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Microdomain Formation in the $CaFe_xMn_{1-x}O_{3-y}$ Ferrites

I. $0.2 \leq x \leq 0.4$

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Electron microscopy and diffraction show that samples of the title system treated at 1400°C in air are formed by the intergrowth of $Ca_2Fe_2O_5$-like domains and/or $CaMnO_3$-like domains. Six sets of microdomains appear to be present in the $x = 0.4$ sample. These results are discussed in terms of oxygen deficiency, compositional variations, and structural relationship within the ferrite-type solid solutions.
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Introduction

The increasing structural complexity that is being discovered in nonstoichiometric solids (*1*) is giving to this subject a prominent role in the chemistry of solid materials (*2*). Complex defects (*3*), extended defects (*4*), and intergrowths (*5*) and, even more complicated, incommensurable structures (*6*) are nowadays "key words" in the studies of solids that, in the past, were supposed to change their composition by the presence of variable amounts of point defects.

More recently, and also from the experimental side, microdomains have been included to explain some cases of compositional variations in the oxidation of several iron perovskites (*7–9*). These microdomains are usually too small, 50–200 Å to a side, to be detected by means of the usual X-ray powder technique, and electron diffraction and microscopy have been essential to obtain evidence of the existence of such small structural entities. Indeed, in all cases in which we have observed microdomains, the X-ray powder pattern gave only evidence of a small cubic subcell (*10*), the real superstructure cell being detected by electron diffraction (*11*).

In order to enlarge our knowledge of the microdomain textured solids we are analyzing by electron microscopy and diffraction, materials which, supposedly having big amounts of, for example, oxygen vacancies, show simple X-ray diffraction patterns.

On the other hand, it is certainly of obvious interest to understand the factors that control the existence of microdomains. With respect to this, the introduction of other cations within the iron-based perovskites appeared to us as a logic extension of our previous work in this field. Among the iron-based mixed B cation perovskites, the system $CaFe_xMn_{1-x}O_{3-y}$ has already been given attention notably by Coates and McMillan (*12*) who found a

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pseudocubic perovskite in the range $CaMnO_3$ ($a = 3.736(2)$)–$CaMn_{0.5}Fe_{0.5}O_{2.75}$ ($a = 3.775(2)$), with the intensity of the superlattice lines decreasing with the increase in iron content and disappearing for $x \geq \frac{1}{4}$.

Afterwards, Banks *et al.* (*13*) have grown, by a flux method, single crystals of the same solid solution, but cubic crystals were only found in the range $0.2 \leq x \leq 0.4$.

More recently, Thomas *et al.* (*14, 15*) have dealt with the related system $CaMnO_{3-y}$ where they have found quite elaborate ordered states based in the structure of $Ca_2Mn_2O_5$ recently determined by Poeppelmeier *et al.* (*16*).

We report in this paper part of our work in the $CaFe_xMn_{1-x}O_{3-y}$ system, in the region $0.2 \leq x \leq 0.4$, in samples prepared at high temperature (~1400°C) in air.

Experimental

Samples of nominal composition $CaFe_xMn_{1-x}O_{3-y}$ ($0.2 \leq x \leq 0.4$) were prepared from a stoichiometric mixture of $CaCO_3$, $MnCO_3$, and α-Fe_2O_3 by heating at 1000°C for 48 hr to remove the carbonate. After such heat treatment, samples were fired at 1100°C and annealed in air at 1400°C for 60 hr. The obtained black materials were quenched to room temperature.

Products have been characterized by X-ray powder diffraction using silicon as internal standard.

Electron diffraction and microscopy have been performed on a SIEMENS ELMISKOP 102 electron microscope, fitted with a double tilting goniometer stage.

Chemical analysis. Total iron in the samples was determined by previously reducing it to the divalent state with a $SnCl_2$ solution in hydrochloric acid. The resulting Fe^{2+} was titrated with a $K_2Cr_2O_7$ solution in the presence of phosphoric acid.

The total manganese content of the samples was obtained after dissolving them in a mixture of nitric and phosphoric acids. Oxidation to permanganate by means of KIO_4 in the presence of phosphoric acid, allowed the manganese content to be determined by spectrophotometry.

The amount of Mn^{4+} was obtained by dissolving the sample in hydrochloric acid and adding potassium iodide solution in the presence of acetilacetone. The iodine liberated was determined by titration with a $Na_2S_2O_3$ solution in the presence of starch.

Total amounts of manganese and iron were also obtained by atomic absorption spectrometry.

A preliminary Mössbauer spectroscopy study indicates the absence of either Fe(IV) or Fe(II) in the samples.

Details about these procedures can be found in Ref. (*17*).

Results and Discussion

Samples of nominal composition $x = 0.2$ were shown by chemical analysis to have the composition $CaFe^{III}_{0.20}Mn^{III}_{0.35}Mn^{IV}_{0.45}O_{2.72}$, which implies a high amount of oxygen deficiency. By X-ray diffraction these solids were found to be tetragonal with a unit cell $a = c = 5.307(1)$ Å, $b = 7.505(1)$ Å, that is, approximately, $a_c\sqrt{2} \times 2a_c \times a_c\sqrt{2}$, where a_c is the pseudocubic unit cell parameter. In this case, $a_c = 3.753$. From density measurements Banks *et al.* (*13*) attributed the composition $CaFe_{0.2}Mn_{0.8}O_{2.70}$ to a similarly prepared sample where no Fe(IV) was found by Mössbauer spectroscopy.

Poepplemeier *et al.* (*16*) have recently shown by single-crystal X-ray diffraction that the material corresponding to $x = 0$, i.e., $CaMnO_3$ is orthorhombic with $a = 5.279$ Å, $b = 7.448(1)$ Å, $c = 5.264(1)$ Å, and a pseudocubic cell edge of $a_c = 3.726$ Å, somewhat lower than the value that we have observed for the $x = 0.2$ sample. This may be attributed to the bigger ionic size and lower oxidation state of both Fe^{3+} and Mn^{3+} with respect to Mn^{4+} (*18*):

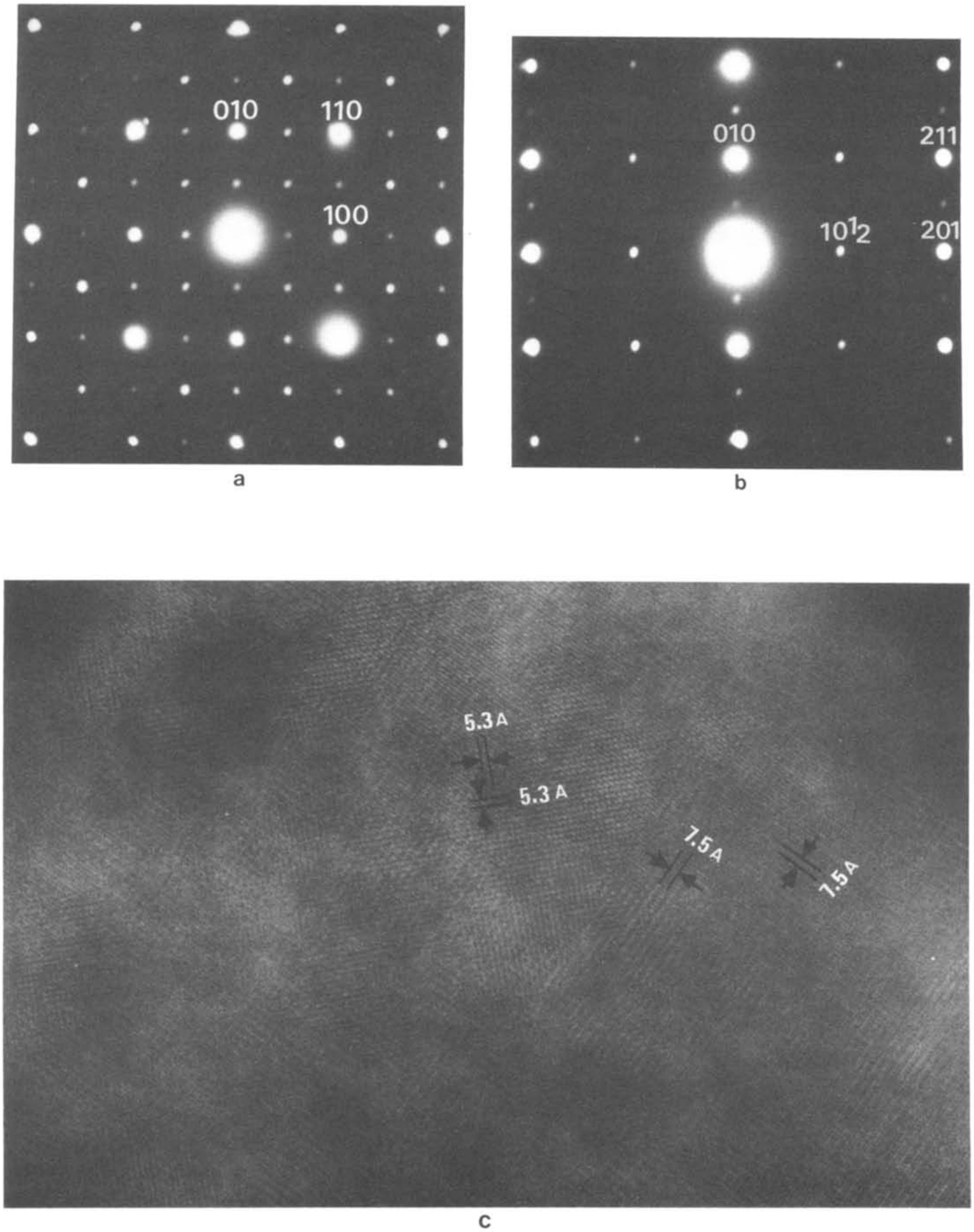

FIG. 1. (a) Electron diffraction pattern of the $x = 0.2$ sample along the $[001]_c$ zone axis. (b) Electron diffraction pattern of the $x = 0.2$ sample along the $[10\bar{2}]_c$ zone axis. (c) Electron micrograph corresponding to the $[001]_c$ zone axis. It can be seen that the perovskite doubled axis is oriented at random in one of the three space directions.

$^{VI}r_{Mn^{4+}} = 0.530$ Å;

$$^{VI}r_{Mn^{3+}} = {}^{VI}r_{Fe^{3+}} = 0.645 \text{ Å}$$

together with the presence of the oxygen deficiency. On the other hand, the presence of Fe^{4+} ($^{VI}r_{Fe^{4+}} = 0.585$ Å) would produce the opposite effect in the unit cell dimensions.

In the electron microscope our $x = 0.2$ sample was shown to have a somewhat more complex nature. Electron diffraction patterns along the pseudocubic $[001]_c$[1] zone axis (Fig. 1a) appeared, at a first sight, as due to a perovskite cell doubled in, at least, two directions: a_c and b_c with the above indexing. Tilting around either a_c^* or b_c^* showed that the third perovskite axis was apparently also doubled. Figure 1b, zone axis $[10\bar{2}]_c$ shows this. Electron microscopy suggests that the real situation is different. Figure 1c, corresponding to the $[001]_c$ orientation, indicates that the crystals are formed by the intergrowth of three types of domains: in each of them, the perovskite doubled axis is oriented at random in one of three space directions. Crystals such as the one shown in Fig. 1c are then examples of three-dimensional multitwinning (3DMT) and are formed by twinned domains of approximately the same size with an average dimension of about 80 Å a side. The multidomain nature of our solid may be the reason for it being, at least metrically, tetragonal both to X-ray and electron diffraction. It is not clear however if the structure within each domain is really tetragonal due to the presence of the multitwinning or if the orthorhombic distortion is so small that it is not detectable by our diffraction cameras.

On the other hand, the fact that, according to chemical analysis, this sample has about 34% Mn^{3+}, would imply, in the high-spin case usual in oxides (*19*), a distortion of the octahedra associated to the well-known Jahn–Teller effect (*20*). The multidomain nature of this sample may produce, by compensation in the different orientations, a nondistorted average. In this connection, it is worth mentioning that spinel-like solid solutions of composition $CuFe_{2-x}Cr_xO_4$ are cubic in the range $0.4 < x < 1.4$ due to a compensation of opposed Jahn–Teller effects (*21*).

Increasing the amount of iron, $x = 0.4$, the superstructure lines disappeared from the powder X-ray diffraction patterns. Simultaneously, the subcell reflections were somewhat broad. A cubic perovskite-like cell of parameter $a_c = 3.776(1)$ Å was obtained. The bigger unit cell size is what one would expect with an increased amount of Fe(III). Chemical analysis gave the approximate composition $CaFe^{III}_{0.4}Mn^{III}_{0.22}Mn^{IV}_{0.38}O_{2.69}$ (cf. Banks *et al.* $CaFe_{0.378}Mn_{0.624}O_{2.70}$ with a cubic cell of $a_c = 3.760(1)$ Å).

By electron microscopy and diffraction this material appeared quite different from a simple perovskite cubic cell. Again, the $[001]_c$ zone axis pattern (Fig. 2a), suggests a doubly doubled perovskite cell. Some streaking is apparent in the spots located at $(0\ k/2\ 0)$ and $(h/2\ 0\ 0)$ with h and k odd. Once again the electron micrograph showed the presence of domains (Fig. 2b). The actual situation is however still more complex than in the $x = 0.2$ sample. Tilting around a_c^* or b_c^* shows that the reciprocal lattice of these crystals has more diffraction maxima than required for a 3DMT cell, as operating in sample $CaFe_{0.20}Mn_{0.80}O_{2.72}$, cf. Fig. 1 above.

Figure 3b shows a $[10\bar{1}]_c$ zone axis pattern where two types of diffraction maxima are discernible:

(a) A series of maxima, schematically shown in Fig. 3a, which can be indexed on the basis of a brownmillerite-type cell. As it is known (*22–24*) the brownmillerite structure is a superstructure of the perovskite cell: $a_c\sqrt{2} \times 4a_c \times a_c\sqrt{2}$, space group *Pnma*, No. 62. In this space group, reflections $0kl$ are only allowed when $k + l = 2n$.

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[1] Subindex c refers to the cubic perovskite unit cell. Subindexes B and T refer to the brownmillerite and $CaMnO_3$-type unit cells, respectively.

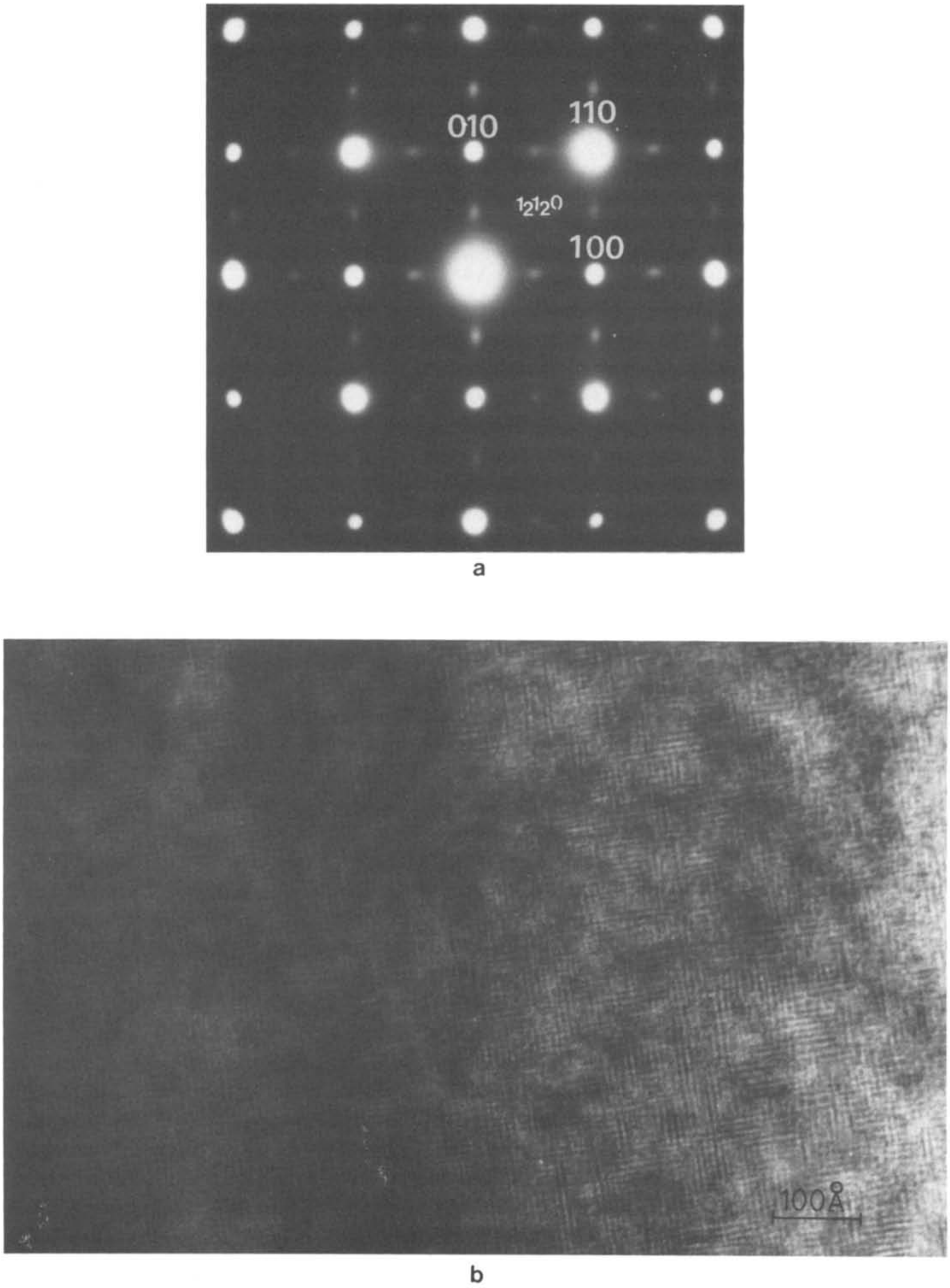

FIG. 2. (a) Electron diffraction pattern of the $x = 0.4$ sample along the $[001]_c$ zone axis. (b) Electron micrograph corresponding to the zone axis in a. A microdomain texture is evident.

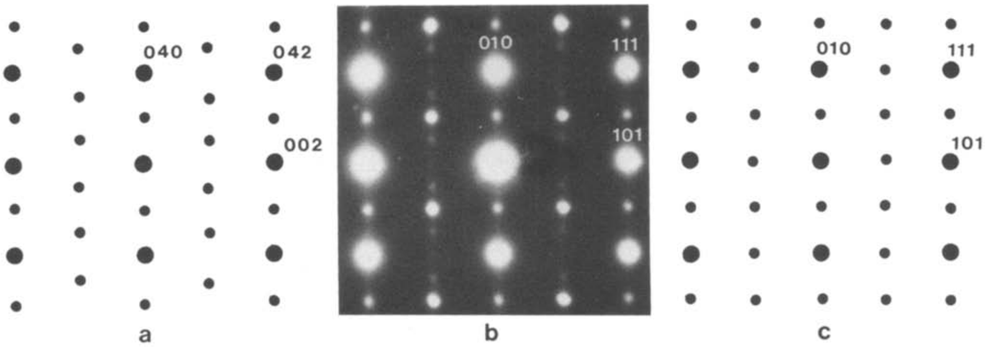

FIG. 3. Electron diffraction pattern corresponding to the $x = 0.4$ sample along the $[101]_c$ zone axis. (b), equivalent to the (a) $[100]_B$ zone axis and (c) zone axis shown in Fig. 1a.

(b) Another group of maxima, as schematized in Fig. 3c. Although these spots would appear to belong to a twice doubled perovskite cell, the above reasoning, regarding both the $x = 0.4$ and the $x = 0.2$ samples, forces us to assign them to a 3DMT pseudocubic structure.

Figure 4, an electron diffraction pattern of this same crystal after a tilt of 26.5° around b_c^*, contains the $[10\bar{2}]_c$ zone axis which confirms the coexistence of both groups of maxima. In particular, the spots appearing at $(h/2\ k/2\ l/4)_c$ with h, k, and l odd confirm the existence of a set of brownmillerite-like domains perpendicular to the two sets already referred to. Also, the spots appearing at $(h\ k\ l/2)_c$ with l odd confirm the presence of a third set of tetragonal $CaMnO_3$-like domains perpendicular to the two sets previously referred to. This set was already apparent from the diffraction maxima appearing in Fig. 2a at the $(h/2\ k/2\ 0)_c$ positions with h and k odd.

In the light of the above reasoning, it appears that the $x = 0.4$ sample is formed by the intergrowth of *six* sets of domains whose corresponding reciprocal lattices are schematically shown, by means of their reciprocal unit cells, in Fig. 5:

—Three sets of domains are characterized by a brownmillerite-type structure and they differ in the relative orientation of their b_B axis:

set α_B: $4a_c \times a_c\sqrt{2} \times a_c\sqrt{2}$

set β_B: $a_c\sqrt{2} \times 4a_c \times a_c\sqrt{2}$

set γ_B: $a_c\sqrt{2} \times a_c\sqrt{2} \times 4a_c$

—Another three sets of domains have the $CaMnO_3$-like structure with a metrically tetragonal cell; they also differ in the relative orientation of their b_T axis:

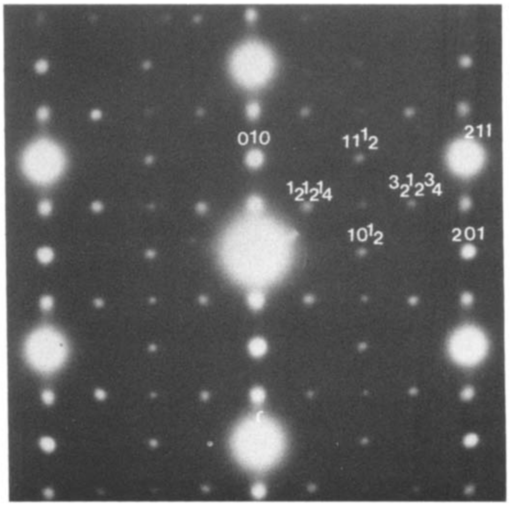

FIG. 4. Electron diffraction pattern corresponding to the $x = 0.4$ sample along the $[10\bar{2}]_c$ zone axis.

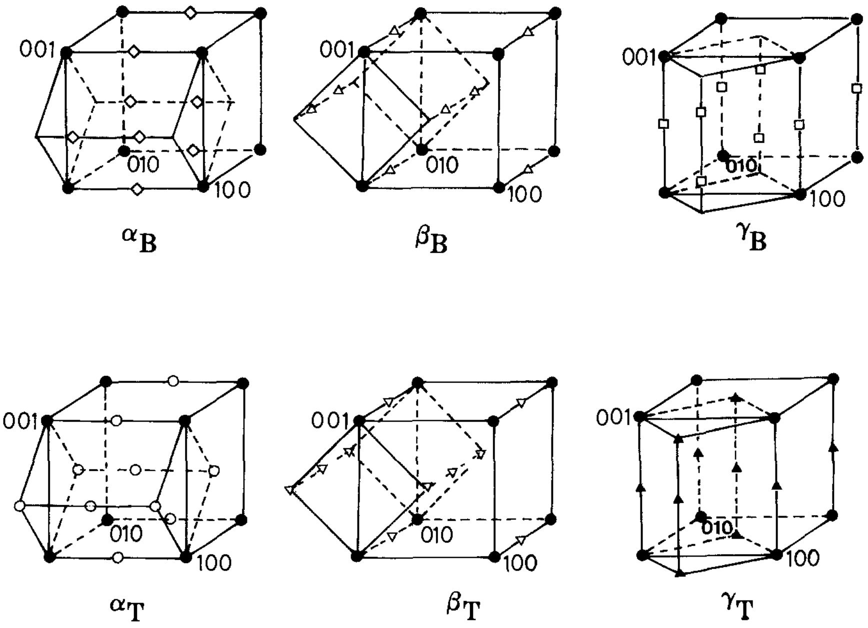

FIG. 5. Schematic representation of the three brownmillerite-type (B) and three CaMnO$_3$-like (T) reciprocal nets.

set α_T: $2a_c \times a_c\sqrt{2} \times a_c\sqrt{2}$

set β_T: $a_c\sqrt{2} \times 2a_c \times a_c\sqrt{2}$

set γ_T: $a_c\sqrt{2} \times a_c\sqrt{2} \times 2a_c$.

The ensemble of these nets has been collected with a common origin in Fig. 6 which represents the true reciprocal unit cell of the crystals of the $x = 0.4$ sample.

It then appears that the $x = 0.4$ sample is formed by the coalescence of *six* sets of microdomains which are characterized by being perovskite superstructures having similar a and c axes and differing in their b axis:

In CaMnO$_3$, $b_T = 2a_c$ due to a tilt of the octahedra (*16*).

In Ca$_2$Fe$_2$O$_5$, $b_B = 4a_c$ due to both a tilt and an alternating sequence of octahedra and tetrahedra where the relative orientation of the tetrahedra recurs every four polyhedra (*22–24*).

Nevertheless some crystal chemical problems arise in assembling together microdomains of a CaMnO$_3$-like solid and a Ca$_2$Fe$_2$O$_5$-like solid. First of all and in common with all previously microdomain tex-

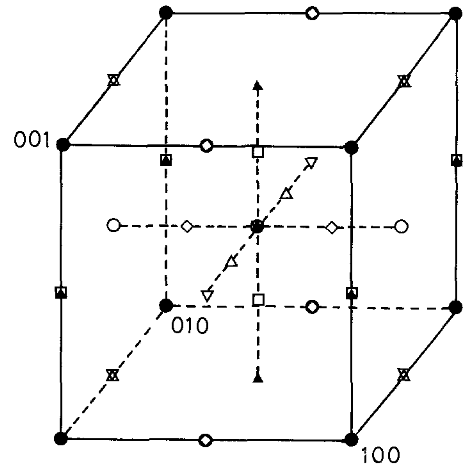

FIG. 6. Complete reciprocal lattice of the $x = 0.4$ sample composed by the juxtaposition of the six reciprocal nets shown in Fig. 5.

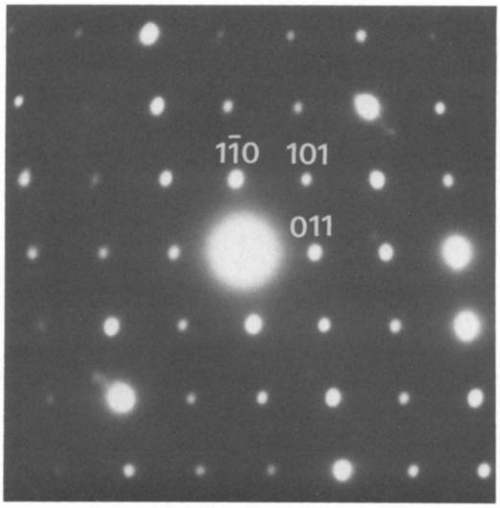

FIG. 7. Electron diffraction pattern of $Ca_2Fe_2O_5$ along the $[1\bar{1}1]_B$ zone axis.

tured solids that we have observed so far (*7–9*), both materials appear tetragonal to electron diffraction, while $Ca_2Fe_2O_5$ is clearly orthorhombic in its "normal state," i.e., outside microdomains. Figure 7 shows a $[1\bar{1}1]_B$ zone axis of $Ca_2Fe_2O_5$ prepared as described in Ref. (*25*). The orthorhombic distortion, $d(011)/d(110) = 1.03$ is obvious.

$CaMnO_3$ is also orthorhombic but the distortion is too small to be observed except with single-crystal X-ray patterns (*16*).

The facility of the intergrowth is then, no doubt, helped by the substitution of manganese by iron, as discussed above. Indeed, the pseudocubic cell dimensions of the solid solution change in the following way

$CaMn_{1-x}Fe_xO_{3-y}$	a_c (Å)
$x = 0$	3.726
$x = 0.20$	3.753
$x = 0.40$	3.776

$Ca_2Fe_2O_5$: $a_c = 3.829$ Å

So that, metrically, the samples in the middle region, x around 0.4, are optimum for intergrowing together if, some iron enters the manganate lattice giving a bigger cell size and also some manganese enters the brownmillerite-like lattice originating a cell contraction. Indeed the $x = 0.2$ sample has 20% iron but only one type of microdomains is formed and no brownmillerite-like domains are observed (see above and Fig. 1b). From $x = 0.5$ onwards a different structure appears (*13*).

The pseudocubic dimension is, certainly, not an absolute measure of the unit cell; we have to use it because, by diffraction methods, the $x = 0.4$ sample appears pseudocubic. However, the very fact that we observe *six* rather than *three* sets of domains, with different reciprocal lattices, is due to the fact that we have two different solids each one having three sets of domains. This will certainly impose structural constraints in the bordering regions between domains. These boundaries are certainly worth of further study.

The study of the $CaFe_xMn_{1-x}O_{3-y}$ system by the combination of electron diffraction and microscopy shows up several interesting facts and first of all the importance of microdomains in the building of mixed oxides.

But it also transpires from the observed facts that two different situations exist at each side of the composition range studied. At small degrees of Mn substitution, up to $x = 0.2$, which, in the high-temperature synthesis conditions employed, implies a Mn^{3+} amount of 34%, three-dimensional multitwinning (3DMT) was observed. No signs of planar ordering was observed for the oxygen-empty positions that such chemical composition suggest: ~1 in every 9 oxygen is absent. Perhaps the oxygen vacancies are just arranged in strings, as already observed by Mössbauer spectroscopy in the closely similar $CaFe_{2y}Ti_{1-2y}O_{3-y}$ (*26*) and $SrFe_xTi_{1-x}O_{3-y}$ (*27*) systems. A detailed Mössbauer study of our samples is currently under way.

At the other side of the composition range, $x = 0.4$, microdomains are also observed but these are of two kinds and arranged in six sets. Three of these sets are analogous to those just discussed for the $x = 0.2$ sample. The other three sets belong to a brownmillerite-type solid where, tetrahedra alternating with octahedra accommodate the oxygen deficiency in a planar ordered way. Under these circumstances we can conclude that the $x = 0.4$ solid is formed by the intergrowth of two different microdomain textured solids: a $CaMnO_3$-like solid where some iron and some vacancies are present but not planarly ordered and another, $Ca_2Fe_2O_5$-like solid, where some Mn is present. This second solid takes care of most of the oxygen deficiency by means of its ordered structure.

The analytical composition is then just an approximate average between a certain amount of each of the extreme terms of the system namely $x = 0$ and $x = 1$ in $CaFe_xMn_{1-x}O_{3-y}$. One can then "decompose" this average composition as

$$CaFe_{0.4}Mn_{0.6}O_{3-y} \leftrightarrow 0.2\ Ca_2Fe_2O_5 + 0.6\ CaMnO_3$$

if we disregard, for the moment, the possible presence of Mn in the $Ca_2Fe_2O_5$ and of Fe in the $CaMnO_3$. The $x = 0.4$ sample that we have studied is just a kind of sophisticated intergrowth (*28*): a supposed anion deficiency is accommodated by the disordered intergrowth of two closely related phases without the need, or without the chance, of a normally ordered arrangement of the anion vacancies in a superstructure. It is worth pointing out in this connection that Coates and McMillan (*12*) concluded that manganese was entering the brownmillerite-like lattice as Mn^{3+}. This is clearly in agreement with the $Ca_2Fe_2O_5$-like solid accounting for the oxygen deficiency that we suggest.

But it is also interesting to mention here that undoped $Ca_2Fe_2O_5$ does not show a microdomain texture when heated up to 1400°C in air. The formation of microdomains in the $Ca_2Fe_2O_5$-like solid, that constitutes part of the $x = 0.4$ crystals, suggest that the presence of Mn is instrumental in facilitating the microdomain formation in $Ca_2Fe_2O_5$. We have shown elsewhere (*8*) that microdomain formation in $Ca_2LaFe_3O_8$ accompanies an oxidation process:

$$Ca_2LaFe_3O_8 + z/2\ O_2 \rightarrow Ca_2LaFe_3O_{8+z}$$

(with $z = 0.235$ at 1400°C in air)

and from this we have suggested that the oxygen excess is likely to be located in the domain walls. Along this line of reasoning, the fact that brownmillerite-like domains are observed here seems to indicate that an oxidation process is taking place. In view of the fact that undoped $Ca_2Fe_2O_5$ does not oxidize in the thermal treatment that our samples have experienced we are forced to admit that part of the manganese is entering $Ca_2Fe_2O_5$ as Mn^{4+} so that some extra oxygen renders possible microdomain formation in the brownmillerite-like $Ca_2Fe_2O_5$. It will certainly be of interest to know the relative amounts and oxidation states of the cations existing within the six sets of domains but this appears to be a difficult goal to achieve.

The marked differences observed between our system and the $CaMnO_{3-y}$ system studied by Thomas *et al.* (*14, 15*) are an interesting reflection of the differences existing between Mn^{3+} and its tendency to have a pyramidal surrounding (*16*) as opposite to Fe^{3+} which certainly prefers to stay in a tetrahedral environment.

Acknowledgments

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References

1. O. T. Sorensen (Ed.), "Nonstoichiometric Oxides," Academic Press, New York (1981).

2. L. Eyring and M. O'Keeffe (Eds.), "The Chemistry of Extended Defects in Nonmetallic Solids," North-Holland, Amsterdam (1970).
3. A. Dominguez Rodriguez, J. Castaing, and R. Marquez, "Basic Properties of Binary Oxides," Publicaciones de la Universidad de Sevilla, Sevilla, Spain (1984).
4. B. G. Hyde, S. Anderson, M. Bakker, C. M. Plug, and M. O'Keeffe, *Prog. Solid State Chem.* **12,** 273 (1979).
5. A. Hussain and L. Kihlborg, *Acta Crystallogr. Sect. A* **32,** 551 (1976).
6. B. G. Hyde and C. Otero, *Acta Crystallogr. Sect. B* **39,** 569 (1983).
7. M. A. Alario-Franco, J. C. Joubert, and J. P. Levy, *Mater. Res. Bull.* **17,** 733 (1982).
8. M. A. Alario Franco, M. J. R. Henche, M. Vallet, J. M. G. Calbet, J. C. Grenier, A. Wattiaux, and P. Hagenmuller, *J. Solid State Chem.* **46,** 23 (1983).
9. M. A. Alario Franco, J. M. Gonzalez Calbet, M. Vallet Regi, and J. C. Grenier, *J. Solid State Chem.* **49,** 219 (1983).
10. J. C. Grenier, F. Menil, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **12,** 79 (1977).
11. M. A. Alario Franco, M. J. R. Henche, M. Vallet, J. C. Grenier, A. Wattiaux, and P. Hagenmuller, *in* "Solid State Chemistry 1982" (R. Metselaar, Ed.), p. 733, Elsevier, Amsterdam (1983).
12. R. V. Coates and J. W. McMillan, *J. Appl. Chem.* **14,** 346 (1964).
13. E. Banks, D. Berkooz, and T. Nakagawa, *Nat. Bur. Stand. (U.S.) Spec. Publ.* **364,** 265 (1972).
14. A. Reller, D. A. Jefferson, J. M. Thomas, and M. Uppal, *J. Phys. Chem.* **87,** 913 (1983).
15. A. Reller, D. A. Jefferson, J. M. Thomas, R. A. Beyerlein, and K. R. Poeppelmeier, *J. Chem. Soc., Chem. Commun.,* 1378 (1982).
16. K. R. Poeppelmeier, M. E. Leonowicz, and J. M. Longo, *J. Solid State Chem.* **44,** 89 (1982).
17. J. Verde, M.Sc. thesis, Universidad Complutense, Madrid (1983).
18. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25,** 925 (1969).
19. A. F. Wells, "Structural Inorganic Chemistry," 4th ed., Oxford Univ. Press, London/New York (1975).
20. H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A* **161,** 220 (1937); **164,** 117 (1938).
21. H. Ohnishi and T. Teranishi, *J. Phys. Soc. Jpn.* **16,** 35 (1961).
22. E. F. Bertaut, L. Blum, and A. Sagnieres, *Acta Crystallogr.* **12,** 149 (1959).
23. A. A. Colville, *Acta Crystallogr. Sect. B* **26,** 1469 (1970).
24. J. Berggren, *Acta Chem. Scand.* **25(10),** 3616 (1971).
25. J. C. Grenier, L. Fournes, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **17,** 55 (1982).
26. J. C. Grenier, F. Menil, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **13,** 329 (1978).
27. T. Blasco, M. Vallet, J. M. Gonzalez Calbet, and J. Rodriguez, *An. Quim.,* in press.
28. M. Vallet Regi, J. Gonzalez Calbet, M. A. Alario Franco, J. C. Grenier, and P. Hagenmuller, *J. Solid State Chem.* **55,** 251 (1984).