

Layered (Cu,Fe) oxides of double perovskite structure. II. Extension of solid solubility of copper in (Ba,La)Y(Cu_{0.5+x}Fe_{0.5-x})₂O_{5+δ} via high-pressure heat treatment

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In this paper, we report successful extension of the solid-solubility limit of copper at the transition element site in the (Ba,La)Y(Cu,Fe)₂O_{5+δ} phase of the double-perovskite “0112” structure. Upon the high-pressure heat treatment at 5 GPa and 1200 °C of the ambient-pressure synthesized samples that contained impurity phases, essentially single-phase samples were obtained for x up to 0.2 in the (Ba_{1-2x}La_{2x})Y(Cu_{0.5+x}Fe_{0.5-x})₂O_{5+δ} system. TEM observations and TEM energy dispersive x-ray analyses for the high-pressure synthesized (Ba_{0.6}La_{0.4})Y(Cu_{0.7}Fe_{0.3})₂O_{5+δ} material showed that the ratio of copper to iron varies in the sample with an average value of Cu:Fe=0.70:0.30, as measured for nine grains. It could thus be concluded that a 0112 phase in which the amount of copper is larger than that of iron in the oxygen pyramid was realized. In order to obtain the copper-rich 0112 phase, simultaneous substitution of the divalent barium site by trivalent lanthanum was found necessary. From ⁵⁷Fe Mössbauer spectroscopy data, the relative intensities of five- and six-coordinated iron atoms were evaluated and the amount of excess oxygen in the structure could be estimated at $\delta \approx 0.23$. Furthermore, both Mössbauer and magnetic-susceptibility measurements of the $x=0.2$ sample showed that the Néel temperature of the copper-rich material is lower than the corresponding transition temperature observed for the material with the stoichiometric $x=0$ composition. Finally, conditions for the successful extension of the copper solubility are discussed and related to the tolerance factor of the 0112 structure. [S0163-1829(99)01201-1]

I. INTRODUCTION

The superconducting cuprate structures built up by alternating $M_mO_{m\pm\delta}$ perovskite or rocksalt blocks (i.e., the “charge-reservoir” block), AO rocksalt planes and $Q_{n-1}Cu_nO_{2n}$ perovskite blocks (i.e., the “infinite-layer” block) are best described as members of a homologous series expressed by $M_mA_2Q_{n-1}Cu_nO_{2+2n+m\pm\delta}$ or $M-m2(n-1)n$.¹ This notation includes also the “02($n-1$) n ” series comprising the existing superconducting cuprate phases in which no $M_mO_{m\pm\delta}$ charge-reservoir block is found. In this series $Q_{n-1}Cu_nO_{2n}$ infinite-layer blocks are separated by a double (AO)₂ layer. Supposing that the layered cuprate structure would be stabilized with only one single AO plane to separate the $Q_{n-1}Cu_nO_{2n}$ blocks, interesting new aspects for testing the present understanding of high- T_c superconductivity appear. First, the structures would

be quite three dimensional. Whether this kind of structure would be superconducting when optimally doped is not known but worth careful clarification. Second, if superconductivity could be induced in this kind of structure, the material would be a promising candidate for exhibiting high irreversibility fields of magnetization (H_{irr}) due to the low anisotropy of the structure.^{2,3} As discussed in our previous papers,^{4,5} the $n=2$ member of this “not-yet-established” “01($n-1$) n ” homologous series would be isomorphous with the “oxygen-deficient double-perovskite” BaY(Cu_{0.5}^(+II)Fe_{0.5}^(+III))₂O₅ compound discovered by Er-Rakho *et al.*⁶ in 1988. In the “0112” structure of BaY(Cu_{0.5}Fe_{0.5})₂O₅ barium and yttrium are ordered along the c axis making the two (Cu,Fe)O₂ planes, which consist of (Cu,Fe)O₅ pyramids, mirror images for each other. Barium (coordination number CN=12) in the single BaO plane shares the apical oxygen atoms of the both (Cu,Fe)O₂ planes,

while yttrium (CN=8) faces the basal planes of the (Cu,Fe)O₅ pyramids (see Fig. 4 in Ref. 5). Within the (Cu,Fe)O₂ planes copper and iron are not ordered but randomly distributed, as was recently concluded from ⁵⁷Fe Mössbauer results⁵ and successfully verified by the convergent-beam-electron-diffraction (CBED) technique.⁷

Besides the stoichiometric BaY(Cu_{0.5}Fe_{0.5})₂O₅ compound,^{6,8} the 0112 structure has been shown to exist for other transition-metal compositions as well, i.e., for BaY(Co_{1-x}Cu_x)₂O₅ at 0.15 ≤ *x* ≤ 0.5,⁹⁻¹¹ and for BaY(Co_{0.5}Cu_{0.5-x}Fe_x)₂O₅ at 0.15 ≤ *x* ≤ 0.3.¹² Complete replacement of Cu with Fe has successfully been done for BaNdFe₂O_{5+δ} and BaSmFe₂O_{5+δ}.¹³ However, there have been no reports on the existence of 0112 compounds in which the amount of copper is larger than that of other transition metals at the transition-metal site in the oxygen pyramid.

From our previous study⁵ (henceforth Paper I) of the 0112 phase, we found that BaY(Cu_{0.5}Fe_{0.5})₂O_{5+δ} is stable at high pressures, and upon the high-pressure heat treatment (at 5 GPa and 1200 °C) the magnetic transition caused by a sort of short-range order⁸ in the normal-pressure synthesized BaY(Cu_{0.5}Fe_{0.5})₂O₅ compound disappears. In the present contribution, successful extension of the solid solubility of copper up to *x* = 0.2 in the (Ba_{1-2*x*}La_{2*x*})Y(Cu_{0.5+*x*}Fe_{0.5-*x*})₂O_{5+δ} system due to high-pressure heat treatment is reported. Simultaneous substitution of divalent Ba by trivalent La was found necessary to compensate the divalent Cu to trivalent Fe replacement. For the characterization of the samples, x-ray diffraction (XRD), a superconducting quantum interference device (SQUID), high-resolution transmission electron microscopy (HRTEM), electron diffraction (ED), energy-dispersive x-ray (EDX) analysis, and ⁵⁷Fe Mössbauer spectroscopy were employed.

II. EXPERIMENT

The (Ba_{1-2*x*}La_{2*x*})Y(Cu_{0.5+*x*}Fe_{0.5-*x*})₂O_{5+δ} (*x* = 0, 0.1, 0.2, and 0.3) samples were prepared from BaCO₃, La₂O₃, Y₂O₃, CuO, and Fe₂O₃ powders. In the present work natural Fe instead of ⁵⁷Fe was used. The mixtures of starting materials were calcined in air at 900 °C for 12 h with an intermediate grinding and sintered in air at 1000 °C for 24 h. Then, small portions (~100 mg) of the obtained powders were separated for the high-pressure heat treatment carried out in a cubic-anvil-type high-pressure apparatus at 5 GPa and 1200 °C for 30 min.

The synthesized samples were checked for phase purity and lattice parameters by x-ray diffraction (MAC Science M18XHF; Cu K_α radiation). The structures were also confirmed by electron diffraction and high-resolution transmission electron microscopy (Hitachi H-9000), and the cation composition of the samples was determined by energy-dispersive x-ray analysis (Kevex Sigma) attached to the electron microscope (TEM-EDX).

The dc magnetization of the samples was measured under an applied field of 1 T with a SQUID magnetometer (Quantum Design MPMSR) in the temperature range of 5–300 K. ⁵⁷Fe Mössbauer spectra of the *x* = 0 (Paper I) and 0.2 samples were recorded at room temperature and at 20 K in transmission geometry. The absorber thickness was approxi-

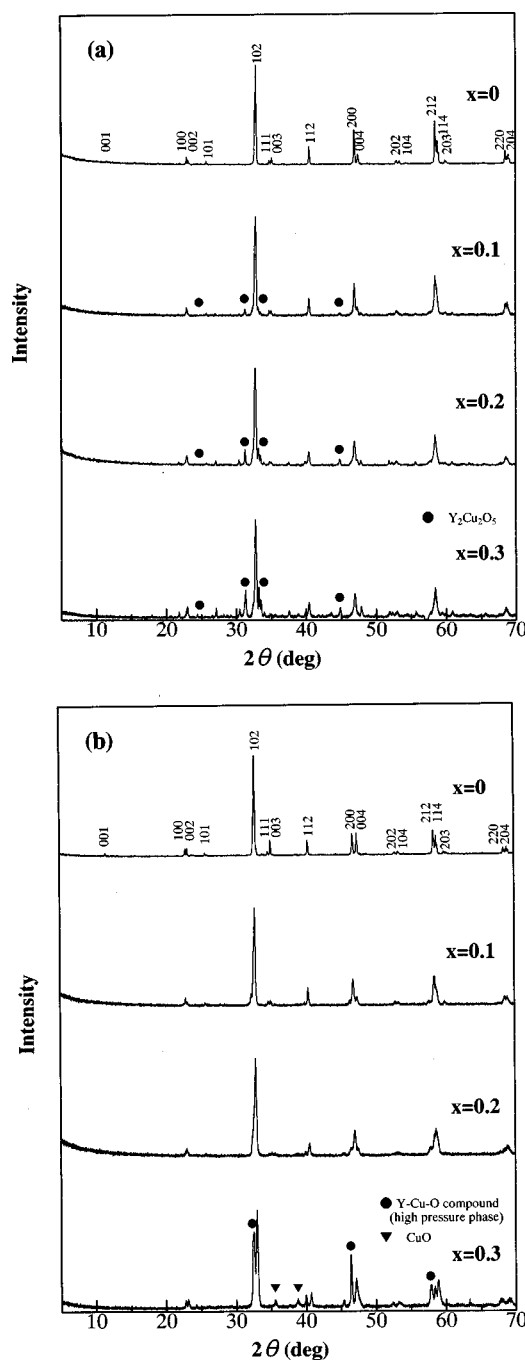


FIG. 1. XRD patterns for the (Ba_{1-2*x*}La_{2*x*})Y(Cu_{0.5+*x*}Fe_{0.5-*x*})₂O_{5+δ} samples (a) synthesized at ambient pressure, and (b) heat treated at high pressure.

mately 20-mg sample per cm². A maximum velocity of 12–15 mm/s and an Amersham ⁵⁷Co:Rh (20 mCi, January 1995) source were used. The 20-K spectrum was fitted for three possible spectral components with the Hamiltonian of combined electric and magnetic interactions and the hyperfine fitting parameters as follows: the internal magnetic field experienced by the Fe nucleus (*B*), the chemical isomer shift relative to α-Fe (Δ), the quadrupole coupling constant (*eQV_{zz}*), the resonance linewidth, and the relative intensity of each component. The internal magnetic field was allowed to be distributed over a certain range of values by supposing a suitable asymmetric distribution.⁵ At 20 K the experimental

linewidth was narrow enough and a simple Gaussian distribution could be applied.

III. RESULTS AND DISCUSSION

Since our preliminary efforts in extending the solubility limit of copper in the $\text{BaY}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ system were unsuccessful, we then shifted to the $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ system believing that the nominally divalent Cu to trivalent Fe substitution would be promoted by a simultaneous replacement of divalent Ba by trivalent La. The XRD patterns obtained for the synthesized $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ samples are shown in Figs. 1(a) and 1(b). In the samples synthesized by a solid-state reaction method at normal pressure, increasing amounts of impurity phases such as $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{La}_4\text{BaCu}_5\text{O}_y$ were detected with increasing x [Fig. 1(a)]. On the other hand, upon the high-pressure heat treatment of the samples at 5 GPa and 1200 °C such impurity phases disappeared and essentially single-phase samples were obtained for x up to 0.2 [Fig. 1(b)]. With increasing La and Cu substitution level x , the c axis decreased while the a axis remained rather unchanged, as shown in Table I.

For the XRD single-phase $(\text{Ba}_{0.6}\text{La}_{0.4})\text{Y}(\text{Cu}_{0.7}\text{Fe}_{0.3})_2\text{O}_{5+\delta}$ sample obtained from the high-pressure heat treatment, electron diffraction and high-resolution transmission electron microscopy studies were carried out. Figures 2(a) and 2(b), respectively, show the electron-diffraction pattern and the corresponding high-resolution electron micrograph of the main phase taken with the incident electron beam along the b axis. Based on the fact that the a and c axes were found perpendicular to each other and the lattice parameters a and c were, respectively, ~ 3.88 and ~ 7.62 Å, the 0112 phase was concluded. From TEM-EDX analysis carried out for several grains, it was found that the synthesized sample was almost of single phase and only traces of impurity phases such as $\text{La}_4\text{BaCu}_5\text{O}_y$ and some Y-Cu-O compound were detected. Furthermore, the TEM-EDX analysis clearly revealed that the copper content was larger than that of iron. The results of the EDX analysis for the 0112 phase are given in Table II. The ratio of copper to iron varied over the sample from 0.81:0.19 to 0.58:0.42. As an average, a Cu:Fe ratio of 0.70:0.30 was obtained. This is identical to the nominal value of 0.7:0.3. As the amount of copper was found larger than that of iron in the oxygen pyramid, the scheme of simultaneous substitution of La and Cu for Ba and Fe sites, respectively, was successfully proven.

The ^{57}Fe Mössbauer spectra recorded for the high-pressure heat-treated $x=0.2$ sample at room temperature and at 20 K in most aspects resemble those obtained for the high-pressure heat-treated stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$

TABLE I. Lattice parameters a and c for the high-pressure heat-treated samples of $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5-x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ with $x=0, 0.1$, and 0.2 .

x	a (Å)	c (Å)
0.0	3.8796(5)	7.6653(7)
0.1	3.867(3)	7.649(7)
0.2	3.878(1)	7.624(4)

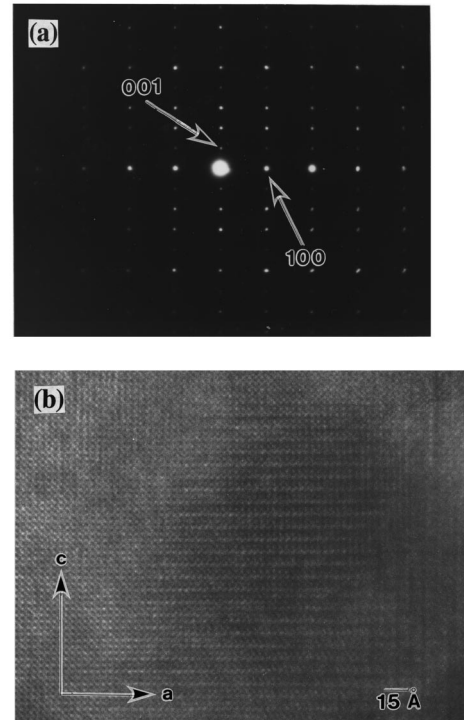


FIG. 2. (a) Electron-diffraction pattern, and (b) HRTEM image for the high-pressure heat-treated $x=0.2$ sample.

sample, Figs. 3(b) and 3(c). However, the room-temperature spectrum is dominated by paramagnetic doublets close to zero velocity. In addition to this, antiferromagnetic sextets start to develop at higher positive and negative velocities, Fig. 3(a). In other words, this is a typical spectrum obtained at a temperature close to the Néel temperature (T_N). Since the paramagnetic features were missing in the room-temperature spectrum of the stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample, it could be concluded that with increasing amount of copper in the oxygen pyramids of the $(\text{Cu,Fe})\text{O}_2$ planes, T_N of the antiferromagnetic transition decreased. The same thing is also seen from the inverse susceptibility versus temperature curves shown in Fig. 4 for both the stoichiometric $x=0$ and the Cu-rich $x=0.2$ samples up to 300 K. The paramagnetic-antiferromagnetic transition occurs around 260 K for the $x=0.2$ sample, but is located above 300 K (around 330 K as shown in Fig. 2 in Paper I) for the $x=0$ sample.

Fitting of the room-temperature Mössbauer spectrum for the $x=0.2$ sample is not feasible due to the strong line broadening. The 20-K spectrum, however, exhibits distinct sextets with narrow linewidths. The outermost lines of the spectrum are doubled in the same way as was observed for the $x=0$ composition, indicating the existence of two oxygen coordinations. The doubling manifests itself, e.g., by the fact that the intensity of the second line in Fig. 3(b) exceeds the intensity of the first line, counting from the left. The internal fields (approx. 50 T) and the isomer shifts (0.3–0.5 mm/s) are typical of high-spin ($S=\frac{5}{2}$) trivalent Fe, in accordance with the findings of Paper I. The two components were assigned to Fe(+III) with a pyramidal and an octahedral (quadrupole coupling constant eQV_{zz} very close to zero, i.e., symmetric electric field) oxygen coordination. Additionally, a

TABLE II. TEM-EDX analysis for the high-pressure heat-treated sample with a nominal composition of $(\text{Ba}_{0.6}\text{La}_{0.4})\text{Y}(\text{Cu}_{0.7}\text{Fe}_{0.3})_2\text{O}_{5+\delta}$. Average ratio of $\text{Cu}:\text{Fe}=0.70:0.30$. Average ratios of $(\text{Ba},\text{La}):\text{Y}:(\text{Cu},\text{Fe})=0.92:0.91:2.1$.

Grain	Ba	La	Y	Cu	Fe	Cu:Fe
1	21.54	1.48	26.42	29.37	21.54	0.58:0.42
2	18.41	2.58	25.44	35.61	17.96	0.67:0.34
3	16.36	7.37	22.04	36.39	17.84	0.67:0.33
4	21.03	1.82	24.10	36.00	17.03	0.68:0.32
5	17.25	5.57	22.86	37.50	16.83	0.69:0.31
6	16.51	4.54	25.51	37.23	16.21	0.70:0.30
7	13.95	10.69	20.91	41.88	12.58	0.77:0.23
8	16.17	9.06	20.90	41.61	12.26	0.77:0.23
9	12.64	10.52	17.46	47.88	11.51	0.81:0.19

component corresponding to $\text{Fe}(\text{IV})$ in an octahedral coordination with a field of ~ 27 T is clearly observed (with a relative intensity of $\sim 16.30\%$). In the $x=0$ sample this component is barely visible (relative intensity of $\sim 3.16\%$), explaining the fact that it was ignored in Paper I and other previous works.⁸ The 27-T component is seen as a shoulder in the right slope of the second line counting from the left in Fig. 3(b). In Table III, results from fitting the 20-K spectra

for the both samples ($x=0$ and 0.2) with these three components are given.

In the case of the stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_{5+\delta}$ sample, the high-pressure heat treatment was shown to increase the amount of excess oxygen δ (Paper I). With coulometric $\text{Cu}(\text{I})/(\text{II})$ titrations the oxygen excess in the high-pressure heat-treated $x=0$ sample was determined at $\delta=0.17\pm 0.01$, while in the normal-pressure synthesized sample oxygen content was found close to the stoichiometric value, i.e., $\delta=0.03\pm 0.01$. It is also possible to estimate the amount of excess oxygen from the Mössbauer components. Supposing that the copper atoms do not attract the excess oxygen atoms, i.e., assuming that all the excess oxygen atoms are within the iron polyhedra, the relative portion of six-coordinated Fe is also a measure of the amount of excess oxygen in the lattice. From a chemical point of view this assumption is quite plausible. According to Table III, the relative portion of six-coordinated iron atoms is 15.44% in the $x=0$ sample and 38.35% in the $x=0.2$ sample. This would lead to δ values of 0.154 for the $x=0$ sample and 0.230 for the $x=0.2$ sample. Interestingly, the estimation obtained for the $x=0$ sample is very close to the value determined by the chemical titration method, i.e., $\delta=0.17\pm 0.01$. To proceed further, the Cu valence values are estimated from the Mössbauer data. Note that, even though the Cu atoms do not attract the excess oxygen atoms they are able to accommodate holes up to a certain limit. From (i) the nominal metal compositions, (ii) estimated oxygen excess values, and (iii) the ratio of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{IV})$ obtained from Mössbauer fit, the following copper valence values are

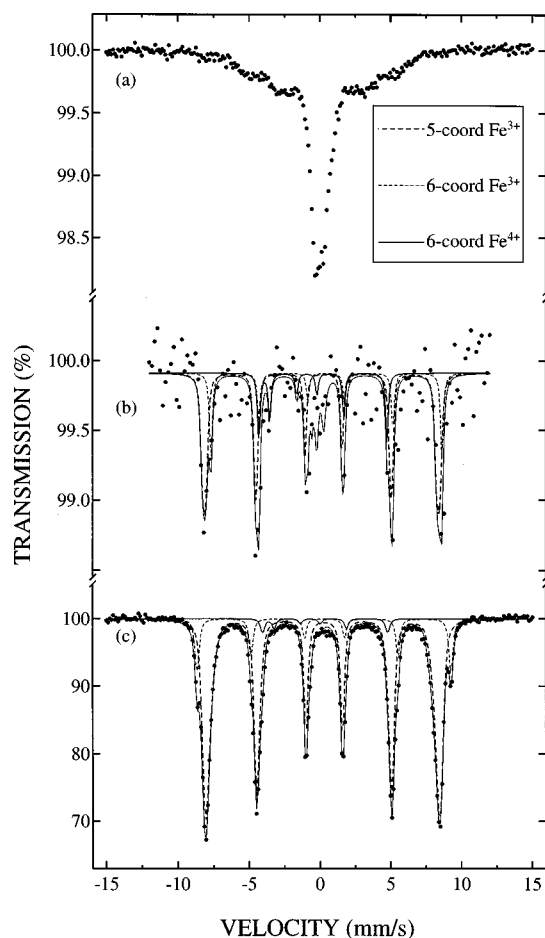


FIG. 3. Mössbauer spectra recorded from the high-pressure heat-treated $x=0.2$ sample (a) at room temperature, and (b) at 20 K. The (c) spectrum was obtained from the high-pressure heat-treated $x=0$ sample at 20 K (Ref. 5). The difference in statistics is due to the fact that ^{57}Fe was used in the synthesis of the latter sample. Component assignments are presented in the legend.

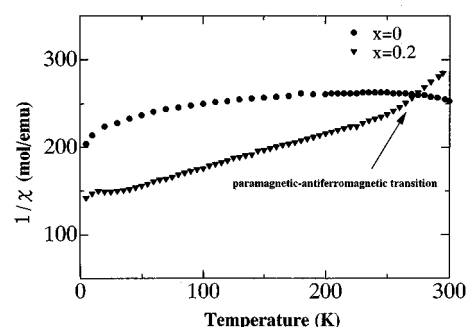


FIG. 4. Inverse susceptibility vs temperature curves of the high-pressure heat-treated $x=0$ (●) and $x=0.2$ (▼) samples. The paramagnetic-antiferromagnetic transition is indicated only when it lies within the temperature range.

TABLE III. ^{57}Fe Mössbauer results for the high-pressure heat-treated samples of $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ with $x=0$ (refit) and 0.2 measured at 20 K.

x	Assigned component	Intensity ^a (%)	Field (T)	Quadrupole coupling (mm/s)	Isomer shift relative to $\alpha\text{-Fe}$ (mm/s)
0	five-coordinated Fe^{3+}	84.56	51.1	-0.33	0.352
	six-coordinated Fe^{3+}	12.28	55.5	-0.05	0.417
	six-coordinated Fe^{4+}	3.16	27.4	2.10	-0.056
	five-coordinated Fe^{3+}	61.64	51.2	-0.31	0.298
0.2	six-coordinated Fe^{3+}	22.05	50.5	0.08	0.558
	six-coordinated Fe^{4+}	16.30	28.07	2.30	-0.256

^aThe intensity of the weak paramagnetic component (see Paper I) was omitted.

obtained: +2.28 in the $x=0$ sample and +2.26 in the $x=0.2$ sample. Finally, for comparison we note that in the $\text{BaY}(\text{Co}_{1-x}\text{Cu}_x)_2\text{O}_5$ ($0.15 \leq x \leq 0.5$) and $\text{BaY}(\text{Co}_{0.5}\text{Cu}_{0.5-x}\text{Fe}_x)_2\text{O}_5$ ($0.15 \leq x \leq 0.3$) systems, copper and iron seem to remain in divalent and trivalent states, respectively, while cobalt is supposed to exhibit mixed valency as represented by the following formulas: $\text{BaY}(\text{Co}_{0.5-x}^{(+II)}\text{Co}_{0.5}^{(+III)}\text{Cu}_x^{(+II)})_2\text{O}_5$ (Refs. 6, 8, and 9) and $\text{BaY}(\text{Co}_x^{(+II)}\text{Co}_{0.5-x}^{(+III)}\text{Cu}_{0.5-x}^{(+II)}\text{Fe}_x^{(+III)})_2\text{O}_5$.¹⁰

The fact that the stabilization of $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ up to $x=0.2$ was realized by the high-pressure heat treatment may be understood by considering the tolerance factor (t) of the 0112 phase. For the 0112 structure built up by stacking rocksalt-type $(\text{Ba},\text{La})\text{O}$, i.e., AO, and perovskite-type $(\text{Cu},\text{Fe})\text{O}_2$ layers the tolerance factor is given by

$$t = d_{\text{Ba,La-O}} / (\sqrt{2}d_{\text{Cu,Fe-O}}), \quad (1)$$

where $d_{\text{Ba,La-O}}$ and $d_{\text{Cu,Fe-O}}$, respectively, are the “optimal” or “expected” bond lengths of the $(\text{Ba},\text{La})\text{-O}$ and $(\text{Cu},\text{Fe})\text{-O}$ bonds as estimated from the corresponding empirically determined ionic-radii data.¹⁴ The tolerance factor provides us with a measure of the bond-length mismatch across the interface of the different layers. Theoretically, deviations from unity reflect the instability of the structure. However, in practice the calculated t value corresponding to the ideal matching may differ somewhat from unity due to the uncertainty in the ionic radii values used in the calculation. For the stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_5$ structure t is 1.056. Since the structure is quite stable under ambient conditions this t value should not be far from the optimal. On the other hand, the fact that the t value is larger than unity explains why the replacement of the larger $\text{Fe}(+III)$ by the smaller $\text{Cu}(+III)$, which would increase the t value further, is not favorable in the $\text{BaY}(\text{Cu},\text{Fe})_2\text{O}_5$ system. Also, empirically it is known that in pyramidal coordination copper possesses average/mixed valence values only in the approximate range of +2.0–+2.3. Therefore, in order to extend the solubility limit of copper in the $(\text{Cu},\text{Fe})\text{O}_2$ plane, an increase in the valence of the A metal and a decrease in the preferred dimension of the rocksalt-type AO layer are simultaneously required. Both requirements are fulfilled when substituting the larger $\text{Ba}(+II)$ ($d_{\text{Ba-O}} = 3.01 \text{ \AA}$) by smaller $\text{La}(+III)$ ($d_{\text{La-O}} = 2.76 \text{ \AA}$). However, in the $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ system t decreases quite strongly with increasing substitution level x . Supposing

that the t value of 1.056 obtained for the stoichiometric $\text{BaY}(\text{Cu}_{0.5}\text{Fe}_{0.5})_2\text{O}_5$ structure is close to the optimal, it becomes probable that with increasing x , the in-plane $\text{Fe}/\text{Cu-O}$ distance needs to be slightly shortened, too. This was achieved by applying high pressure during the synthesis, since the excess oxygen that was incorporated into the structure upon the high-pressure heat treatment is likely to shorten the in-plane $\text{Fe}/\text{Cu-O}$ bond length by increasing the valence value of the Cu/Fe atoms. Finally, we note that this kind of mapping of the tolerance limits for the stability of the 0112 structure is indispensable for finding the proper conditions for stabilizing the structure with totally iron-free CuO_2 planes.

IV. CONCLUSIONS

This study demonstrated an extension of the solid-solubility limit of copper in the $(\text{Ba}_{1-2x}\text{La}_{2x})\text{Y}(\text{Cu}_{0.5+x}\text{Fe}_{0.5-x})_2\text{O}_{5+\delta}$ system. Via high-pressure heat treatment at 5 GPa and 1200 °C, a 0112 compound in which the amount of copper is larger than that of iron in the oxygen pyramid was successfully obtained for the first time. The successful synthesis by the simultaneous substitution of La for the Ba site and Cu for the Fe site could be explained also by considering the tolerance factor of the layered 0112 structure. ^{57}Fe Mössbauer results revealed a presence of a notable amount of excess oxygen in the high-pressure heat-treated samples. Furthermore, not only the average Fe valence but also the average Cu valence could be estimated from the Mössbauer data. A decrease of T_N with increasing x was observed. This can be understood as a consequence of a weakening of the antiferromagnetic coupling due to the replacement of high-spin trivalent ($S = \frac{5}{2}$) iron by divalent ($S = \frac{1}{2}$) copper.

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