A New Perovskite-Type Compound: $Ca_4Fe_2Ti_2O_{11}$

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A new perovskite-related oxide with a composition $Ca_4Fe_2Ti_2O_{11}$ has been found in the $Ca_2Fe_2O_5$–$CaTiO_3$ system. Synthesis and characterization by X-ray diffraction and electron microscopy are reported. A model based on a stacking sequence of . . . OOOTOOOT' . . . along the b axis of this material, corresponding to the structure of a compound with $n = 4$ in the $A_nM_nO_{3n-1}$ series, is proposed. © 1987 Academic Press, Inc.

Introduction

Nonstoichiometry in perovskite-related oxides, AMO_3 (*1*), has been widely studied. The substitution of either A or M cations by other ions of lower oxidation state leads to the formation of nonstoichiometric compounds with the general formula AMO_{3-y}. The composition range of these materials varies from AMO_3 to $AMO_{2.5}$, i.e., from a compound with a complete anionic sublattice to another in which one of six anionic sites is vacant, a brownmillerite-type structure being frequently obtained (*2*). However, due to the close analogy existing between both structural types, Wadsley (*3*) predicted the existence of ordered phases with an AMO_{3-y} ($0 \leq x \leq 0.5$) composition. These phases have been reported by Grenier *et al.* (*4*) who described a structural model in which $n - 1$ layers of octahedra alternate with a layer of tetrahedra along their b axis, having the general formula $A_nM_nO_{3n-1}$ and $y = 1/n$. Up to now, only three members of this family have been isolated:

$n = 2$, corresponding to the brownmiller-

ite-type structure, $AMO_{2.5}$, in which an octahedral layer alternates with a tetrahedral layer, following the . . . OTOT' . . . stacking sequence due to the relative orientation of the tetrahedra along the b axis (Fig. 1a),

$n = 3$, i.e., the $AMO_{2.67}$ material (*4*) in which two octahedral layers alternate with one tetrahedral layer with a . . . OOTOOT . . . sequence (Fig. 1b), and

$n = \infty$, i.e., the perovskite structure, AMO_3, where only $[MO_6]$ octahedra are present (Fig. 1c).

Efforts to obtain new ordered phases having this general formula have led to materials showing disordered intergrowths among these three structural types (*5–7*). In this paper we describe the synthesis and characterization, by X-ray powder diffraction and electron microscopy, of an $n = 4$ type compound of this series having an $AMO_{2.75}$ composition.

Experimental

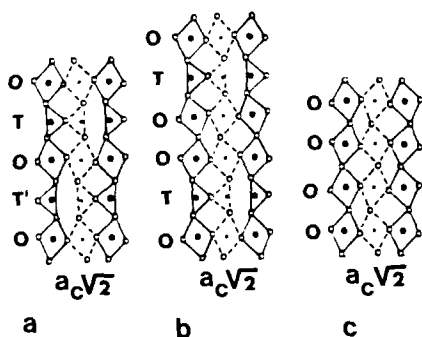The $Ca_4Fe_2Ti_2O_{11}$ sample has been prepared from the corresponding stoichio-

FIG. 1. Structural models corresponding to the three members of the $A_nM_nO_{3n-1}$ series. (a) Brownmillerite. (b) $AMO_{2.67}$ type material. (c) Perovskite.

metric amounts of $CaCO_3$, α-Fe_2O_3, and TiO_2 (anatase). The mixture was heated at 1000°C for 24 hr to decompose the carbonate and, then, fired at 1350°C in air for 48 hr. In order to obtain an ordered material the product was annealed at 1100°C in air for 45 days. Finally, an annealing at 1100°C under low partial oxygen pressure ($pO_2 \simeq 10^{-5}$ atm) was necessary to reduce Fe(IV) to Fe(III). A homogeneous brown powder was obtained.

Total amounts of calcium, iron, and titanium were confirmed by atomic absorption spectrometry. The oxidation state of iron was determined by chemical analysis with $K_2Cr_2O_7$ solution after dilution in 3 N HCl with an excess of Mohr's salt, confirming that all iron was in the III state of oxidation.

Electron microscopy was carried out on a JEOL 200 CX electron microscope equipped with a ±30° goniometer stage, kindly lent to us by the INPG, Grenoble, France.

Results and Discussion

Figure 2 shows the X-ray diffraction powder pattern of the Ca$_4$Fe$_2$Ti$_2$O$_{11}$ sample. According to previous papers (2, 5), the observed diffraction peaks correspond to a material with orthorhombic symmetry and $\sim a_c\sqrt{2} \times na_c \times a_c\sqrt{2}$ parameters, a_c being the cubic perovskite unit cell parameter. However, such diffraction patterns are difficult to index since n can, in principle, have various values and other phases with similar parameters and overlaping diffraction peaks can be obtained. In order to solve this possible ambiguity a study by electron diffraction and microscopy was performed.

Figure 3a shows the electron diffraction pattern along [010] of this new phase, parallel to the [010]$_c$ direction of the perovskite substructure. This pattern confirms the orthorhombic distortion showing a ratio $a^*/c^* = 1.01$. The order along this direction is shown in the corresponding electron micrograph (Fig. 3b).

The electron diffraction pattern along [10$\bar{1}$] parallel to [100]$_c$ is shown in Fig. 4a. An eightfold superlattice of the perovskite structure along the b axis can be observed. The corresponding electron micrograph
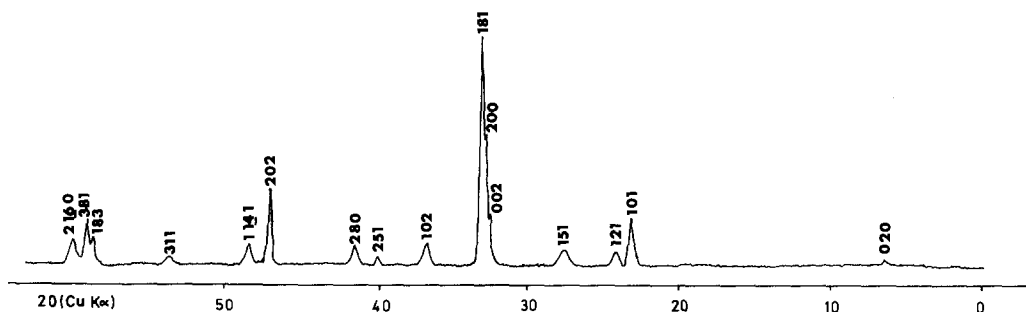

FIG. 2. X-ray diffraction powder pattern of the Ca$_4$Fe$_2$Ti$_2$O$_{11}$ sample (λCu$K\alpha$).
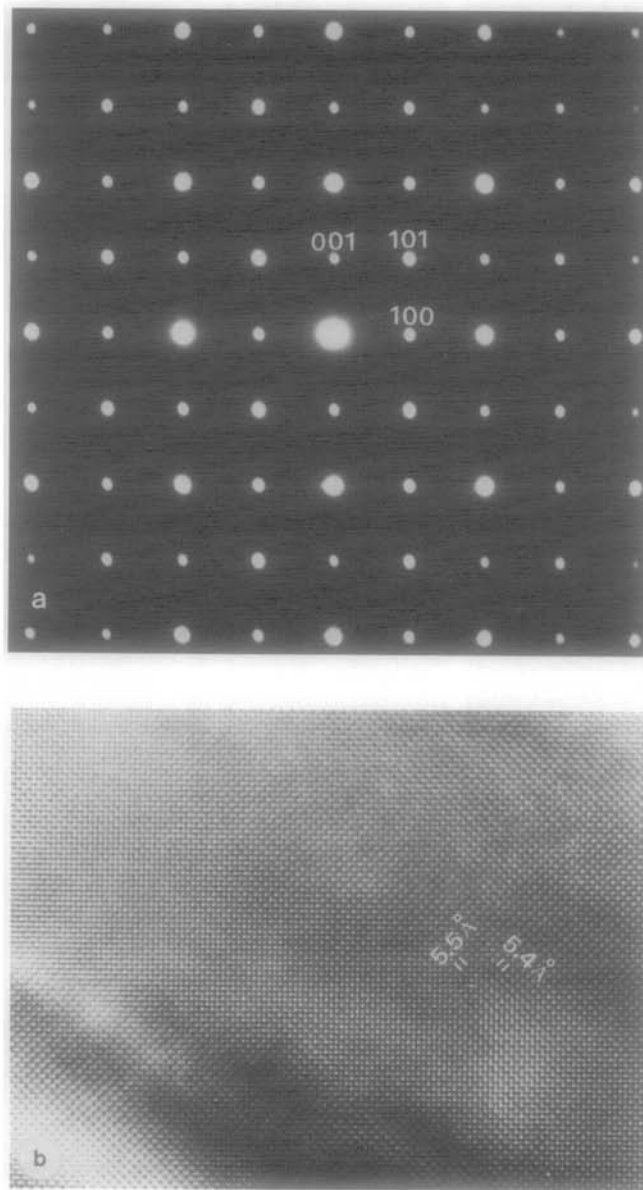
Fig. 3. (a) The electron diffraction pattern of $Ca_4Fe_2Ti_2O_{11}$ along $[010]\|[010]_c$. (b) The corresponding electron micrograph.

shows ordered fringes with a d spacing of 30.2 Å $= 8a_c$ (Fig. 4b).

From the electron diffraction data all the X-ray diffraction maxima can be indexed on an orthorhombic unit cell with $\sim a_c\sqrt{2} \times 8a_c \times a_c\sqrt{2}$ parameters. Unit cell parame-

ters, d spacings, and (hkl) indexes are presented in Table I.

Figure 5a shows the electron diffraction pattern with $[100]\|[10\bar{1}]_c$ where $(0kl)$ reflections only appear when $k + 1 = 2n$. This is reflected in the corresponding electron mi-
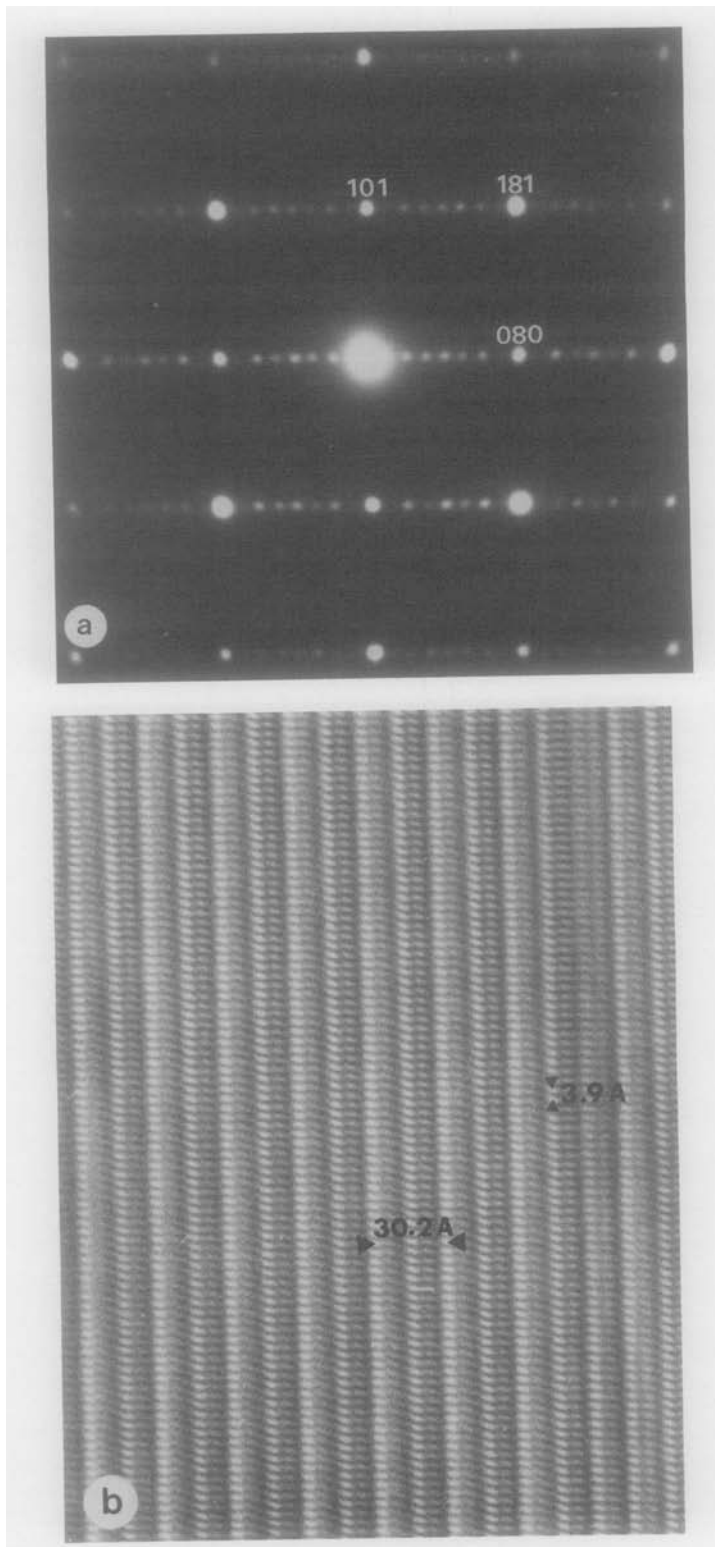
FIG. 4. (a) The electron diffraction pattern of the $n = 4$ term of the $A_n M_n O_{3n-1}$ series along the $[10\bar{1}]\|[100]_c$ zone axis. (b) The corresponding electron micrograph.
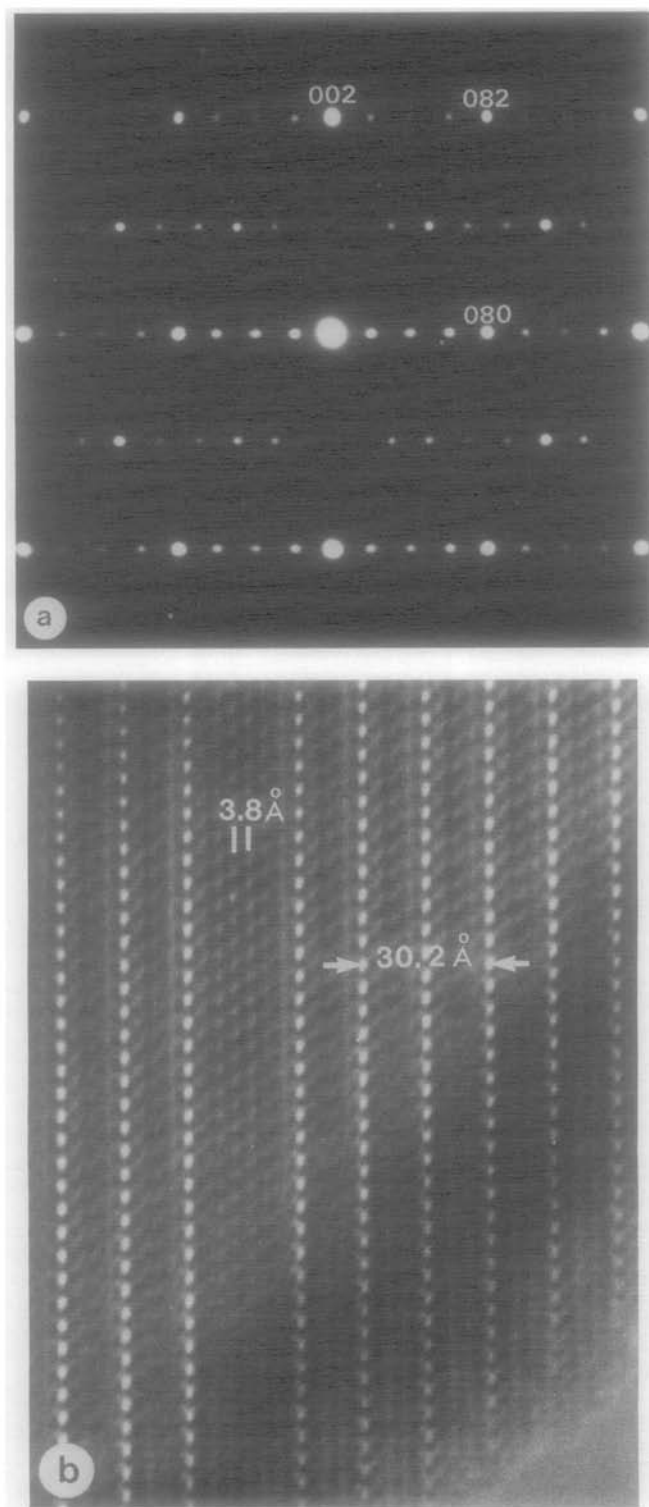
FIG. 5. (a) The electron diffraction pattern of the sample along $[100]\|[10\bar{1}]_c$. (b) The corresponding electron micrograph showing the true d spacing along the b axis.

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TABLE I

X-RAY DIFFRACTION POWDER DATA
($\lambda_{CuK\alpha} = 1.5418$ Å) FOR THE
$Ca_4Fe_2Ti_2O_{11}$ SAMPLE

$a = 5.437(1)$ Å
$b = 30.22(1)$ Å $V = 901.9(3)$ Å^3
$c = 5.489(1)$ Å

d_{obs} (Å)	d_{calc} (Å)	khl	I/I_0
15.107	15.112	020	2
3.866	3.863	101	15
3.753	3.742	121	8
3.263	3.255	151	2
2.742	2.744	002	30
2.716	2.718	200	50
2.698	2.700	181	100
2.449	2.450	102	5
2.264	2.259	251	3
2.207	2.207	280	6
1.930	1.931	202	35
1.886	1.884	1141	12
1.718	1.718	$\overline{3}11$	3
1.572	1.576	183	13
1.566	1.567	381	16
1.551	1.553	$\overline{2}160$	11

crograph (Fig. 5b) in which the repeating interval, along the b axis, is 30.2 Å. This contrast is also observed in a brownmillerite-type structure (6) and corresponds to the relative orientation of the tetrahedra along the b axis. Moreover, Bando et al. (8, 9) have synthesized a material with a composition of $Ca_4YFe_5O_{13}$ in which [FeO$_6$] octahedra and [FeO$_4$] tetrahedra follow the stacking sequence . . . OTOOTO T'OOT'O . . . . Structure images interpreted on the basis of the calculated images indicate that tetrahedra intergrown between two octahedra are disposed in the same orientation while tetrahedral layers separated by only one octahedra layer are tilted in a different way along the b axis. According to that, and on the basis of the image shown in Fig. 5b, a structural model can be proposed for $Ca_4Fe_2Ti_2O_{11}$ following a stacking sequence . . . OOOTOOOT'

. . . and, due to the relative orientation of the tetrahedra, the unit cell along the b axis is eight times the a_c perovskite axis (Fig. 6).

A previous study by electron microscopy of the so-called $Ca_2Ti_{2-2x}Fe_{2x}O_{6-x}$ solid solution (5) shows a one-dimensional lattice image in which some microdomains corresponding to the compound with $n = 4$ were present. Lattice fringes characterized by a $d = 15.1$ Å spacing were interpreted as due to a stacking sequence . . . OOOTOOOT . . . . However, the electron diffraction pattern of our sample along [$10\overline{1}$] (Fig. 4a) and the high-resolution micrograph along the [100] zone axis (Fig. 5b) show, conclusively, that $Ca_4Fe_2Ti_2O_{11}$ must be described as an eightfold superstructure of the perovskite structure due to the relative orientation of the tetrahedra, as shown in Fig. 6.

The above results show the existence of a new phase corresponding to the homologous series $A_nM_nO_{3n-1}$ and confirm that the ordered intergrowth of the end members of this family, i.e., where $n = 2$ and $n = \infty$, can lead to an infinite number of different sequences and, consequently, of different structures. Thus, while the structure of
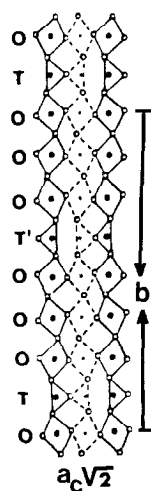

FIG. 6. The structural model proposed for the $A_4M_4O_{11}$ material.

compounds with $n = 3$ can be described as an ordered intergrowth between a perovskite unit cell and half a brownmillerite unit cell, the structure of compounds with $n = 4$ is formed by the ordered intergrowth of two perovskite unit cells and half a brownmillerite unit cell. However, the attainment of an ordered perovskite-related material with a relatively low vacancy concentration ($y = 0.25$) requires long annealing time, so the presence of stacking faults in these materials is relatively frequent. Figure 5b shows such a phenomenon, where lattice fringes with interplanar spacings of 3.8 Å, corresponding to the stacking sequence . . . OOOOOO . . . characteristic of the perovskite structure, alters the normal stacking sequence in phases with $n = 4$. This fact makes it difficult to obtain an ordered compound of this series with higher n values and, consequently, a lower vacancy concentration, but attempts to obtain such compounds by increasing the annealing time are in progress.

On the other hand, from the comparison of the structure of the compounds in the $A_n M_n O_{3n-1}$ series hitherto isolated, it seems that compounds in which n is odd have a $b = na_c$ parameter, while those in which n is even have a $b = 2na_c$ parameter. Determination of the structure of $Ca_4Fe_2Ti_2O_{11}$ by the Rietveld method of X-ray powder diffraction and some image calculations is in progress.

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