$YBaCuFeO_{5+\delta}$: A Novel Oxygen-Deficient Perovskite with a Layer Structure

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A novel ordered oxygen-deficient perovskite with a layer structure, $YBaCuFeO_{5+\delta}$, was isolated. It was characterized by chemical analysis, Mössbauer spectroscopy, and magnetic susceptibility measurements versus temperature. Its structure was determined by powder neutron diffraction. It crystallizes in the tetragonal system with $a = 3.867$ Å $\simeq a_p$ and $c = 7.656$ Å $\simeq 2a_p$. The structure can be described as formed of $[CuFeO_5]_\infty$ double layers of corner-sharing CuO_5 and FeO_5 pyramids, perpendicular to **c**. The cohesion between the layers is ensured by ytterium planes whereas the barium ions are located inside the layers. The relationships of this structure with those of $YBa_2Cu_3O_{7-\delta}$ and $LaBa_2Cu_3O_{7-\delta}$ are discussed. © 1988 Academic Press, Inc.

Introduction

The mixed-valence copper perovskites form, among the oxygen-deficient perovskites, a rather large family which has recently been studied for its ability to exhibit superconducting properties. One striking feature of those oxides deals with their high oxygen deficiency and with the fact that the oxygen vacancies are ordered leading to various superstructures of the ideal perovskite cubic cell. One can indeed distinguish three-dimensional frameworks such as $BaLa_4Cu_5O_{13+\delta}$ (*1, 2*) and $La_{8-x}Sr_x Cu_8O_{20-\varepsilon}$ (*3, 4*), which exhibit metallic conductivity but not superconductivity, from the two-dimensional structures such as that of the tetragonal oxide $LaBa_2Cu_3O_{7-\delta}$ (*5, 6*) and the orthorhombic oxide $YBa_2Cu_3O_{7-\delta}$ (*7–11*) which are superconductors known for their high critical temperatures. Another example deals with the oxide $Ba_3 La_3Cu_6O_{14+\delta}$ (*12–14*), whose bidimensional character for $\delta = 0$ does not lead to any

superconductivity. It is well known that the partial replacement of copper by other ions, magnetic (Ni^{2+}, Fe^{3+}) and nonmagnetic (Zn^{2+}, Al^{3+}), will tend to destroy the superconductivity, but the mechanism is by far not clear at the present time. Thus it appears that the study of the replacement of copper by iron will be useful in order to understand all of these phenomena. In a recent paper (15) we have studied the magnetic and electrical properties of a new family of perovskites $La_{0.5}Ba_{0.5}Fe_{1-x}Cu_x$ $O_{2.75-x/2+\delta}$ ($0 \ll x \ll 0.8$) in which copper and iron exhibit the mixed valence: Cu(II)–Cu(III) and Fe(III)–Fe(IV). This latter oxide is characterized by cubic symmetry, i.e., by a disordered distribution of the anionic vacancies in spite of its high oxygen deficiency. The present work deals with the synthesis and the structural study of a new oxygen-deficient perovskite $YBaFeCuO_5$ characterized by a lamellar structure.

Experimental

Synthesis

Samples were prepared by solid-state reactions in platinum crucibles from appropriate mixtures of dried oxides CuO, Fe_2O_3, Y_2O_3, and carbonate $BaCO_3$. The powders were ground, heated in air at 900°C for 12 hr, crushed, fired at 1000°C for 24 hr, quenched to room temperature, and finally annealed in air at 400°C for 24 hr.

Chemical Analysis

To determine the mean oxidation state of the transition metal ions and consequently the oxygen content, chemical analysis was carried out by redox back titration using standard solutions of Fe^{2+} and potassium dichromate as described elsewhere (3).

Structural Analysis

The cell parameters were determined from X-ray powder diffraction patterns ob-

tained with a Philips diffractometer using $CuK\alpha$ radiation. The space groups were determined by electron diffraction using a Jeol 120 CX electron microscope. For structural studies, powder diffraction data were collected with the high-resolution diffractometer D2B at the Institute Laue-Langevin with $\lambda = 1.6002$ Å from 10° to 148° in steps of 0.025° in 2θ. Calculations were done with a profile refinement of a diffraction lines program (16, 17). The following scattering amplitudes (all in 10^{-12} cm) were used (18): 0.525(Ba), 0.772(Cu), 0.954(Fe), 0.775(Y), 0.580(O).

Magnetic Measurements

Magnetic susceptibility was measured as a function of temperature in the range 100–800 K by the Faraday method using a Cahn RG microbalance. The Mössbauer spectrum was obtained at room temperature with a spectrometer in conjunction with a multichannel analyzer. The velocity transducer was calibrated by reference to the Mössbauer spectra of metallic iron. The recorded spectrum was compared to that calculated with a refinement program (19).

Results and Discussion

The study of the system $YBaFe_{2-x}Cu_x$ $O_{5.5-x/2+\delta}$ allows only one compound to be isolated for $x = 1$. Chemical analysis shows a very weak excess of oxygen ($\delta = 0.02 \mp 0.01$) leading to the composition $YBaFe$ $CuO_{5.02}$ and involving copper and iron mainly in the oxidation state (II) and (III), respectively. The pervoskite-related X-ray diffraction pattern indicates a tetragonal cell with the following parameters $a = b = 3.867$ Å $\simeq a_p$; $c = 7.656$ Å $\simeq 2a_p$. The density measurement ($d_{exp} = 6.17$) agrees with one $YBaFeCuO_{5.02}$ species per cell ($d_{cal} = 6.17$).

The magnetic susceptibility measurements as a function of temperature (Fig. 1) suggest the presence of an antiferromag-

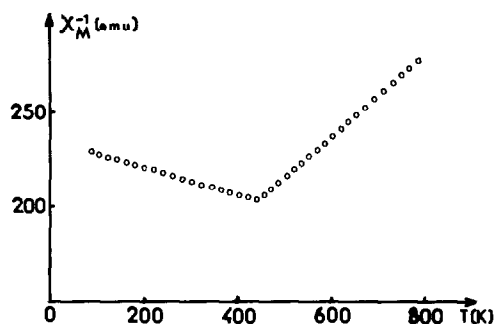FIG. 1. Variation of χ_M^{-1} as a function of absolute temperature for the oxide YBaCuFeO$_{5.02}$.

FIG. 2. Mössbauer spectrum at room temperature of the oxide YBaCuFeO$_{5.02}$.

netic order below 460 K. The magnetic order is supported by the Mössbauer spectrum recorded at room temperature (Fig. 2). Although the resolution of this spectrum was low, it could not be fitted with only one Fe contribution. In Table I the Mössbauer parameters obtained after refinement with two contributions for Fe ions are given. The values are in agreement with Fe^{3+} ions in two different distorted environments (20).

In order to determine with accuracy the position of the oxygen vacancies in the cell of this new oxygen-deficient perovskite, a structural study was carried out by powder neutron diffraction. From X-ray, neutron, and electron diffraction patterns, no conditions of reflection are observed. This leads to eight possible space groups. Referring to the perovskite structure and in order to minimize the number of variable parameters, the most symmetrical space group which allows two different sites for iron and copper ions—$P4mm$—was chosen. Data were collected in the paramagnetic domain: $T = 500$ K. At this temperature the cell parameters were found to be $a = 3.893(2)$ Å, $c = 7.751(3)$ Å.

First calculations were carried out in a nonoxygen-deficient model:

Y and Ba were statistically distributed over two 1(a) sites (0, 0, z) with $z = 0.0$ ((Y,Ba)$_1$) and $z = 0.5$ ((Y,Ba)$_2$).
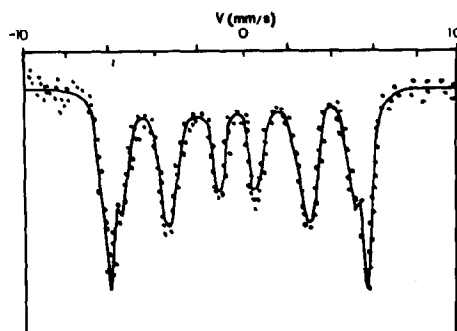
0.62Cu + 0.38Fe were distributed in the 1(b) site ($\frac{1}{2}$, $\frac{1}{2}$, z) with $z = 0.25$ ((Cu,Fe)$_1$), and 0.38Cu + 0.62Fe in the 1(b) site with $z = 0.75$ ((Cu,Fe)$_2$), according to the Mössbauer results.

O(1) and O(2) in 1(b) with $z = 0.0$ and $z = 0.5$; O(3) and O(4) in 2(c) with $z = 0.25$ and $z = 0.75$

For these atomic positions which correspond to those of the ideal perovskite and isotropic thermal factors of 1 Å^2, the nuclear R factor R_n (R factor calculated on the integrated intensities) was 0.643. This factor was lowered to 0.117 after refinement of the variable atomic coordinates and thermal factors. The B factors resulting from this calculation for (Y,Ba)$_1$: $B = 1.97$ Å^2, (Y,Ba)$_2$: $B = -0.33$ Å^2, and O(2): $B = 54.7$ Å^2 suggested an ordered distribution of barium and yttrium over the 1(a) sites and that the O(2) oxygen was missing. Barium and yttrium were then located in (Y,Ba)$_1$

TABLE I

MÖSSBAUER PARAMETER, ISOMER SHIFT (δ), QUADRUPOLAR SPLITTING (SQ), AND HYPERFINE FIELD (H)

Site	Fe (%)	δ (mm/sec)	SQ (mm/sec)	H (hG)
1	62	0.304	−0.014	370
2	38	0.310	0.006	339

TABLE II

VARIABLE PARAMETERS AFTER REFINEMENT OF THE
STRUCTURE (SPACE GROUP $P4mm$)

Site	Atoms	x	y	z	B
1(a)	Ba	0.0	0.0	0.0226(22)	0.82(6)
1(a)	Y	0.0	0.0	0.5112(3)	0.58(4)
1(b)	$(Cu/Fe)_1$	0.5	0.5	0.2738(5)	0.47(11)
1(b)	$(Cu/Fe)_2$	0.5	0.5	0.7387(6)	0.86(14)
1(b)	O(1)	0.5	0.5	0.0149(23)	1.68(8)
2(c)	O(3)	0.5	0.0	0.3331(9)	1.09(17)
2(c)	O(4)	0.5	0.0	0.7028(9)	0.89(13)

and $(Y,Ba)_2$ sites, respectively, and the
O(2) oxygen was removed from the struc-
ture. Final refinement including this last
hypothesis led to $R_n = 0.081$ ($R_p = 0.17$,
$R_{exp} = 0.15$)[1] for the coordinates and B
values given in Table II. Attempts at calcu-
lation with other Cu–Fe distributions over
the two 1(b) sites did not allow lowering of
the R factors. Since the excess oxygen
content was very low ($\delta = 0.02$), the for-
mula $YBaCuFeO_5$ was assumed in the final
calculation.

The structure of this oxide (Fig. 3) can be
described as an ordered oxygen-deficient
perovskite which exhibits a great similarity
to the structures of $YBa_2Cu_3O_{7-\delta}$ (7–11)
and $LaBa_2Cu_3O_{7-\delta}$ (5, 6). The barium and
yttrium ions form planes perpendicular to
c, which alternate according to the se-
quence Ba–Y–Ba . . . , whereas the se-
quence Ba–Ba–Y–Ba–Ba . . . is observed
for the other two structures. Moreover, the
oxygen vacancies are located at the same
level as the yttrium ions in the three struc-
tures, so that they all exhibit layers of
polyhedra whose cohesion is ensured by
yttrium ions. The layers $[CuFeO_5]_\infty$ of
$YBaFeCuO_5$ are themselves built up from
double layers of corner-sharing CuO_5 and
FeO_5 pyramids, whereas triple layers of

[1] R_p is the R factor calculated on the lines
profile and R_{exp} is the R factor expected from the
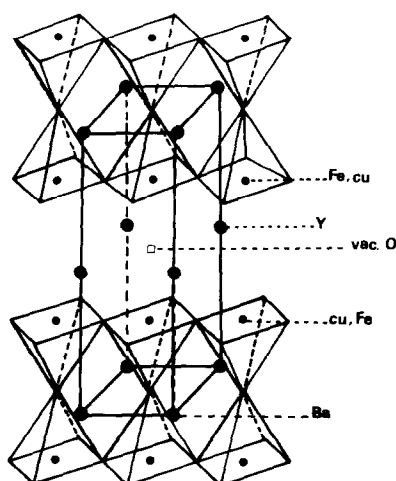statistic.

FIG. 3. Structure of the oxide for the ideal composi-
tion $YBaCuFeO_5$.

polyhedra are observed, for instance, in
$YBa_2Cu_3O_7$. It is worth pointing out that in
all those compounds the barium ions are
located inside the layers.

The different interatomic distances (Ta-
ble III) are in agreement with the sizes of
the elements (21). In particular, the Y–O
distances range from 2.38 to 2.44 Å while
the Ba–O distances range from 2.75 to 3.14
Å. Two kinds of CuO_5 pyramids are ob-
served whose distorsions are different: the
first type exhibits five $(Cu,Fe)_1$–O equiva-
lent distances close to 2.00 Å, while the
second one is characterized by four short
$(Cu,Fe)_2$–O distances (1.96 Å) and one
longer distance (2.13 Å).

Curiously, the most distorted square pyr-

TABLE III

INTERATOMIC DISTANCES

M–O	Distance (Å)	M–O	Distance (Å)
Ba–O(1)	2.753(1) × 4	(Cu/Fe)1–O(1)	1.998(19) × 1
Ba–O(3)	3.086(2) × 4	(Cu/Fe)1–O(3)	1.999(2) × 4
Ba–O(4)	3.143(2) × 4		
		(Cu/Fe)2–O(1)	2.130(19) × 1
Y–O(3)	2.383(1) × 4	(Cu/Fe)2–O(4)	1.966(1) × 4
Y–O(4)	2.444(1) × 4		

amid is that mainly occupied by Fe^{3+} ions (62%); but such distorted environments have been previously observed for this cation: for instance, in $LaSrFeO_4$ (22) the FeO_6 octahedron exhibits four short Fe–O distances at 1.94 Å and two long distances at 2.15 Å.

The only possibility of locating the excess of oxygen with respect to the formulation $YBaFeCuO_5$ corresponds to the site 1(b) ($z = 0.5$). This site is here almost empty (2% of occupancy) and the calculations cannot be considered as significant.

These results show clearly that $YBaFeCuO_{5+\delta}$ can be considered as a layer structure. A systematic study is in progress to understand the role of the rare-earth ion in the structure. It can already be stated that this bidimensional character is also observed in the case of the gadolinium oxide $GdBaFe_{2-2x}Cu_{2x}O_{5.5-x+\delta}$ ($0.50 \leq x \leq 0.60$ and $\delta \approx 0.03$) (23). Very different results are observed by replacing yttrium with samarium and neodynium: the mixed valence of copper and iron appears whereas the bidimensional character of the structure disappears.

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