

A New Perovskite-Related Compound $Y_2Ba_3Cu_3Co_2O_{12}$

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A new perovskite-related compound, $Y_2Ba_3Cu_3Co_2O_{12}$, has been synthesized by solid state reaction. Its structure is tetragonal with $a = 3.878(2)$ Å and $c = 19.193(8)$ Å; XRD and HREM investigations indicate that it consists of a regular intergrowth of $YBa_2(Cu, Co)_3O_7$ and $YBa(Cu, Co)_2O_5$. Possible modifications of this compound by chemical substitution are discussed. © 1995

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INTRODUCTION

Since the discovery of the high- T_c oxide superconductor $YBa_2Cu_3O_{7-\delta}$ several years ago, many investigators have sought to modify its structure and consequently its electronic properties. There are two possible avenues of approach for the structural chemist. The simplest way is to alter the composition either by control of the oxygen content of the lattice or by chemical substitution of the constituent metal atoms while still maintaining the basic structure: electronic properties will change accordingly. The second method is to search for phases closely related to $YBa_2Cu_3O_{7-\delta}$ and to investigate possible intermediate phases. For example, $YBa_2Cu_4O_8$ has a very similar structure to $YBa_2Cu_3O_{7-\delta}$ except that it contains double Cu-O chains replacing the single Cu-O chain in the latter. $YBa_2Cu_4O_8$ was also found to be a high T_c superconductor (1), and several intergrowths between the two phases have been reported (2). Another perovskite-related compound which has possibilities in the context of intermediate compound formation is $YBaCuMO_5$ ($M = Co$ or Fe) (3, 4). This can be regarded as being derived from $YBa_2Cu_3O_7$ by removing one Ba-O layer and the accompanying Cu-O chain which is originally sandwiched between the two Ba-O layers. The component of the structure responsible for superconductivity in $YBa_2Cu_3O_{7-\delta}$ is believed to be the Cu-O planes, in which the copper atoms are linked by oxygen in a highly covalent manner rather than as isolated Cu^{3+} and Cu^{2+} ions. Although these Cu-O planes are maintained in $YBaCuMO_5$, their covalent nature is destroyed by the guest cations, Co^{3+} or Fe^{3+} , and the density of the itiner-

ant charge carriers in the material is reduced. Consequently this material has been found to be an insulator in its pure state.

Recently a series of specimens corresponding to the compositions $YBaCu_{1-x}Co_{1+x}O_5$ ($0 < x < 1$) has been prepared and investigated in our laboratories (5). All the specimens prepared were found to be completely isostructural with $YBaCuCoO_5$, indicating complete solid solubility. The most interesting compound in this range is the end member, $YBaCo_2O_5$, in which the cobalt possesses a nominally mixed valence of Co^{2+} and Co^{3+} . In addition, after annealing in pure oxygen, excess oxygen can be introduced into the anion vacancies in the yttrium layer in $YBaCo_2O_5$ to form a $3 \times 3 \times 1$ superstructure. These excess oxygen anions are mobile and can be removed by annealing the specimen in a 20% oxygen/80% argon mixture. They are also eliminated by electron beam irradiation in the electron microscope. Consequently, we may then assume that this compound might be a good charge reservoir when intergrown with a superconducting phase such as $YBa_2Cu_3O_{7-\delta}$. A schematic outline of the structure of such an intergrowth is shown in Fig. 1. Intergrowth of the two compounds can be expected because the dimensions of the (001) planes in these two compounds are very similar. Bearing in mind that one of the greatest limitations of $YBa_2Cu_3O_{7-\delta}$ is the surface structure which readily decomposes into a thick amorphous coating (6) and severely reduces the intergranular critical current density, we might expect that an intergrowth compound would have a more stable surface structure, as found in pure $YBaCo_2O_5$, and hence offer a means of surmounting this limitation. In this present work, therefore, we report the synthesis and structural characterization of the regular intergrowth of $YBa_2(Cu, Co)_3O_7$ and $YBa(Cu, Co)_2O_5$, which constitutes a new perovskite-related phase of composition $Y_2Ba_3Cu_3Co_2O_{12}$.

EXPERIMENTAL

Ceramic specimens of $Y_2Ba_3Cu_3Co_2O_{12}$ were prepared initially by heating stoichiometric mixtures of Y_2O_3

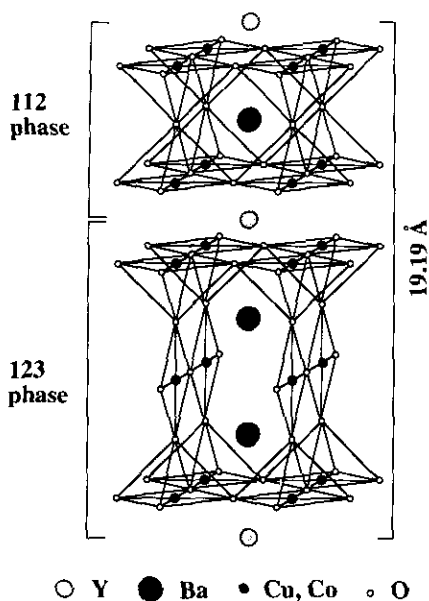


FIG. 1. Structural model of $Y_2Ba_3Cu_3Co_2O_{12}$, an intergrowth of $YBa_2Cu_3O_7$ (123 phase) and $YBaCo_2O_5$ (112 phase).

(99.999%), $BaCO_3$ (99.999%), CuO (99.999%), and CoO (>99%) at $950^\circ C$ in pure oxygen for 48 hr. The specimens were then quenched to room temperature, reground with an agate mortar and pestle, pressed into a pellet, and reheated at $980^\circ C$ for another 5 days. Compositional homogeneity of all specimen was investigated using energy dispersive X-ray spectrometry (EDS) on a JEOL JEM-2010 electron microscope. Initial phase identification in each specimen was by X-ray powder diffractometry (XRD), subsequent structural characterization being based on selected area electron diffraction (SAED) and high resolution electron microscopy (HREM), both carried out in a JEOL JEM-200CX electron microscope operated at 200 kV and having a modified specimen stage with objective lens parameters $C_s = 0.41$ mm and $C_c = 0.95$ mm (7), giving an interpretable point resolution of about 1.85 Å. HREM images were recorded at a magnification of ca. 475,000, after careful correction for the effects of objective astigmatism and incident beam inclination using the granularity of the amorphous carbon support film. Structural models based on these images were tested by computer image simulation according to the multislice method (8, 9) in which the commercially available CERIOUS HRTEM program developed by Cambridge Molecular Design Ltd. was used.

RESULTS AND DISCUSSION

For all specimens, the observed XRD peaks can be indexed on the predicted tetragonal unit cell with $a = 3.878$ Å and $c = 19.193$ Å (Fig. 2). Although the $(hk0)$

reflections from $YBa_2Cu_3O_7$ (the 123 phase), $YBaCo_2O_5$ (the 112 phase) and the new compound cannot be resolved because of the similarity of the a -dimensions of the tetragonal unit cell; no $(h0l)$ and $(00l)$ peaks from the first two compounds are visible in the diffractometer profile of Fig. 2. Accurate control of the annealing temperature was crucial to the preparation of $Y_2Ba_3Cu_3Co_2O_{12}$, which appeared to have a very narrow range of thermal stability. At temperatures below $950^\circ C$ a green phase, Y_2BaCuO_5 , was the stable product, whereas at temperatures greater than $1000^\circ C$ the 123 phase was unstable and only the 112 phase could be detected by XRD. If the temperature was held at approximately $980^\circ C$ for 2 days an irregular intergrowth of the 123 and 112 phases was indicated in the HREM images. X-ray powder diffractometry indicated only the presence of the 123 phase. However, on prolonged annealing (>5 days) at $980^\circ C$ under atmospheric pressure the ordered intergrowth was formed, presumably resulting from a gradual ordering of the initially disordered 112 and 123 components.

In the test for compositional homogeneity using EDS, 30 particles were randomly chosen from the specimen. Monophasic $YBaCo_2O_5$ and a crushed single crystal of pure $YBa_2Cu_3O_7$ were used as reference materials, and the metal atom ratios in the crystals of the new compound were calculated from the relative intensities of BaL , $CoK\alpha$, $CuK\alpha$, and $YK\alpha$ emission lines. Only thin edge areas of the crystals were selected for examination and the ratio of $YK\alpha/YL\alpha$ emissions was checked in each case to ensure that there was no significant energy dependent X-ray absorption occurring either in the crystal under examination or in neighboring crystals on the specimen grid. The final metal atom ratios obtained were $Y : Ba : Cu : Co = 2.08(6) : 3.00(4) : 2.9(1) : 2.02(4)$. No crystals of separate 123 or 112 phases were detected and the homogeneity of the sample was thus confirmed. A typical EDS spectrum of the new compound is shown in Fig. 3.

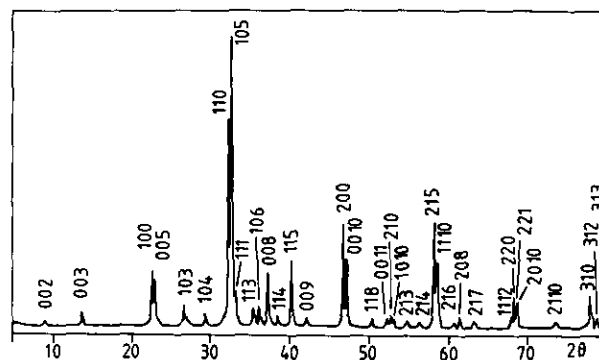


FIG. 2. Powder XRD pattern of $Y_2Ba_3Cu_3Co_2O_{12}$ indexed onto a tetragonal unit cell with $a = 3.878$ Å and $c = 19.193$ Å.

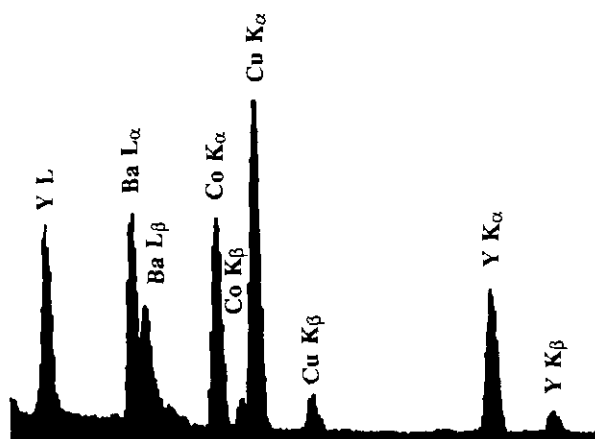


FIG. 3. EDS spectrum of $Y_2Ba_3Cu_3Co_2O_{12}$.

The detailed structure was then investigated using SAED and HREM. All the SAED patterns could be indexed on a tetragonal unit cell with $a = 3.87 \text{ \AA}$ and $c = 19.2 \text{ \AA}$, these being in excellent agreement with the XRD results. No superlattices were observed in the SAED patterns. Figure 4 shows two typical HREM images and the corresponding SAED patterns of $Y_2Ba_3Cu_3Co_2O_{12}$ viewed down the [100] and [001] directions. The c -axis with a dimension of 19.2 \AA corresponding to 10 metal atom layers was revealed in Fig. 4a and the tetragonal symmetry is confirmed in the micrograph of Fig. 4b. Using the structural model shown in Fig. 1 with a random 1:1 occupation of copper and cobalt cations in both the octahedral and pyramidal sites, the contrast in both of the HREM images in Fig. 4 can be reproduced by image simulation. For Fig. 4a, the detailed image contrast could be matched in two areas with clearly different specimen thicknesses and objective lens defocus. Instrumental resolution was insufficient to allow any deductions regarding the oxygen atom positions. Nevertheless, these results show that the chemically designed compound of $Y_2Ba_3Cu_3Co_2O_{12}$ has been successfully synthesized and, within the limitations imposed by microscope resolution, its structure is exactly as predicted.

Specimens of this new phase did not exhibit any superconducting properties in magnetic susceptibility measurements at temperatures down as far as 4 K. We believe that this is due to the high concentration of cobalt in the structure. Cobalt is present in the 112 solid solution series $YBaCu_{1-x}Co_{1+x}O_5$ ($0 < x < 1$) and can also substitute for up to 24% of the copper in $YBa_2Cu_3O_7$ (10). In the latter case, the superconducting T_c falls dramatically as the cobalt content increases. We must therefore assume that in $Y_2Ba_3Cu_3Co_2O_{12}$, a large proportion of the cobalt atoms replace copper in the $YBa_2Cu_3O_7$ component, producing an intergrowth of $YBa_2(Cu, Co)_3O_7$ and $YBa(Cu,$

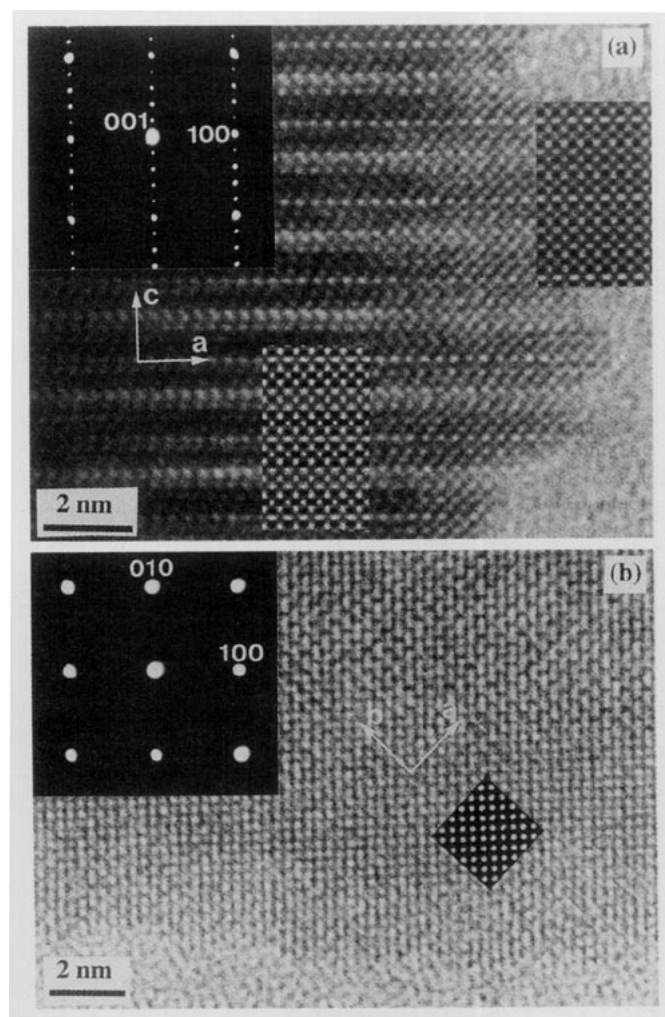


FIG. 4. HREM images and the corresponding SAED patterns of $Y_2Ba_3Cu_3Co_2O_{12}$ viewed down the (a) [100] and (b) [001] zone axes. The insets are computer simulated images from a structural model shown in Fig. 1 with the specimen thicknesses and lens defocus values of (a) 11.60 \AA and -750 \AA (right), 30.94 \AA and -600 \AA (left), and (b) 48.17 and -200 \AA .

$Co)_2O_5$ rather than the ideal intergrowth of $YBa_2Cu_3O_7$ and $YBaCo_2O_5$. We have also found that the cobalt content in the 112 phase cannot be reduced beyond the 1:1 composition of $YBaCuCoO_5$ and, for example, a preparation with a nominal composition of $YBaCu_{1.2}Co_{0.8}O_5$ led to a mixture of phases comprising mainly $YBaCuCoO_5$ with several other minor impurities. Consequently, a nominal copper valence of 2 cannot be exceeded in the 112 phase. The logical composition to prepare is therefore $Y_2Ba_3Cu_4CoO_{12}$, which should have all the cobalt concentrated in the 112 component. However, preparation of the series $Y_2Ba_3Cu_{4-x}Co_{1+x}O_{12}$ reveals that unless x is greater than 0.75 a multiphase assemblage is produced, consisting of $Y_2Ba_3Cu_{3.25}Co_{1.75}O_{12}$ and several minor phases, the most prominent being Y_2BaCuO_5 ,

BaCuO₂ and a cobalt-substituted 123 phase. This suggests that for the intergrowth structure to form, substitution of some cobalt in the 123 component is essential, either to remove a lattice mismatch, which is unlikely, or more probably to provide a residual electrical charge on alternate structural components, as is found in some other intergrowth structures (11).

In conclusion, a new perovskite-related compound, Y₂Ba₃Cu₃Co₂O₁₂, has been synthesized and the arrangement of the metal atoms in its structure has been determined by XRD and HREM studies. Owing to the insensitivity of both the HREM imaging and powder XRD refinement techniques, the distribution of the copper and cobalt cations at the lattice sites could not be determined in the new phase, but investigation by neutron diffraction is feasible and is being explored. Many other possibilities exist for further chemical modification. Although reduction of the cobalt concentration in Y₂Ba₃Cu₃Co₂O₁₂ beyond Y₂Ba₃Cu_{3.25}Co_{1.75}O₁₂ has proved impracticable under conditions of normal atmospheric pressure, control of the partial pressure of oxygen remains to be tested. Other possibilities include the replacement of Y³⁺ by Ce⁴⁺ or Ba²⁺ by La³⁺ to stabilize the 112 component when the cobalt concentration in this part is reduced. Consequently, this new compound may still be regarded as a parent structure of future superconductors, if appropriate chemical modification can be found.

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