selected Bond Distances for $CaBiO_2Cl$**

| | | | | | |
|---|---|---|---|---|---|
| Bi–Cl | ×2 | 3.430(2) | Ca–Cl | ×2 | 3.053(3) |
| Bi–Cl | | 3.470(2) | Ca–Cl | | 2.778(4) |
| Bi–O(1) | ×2 | 2.263(1) | Ca–O(1) | | 2.520(4) |
| Bi–O(1) | | 2.196(3) | Ca–O(2) | ×2 | 2.316(2) |
| Bi–O(2) | | 2.060(2) | Ca–O(2) | | 2.346(4) |

**TABLE 4**
**Final Atomic Parameters for $SrBiO_2Cl$**

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}/\text{Å}^2$ | $U_{22}/\text{Å}^2$ | $U_{33}/\text{Å}^2$ | $U_{\text{iso}}/\text{Å}^2$ |
|---|---|---|---|---|---|---|---|---|
| Bi | 4*c* | 0 | 0.0824(1) | 0.25 | 0.037(1) | 0.043(1) | 0.026(1) | |
| Sr | 4*c* | 0 | 0.3879(2) | 0.25 | 0.022(3) | 0.034(3) | 0.029(2) | |
| O | 8*e* | 0.241(2) | 0 | 0 | | | | 0.045(5) |
| Cl | 4*c* | 0 | 0.7442(6) | 0.25 | | | | 0.048(3) |

*Note.* $U_{12} = U_{13} = U_{23} = 0$.

ordered superstructure, $a \sim 2a_{\text{ideal}}$, $b \sim b_{\text{ideal}}$, $c \sim c_{\text{ideal}}/2$, with a concommitant lowering of symmetry to primitive monoclinic. The cation ordering present in both systems may be attributed to the distorted coordination requirements of the stereochemically active Bi $6s^2$ lone pair, leading to rather short Bi–O distances and long Bi–Cl distances. In the case of $CaBiO_2Cl$, however, the additional effect of the smaller size of the $Ca^{2+}$ cation must also be taken into account. This has the significant result of reducing the coordination number of both cations from 8 (4O + 4Cl) to 7 (4O + 3Cl) and also in reducing the chloride ion coordination number from 8 to 6. This can be clearly seen in Figs. 5 and 6, where views parallel and perpendicular, respectively, to the $[CaBiO_2]$ layers are shown. Figure 6 should be contrasted with Fig. 4, showing the analogous view for the Sr and Ba compounds. The main difference is the replacement of the "chloride square" of the ideal square antiprism with a triangle.

Comparing the details of the present structures to that of $BaBiO_2Cl$, it is apparent that although $CaBiO_2Cl$ has a much more distorted overall structure, the environment around the $Bi^{3+}$ cation is in fact more regular. Bi–O bond lengths in the range 2.06–2.26 Å and Bi–Cl bond lengths of 3.43–3.47 Å in $CaBiO_2Cl$ may be contrasted with those of 2.18 Å and 3.65–3.67 Å, respectively, in $BaBiO_2Cl$. The exceptionally long Bi–Cl bond lengths in the latter in fact suggest that the Bi is best regarded as only coordinated to oxygen in that case. The corresponding bond lengths in $SrBiO_2Cl$ are intermediate between the Ca and Ba analogs with Bi–Cl distances of 3.49–3.53 Å. The Bi geometry in $CaBiO_2Cl$ is closer to that in the triple fluorite layer phase $Bi_2LaO_4Cl$ (5) (Bi–O = 2.252 Å, Bi–Cl = 3.392 Å); nevertheless in every case it is apparent that the Bi 6*s* lone pair is accommodated on the chloride side of the Bi atom. The only other previously characterized Ca or Sr oxychlorides are the isostructural $BiM_3O_3Cl_3$ ($M$ = Ca, Sr) (16). These compounds have five-coordinated Bi (3O + 2Cl) with short Bi–O lengths of ~ 2.06 Å and intermediate Bi–Cl lengths of 3.47 Å; the structures are layered, but unrelated to the Sillen phases.

**TABLE 5**
**Selected Bond Distances for $SrBiO_2Cl$**

| | | | | | |
|---|---|---|---|---|---|
| Bi–Cl | ×2 | 3.527(5) | Sr–Cl | ×2 | 3.240(4) |
| Bi–Cl | ×2 | 3.491(4) | Sr–Cl | ×2 | 3.367(4) |
| Bi–O | ×4 | 2.211(7) | Sr–O | ×4 | 2.465(7) |

### *Comments on the Existence of Sillen Copper Oxide Intergrowths*

In the present study, and in our previous work on $Bi_2LaO_4Cl$ (5), we have attempted to form ordered intergrowths between Sillen phases and layered Ruddlesden–Popper cuprates. This possibility was suggested by Zhu *et al.* (11), who went as far as postulating a model for "$Bi_{2.4}Ca_{3.1}CuO_{6-y}Cl_5$" (II), which may be regarded as a X1:X2:$Ca_2CuO_2Cl_2$ intergrowth (i.e., approx. $M_2O_2Cl$:$M_2O_2Cl_2$:$Ca_2CuO_2Cl_2$). Note, however, that this proposed model is rather tentative as it is based only on a comparison of integrated X-ray powder intensities. Zhu *et al.* prepared their phase by reaction of an X1X3 phase "$Bi_{1.7}Ca_{2.7}O_{4-y}Cl_4$" (I) with excess $CaCl_2$ (although Cu is

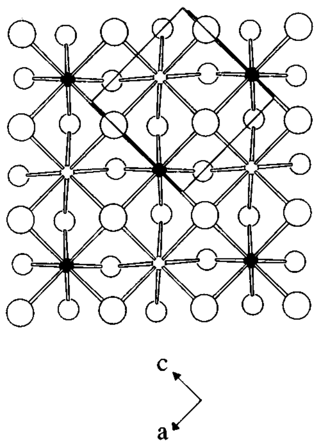

FIG. 4. Structure of $SrBiO_2Cl$ along [010] showing ordered cation arrangement.

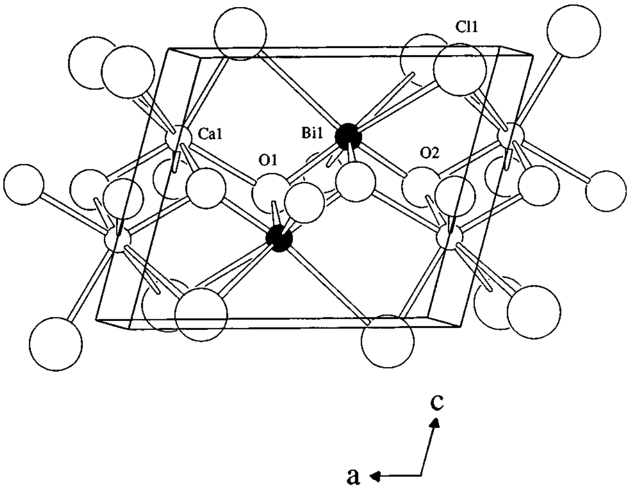

**FIG. 5.** Structure of $CaBiO_2Cl$ along [010].

present in the first stage of the reaction). Our serendipitous preparation of $CaBiO_2Cl$ arose from an attempt to prepare an idealized version of compound II directly. Copper was not incorporated into our phase, although we note that if the same reaction is carried out under nitrogen instead of air, loss of chlorine does not occur, and copper is incorporated into the product, which may be indexed similarly to Zhu's compound I ($c \sim 16.8$ Å). This material hydrates readily on exposure to moist air, leading to a product with $c \sim 20$ Å, apparently analogous to Zhu's compound II. Reaction of compound I with excess $CuCl_2$ results in an X3 phase which also readily picks up water in moist air to give a phase with $c \sim 27$ Å. We believe Zhu's compound II to be a hydrated Sillen X1X3-like phase with Cu incorporated into the middle of the central chloride layer of the X3 subunit, as is known to occur for Ca in Sillen's original X3 phase. If this is correct there are no $CuO_2$ planes in the material reported by Zhu *et al.* We are currently carrying out further studies on these systems by powder diffraction methods.

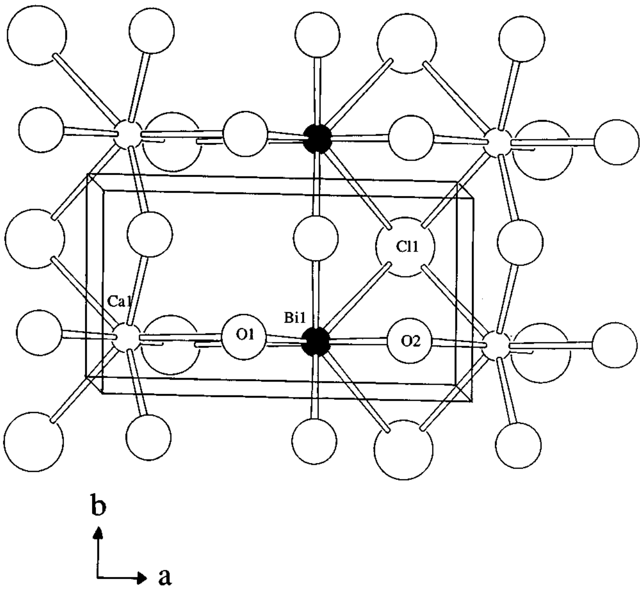

**FIG. 6.** Structure of $CaBiO_2Cl$ along [001].

## ACKNOWLEDGMENTS

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