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Communications

Ordering of La^{3+} Ions in the Bi^{3+} Sublattice of Layered Oxychloride Catalysts

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Although the ionic radii of trivalent bismuth and lanthanum are similar (96 and 106 pm, respectively), the structures of many pairs of corresponding ternary compounds (Bi_2CuO_4 ¹ and La_2CuO_4 ², for instance) are quite different from one another. This is attributed to the presence of the lone pair of electrons in Bi^{3+} and the specific local stereochemical requirements associated with it.

Lattice sites normally occupied by Bi^{3+} ions in layered oxyhalides may, however, be tenanted by a variety of alkali-metal and alkaline-earth-metal ions. This occurs in the family of catalysts upon which we have recently reported,^{3,4} $\text{M}\text{Ca}_2\text{Bi}_3\text{O}_4\text{Cl}_6$ ($\text{M} = \text{Li}, \text{Na}$). And in the families of so-called warm superconductors containing bismuth (for example, those possessing⁵ the formulas $\text{Bi}_2\text{Sr}_{2-x}\text{CaCu}_2\text{O}_8$ and $\text{Bi}_{2+x}\text{Ca}_{1-x}\text{Sr}_2\text{Cu}_2\text{O}_{8+x}$) there are indications that Bi^{3+} and Ca^{2+} may occupy similar sites. In the new type of catalyst for selective oxidation of methane,⁷ $\text{Cs}_2\text{Bi}_{10}\text{Ca}_2\text{-}$

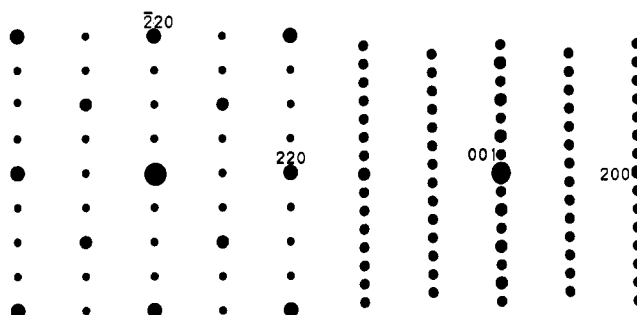


Figure 1. Schematic drawings of the selected area diffraction patterns of $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ viewed down $[001]$ with the $2\sqrt{2}.\sqrt{2}$ supermesh (left side) and down $[010]$ with the 2.1 supermesh (right side). Indexing is according to the BiOCl sublattice. Note that the magnifications are not the same for the left and right sides.

$\text{Cl}_{12}\text{O}_{16}$, there are also clear indications that Bi^{3+} and Ca^{2+} ions are not distributed at random among the (Bi^{3+}) sites of the layered structure.

Our interest in the solid solutions $\text{Bi}_{1-x}\text{La}_x\text{OCl}$ stems from two sources. First, several compounds derived from BiOCl are good catalysts for the selective oxidation of methane.^{2,3,7,8} Second, many solid solutions of mixed oxides containing bismuth display remarkably wide varieties of superlattice ordering.^{9,10} BiOCl itself is a good catalyst in the present context inasmuch as it yields ratios of ethene to ethane of 30 to 60, depending upon the precise conditions of oxidation. But it suffers from the disadvantage of losing chlorine during use. This loss can be greatly arrested,⁸ but at the expense of diminished catalytic performance, by replacing some of the Bi^{3+} ions with either La^{3+} or Sm^{3+} . (Both LaOCl and SmOCl are isostructural with BiOCl .)

Samples of $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ were made from a paste of the respective pure end members by using a 1 mol L^{-1} solution

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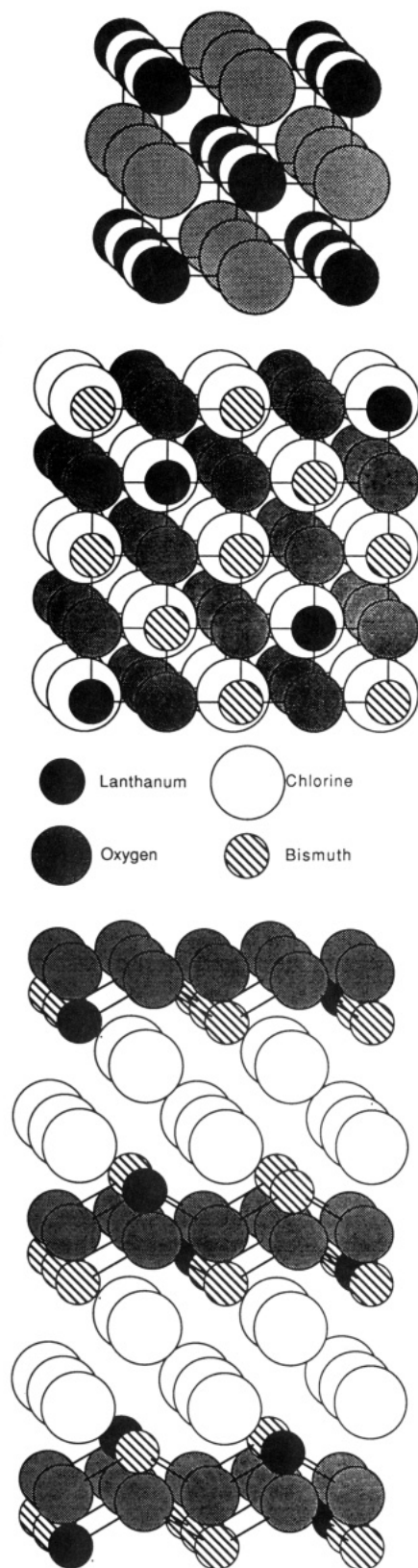


Figure 2. Comparison, roughly to scale, of the size and content of (top) the BiOCl (or LaOCl) structure with (middle and bottom) the $\sqrt{2.2}\sqrt{2.2}$ superlattice of the $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ structure.

of ammonium chloride. This was subjected to slow evaporation in an alumina crucible, thorough washing to remove excess chloride, compaction into tablets, and then heating for 72 h at 450 °C and 6 h at 900 °C. Phase purity was established by X-ray powder diffractometry. The spatial uniformity and homogeneity of the powdered product were

deduced from energy-dispersive X-ray microanalysis carried out using a JEOL-200CX electron microscope on a randomly selected set of 20 microcrystallites. The ratio of the $L\alpha$ lines of Bi and La was used for this purpose. (Since the Cl K and Bi M lines markedly overlap, it was not possible to probe the spatial uniformity of the anionic content.)

The X-ray diffractogram of the $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ was the same in appearance as that which we have previously published⁸ for both pure BiOCl and $\text{Bi}_{0.5}\text{La}_{0.5}\text{OCl}$. It is not in general feasible, as we have shown elsewhere⁹ for other solid solutions containing bismuth and oxygen, readily to discern, from X-ray diffractograms, evidence of any superlattice ordering. With use of electron diffraction, however, superlattice formation is readily apparent (see Figure 1, which shows typical selected area diffraction patterns down two high-symmetry directions).

It is clear that, compared with the structure of the pure BiOCl¹¹ ($a_0 = 38.9$, $c_0 = 73.7$ pm, space group $P4/mmm$), the 3:1 solid solution of Bi^{3+} and La^{3+} yields a new unit cell related to the parent one as shown in Figure 2, the relevant superlattice factors being $\sqrt{2}$, $2\sqrt{2}$, and 2. On the basis of this idealized superstructure, we have computed, by the multislice method,^{9,12} the expected high-resolution microscopic image and compared it with that observed under the appropriate^{13,14} electron optical and other conditions. The correspondence is good, and, in particular, the real-space image confirms the reality of the doubling of the c axis repeat in the $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ ordered, solid solution.

We have also examined, by selected area electron diffraction, specimens of the 1:3 and 1:1 solid solution ($\text{Bi}_{0.25}\text{La}_{0.75}\text{OCl}$ and $\text{Bi}_{0.5}\text{La}_{0.5}\text{OCl}$, respectively). No superlattice spots are seen in the former (down the 001 and $1\bar{1}1$ zone axes); and with the latter some incommensurate satellite diffraction spots appear along the $[1\bar{1}2]$ direction.

Careful measurement of the diffraction patterns of the $\text{Bi}_{0.75}\text{La}_{0.25}\text{OCl}$ revealed the presence of a slight lattice distortion away from the idealized orthorhombic state, the γ angle being ca. 91°. Crystals of this composition also show a slight tendency to exhibit twinning. The subtlety of the dependence of catalytic performance on cation ordering in the solid is underlined by this work.

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Low-Temperature Chemical Vapor Deposition of High-Purity Copper from an Organometallic Source

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Thermal chemical vapor deposition (CVD) of copper has been reported from several inorganic sources including