Crystal structure of Sr$_4$OCl$_6$

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ABSTRACT.- The compound Sr$_4$OCl$_6$ was synthesized and its crystal structure was determined by using a ferroelectrically single domain crystal. The structure is similar to those of other M$_4$OCl$_6$ compounds where M=Ca,Yb,Eu,Sm and Ba. Interatomic distances are compared with these compounds. The Raman spectra of Sr$_4$OCl$_6$ and Ba$_4$OCl$_6$ are compared.

INTRODUCTION

Crystals of the general formula M$_4$OX$_6$ with M=Sr,Ba and X=Cl,Br have recently been shown to present interesting properties as X-ray phosphors when doped with Eu(II) [1,2]. Our interest in these compounds arises from our research on room temperature photochemical hole burning on Sm(II) in mixed alkaline earth fluorohalides [3]. Solid solutions of M$_4$OX$_6$ have been reported to form [4]. However, the current knowledge on these compounds remains scarce. Besides
the crystal structures of Ba₅OCl₆ [5] and Ca₅OCl₆ [6], there are only the structures of the compounds with M=Eu,Sm and Yb [7-9] which have been determined. In this work, we present the crystal structure of Sr₄OCl₆ as well as the first room temperature Raman spectra of M₄OCl₆ with M=Sr,Ba. The title compound was chosen because of the similarity of the ionic radii of Sr²⁺ and Sm²⁺.

EXPERIMENTAL

Small needle shaped crystals with hexagonal, close to trigonal noncentrosymmetric section, were obtained by slow cooling from 1100°C to 900°C (10 hours) of a stoichiometric melt of SrO and SrCl₂ contained in a pyrolytic graphite crucible under argon atmosphere.

Table I - Conditions of structure analysis for Sr₄OCl₆.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P 6₃mc [186]</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>a (pm)</td>
<td>945.13(4)</td>
</tr>
<tr>
<td>c (pm)</td>
<td>720.36(10)</td>
</tr>
<tr>
<td>V (10⁶pm³)</td>
<td>557.27(10)</td>
</tr>
<tr>
<td>X-ray density (gcm⁻³)</td>
<td>3.452</td>
</tr>
<tr>
<td>Molar mass (gmol⁻¹)</td>
<td>579.21</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.22 x 0.27 x 0.84</td>
</tr>
<tr>
<td>Absorption coefficient (cm⁻¹)</td>
<td>2.042</td>
</tr>
<tr>
<td>Diffractometer / radiation</td>
<td>STOE, /MoKα</td>
</tr>
<tr>
<td>Scan method</td>
<td>ω / Δ</td>
</tr>
<tr>
<td>Measured intensities</td>
<td>9588</td>
</tr>
<tr>
<td>Analytical integration (Tₘin/max)</td>
<td>0.021/0.083</td>
</tr>
<tr>
<td>Rₛᵡ</td>
<td>0.067</td>
</tr>
<tr>
<td>Independent intensities</td>
<td>486</td>
</tr>
<tr>
<td>Used reflections (Fᵢ&gt;3σ(Fᵢ))</td>
<td>451</td>
</tr>
<tr>
<td>No. of refined parameters</td>
<td>26</td>
</tr>
<tr>
<td>R(Rₛ)</td>
<td>0.034 (0.024)</td>
</tr>
<tr>
<td>Max.shift/esd</td>
<td>0.032</td>
</tr>
<tr>
<td>Residual e⁺ density (eÅ⁻³)</td>
<td>2.5 (-2.4)</td>
</tr>
<tr>
<td>Absolute structure factor</td>
<td>1.014(13)</td>
</tr>
</tbody>
</table>
These crystals are not extremely moisture sensitive. A small sample was left overnight in air and did not show any surface damage and its Raman spectrum remained unchanged. The crystal used for the single crystal X-ray diffraction yielded constant reference reflection intensities through the entire data collection cycle extending over several days.

Conditions of X-ray collection and refinement using the refinement package XTAL 3.2 [10] are summarized in Table 1. Starting atomic coordinates were taken from Ref. [5].

Raman spectra were obtained at room temperature using a backscattering geometry. The laser excitation wavelength is 488nm. The slit width of 0.2 mm corresponds to a spectral resolution of ca. 2 cm\(^{-1}\).

**Table II - Atomic positions and isotropic displacement parameters in pm\(^2\):**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(_{iso})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl1</td>
<td>6(c)</td>
<td>0.13966(10)</td>
<td>0.86034(10)</td>
<td>0.2862(3)</td>
<td>211(4)</td>
</tr>
<tr>
<td>Cl2</td>
<td>6(c)</td>
<td>0.53322(9)</td>
<td>0.46678(9)</td>
<td>0.1068(3)</td>
<td>188(4)</td>
</tr>
<tr>
<td>Sr1</td>
<td>6(c)</td>
<td>0.80372(3)</td>
<td>0.19628(3)</td>
<td>0.39545</td>
<td>147(2)</td>
</tr>
<tr>
<td>O</td>
<td>2(b)</td>
<td>1/3</td>
<td>2/3</td>
<td>0.000(3)</td>
<td>140(20)</td>
</tr>
<tr>
<td>Sr2</td>
<td>2(b)</td>
<td>1/3</td>
<td>2/3</td>
<td>0.3261(3)</td>
<td>184(2)</td>
</tr>
</tbody>
</table>

**Anisotropic atomic displacement parameters in pm\(^2\):**

<table>
<thead>
<tr>
<th>Atom</th>
<th>U(_{11})</th>
<th>U(_{22})</th>
<th>U(_{33})</th>
<th>U(_{12})</th>
<th>U(_{13})</th>
<th>U(_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl1</td>
<td>162(4)</td>
<td>U(_{11})</td>
<td>254(9)</td>
<td>40(5)</td>
<td>25(3)</td>
<td>-U(_{13})</td>
</tr>
<tr>
<td>Cl2</td>
<td>187(4)</td>
<td>U(_{11})</td>
<td>196(7)</td>
<td>98(6)</td>
<td>11(3)</td>
<td>-U(_{13})</td>
</tr>
<tr>
<td>Sr1</td>
<td>136(2)</td>
<td>U(_{11})</td>
<td>187(3)</td>
<td>82(2)</td>
<td>-6(1)</td>
<td>-U(_{13})</td>
</tr>
<tr>
<td>O</td>
<td>2U(_{12})</td>
<td>2U(_{12})</td>
<td>140(40)</td>
<td>68(9)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sr2</td>
<td>2U(_{12})</td>
<td>2U(_{12})</td>
<td>136(5)</td>
<td>104(1)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

[The anisotropic displacement factor in the structure factor expression is: U\(_g\)=exp-2π\(^2\)(U\(_{11}\)h\(^2\)a\(^2\)+U\(_{22}\)k\(^2\)b\(^2\)+U\(_{33}\)l\(^2\)c\(^2\)+2U\(_{12}\)hka\(^*\)b\(^*\)+2U\(_{13}\)hla\(^*\)c\(^*\)+2U\(_{23}\)klb\(^*\)c\(^*\))].
Fig. 1 - Selected interatomic distances of $M_4OCl_6$ as a function of $M^{3+}$ ionic radius.

RESULTS AND DISCUSSION

Standardized [11] atomic positions are given in Table II and selected interatomic distances in Table III.

The structure of $Sr_4OCl_6$ compares to the other oxy-chlorides studied so far. Fig. 1 shows the variation of some interatomic distances as a function of the ionic...
radius of the metal atoms. As expected, only minor differences are found for the Sr compound compared to the Eu\textsubscript{3}OCl\textsubscript{6} and Sm\textsubscript{3}OCl\textsubscript{6} crystals [6,8]. The distances vary almost linearly as a function of ionic radius.

![Crystal Structure Diagram](image)

**Fig 2.** Projection along c of the crystal structure of Sr\textsubscript{3}OCl\textsubscript{6}. Sr atoms are in black, Cl1 in white and Cl2 in grey. The O atoms are located in the center of the almost perfect Sr\textsubscript{3}O tetrahedra.

The structure is characterized by empty channels centered at the origin along the c-axis (see Fig.2). These channels may be viewed as empty face-sharing (slightly distorted) octahedra with distances of 291.0(2) pm between the virtual center and all 6 Cl ions. The angles are 85.74(5)° and 94.26(5)°. The Cl-Cl distance of the channel triangle is 396.0(2) pm for Sr\textsubscript{3}OCl\textsubscript{6} and increases up to ~ 435(2) pm for the Ba\textsubscript{3}OCl\textsubscript{6}. Located next to the less dense (empty) tricapped trigonal columns is a rather compact environment around Sr1 with coordination number (CN) 8 and distances close to the sum of ionic radii. Next to the latter comes a region
(CN=10) with longer interatomic distances around the metal ion Sr2; average distances are about 10% longer than the sum of the ionic radii.

The ionic radius of Cl is 181 pm, so the shortest distance of 347.2(1) pm observed between Cl1 and Cl2 is rather short and can only be explained by the particular geometrical constellation of the chloride ions surrounding the Sr₄O tetrahedron.

Compounds with chemical composition of A₄BX₆ exist also as anti-type (Na₆ZnO₄) [12] compounds. Disordered systems on the X position were found for both types e.g. Ba₄O(Cl,Br)₆ [4] or Na₃SrTaP₄ [13].

Table III - Selected interatomic distances (pm) with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th></th>
<th>Sr₂</th>
<th></th>
<th>Sr1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-O</td>
<td>235.1(1)</td>
<td>-O</td>
<td>236.7(3)</td>
</tr>
<tr>
<td></td>
<td>-Cl₂</td>
<td>x3 297.7(2)</td>
<td>-Cl₁</td>
<td>296.4(2)</td>
</tr>
<tr>
<td></td>
<td>-Cl₁</td>
<td>x3 318.3(1)</td>
<td>-Cl₁</td>
<td>x2 297.1(1)</td>
</tr>
<tr>
<td></td>
<td>-Cl₂</td>
<td>x3 363.3(2)</td>
<td>-Cl₂</td>
<td>x2 303.8(2)</td>
</tr>
<tr>
<td></td>
<td>-Sr₁</td>
<td>x3 382.8(1)</td>
<td>-Sr₁</td>
<td>x2 388.60(6)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cl₁</th>
<th></th>
<th>Cl₂</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-O</td>
<td>x2 347.2(1)</td>
<td>Cl₂</td>
<td>x2 336.1(3)</td>
</tr>
<tr>
<td></td>
<td>-Cl₂</td>
<td>x2 363.7(2)</td>
<td>-O</td>
<td>x2 357.7(8)</td>
</tr>
<tr>
<td></td>
<td>-Cl₁</td>
<td>x4 426.6(3)</td>
<td>-Cl₁</td>
<td>x2 396.0(2)</td>
</tr>
<tr>
<td></td>
<td>-O</td>
<td>x3 378.2(5)</td>
<td>Cl₂</td>
<td>x2 376.2(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x2 378.4(2)</td>
</tr>
</tbody>
</table>
Raman spectra

Figure 3 presents partially polarized Raman spectra of Sr$_4$OCl$_6$ and Ba$_2$OCl$_6$. Group theory predicts that the zone center optical vibrational modes transform as $7A_g + 3A_u + 3B_g + 8B_u + 10E_g + 11E_u$. The Raman active modes transform as $A_i (x^2+y^2,z^2)$, $E_i (xz, yz)$ and $E_u (x^2-y^2, xy)$.

The observed spectra reveal indeed some similarities. There is in both cases a group of 3 bands at high Raman shift around ca. 390 and 340 cm$^{-1}$ respectively. This group is well separated from the remaining spectrum and can be assigned to metal-oxygen vibrations. Indeed, if one considers theoretically an isolated $M_4\text{O}^{6-}$ ion of ideal tetrahedral symmetry, the application of standard site group analysis [14,15] shows that its antisymmetric stretching vibration (of $F_2$ symmetry) transforms in the crystal on a $C_3v$ site as $A_i + B_2 + E_i + E_u$. Keeping in mind that the $B_2$ mode is not Raman active, it is interesting to note that the 3 bands observed present indeed different polarization behavior. Additionnally, it is useful to compare the overall separation of these bands. This separation is about 37 cm$^{-1}$ in the Sr$_4$OCl$_6$ crystal, while it reaches 52 cm$^{-1}$ in the Ba$_2$OCl$_6$ crystal. This increased splitting can be associated with the stronger deviation from tetrahedral symmetry in the Ba crystal as shown by the difference in the metal-oxygen bond length (see Fig. 1). Preliminary Raman measurements on very hygroscopic Ca$_4$OCl$_6$ samples present 3 similar bands at 417, 422 and 463 cm$^{-1}$. These data yield thus a separation of 45 cm$^{-1}$, in agreement with the above argument. However, these spectra of Ca$_4$OCl$_6$ need to be confirmed on a single crystal kept under controlled atmosphere.

The precise assignment of the bands appearing at lower frequencies is difficult, as there are many different modes predicted by group theory.

By analogy with the Raman spectra of BaFCl and SrFCl and related mixed crystals [16,17], one may expect the metal chloride stretching modes as relatively
strong bands between 140 and 200 cm⁻¹, but there are also metal-oxygen motions which can appear in this spectral range.

Fig. 3 - Partially polarized Raman spectra of Sr₂OCl₆ (A) and Ba₂OCl₆ (B) at 20°C.

The imperfections of the polarizations arise from internal reflections in the very small (ca 0.5x0.5x2mm³) crystals used for these measurements. The laboratory frame axis Z is parallel to the c crystallographic axis of the crystal.

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REFERENCES


