

Novel Oxygen Vacancy-ordered Phases of $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ prepared by the Topotactic Reduction of the Perovskite Oxides, $\text{Ca}_3\text{Fe}_{3-x}\text{Mn}_x\text{O}_{9-y}$ ($0 < y < 1.5$)

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Octahedral (O), tetrahedral (T), and square pyramidal (SP) co-ordination polyhedra of the transition metal ions are shown to coexist in oxides of the type $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$; these oxides transform on heating to the brownmillerite structure with only O and T co-ordination polyhedra.

Novel metal oxides exhibiting superstructures due to the ordering of anion or cation vacancies constitute an important recent development in the chemistry of inorganic solids.^{1,2} For example, an unusual oxide of nickel, $\text{La}_2\text{Ni}_2\text{O}_5$, ($n = 2$ in the $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$ series) where the Ni^{2+} ions are present both in octahedral and square planar co-ordination has been recently

reported.³ $\text{Ca}_2\text{Fe}_2\text{O}_5$ [brownmillerite (BM) structure] possessing alternate sheets of octahedra and tetrahedra along the b -axis of an orthorhombic unit cell⁴ and $\text{Ca}_2\text{Mn}_2\text{O}_5$ possessing sheets of square pyramids along the c -axis of an orthorhombic unit cell⁵ are two well-known examples of such oxides in the perovskite family¹ (Figures 1 and 2). It is of considerable

Table 1. Composition and unit cell parameters of $\text{Ca}_3\text{Fe}_{3-x}\text{Mn}_x\text{O}_{9-y}$ ($0 < y < 1.5$) and oxides obtained by hydrogen reduction.

Composition	Perovskite oxides			Composition	Oxides obtained by reduction		
	a	b	c		a	b	c
$\text{Ca}_3\text{Fe}_2\text{MnO}_8$	5.37	11.14	5.50	$\text{Ca}_3\text{Fe}_2\text{MnO}_{7.5}$ ($\equiv \text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$)	5.53	11.20	10.83
$\text{Ca}_3\text{Fe}_{1.5}\text{Mn}_{1.5}\text{O}_{8.1}^a$	5.35	11.19	5.44	$\text{Ca}_3\text{Fe}_{1.5}\text{Mn}_{1.5}\text{O}_{7.5}$ ($\equiv \text{Ca}_2\text{FeMnO}_5$)	5.53	11.06	10.86
$\text{Ca}_3\text{FeMn}_2\text{O}_{8.35}^a$	5.32	11.26	5.42	$\text{Ca}_3\text{FeMn}_2\text{O}_{7.5}$ ($\equiv \text{Ca}_2\text{Fe}_{0.67}\text{Mn}_{1.33}\text{O}_5$)	5.48	11.20	10.20

^a The stoichiometric excess of oxygen is likely to be accommodated by converting part of the tetrahedra into octahedra or square pyramids.

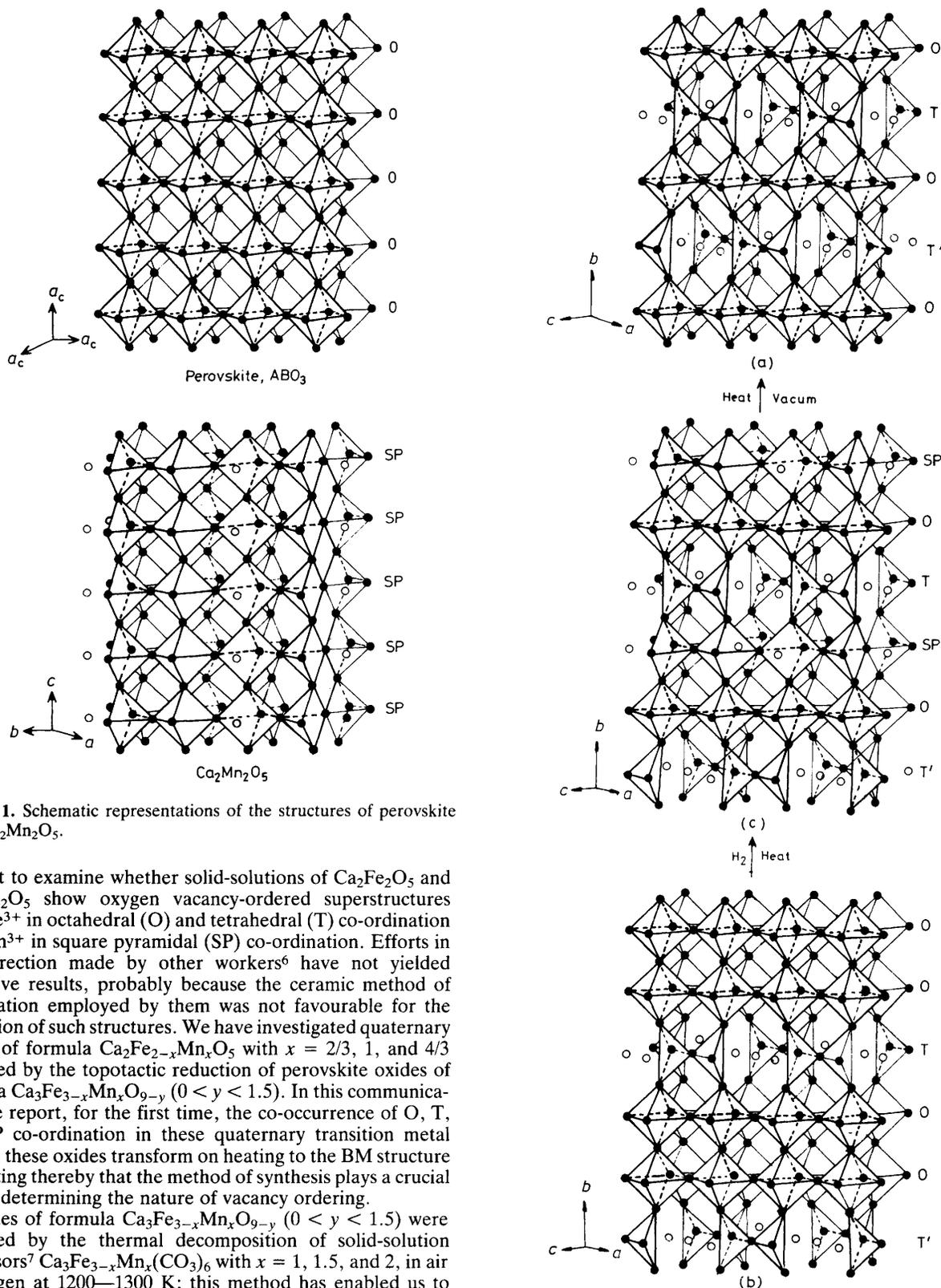


Figure 1. Schematic representations of the structures of perovskite and $\text{Ca}_2\text{Mn}_2\text{O}_5$.

interest to examine whether solid-solutions of $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Mn}_2\text{O}_5$ show oxygen vacancy-ordered superstructures with Fe^{3+} in octahedral (O) and tetrahedral (T) co-ordination and Mn^{3+} in square pyramidal (SP) co-ordination. Efforts in this direction made by other workers⁶ have not yielded definitive results, probably because the ceramic method of preparation employed by them was not favourable for the formation of such structures. We have investigated quaternary oxides of formula $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ with $x = 2/3, 1,$ and $4/3$ prepared by the topotactic reduction of perovskite oxides of formula $\text{Ca}_3\text{Fe}_{3-x}\text{Mn}_x\text{O}_{9-y}$ ($0 < y < 1.5$). In this communication we report, for the first time, the co-occurrence of O, T, and SP co-ordination in these quaternary transition metal oxides; these oxides transform on heating to the BM structure suggesting thereby that the method of synthesis plays a crucial role in determining the nature of vacancy ordering.

Oxides of formula $\text{Ca}_3\text{Fe}_{3-x}\text{Mn}_x\text{O}_{9-y}$ ($0 < y < 1.5$) were prepared by the thermal decomposition of solid-solution precursors⁷ $\text{Ca}_3\text{Fe}_{3-x}\text{Mn}_x(\text{CO}_3)_6$ with $x = 1, 1.5,$ and 2 , in air or oxygen at 1200–1300 K; this method has enabled us to prepare a wider range of compositions of the oxides than normally obtained by the ceramic method⁸ as shown in Table 1. X-Ray powder diffraction and electron diffraction patterns of these oxides show them to have an orthorhombic unit cell (see Table 1 for unit cell data) corresponding to the $n = 3$ member of the $\text{A}_n\text{B}_n\text{O}_{3n-1}$ series⁹ with BM type of oxygen vacancy ordering.

Figure 2. Schematic representations of the structures of (a) $\text{Ca}_2\text{Fe}_2\text{O}_5$ (BM), (b) $\text{Ca}_3\text{Fe}_2\text{MnO}_8$, and (c) $\text{Ca}_3\text{Fe}_2\text{MnO}_{7.5} \equiv \text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$. (c), with SP, O, T polyhedra transforms to the BM structure on heating *in vacuo*. (●: oxygen; ○: oxygen vacancy; metal ions are not shown).

Careful reduction of the perovskite oxides in dilute hydrogen ($H_2:N_2$ mixture with a 1:5 volume ratio) at 600 K in a thermogravimetric balance gave oxides of general formula $Ca_3Fe_{3-x}Mn_xO_{7.5}$ with $x = 1, 1.5,$ and 2 (Table 1, Figure 2), all of which possess an orthorhombic unit cell with the c -axis doubled compared to that in the parent oxides. The unit cell parameters of these oxides from X-ray diffraction (Table 1) bear the following relations to the cubic perovskite cell: $a \approx \sqrt{2}a_c$, $b \approx 3a_c$, and $c \approx 2\sqrt{2}a_c$. We readily see that this supercell is related to both the $n = 3$ member of the $A_nB_nO_{3n-1}$ series ($b \approx 3a_c$) and to $Ca_2Mn_2O_5$ ($a \approx \sqrt{2}a_c$ and $c \approx 2\sqrt{2}a_c$) suggesting that oxygen vacancy ordering is likely to involve features of both the parent oxide and $Ca_2Mn_2O_5$.

An electron diffraction investigation of $Ca_3Fe_2MnO_{7.5}$ not only confirms the unit cell dimensions derived from X-ray diffraction but also provides information related to vacancy ordering. Thus, the $[010] \equiv [001]_c$ zone-axis electron diffraction pattern is similar to the $[001]$ zone-axis pattern of $Ca_2Mn_2O_5$, showing three superlattice reflections along $[110]_c$; accordingly the pattern shows $a \approx \sqrt{2}a_c$ and $c \approx 2\sqrt{2}a_c$ relationships characteristic of an ordered SP layer. Furthermore, the diffraction pattern differs from that of the parent oxide, $Ca_3Fe_2MnO_8$ (with OOT sequence) in the corresponding zone-axis. The $[201] \equiv [100]_c$ zone-axis pattern which shows a tripling of the perovskite cell along the b -direction as in the parent $Ca_3Fe_2MnO_8$ reveals that the three-layer repeat in this direction is retained in the reduction product. The most probable superstructure of the oxide which accounts for both the composition and the electron diffraction patterns is therefore one involving a sequence of SP, O, and T polyhedra along the b -direction, Figure 2(c). The structure results from the topotactic reduction of the O layers of Mn^{4+} in $Ca_3Fe_2MnO_8$ to SP layers of Mn^{3+} in $Ca_3Fe_2MnO_{7.5}$, the oxygen vacancies being ordered along the $[100]$ as in $Ca_2Mn_2O_5$ (Figure 1). The topotactic relation between $Ca_3Fe_2MnO_8$, Figure 2(b), and $Ca_3Fe_2MnO_{7.5}$, Figure 2(c), can be expressed as $(100)_b || (100)_c$, $(010)_b || (010)_c$ and $(001)_b || (002)_c$.

X-Ray diffraction data of $Ca_3Fe_{1.5}Mn_{1.5}O_{7.5}$ and $Ca_3FeMn_2O_{7.5}$ (Table 1) also suggest the presence of three

polyhedral layers (O, T, and SP) in these oxides. Electron diffraction patterns however reveal that the polyhedra are not ordered. The disorder is likely to be due to the random occupancy of the O and SP sites by Mn^{3+} and Fe^{3+} ions; the T sites (occupied by Fe^{3+}) would however be ordered. It is also possible that the disorder in the polyhedral layers results from the disordered polyhedral arrangement in the parent oxides themselves.

Both $Ca_3Fe_2MnO_{7.5}$ and $Ca_3Fe_{1.5}Mn_{1.5}O_{7.5}$ transform to the BM structure ($a = 5.32-5.30$, $b = 15.13-15.29$, and $c = 5.48-5.46$ Å) on heating at 1150 K *in vacuo* without change in stoichiometry (Figure 2). This transformation to the BM structure suggests that the formation of structures with ordered or disordered arrangements of O, T, and SP polyhedra is due to the method of preparation rather than the site preference energies. One would expect $Ca_2Mn_2O_5$ itself to transform to the BM structure on heating, but unfortunately it decomposes to the component oxides.

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