Three New Ordering Schemes for Oxygen Vacancies in $CaMnO_{3-x}$ Superlattices based on Square-pyramidal Co-ordination of Mn^{3+}

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Electron diffraction and high resolution electron microscopy have brought to light three new ordered structures in a material of composition $CaMnO_{(2.50 \pm 0.02)}$; in all these structures as well as in another analogous oxide, $CaMnO_{2.75}$, the original features of the perovskite structure are preserved, thus offering an explanation for the facile loss and uptake of oxygen properties that these selective oxidation catalysts possess.

When perovskites (ABO_3) are rendered grossly anion-deficient (ABO_{3-x} with $0<x<0.5$) by progressive reduction, there comes a point, clearly identified by *X*-ray diffraction analysis, magnetic measurements, and Mössbauer resonance studies,[1] when the vacancies adopt long-range order. In $CaFeO_{2.5}$ (which is the mineral brownmillerite[2]) and related systems such as $Ca_4YFe_5O_{13}$[3] or $Ca_2Fe_2O_5$–$LaFeO_3$[1] it has been established that the grossly defective structure is made up of separate sheets of corner-linked (MO_4) tetrahedra and corner-linked MO_6 octahedra. Recently, however, Longo *et al.*[4] found that in $CaMnO_{2.5}$ and $Ca_2MnO_{3.5}$ a hitherto unknown ordering scheme of oxygen vacancies (in perovskite-related structure) exists where Mn^{3+} cations are in essentially square-pyramidal co-ordination.

Effectively, in these compounds, unlike the grossly non-stoicheiometric shear- or block-structures,[5] the final 'defective' structure preserves the essential features of its stoicheiometric precursor [Figure 1(a) and (b)]. The oxygen vacancies occur in all layers to the same extent, and each sheet has a composition $CaMnO_{2.5}$, there being C_{4v} (square-pyramidal) co-ordination around the Mn^{3+} cation. In the course of a high-resolution electron microscopic study of $CaMnO_{2.5}$ we have, in addition to confirming the structure proposed by Longo,[4] discovered minor amounts of three other phases with different oxygen vacancy ordering schemes which again entail the essential feature of the parent structure and again implicate Mn^{3+} cations in square-pyramidal co-ordination. Samples prepared by reduction in hydrogen at 300 °C were too polycrystalline for study by electron diffraction, but those prepared at 600 °C in H_2–H_2O (1 : 1000) were quite satisfactory.

Electron diffraction patterns[6] (schematized in Figures 2, 3, and 4) revealed the existence of these new structures, which are drawn in their idealized form. It is to be noted that, in all these structures, each Mn^{3+} cation is five-co-ordinated (square-pyramidal). The diffraction patterns and unit cell dimensions rule out a structure in which there are alternating sheets of linked MnO_4 and MnO_6 polyhedra as in brownmillerite. The square unit cell of Figure 2 is compatible only with the composition $CaMnO_{2.5}$. In the cells of Figures 3 and 4, where there are three and four vacancies per cell, respectively, it is possible that some of the vacancies could be filled, thereby producing stoicheiometries other than $CaMnO_{2.5}$. Thus, if, in Figure 3, one of the three oxygen vacancies were occupied the stoicheiometry would then be 2.667, but the superlattice would be unchanged. Likewise, in Figure 4, if one of the four oxygen vacancies were occupied the new stoicheiometry would be 2.625. The superlattice phases represented by Figures 3 and 4 refer to minority constituents, which are detectable only by electron diffraction. *X*-Ray powder diffraction and neutron powder diffraction measurements reveal the presence of a single phase, that represented by Figure 1(b). No *in situ* analytical technique (such as *X*-ray emission spectrometry or electron energy loss spectroscopy) is sensitive enough to

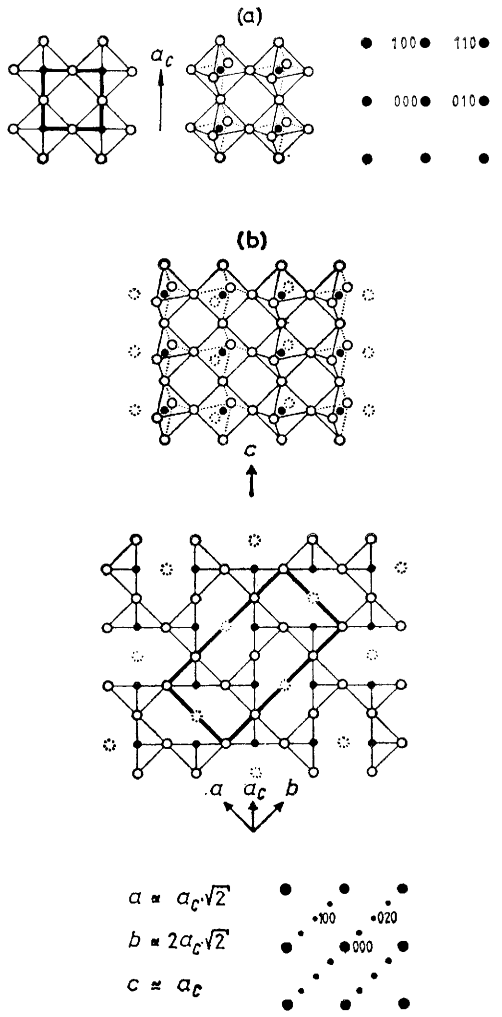

Figure 1. Schematic representation of the structures and electron diffraction patterns for $CaMnO_3$ and $CaMnO_{2.5}$.[4] (a) Projection along [001], slice parallel (100), and [001] zone-axis electron diffraction pattern for $CaMnO_3$. (b) Slice parallel ($\bar{1}20$), projection along [001], and [001] zone-axis pattern for $CaMnO_{2.5}$. (Full open circles: oxygen; dotted open circles: oxygen vacancies; filled circles: manganese; calcium ions are not shown).

detect surplus oxygen beyond that corresponding to $CaMnO_{2.5}$.

Our work has also brought to light a new, ordered structure in $CaMnO_{2.75}$ ($a = 5.35$, $b = 21.0$, $c = 7.47$ Å) again based on a 50:50 mixture of interconnecting MnO_5 square pyramids and MnO_6 octahedra. In another sample, we have also discovered evidence for an ordered structure of composition[7] $CaMnO_{2.8}$ which has a tendency to form intergrowths with the structures of formulae $CaMnO_{2.75}$ and $CaMnO_{3.0}$. This material was prepared by partial reduction of $CaMnO_3$ at 500 °C using H_2 gas. The initial, fully oxidized, perovskite crystals were grown in a $CaCl_2$ melt at 900 °C.

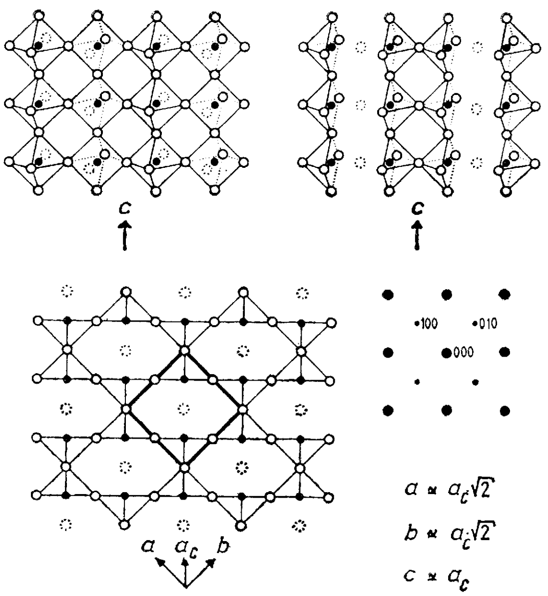

Figure 2. Slices parallel ($\bar{1}10$) and (110) respectively, projection along [001], and [001] zone-axis electron diffraction pattern for $CaMnO_{2.5}$.

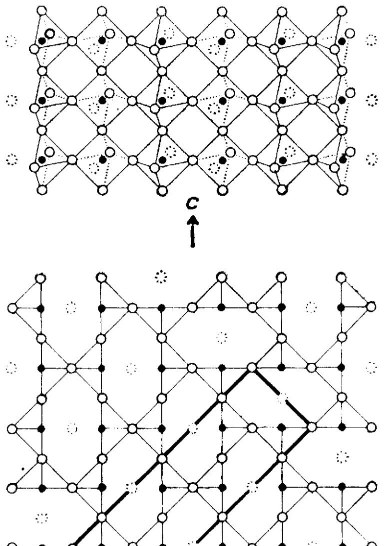

Figure 3. Slice parallel ($\bar{1}30$), projection along [001], and [001] zone-axis electron diffraction pattern for $CaMnO_{2.6}$.

Apart from their intrinsic structural importance,[8] the discovery of this family of well ordered, grossly non-stoicheiometric, perovskite-related oxides is of considerable relevance in heterogeneous catalysis, since ternary oxides of this kind function as selective oxidizing agents. Whereas the formation of WO_{3-x}, NbO_{3-x}, and TiO_{2-x} involves collapse and shear following elimination of oxygen, in the compounds discussed here there is only relatively minor structural reorganization accompanying oxygen removal. This fact could well account for the facile and reversible displacement of oxygen from this kind of perovskite structure and, in turn, explain why these structures have such promising[9] catalytic activity.

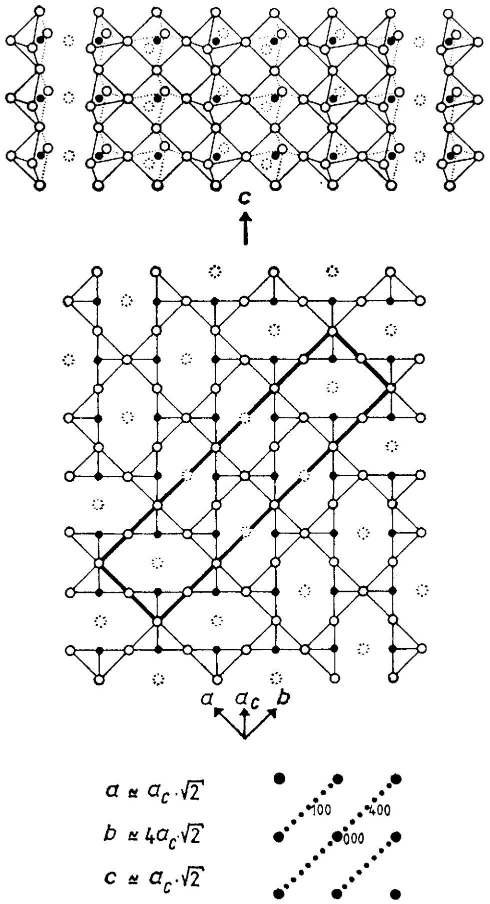

Figure 4. Slice parallel ($\bar{1}40$), projection along [001], and [001] zone-axis electron diffraction pattern for $CaMnO_{2\cdot5}$.

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