

Solid Solution of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ ($0 \leq x \leq 1$) and Its Intergrowth with $\text{YBa}_2\text{Cu}_3\text{O}_7$

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Solid-solution materials of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ ($0 \leq x \leq 1$) have been synthesized by solid-state reaction. Using the XRD and HREM techniques, their structures were determined to be related to the defect perovskite structure and have tetragonal unit cells with $a \approx 3.88$ and $c \approx 7.52$ Å. Annealing YBaCo_2O_5 in pure oxygen leads to a $3 \times 3 \times 1$ tetragonal superstructure which can be eliminated by electron beam irradiation or by annealing the specimen in argon, implying the existence of excess oxygen in the yttrium layer. A model for this superstructure with a composition of $\text{Y}_9\text{Ba}_9\text{Co}_{18}\text{O}_{49}$ has been suggested and supported by computer simulations of the HREM images. Irregular intergrowth of YBaCo_2O_5 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ has also been observed from a specimen with a nominal composition of $\text{Y}_2\text{Ba}_3\text{Cu}_3\text{Co}_2\text{O}_{12}$.

Introduction

Recently, a new perovskite-related compound, YBaCo_2O_5 , was synthesized, and its structure determined by X-ray diffractometry (XRD) and selected area electron diffraction (SAED)¹ to be isomorphous with YBaCuCoO_5 ² or YBaCuFeO_5 .³ YBaCuCoO_5 can be produced not only in a ceramic form but also in large single crystals.⁴ Its structure can be regarded as a derivative of the high- T_c superconducting phase, $\text{YBa}_2\text{Cu}_3\text{O}_7$, achieved by removing one Ba-O layer and the Cu-O chain originally sandwiched by two Ba-O layers (Figure 1) with 50% of the remaining copper atoms being substituted by cobalt. In YBaCo_2O_5 , therefore, all of the copper sites are occupied by the cobalt cations.

Cobalt usually exists as Co^{2+} in simple compounds but prefers a higher oxidation state, Co^{3+} , octahedrally coordinated by anions in most complexes.⁵ Therefore, it is more likely that the cobalt cations in YBaCuCoO_5 are in the 3+ state and the copper cations are in the 2+ state. In YBaCo_2O_5 , the average charge valence for cobalt is 2.5+. In other words, cobalt exists in both the 2+ and 3+ states in the Cu-free phase. Furthermore, after annealing the specimen of YBaCo_2O_5 in pure oxygen atmosphere, a $3 \times 3 \times 1$ superstructure was observed on the SAED patterns.¹ It was therefore assumed that excess oxygen atoms had been introduced into the yttrium layer, partially occupying the anion vacant sites in an ordered arrangement. Consequently, the cobalt cations in YBaCo_2O_5 can be further oxidized from $\text{Co}^{2.5+}$ to Co^{3+} .

The structural similarity of YBaCuCoO_5 and YBaCo_2O_5 implies that a solid solution may cover the whole com-

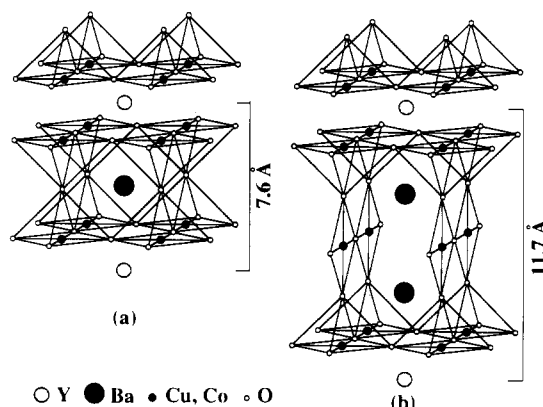


Figure 1. Structural models of (a) YBaCuCoO_5 and (b) $\text{YBa}_2\text{Cu}_3\text{O}_7$.

positional range between these two compounds. The system of $\text{YBaCu}_x\text{Fe}_{2-x}\text{O}_5$ has been previously studied and only one compound was isolated, i.e., YBaCuFeO_5 .³ Up to date, no parallel studies for the system of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ have been reported. On the other hand, since $\text{YBa}(\text{Cu},\text{Co})_2\text{O}_5$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ belong to the same structural family of $\text{YBa}_n(\text{Cu},\text{Co})_{n+1}\text{O}_{3+2n}$ (Figure 1) intergrowth between these two phases along the c axes is possible.

In this work, synthesis and the structure determination of the solid solution of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ with $0 \leq x < 1$ by XRD and high-resolution electron microscopy (HREM) are presented. Irregular intergrowth of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and YBaCo_2O_5 phases observed in the HREM studies from a specimen with a nominal composition of $\text{Y}_2\text{Ba}_3\text{Cu}_3\text{Co}_2\text{O}_{12}$ is also presented. Future development of these solid-solution materials is discussed.

Experimental Section

Polycrystalline specimens of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ with $x = 0, 0.25, 0.5, 0.75,$ and 1 were prepared by heating stoichiometric mixtures of Y_2O_3 (99.999%), BaCO_3 (>99%), CuO (99.999%), and CoO (>99%) in air at 1000 °C for 48 h. The specimen was quenched to room temperature, reground in an agate mortar and pestle, pressed into a pellet, and reheated at 1100 °C in pure oxygen for

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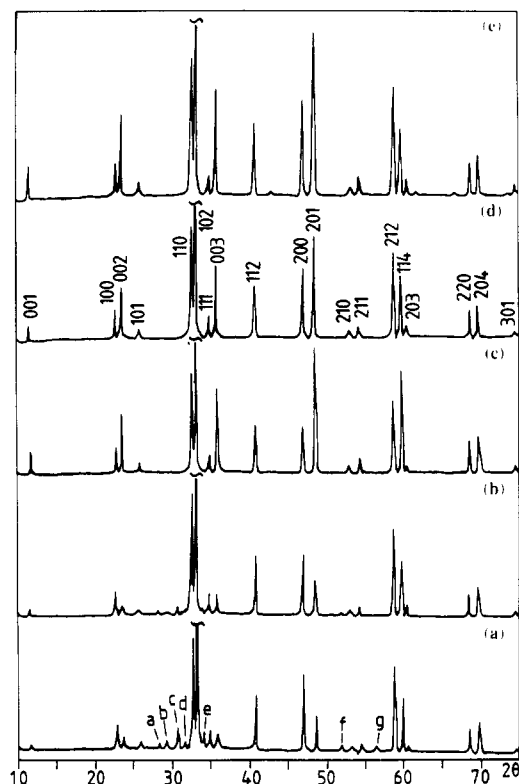


Figure 2. XRD spectra of the solid solution materials of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_{5+y}$, with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$. The spectrum of (d) is indexed onto a tetragonal unit cell with $a = 3.876$ and $c = 7.536$ Å. The marked peaks in (a) are from a $3 \times 3 \times 1$ superstructure.

another 48 h followed by quenching to room temperature. A mixture of oxides with a nominal composition of $\text{Y}_2\text{Ba}_3\text{Cu}_3\text{Co}_2\text{O}_{12}$ was heated at 980 °C in pure oxygen atmosphere for 48 h and then quenched to room temperature. Homogeneity of the specimens was examined by energy-dispersive X-ray spectrometry (EDS) on a JEOL EM-2010CX electron microscope. Initial characterization of the specimens was by XRD. Further structural examination was based on analysis of the SAED patterns and HREM images, both being obtained on a JEOL EM-200CX electron microscope operated at 200 kV with a modified specimen stage⁶ with objective lens parameters $C_s = 0.41$ mm and $C_c = 0.95$ mm, giving an interpretable point resolution of about 1.85 Å. Computer image simulations were performed according to the multislice method^{7,8} using the cerius HRTEM program developed by Cambridge Molecular Design Ltd.

Results and Discussion

The XRD spectra from all the prepared specimens of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ (Figure 2) are very similar to each other and can be indexed to a YBaCuCoO_5 -like⁴ tetragonal unit cell, except that there are some additional weak peaks observed from cobalt-rich specimens (Figure 2a,b). The basic unit-cell parameters of each composition are listed in Table 1. The unit-cell volume slightly decreases with an increase of the cobalt concentration.

Using single crystals of YBaCuCoO_5 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ as references in the EDS studies, the average metal composition from 20 particles randomly chosen from each specimen was obtained to be very close to the starting composition (Table 2). Consequently, all the specimens

Table 1. Tetragonal Unit-Cell Parameters of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$

x	a (Å)	c (Å)	vol (Å ³)
1.0	3.878(1)	7.542(2)	113.4(1)
0.75	3.876(1)	7.536(2)	113.22(9)
0.5	3.879(4)	7.508(7)	113.0(3)
0.25	3.876(2)	7.512(4)	112.86(6)
0.0 ^a	3.867(2)	7.484(4)	111.91(6)
0.0 ^b	3.871(2)	7.492(4)	112.27(7)

^a After annealing in pure oxygen. ^b After annealing in argon.

Table 2. Metal Compositions of the Solid-Solution Materials of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ Determined by EDS

starting composition	Y	Ba	Cu	Co
YBaCuCoO_5	1.00(4)	1.00(2)	0.92(9)	1.07(5)
$\text{YBaCu}_{0.75}\text{Co}_{1.25}\text{O}_5$	0.97(1)	0.99(2)	0.79(4)	1.26(2)
$\text{YBaCu}_{0.5}\text{Co}_{1.5}\text{O}_5$	1.02(2)	1.02(2)	0.46(2)	1.52(3)
$\text{YBaCu}_{0.25}\text{Co}_{1.75}\text{O}_5$	1.02(3)	0.99(2)	0.26(3)	1.73(3)
YBaCo_2O_5	1.00(2)	1.00(2)	0	1.99(2)

prepared are single phases in terms of chemical composition, despite the unindexed XRD peaks from $\text{YBaCu}_{0.25}\text{Co}_{1.75}\text{O}_5$ and YBaCo_2O_5 (Figure 2). To determine the exact compositional range of the solid solution, another specimen with a nominal composition of $\text{YBaCu}_{1.2}\text{Co}_{0.8}\text{O}_5$ was also prepared under the same preparation conditions as those for the other samples. The EDS results indicated that the majority phase in the specimen was YBaCuCoO_5 . Several minor phases, e.g., Y_2CuO_4 , Y_2BaCuO_5 , $\text{YBa}_2\text{Cu}_3\text{O}_7$, etc., were also detected. Therefore, the solid solution of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ can be produced at room temperature in the compositional range with $0 \leq x \leq 1$.

The iron and cobalt cations have very similar chemical properties and ionic radii. Fe- and Co-containing compounds are usually isomorphous. Why the preparation of a solid solution of $\text{YBaCu}_x\text{Fe}_{2-x}\text{O}_5$ was not successful³ remains unknown.

The oxygen concentration of the single crystals of YBaCuCoO_5 was previously determined using a wavelength-dispersive spectrometer mounted in an electron microprobe apparatus (EPMA) to be 4.9(1).⁴ Therefore, similar to the high- T_c superconducting phases of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$, no oxygen atoms occupy the anion vacancies in the yttrium layer of YBaCuCoO_5 .

In the HREM studies, a simple structure shown in Figure 1a without any superstructure was confirmed for YBaCuCoO_5 . Figure 3 shows a principal HREM image and the corresponding SAED pattern of YBaCuCoO_5 viewed down the [010] zone axis. The inset of Figure 3 is a computer simulated image calculated from the structural model of Figure 1a with an average occupation of copper and cobalt on the pyramid sites. The observed image contrast has been reproduced. Evidence of ordering of the copper and cobalt cations was never detected.

In agreement with the XRD results, all the SAED patterns and HREM images obtained from $\text{YBaCu}_{0.75}\text{Co}_{1.25}\text{O}_5$ and $\text{YBaCu}_{0.5}\text{O}_5$ were identical to those from YBaCuCoO_5 . The average charge valence of cobalt in these compositions varies with the ratio of Cu:Co, i.e., cobalt exists as Co^{3+} in YBaCuCoO_5 , $\text{Co}^{2.8+}$ in $\text{YBaCu}_{0.75}\text{Co}_{1.25}\text{O}_5$, and $\text{Co}^{2.67+}$ in $\text{YBaCu}_{0.5}\text{Co}_{1.5}\text{O}_5$.

Among the prepared samples, the most interesting one is the Cu-free YBaCo_2O_5 . The additional peaks on the XRD spectrum shown in Figure 2a could not be eliminated by annealing the specimen in pure oxygen for a longer time. However, after annealing the sample in argon or nitrogen at 900 °C for 24 h, all the extra peaks disappeared

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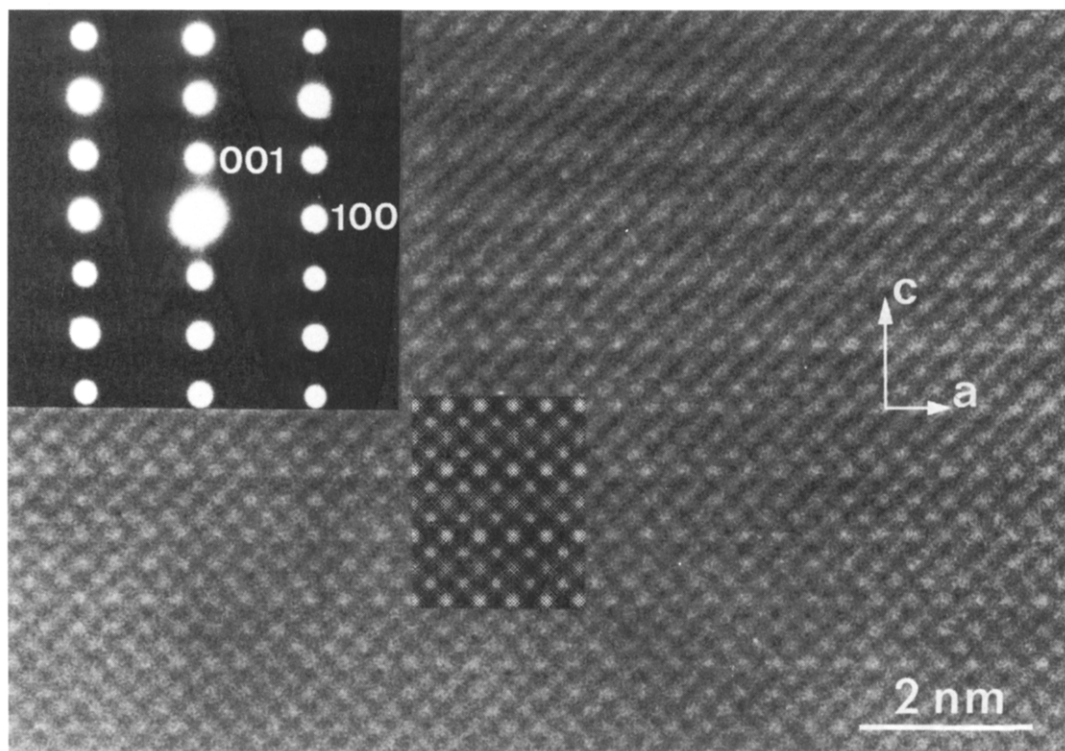


Figure 3. HREM image and the corresponding SAED pattern from YBaCuCoO_5 viewed down the $[010]$ zone axis. The inset is a computer-simulating image from a structural model shown in Figure 1a with an average occupation of copper and cobalt on the pyramid sites. Specimen thickness of 19.30 Å and lens defocus of -600 Å were used in the calculation.

and the remaining XRD peaks were perfectly indexed to a YBaCuCoO_5 -like unit cell.¹

The parallel SAED and HREM studies revealed a $3 \times 3 \times 1$ superstructure only from the Cu-free specimen synthesized in pure oxygen but from neither those after annealing in argon and nitrogen nor the Cu-containing samples. Figure 4 shows a HREM image of such a superstructure when viewed down the $[001]$ zone axis. The corresponding SAED pattern on the top left corner of Figure 4 is indexed onto the YBaCuCoO_5 -like basic unit cell. A 3×3 superlattice is clearly observed both on the SAED pattern and the HREM image. Using this $3 \times 3 \times 1$ superunit cell, all the additional XRD peaks in Figure 2a have been indexed, e.g., the marked peak a can be indexed as the (202) reflection, b as (212), c as (400), d as (410), e as (411), f as (214), and g as (622).

Under the electron beam irradiation with a beam current of ca. 120 μA and screen brightness of 130 PA/cm^2 , the SAED pattern with the superstructure (Figure 5a) remained unchanged. However, when the screen brightness was increased to 150 PA/cm^2 , the satellite diffraction spots suddenly disappeared. Eventually, the SAED pattern became the same as the normal one obtained from other specimens (Figure 5b). An opposite procedure was not achieved under the operating conditions of the electron microscope. Practically, a reduction rather than an oxidation process usually takes place under the electron beam irradiation in the high vacuum system (ca. 2×10^{-7} Torr) inside the electron microscope. The removal of oxygen from metal oxide crystals by electron beam irradiation are often observed in other materials,⁹ leading to the formation of superstructures based on the ordering of oxygen vacancies. In many perovskite-related crystals,

superstructures are formed due to the ordering of cations (e.g., an ordering of Bi^{3+} and Bi^{5+} in BiBaO_3) and lattice distortion (e.g., distortion of CuO_6 octahedra in La_2CuO_4). However, such an ordering and lattice distortion unlikely give rise to a $3 \times 3 \times 1$ superstructure. Therefore, the superstructure in YBaCo_2O_5 after annealing in pure oxygen is assumed to relate to an ordering of excess oxygen and the composition of the compound becomes $\text{YBaCo}_2\text{O}_{5+x}$. After annealing in argon, the sample was reduced to YBaCo_2O_5 .

Some additional weak peaks are also found on the XRD spectrum of $\text{YBaCu}_{0.25}\text{Co}_{1.75}\text{O}_5$ (Figure 2b). The sample is therefore assumed to contain excess oxygen as well, giving rise to a composition of $\text{YBaCu}_{0.25}\text{Co}_{1.75}\text{O}_{5+x}$. However, no superstructure was observed in the SAED and HREM studies from this specimen. One possible reason of this is that the sample lost excess oxygen immediately when it was transferred into the vacuum chamber of the electron microscope or when it was exposed to the electron beam. It is also possible that the amount of the excess oxygen ions in $\text{YBaCu}_{0.25}\text{Co}_{1.75}\text{O}_{5+x}$ is much less than that in $\text{YBaCo}_2\text{O}_{5+x}$ and these ions are mobile, losing the ordered arrangement under the electron beam exposure.

It is noted that cobalt usually exists in a mixed valence of 2+ and 3+ in an oxide form. For example, Co_2O_3 is not definitely established. CoO will be easily oxidized in oxygen above 400 °C to form Fe_3O_4 -like Co_3O_4 , which contains tetrahedrally surrounded Co^{2+} and octahedrally surrounded Co^{3+} cations. When excess oxygen ions enter the structure of YBaCo_2O_5 , it is almost certain that the oxygen ions must occupy the anion vacancies in the yttrium layer to link two CoO_5 pyramids, since, unlike $\text{YBa}_2\text{Cu}_3\text{O}_7$, there is no other space in YBaCo_2O_5 which can accommodate extra oxygen (Figure 1). It is not difficult to understand

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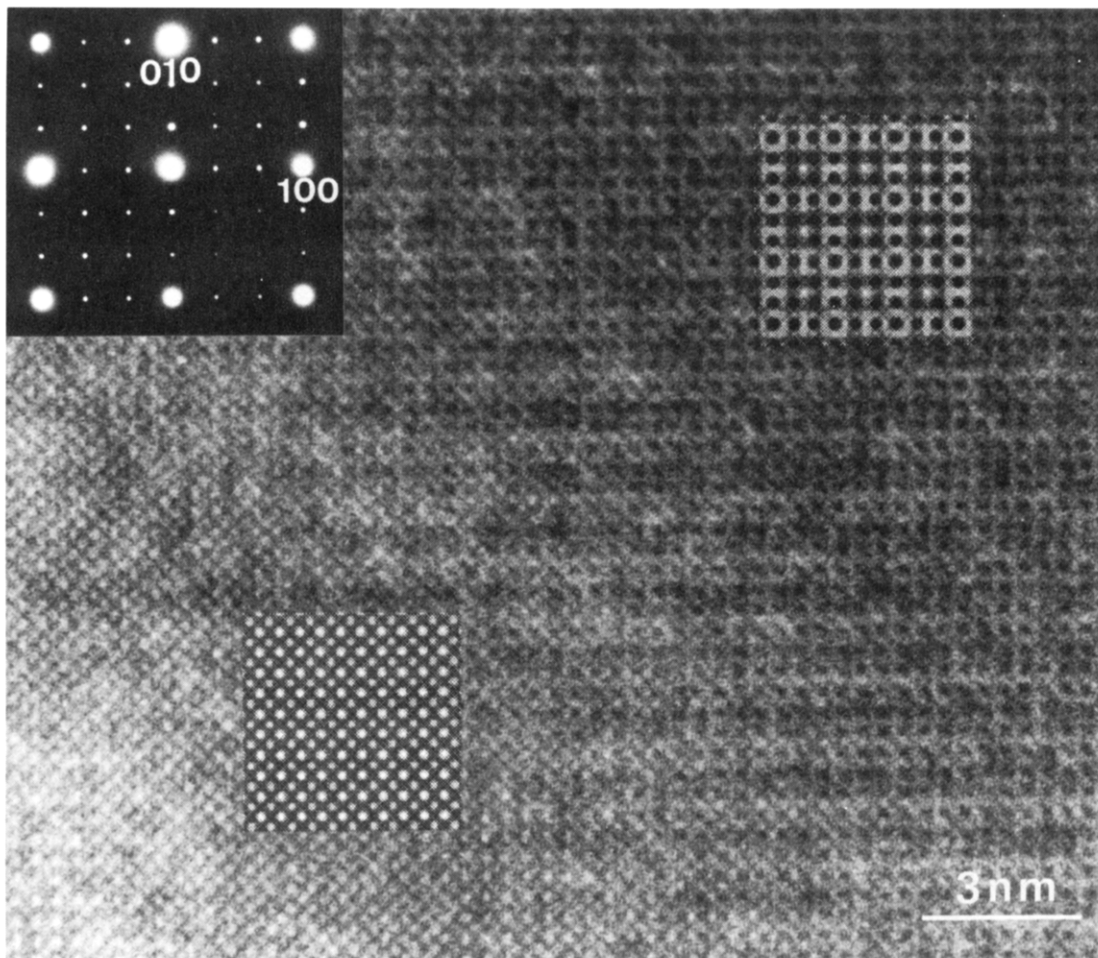


Figure 4. HREM image and the corresponding SAED pattern from $\text{YBaCo}_2\text{O}_{5+x}$ after annealing in pure O_2 . The SAED pattern is indexed to the basic unit cell. The insets are simulated images calculated from a structural model shown in Figure 6c. Specimen thicknesses are 7.6 (left) and 38.0 Å (right). Lens defocuses are -600 (left) and -700 Å (right).

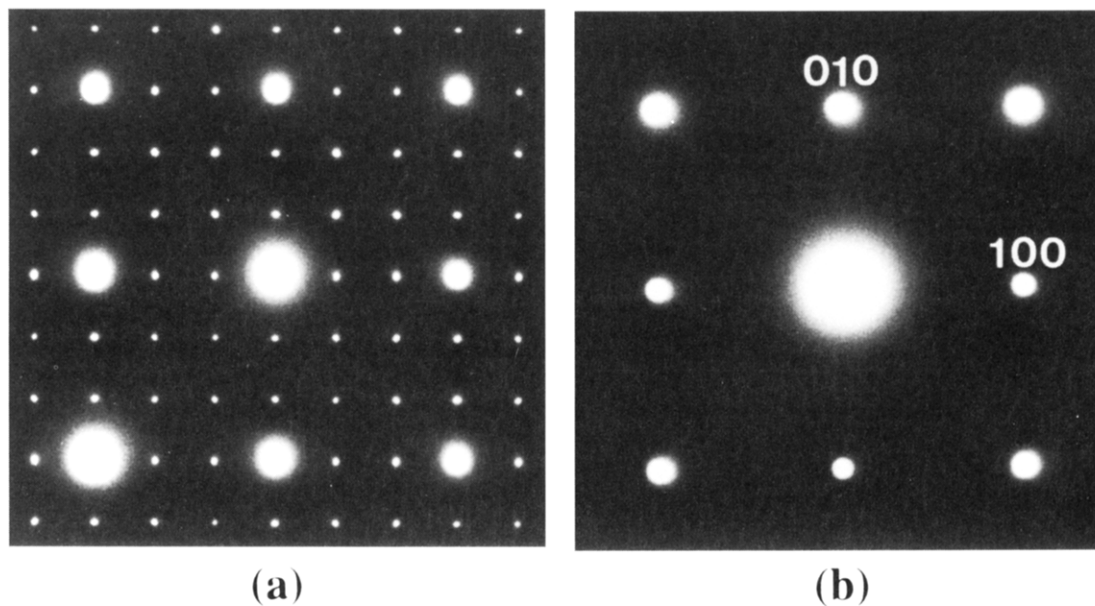


Figure 5. (a) Original SAED pattern from $\text{YBaCo}_2\text{O}_{5+x}$ after annealing in pure oxygen, showing 3×3 superlattice. (b) SAED pattern from the same crystal after electron beam irradiation in less than one second with the screen brightness of 150 PA/cm^2 .

that filling the anion vacancies in the yttrium layer with oxygen (Figure 1a) during the preparation of the specimen will affect the morphology of the crystals, i.e., the crystals become more isometric in comparison with sheetlike crystals of YBaCuCoO_5 . Therefore, the observed relative

intensities of the $(00l)$ peaks on the XRD spectrum are significantly higher from $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ ($x \geq 0.5$; Figure 2c-e) than those from the specimens with $x \leq 0.25$, in which excess oxygen was assumed to present indicated by the additional peaks on the XRD spectra (Figure 2a,b).

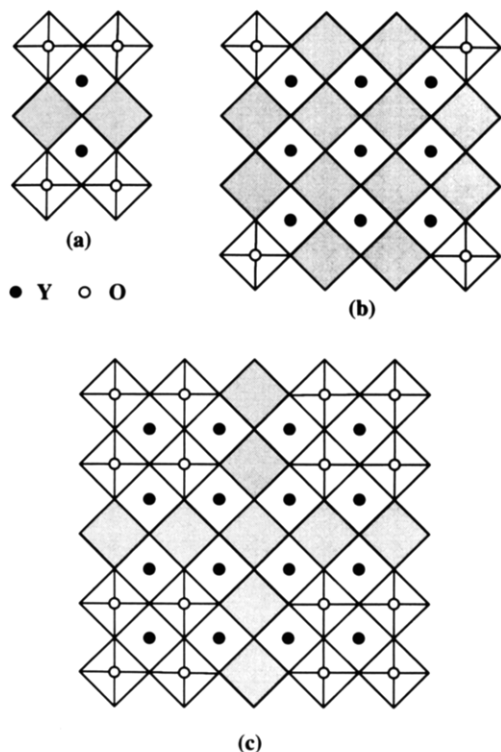


Figure 6. Schematic drawings of the (ab) planes at the yttrium layer in $\text{YBaCo}_2\text{O}_{5+x}$. The shadowed squares represent the original Co–O planes. Open circles represent extra oxygen ions occupying the oxygen vacancies in the yttrium layer to form CoO_6 octahedra. (a) A 2×1 arrangement corresponding to a composition of $\text{Y}_2\text{Ba}_2\text{Co}_4\text{O}_{11}$. (b) The simplest 3×3 superstructure with a composition of $\text{Y}_9\text{Ba}_9\text{Co}_{18}\text{O}_{46}$, and (c) the final 3×3 superstructure with a composition of $\text{Y}_9\text{Ba}_9\text{Co}_{18}\text{O}_{49}$.

If all cobalt atoms in $\text{YBaCo}_2\text{O}_{5+x}$ are oxidized to $3+$, the composition becomes $\text{Y}_2\text{Ba}_2\text{Co}_4\text{O}_{11}$. The simplest model for this composition is a 2×1 superstructure on the (ab) plane (Figure 6a). Such a superstructure was never observed in our HREM studies. The reason might be that a one-dimensional ordering of CoO_5 pyramids and CoO_6 octahedra would give rise to too much lattice stress inside the structure. Second possible model with the one excess oxygen atom in the yttrium layer of a $2 \times 2 \times 1$ superstructure has a two-dimensional arrangement of CoO_6 octahedra. The composition becomes $\text{Y}_4\text{Ba}_4\text{Co}_8\text{O}_{21}$ with an average charge valence of $2.75+$ for cobalt. Again we have not observed such a superstructure. Adding one oxygen atom into the yttrium layer in a $3 \times 3 \times 1$ superunit cell gives the simplest model to match the observed unit cell (Figure 6b). It has a composition of $\text{Y}_9\text{Ba}_9\text{Co}_{18}\text{O}_{46}$ with an average charge valence of $2.61+$ for cobalt. Using this model, the observed SAED patterns can be reproduced in the computer simulations, but the calculated relative intensities of the satellite diffraction spots with a specimen thickness of up to 200 \AA are much weaker than those experimentally observed. Simulated HREM images viewed down the $[001]$ direction of this model with the specimen thickness from 10 to 200 \AA and lens defocus from 0 to -2000 \AA gave no 3×3 fringes as strong as the observed ones (Figure 4), unless significant lattice distortion or atomic shift was made in the model.

To find out whether the superstructure resulted mainly from an ordering of excess oxygen atoms in the yttrium layer, a mass-loss measurement has been performed.¹ The oxidized specimen of $1.6600(2) \text{ g}$ lost $0.0245(2) \text{ g}$ in mass after being annealing in pure argon at $1000 \text{ }^\circ\text{C}$ for 24 h .

The reduced specimen was then reannealed in pure oxygen at $1000 \text{ }^\circ\text{C}$ for another 24 h . The mass of the sample went back to $1.6608(2) \text{ g}$. Assuming the reduced sample has an ideal composition of YBaCo_2O_5 , this mass loss corresponds to an x value in the oxidized sample, $\text{YBaCo}_2\text{O}_{5+x}$, of ca. 0.4 . The real average charge valence of cobalt in this specimen is accordingly $2.9+$. Therefore, an ordering of the excess oxygen atoms must be responsible for the superstructure and the average composition of $\text{YBaCo}_2\text{O}_{5.4}$ for the oxidized sample must be considered in the construction of the superstructural model.

It has to be mentioned that the reversible process of mass loss described above cannot be achieved when pure nitrogen was used instead of pure argon. No significant mass loss was observed after annealing the oxidized sample in pure nitrogen. After annealing the reduced specimen (after treatment in pure argon) in pure nitrogen, the mass of the specimen went up to about the same as that of the oxidized sample. The mass of the specimen after being annealed in pure nitrogen did not lose even the specimen was heated in pure argon at $1000 \text{ }^\circ\text{C}$ for 48 h . It was assumed that YBaCo_2O_5 might absorb nitrogen to form some kinds of N-containing compounds.

The final model for $\text{YBaCo}_2\text{O}_{5+x}$ was then proposed as shown in Figure 6c. Four oxygen atoms in a square unit were introduced into the yttrium layer to form a complete perovskite block, CoYO_3 , in the $3 \times 3 \times 1$ superunit cell. The composition becomes $\text{Y}_9\text{Ba}_9\text{Co}_{18}\text{O}_{49}$ or $\text{YBaCo}_2\text{O}_{5.44}$, in which the average charge valence for cobalt is $2.94+$. On the basis of this ideal model, the SAED pattern shown in Figure 5a and others with the satellite diffraction spots have been reproduced in the computer simulations. The observed HREM image shown in Figure 4 was also reproduced using the computer-image simulation technique. As one can see, the image contrast in both the edge and bulk areas of the crystal with different specimen thickness can be matched by the calculated images. Other observed HREM images viewed down different zone axes have also been simulated by the same method. Consequently, the principle of the proposed model for the $3 \times 3 \times 1$ superstructure in $\text{YBaCo}_2\text{O}_{5+x}$ is basically correct. Other ordered, partially ordered or even disordered arrangements of excess oxygen in the yttrium layer of the compound with different oxygen content may also be possible depending on the preparation conditions.

The vacancies in the Y layer of YBaCo_2O_5 are the only possible sites for the excess oxygen, although the space in the layer is relatively small. In the proposed model (Figure 6c), the perovskite units of YCoO_3 together with the perovskite units of BaCoO_3 present. To form a perovskite lattice, the lattice tolerance factor, $t = (R_A + R_O)/[\sqrt{2}(R_B + R_O)]$, must lie between 0.8 and 1.0 , where R_A , R_B , and R_O are the radii of the relevant ions, i.e., $R_A = 0.893 \text{ \AA}$ for Y^{3+} , 1.34 \AA for Ba^{2+} , $R_B = 0.63 \text{ \AA}$ for Co^{3+} , and $R_O = 1.32 \text{ \AA}$ for O^{2-} . The t values for $\text{Ba}^{2+}\text{Co}^{3+}\text{O}_3$ and $\text{Y}^{3+}\text{Co}^{3+}\text{O}_3$ lattices are 0.96 and 0.80 , respectively. Therefore, both BaCoO_3 and YCoO_3 can possibly form the perovskite structure.

Nevertheless, the solid solution of $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ presented in this work is a new series of Co-containing materials, and its end member, YBaCo_2O_5 , is the first example we know so far to demonstrate the capability to accommodate oxygen ions in the yttrium layer of the Y-containing perovskite cuprates. In addition, these excess oxygen ions are mobile and there is no significant difference

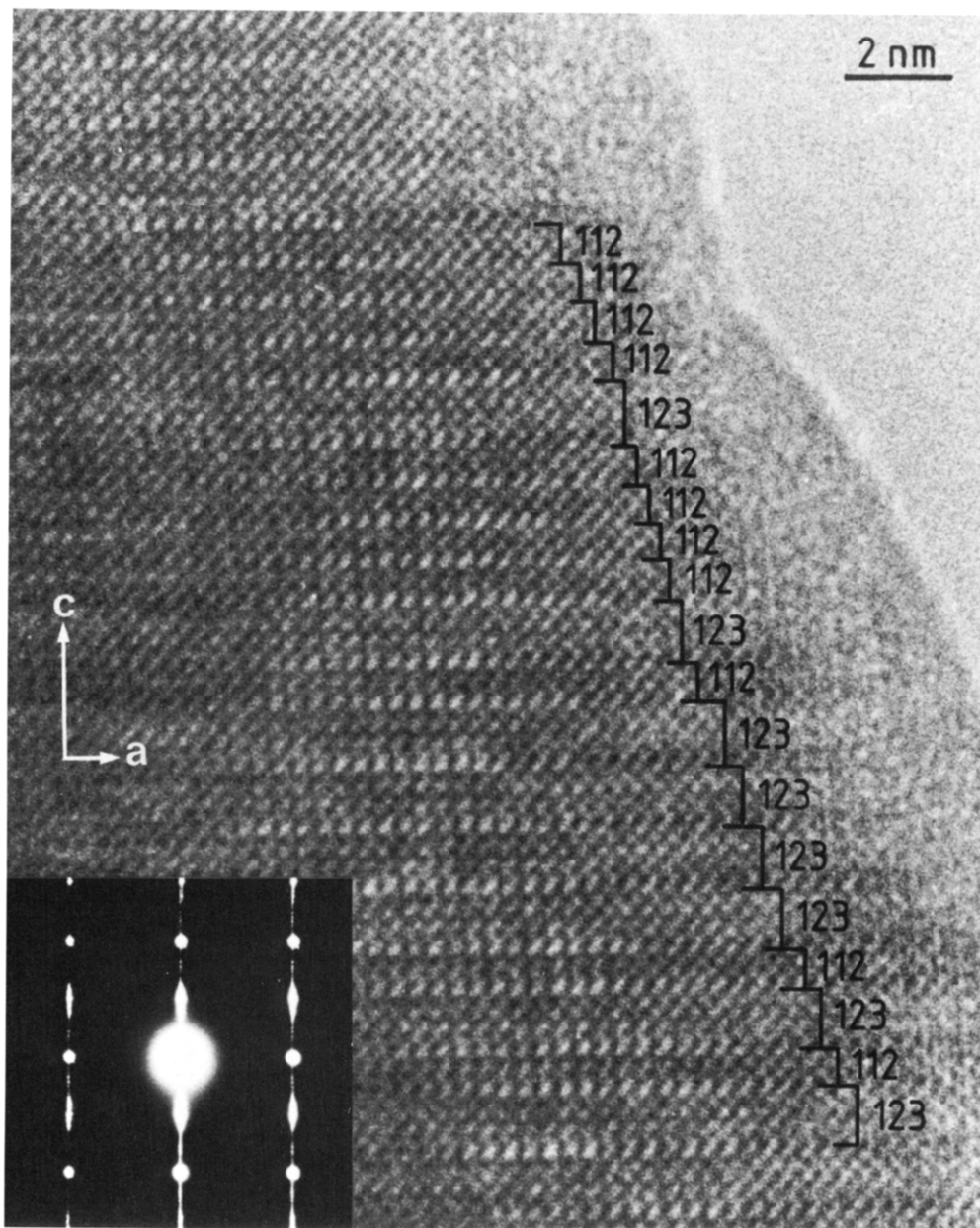


Figure 7. HREM image from the specimen with a nominal composition of $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{Co}_2\text{O}_{12}$, showing an irregular intergrowth of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) and YBaCo_2O_5 (112) phases.

of the basic unit cell parameters between the reduced and oxidized forms of $\text{YBaCo}_2\text{O}_{5+x}$ (Table 1). The mobility of the excess oxygen ions in the sample allows us to modify the charge valence of the cobalt cations in the material. In the other compositions, $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$, the average charge valence of cobalt depends on the ratio of Cu:Co.

On the other hand, chemical substitution can also change the charge density at cobalt in YBaCo_2O_5 . For example, substitution of yttrium by calcium in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase is well-known.¹⁰ If this can also be achieved in YBaCo_2O_5 to form a new solid solution of $\text{Y}_{1-x}\text{Ca}_x\text{BaCo}_2\text{O}_5$, the average charge valence of cobalt will be increased.

Another interesting feature of the $\text{YBaCu}_x\text{Co}_{2-x}\text{O}_5$ solid solution is its structural similarity to $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Figure 1). Both of these phases actually belong to the same structural family to $\text{YBa}_n(\text{Cu},\text{Co})_{n+1}\text{O}_{3+2n}$. An intergrowth of these two phases along the *c* axes is possible and the

physical properties of the high- T_c superconducting phase may therefore be modified.

Figure 7 shows a HREM image taken from the prepared specimen with a nominal composition of $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{Co}_2\text{O}_{12}$. An irregular intergrowth of the YBaCo_2O_5 (112) and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) phases can be clearly observed. No individual 112 and 123 crystals were detected in the EDS studies.

The material did not show a superconducting property. Bearing in mind that cobalt not only can exist in the 112 phase but also can substitute copper in $\text{YBa}_2\text{Cu}_3\text{O}_7$, it is quite possible that the cobalt cations present in both the 112 and 123 components in the specimen and destroy the superconducting property of the 123 component.

In addition, it has been found that the annealing temperature for the synthesis of a monophasic $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{Co}_2\text{O}_{12}$ is crucial. When the temperature is too low (<950 °C), a green phase, Y_2BaCuO_5 is produced. If the temperature is too high (>1000 °C), the 123 phase is unstable and isolated 112 phase can be detected by XRD.

(10) Manthiram, A.; Lee, S. J.; Goodenough, J. B. *J. Solid State Chem.* 1988, 73, 278.

Consequently, a long-time annealing at about 980 °C in oxygen might be necessary in preparation of a regularly intergrown compound of $Y_2Ba_2Cu_3Co_2O_{12}$. A new specimen has been recently prepared by annealing at 980 °C for 1 week. HREM examination reveals that more than 90% crystal areas have been rearranged into the 1:1 intergrowth of the 112 and 123 phases.

In conclusion, solid solution materials of $YBaCu_xCo_{2-x}O_5$ ($0 \leq x \leq 1$) have been synthesized and their structures determined using XRD and HREM. The average charge valence of cobalt in the Cu-containing specimens can be varied by changing the ratio of Cu:Co and that in the Cu-

free compound can be varied by control of the oxygen content. An intergrowth of the $YBa(Cu,Co)_2O_5$ and $YBa_2(Cu,Co)_3O_7$ phases has been observed by HREM. Synthesis of the new solid solution materials of $Y_2Ba_3(Cu,Co)_5O_{12}$ is carried out. Neutron diffraction studies for the determination of oxygen positions in $YBaCo_2O_{5+x}$, possible ordering of copper and cobalt in $YBaCu_xCo_{2-x}O_5$ and the distribution of cobalt in $Y_2Ba_3Cu_3Co_2O_{12}$ are under way.

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