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Electron Microscopy and Diffraction of Barium–Lanthanum Ferrites: $Ba_xLa_{1-x}FeO_{3-y}$

M. PARRAS,* M. VALLET-REGI,* J. M. GONZÁLEZ-CALBET,[1],* M. ALARIO-FRANCO,* AND J. C. GRENIER†

*Facultad de Ciencias Químicas, Dpto. Química Inorgánica, Universidad Complutense, 28040-Madrid, Spain; and †Laboratoire de Chimie du Solide du CNRS, 33405 Talence-Cedex, France

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The system formed by $Ba_2Fe_2O_5$ and $LaFeO_3$ has been studied at the microstructural level. Four different phases, which are metrical multiples of the perovskite cubic cell, appear as a function of the Ba/La ratio. Their microstructure ranges from three-dimensional multitwinning, as in $LaFeO_3$, to an apparently stoichiometric line phase of $Ba_2Fe_2O_5$ composition with parameters $a = 23.40(1)$ Å, $b = 11.71(1)$ Å, $c = 7.05(1)$ Å, and $\beta = 98°3(1)'$. For $0 < x < 0.25$, cubic regions appear within a $LaFeO_3$ matrix. When $x = 0.33$, a double perovskite cell is intergrown with a single one. Such a single cubic perovskite is the only phase obtained in the $0.33 < x < 0.66$ range. © 1988 Academic Press, Inc.

Introduction

Due to the interest in perovskite-related ferrites, much work has been devoted to nonstoichiometry in orthoferrites (*1–3*). In particular, our recent work in the $Ca_xLa_{1-x}FeO_{3-y}$ system has shown interesting and novel ways of accommodating compositional variations (*4, 5*). On the other hand, the Ba–Fe–O phase diagram has also been widely investigated though not conclusively (*6–8*). Recent work (*9*) has shown that presumably due to the bigger size of barium, oxygen vacancy ordering occurs in an original way, as recently seen in the case of $Ba_2Fe_2O_5$ whose structure has a unit cell different from the usual brownmillerite structure of $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$ (*10, 11*).

In an attempt of clarify some of the microstructural aspects of these ferrites, we have undertaken a study of the substitution of lanthanum by barium in the $Ba_xLa_{1-x}FeO_{3-y}$ system, in samples of intermediate composition between $LaFeO_3$ and nonstoichiometric $BaFeO_{3-x}$. As will be seen below, these materials contain mixed valencies of iron (Fe^{3+}, Fe^{4+}) and the ordered states observed along the composition range are very different.

Experimental

Samples of the $Ba_xLa_{1-x}FeO_{3-y}$ system were prepared by heating stoichiometric mixtures of $BaCO_3$, La_2O_3, and α-Fe_2O_3 of analar quality in air at 1300°C for 3 days. The homogeneous black products were quenched to room temperature in the alumina crucibles used for synthesis.

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[1] To whom correspondence should be addressed.

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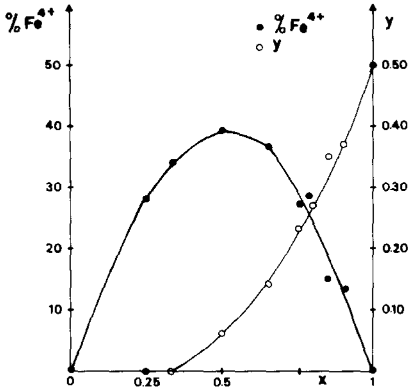

FIG. 1. Variation of the Fe^{4+} amount and of the oxygen deficiency versus x.

Powder X-ray diffraction was performed using a SIEMENS D-500 diffractometer with a graphite monochromator and $CuK\alpha$ radiation.

Electron diffraction and microscopy have been undertaken using a SIEMENS-ELMISKOP 102 electron microscopy fitted with a double tilting goniometer stage.

The average oxidation state of iron was determined by chemical analysis with $K_2Cr_2O_7$ solution after reaction in 3*N* HCl with a known excess of Mohr's salt. The results were confirmed by thermogravimetric analysis using a Cahn balance equipped with a furnace allowing the simultaneous determination of the weight loss and reaction temperature. The sample (~80 mg) was usually reduced by hydrogen at 400°C and 250 Torr, according to the following reaction:

$$Ba_xLa_{1-x}Fe^{4+}_yFe^{3+}_{1-y}O_{3-(x-y)/2} \xrightarrow{H_2} Ba_xLa_{1-x}Fe^{3+}O_{3-x/2}$$

Results and Discussion

The average composition of the samples obtained by chemical and thermogravimetric analysis is shown in Fig. 1. It can be seen that the amount of Fe^{4+} increases steadily with barium substitution until it attains 50%. Then, it decreases as steadily in the same manner. On the other hand, the oxygen deficiency with respect to the perovskite composition starts at a lanthanum substitution slightly above 33% and increases continuously.

The powder X-ray data shows three crystallographically distinct phases and an intermediate two-phase region. According to the stoichiometry, the unit cells are:

$0 \leq x \leq 0.25$: Lanthanum orthoferrite type (*12*) with parameters related to the a_c perovskite cell,[2] $a_c\sqrt{2} \times a_c\sqrt{2} \times 2a_c$; a = 5.553(2) Å, b = 5.567(2) Å, and c = 7.867 (3) Å for $LaFeO_3$ and a = 5.554(4) Å, b = 5.567(2) Å, and c = 7.867(4) Å for $x = 0.25$.

$0.25 < x \leq 0.66$: Simple cubic perovskite. Cell parameter, a_c where a = 3.933(1) Å for $x = 0.33$, a = 3.942(1) Å for $x = 0.5$, and a = 3.948(1) Å for $x = 0.66$.

$0.66 < x \leq 0.99$: Mixture of cubic perovskite and monoclinic $Ba_2Fe_2O_5$.

$x = 1$: Monoclinic $Ba_2Fe_2O_5$ (*9*). Cell parameters, $14a_c/\sqrt{6} \sin\beta \times 2\sqrt{2}a_c \times 7a_c/\sqrt{17} \sin\beta$, i.e., a = 23.40(1) Å, b = 11.71(1) Å, c = 7.05 Å, and $\beta = 98°3(1)'$.

If these cells are reduced to the basic perovskite cell we observe a continuous increase in a_c with the composition. This is an interesting result because in addition to the size difference between Ba^{2+} and La^{3+}—XII $r_{Ba^{2+}}$ = 1.61 Å and VIII $r_{La^{3+}}$ = 1.16 Å (*13*)—some trivalent iron is oxidized at the early stages of the substitution (see Fig. 1). As, indeed, Fe^{4+} is smaller than Fe^{3+}—0.585 and 0.645 Å, respectively (*13*)—it appears that the size of the alkali-metal ion overrides the small decrease necessarily produced in the lattice by the smaller and more highly charged Fe^{4+} ions. This is enhanced by the fact that for substitutions

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[2] Subindex c refers to the cubic perovskite unit cell.

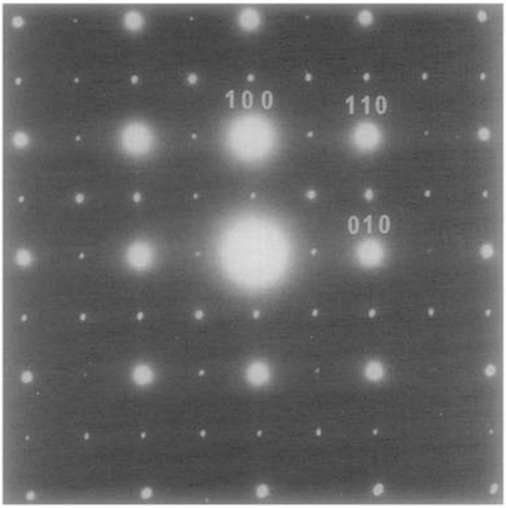

FIG. 2. Electron diffraction pattern of the $x = 0.25$ sample along the $[001]_c$ zone axis.

with $x > 0.50$, oxygen vacancies and the corresponding decreasing Fe^{4+} concentration (Fig. 1) should help to increase the basic cell size.

However, the electron diffraction and microscopy results show a somewhat different situation.

When $x = 0$, and as previously shown (*5*), we found a $LaFeO_3$-type basic cell (henceforth called *L*) which is three-dimensionally multitwinned, that is to say, three-dimensional twin domains in which the double perovskite axis is randomly directed along one of the three possible directions.

Introducing barium introduces an interesting case of an intergrowth "phase mixture" in which, within the same crystal, we can observe regions of L and of another phase which appears to be a double perovskite. Figure 2 shows a diffraction pattern of the $x = 0.25$ composition which seems similar to that of the L-phase along $[001]_c$. But, the corresponding micrograph (Fig. 3) reveals domains with the perovskite cell alternatively doubled in two directions and some areas where fringes separated by 3.9 Å are crossing at 90°. Although these regions could be assigned to a single cubic

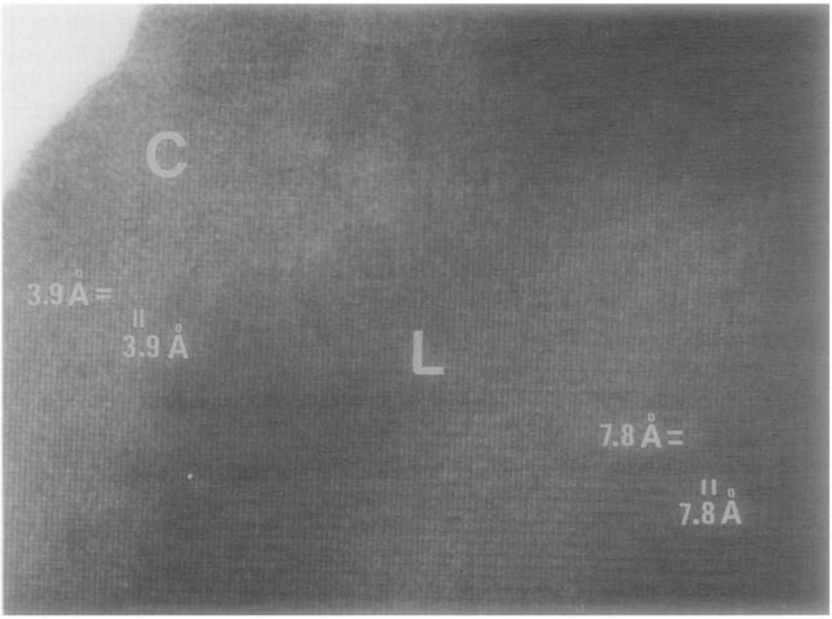

FIG. 3. Corresponding electron micrograph showing L twin domains intergrowth with a cubic perovskite (C).

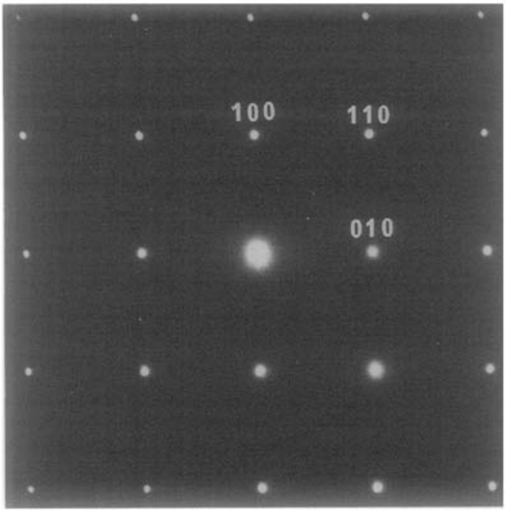

FIG. 4. Electron diffraction pattern of the crystal shown in Fig. 3 corresponding to the domain called C.

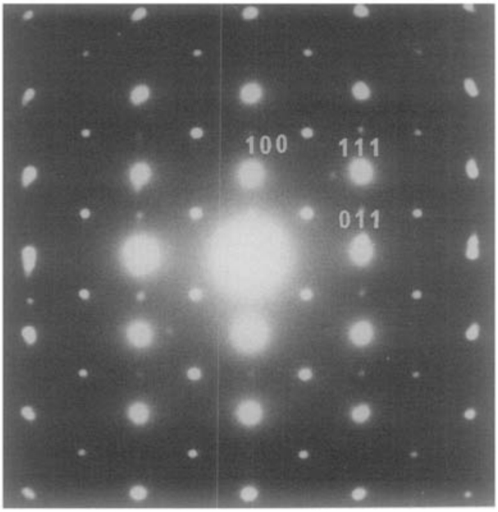

FIG. 6. Electron diffraction pattern of the crystal shown in Fig. 3 along the $[01\bar{1}]_c$ zone axis.

perovskite (Fig. 4), tilting 45° around a_c^* shows an extra spot (located at 1/2 1/2 1/2) which should not appear unless this region corresponds to a double perovskite cell (Fig. 5). If we use a larger selected area aperture, a combined pattern is observed (Fig. 6). Figure 7 shows the reciprocal sections corresponding to Figs. 2, 4, 5, and 6, respectively.

When $x = 1/3$, i.e., $Ba_{1/3}La_{2/3}FeO_3$ (or $BaLa_2Fe_3O_9$), only a double perovskite pattern appears as opposed to the simple cubic pattern observed by X-ray diffraction. The corresponding image is given in Fig. 8. Some regions of this crystal, however, only show a single 3.9-Å cubic cell. It is worth emphasizing that beginning with this barium content (33%), oxygen vacancies appear in the structure (Fig. 1).

This single cubic cell is the dominant characteristic of all samples with $1/2 \leq x \leq$

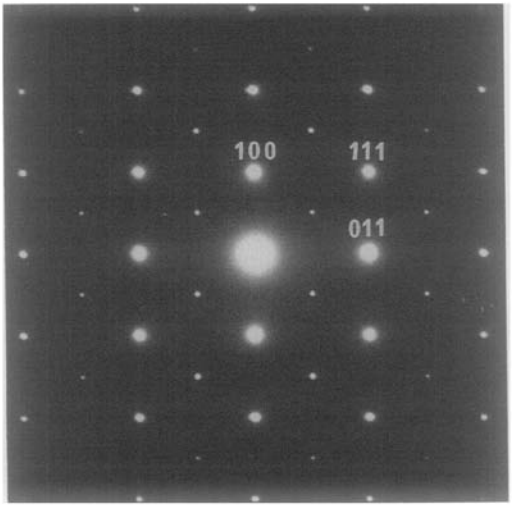

FIG. 5. Electron diffraction pattern of the C domain along the $[01\bar{1}]_c$ zone axis corresponding to a double perovskite.

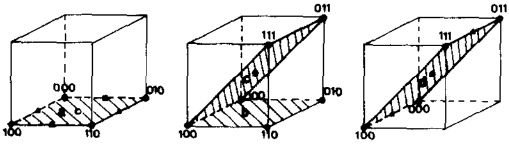

FIG. 7. Schematic representation of the above electron diffraction patterns within a reciprocal net corresponding to a single cubic perovskite substructure. Shadowed planes in (a), (b), (c), and (d) correspond to Figs. 2, 4, 5, and 6, respectively.

FIG. 8. Electron micrograph of the $x = 1/3$ sample along the $[01\bar{1}]_c$ zone axis showing domains of a double perovskite in the matrix of a single one.

2/3, both in X-ray and electron diffraction patterns.

For higher barium content ($x > 2/3$) this cubic cell appears in a normal two-phase mixture, i.e., nonintergrowth, with $Ba_2Fe_2O_5$ which is the only phase appearing at $x = 1$.

One of the most interesting compositions found in this system corresponds to $x = 1/3$ where, as we have already mentioned, a double perovskite cell coexists with crystal regions where the structure is simple cubic. Although in that kind of hybrid crystal it is very complicated, if at all possible, to establish in detail the real structure, the fact that, according to the chemical analysis we do not have oxygen vacancies at this composition (see Fig. 1), implies that the doubling of the unit cell is related to barium–lanthanum ordering in the A position. This is likely associated to a Fe^{3+}–Fe^{4+} ordering provided that, for electrostatic reasons, those cations are also in a 1 : 1 ratio in the domains. If this is correct, the nondouble crystal regions should correspond to those where, for reasons which are not obvious, such order has not been established. In this way, the Ba–La ordering is such that each barium atom is surrounded by lanthanum atoms and therefore, a lanthanum atom has barium atoms as closest A neighbors; a similar situation may happen for Fe^{3+} and Fe^{4+} ions. Unfortunately, the electron scattering factors of Ba^{2+} and La^{3+} are so close that this order cannot be distinguished by X-ray or electron diffraction.

Nevertheless, one would expect that the size and charge differences existing between these two cations will strongly modify the structure around the A position. If in the most simple model, Ba (XII $r_{Ba^{2+}} = 1.61$ Å) expands the lattice while La (XII $r_{La^{3+}} =$

1.36 Å) contracts it, this will introduce a distortion of the (Fe–O_6) octahedra which in the described Ba–La order will result in a double cell similar, for example, to that observed in $Sc(OH)_3$ (*14*) where it happens due to H-bonding, or in $A_2BB'O_6$ perovskites such as in Ba_2NaReO_6 (*15*). One may wonder why the whole crystal is not ordered in the same way. This seems simply due to the composition $Ba_{1/3}La_{2/3}FeO_6$ not being adequate for an ordering described since this requires equal proportion of Ba and La. If this is correct, it will then appear obvious that when $x = 0.50$—when the Ba/La ratio is equal to 1—this ordering would naturally establish itself. However, as shown in Fig. 1, the experimental conditions that we have used in the synthesis give rise to some oxygen vacancies (6%) and this modifies the structure in such a way so that no order is achieved. Consequently, with a random distribution of La–Ba atoms, Fe^{3+}–Fe^{4+} ions and oxygen vacancies, the unit cell is simple cubic with $a = 3.942(1)$ Å.

We may note that the composition corresponding to $Ba_2LaFe_3O_9$ is cationically analogous to $Ba_2YCu_3O_{9-x}$ of superconducting fame (*16*). Unfortunately, these ferrites do not seem to be superconducting, down 4.2 K but rather they show an antiferromagnetic order to a temperature of 370 K.

When $2/3 < x < 1$, a "classical phase mixture" is observed, that is, separate crystal of the simple cubic symmetry coexist with those of monoclinic $Ba_2Fe_2O_5$ (*9*).

The results presented above show that the Ba–La–Fe–O system is complicated, particularly from a microstructural point of view. Indeed for just one temperature, 1300°C, and one oxygen pressure ($P_{O_2} = 0.2$ atm) no less than four different structures exist and they are either in microdomains of one phase or intergrowths of ordered and disordered regions within a single crystal; also as normal phase mixtures and at least in one case, $Ba_2Fe_2O_5$, as a single phase. This is certainly a behavior well away of the "classical" solid solution usually expected in this type of nonstoichiometric perovskites.

Accordingly, it can be concluded that, even if in formal terms the calcium and barium–lanthanum ferrites are similar, they are very different in microstructural terms. The ordered intergrowth between $LaFeO_3$ and $Ca_2Fe_2O_5$ does not seem to occur between $LaFeO_3$ and $Ba_2Fe_2O_5$. This is certainly due to the fact that although metrically $Ba_2Fe_2O_5$ is a perovskite superstructure, its real structure (*9*) is very different from orthorhombic $LaFeO_3$ so that intergrowth is not possible. Nevertheless, some very interesting ordering states of the A cation have been observed in the basic system. There are, however, some intergrowths between ordered and disordered, i.e., double and single cubic perovskite type structure due to this A cation ordering.

Mössbauer spectroscopy is in progress and will be reported in due course.

Acknowledgments

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