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Stability Field of Layered Cuprate $Ca_{1-x}Sr_xCuO_2$ ($x \sim 0.1$) at 1000°C under Oxygen Atmosphere

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Powdered samples of layered cuprate $Ca_{1-x}Sr_xCuO_2$ with a tetragonal structure were prepared at 1000°C under flowing oxygen, and their lattice constants a and c were determined as a function of x. The cuprate is stable as a single phase in the range of $x = 0.09$–0.15 in which the a and c axes expand 0.14 and 0.45%, respectively. The $x = 0.14$ and $x = 0.09$ phases so far reported correspond to both end members.

Introduction

High-T_c superconductors in the system (Bi, Tl)$_m$ (Sr, Ba)$_2$Ca$_n$–Cu$_n$O$_{2n+4}$ are characterized by a structure comprising planar CuO_2 layers separated by planes of Ca atoms (*1*, *2*). A similar structure without any trivalent or quardrivalent counter cations was obtained as layered cuprates with the compositions $Ca_{0.86}Sr_{0.14}CuO_2$ and $Ca_{0.91}Sr_{0.09}CuO_2$ by Siegrist *et al.* (*3*) and Yamane *et al.* (*4*), respectively. These compounds were not made to superconduct, but electron-doped superconductivity at 40 K was reported on the isostructural compound $Sr_{1-y}Nd_yCuO_2$ prepared under high pressure (*5*). Superconductivity at 60 and 90 K was also observed on a similar structure in the Ba–Sr–Cu–O system prepared using high pressure (*6*, *7*).

These findings suggest the importance of the layered cuprate $Ca_{1-x}Sr_xCuO_2$ as the parent compound of the high-T_c superconductors. However, neither the stability field of the layered cuprate at 1 atm nor the relationship between the $x = 0.14$ and $x = 0.09$ phases has been established. An attempt was thus made to clarify the phase relation in the system $Ca_{1-x}Sr_xCuO_2$ with $x \sim 0.1$ at 1000°C under oxygen atmosphere.

Experimental

Samples were prepared by the solid-state reaction of $CaCO_3$, $SrCO_3$, and CuO (99.99% Rare Metallic). The mixed powder with the nominal composition of $Ca_{1-x}Sr_xCuO_2$ ($x = 0.06$–0.16) was heated at 1000°C for 12 hr in flowing oxygen, cooled to room temperature, and then reground. This procedure was repeated four times. Powder X-ray diffractograms were recorded with an XD-3A Shimazu diffractometer using Cu*Kα* radiation and silicon was used as an external standard. The data were collected in the angular range 20–130° (2*θ*). Lattice constants were calculated by the least-squares method

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TABLE I

X-RAY CHARACTERIZATION OF SAMPLES WITH THE NOMINAL COMPOSION $Ca_{1-x}Sr_xCuO_2$ FIRED AT 1000°C UNDER FLOWING OXYGEN

Sample no.	x	Product
1	0.06	SS + CC2 + C2C
2	0.07	SS + C2C
3	0.08	SS
4	0.09	SS
5	0.10	SS
6	0.11	SS
7	0.12	SS
8	0.13	SS
9	0.14	SS
10	0.15	SS
11	0.16	SS + S2C + CC2 + C2C

Note. (SS) solid solution $Ca_{1-x}Sr_xCuO_2$, (S2C) Sr_2CuO_3, (CC2) $CaCu_2O_3$, (C2C) Ca_2CuO_3.

using absolute 2θ values of 18 reflections obtained.

Results and Discussion

Table I summarizes the X-ray characterization of the resulting samples with the nominal composition $Ca_{1-x}Sr_xCuO_2$. X-ray diffraction patterns of several fired samples are shown in Fig. 1. For $0.08 < x < 0.15$, only a layered cuprate phase similar to those reported by Siegrist *et al.* (*3*) and by Yamane *et al.* (*4*) was observed in the X-ray diffraction patterns, while for $x < 0.08$ and $x = 0.16$ it coexisted with a small amount of one to three of $CaCu_2O_3$, Ca_2CuO_3, and Sr_2CuO_3. The X-ray diffraction peaks for the layered cuprate phase were indexed on the basis of a tetragonal cell. The lattice constants (a and c) thus evaluated for the tetragonal phase in the fired samples are plotted as a function of x in Fig. 2, along with the cell volume v. The values of a and c for the $x = 0.09$ product in this study are in good agreement with $a = 3.8581$ and $c = 3.1997$ Å reported by Yamane *et al.* (*4*). Those for the $x = 0.11$ product are slightly larger than $a = 3.8611$ and $c = 3.1995$ Å obtained by Siegrist *et al.* (*3*), probably because the powder sample used in this study is more expanded in the crystal lattice than small single crystals in the latter. In the range of $x = 0.09$–0.14, the a, c, and v values increase linearly with an increase in the Sr content x, while they remain nearly constant in the ranges of $0.08 < x < 0.09$ and $x > 0.14$. The latter fact suggests that the solid solution $Ca_{1-x}Sr_xCuO_2$ is stable as a single phase in the range of $x = 0.09$–0.14. Both end members in the stability field of the solid solution

FIG. 1. X-ray diffraction patterns of powdered samples with the nominal composition $Ca_{1-x}Sr_xCuO_2$ fired at 1000°C under flowing oxygen. x : 0.06 (a), 0.09 (b), 0.11 (c), 0.14 (d), and 0.16 (e). Peak assignment: ○, $CaCu_2O_3$; △, Ca_2CuO_3, □, Sr_2CuO_3; none, layered solid solution.

correspond to the layered cuprates $Ca_{0.91}Sr_{0.09}CuO_2$ and $Ca_{0.86}Sr_{0.14}CuO_2$ so far reported. The *a* and *c* axes expand by 0.14 and 0.45%, respectively, with an increasing x from 0.09 to 0.14. The relatively large expansion of *c* axis is ascribable to the substitution of Sr for Ca, smaller in size, in the (Ca, Sr) plane sandwiched by plannar CuO_2 sheets. The plots of *a*, *c*, and *v* against x for $x < 0.08$ suggest that there would exist another stability field of the isostructural solid solution $Ca_{1-x}Sr_xCuO_2$ which coexists with extra phases $CaCu_2O_3$ and/or Ca_2CuO_3.

Yamane *et al.* (*4*) observed that their samples with $x = 0.08$ and 0.10 fired at 1000°C under flowing oxygen yield a mixture of the layered cuprate and two extra phases and concluded that the range of x available for the formation of the layered cuprate as a single phase would be extremely narrow. On the other hand, the present study showed that the stability field of the layered cuprate obtainable as a single phase is as wide as $x = 0.09$–0.14. This is probably because powder samples used in the present study take up oxygen much more feasibly than pellet samples employed by Yamane *et al.* (*4*). In fact, we also observed that a pellet sample with the nominal composition of $x = 0.11$ fired under the same condition as above yielded a slight amount of Ca_2CuO_3 and $CaCu_2O_3$ as extra phases coexisting with the layered cuprate, as shown in Fig. 3. Furthermore, powder samples with the nominal composition $x = 0.09$–0.14 fired at 1000°C in air decreased remarkably in the fraction of the layered cuprate. These observations suggest that the formation of the layered cuprate would be lowered in rate by a decrease in the partial pressure of oxygen in the atmosphere or by a decrease in the diffusivity of oxygen into the crystals, as pointed out by Yamane *et al.* (*4*).

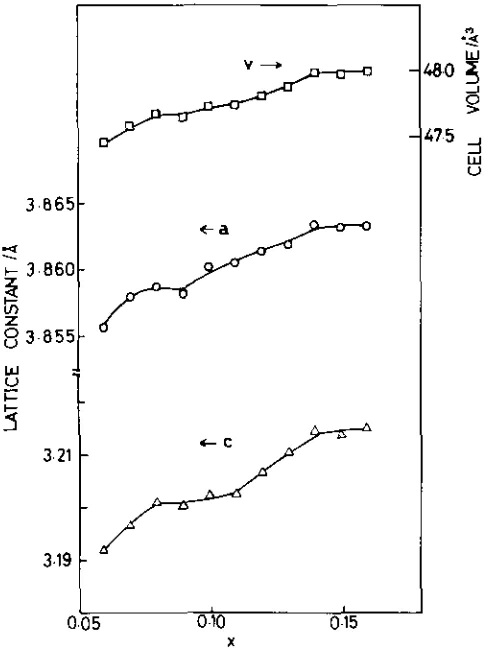

FIG. 2. Lattice constants and cell volume of layered cuprate $Ca_{1-x}Sr_xCuO_2$ as a function of x. For $x < 0.08$ and $x > 0.15$, x means the nominal composition of a mixture containing layered cuprate as the major phase.

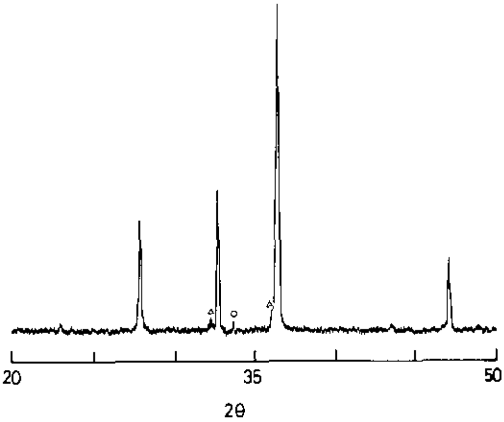

FIG. 3. X-ray diffraction pattern of a pellet sample with the nominal composition $Ca_{0.89}Sr_{0.11}CuO_2$ fired at 1000°C under flowing oxygen. Key as in Fig. 1.

A further attempt is underway to make the layered cuprate superconducting by electrochemical oxidation or reduction.

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