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Dependence of Lattice Parameters and T_c on the Hole Concentration Determined by Precise Measurement of the Oxygen Content of $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca)

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Systematic precise measurements of oxygen content have been performed on sintered samples of $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) superconducting oxides by both thermogravimetry and iodometry. The hole concentration, P, has been estimated by using the obtained oxygen content on the basis of charge neutrality. Lattice parameters and superconductivity of the samples have been measured by X-ray powder diffraction analysis and electrical resistivity or ac magnetic susceptibility measurement, respectively. The lattice parameter, a, depended on both P and the average ionic radius of the La^{3+} site and c depended on the average ionic radius of the La^{3+} site, volume compensation, and oxygen defect. Orthorhombicity (defined by $2(b - a)/(a + b)$) depended on P. Superconductivity appeared at the same hole concentration, $P = 0.10$, regardless of the kind of alkaline-earth metal used. A linear relation between T_c and Cu–O_I bond length within the basal plane in the structure was recognized only in the case where the hole quantity, P, was constant.

1. Introduction

$M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) with the K_2NiF_4 structure containing copper ion is the first high temperature superconducting oxide discovered by Bednorz and Müller (*1*). Kishio *et al.* (*2*) have shown a linear relation between T_c and Cu–O_I bond length within the basal plane in the tetragonal structure, although they have not measured oxygen content for this system. We have systematically measured the oxygen content and revealed a relation between crystal lattice and superconductivity for this system (*3*). Torrance *et al.* (*4*) have shown a correlation between T_c and hole concentration, P, for the case of M = Sr in this system. Axe *et al.* (*5*) and Suzuki and Fujita (*6*) have revealed an anomaly of T_c at $x = 0.125$ for the case of M = Ba in this system. However, there are few reports for the case of M = Ca in this system, and it is not known whether the relation between T_c and P or the Cu–O_I bond length is intrinsic.

In this paper, we report synthesis of sintered samples of $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) and experimental results on the oxygen content, lattice parameters, and superconductivity determined by thermogravimetry, iodometry, X-ray powder diffraction analysis, electrical resistivity, and ac mag-

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netic susceptibility measurements. So far, changes in the lattice parameters and the superconducting transition temperature have been plotted versus the alkaline-earth metal content, x. In the present study, we examined the correlation between crystal lattice and superconductivity and clarified the relation between T_c and P or between T_c and the Cu–O$_I$ bond length. Second, we discuss systematically the similarity and disparity among the samples having three kinds of alkaline-earth metals. Finally, we reveal a relation between T_c and the Cu–O$_I$ bond length at constant hole concentration from the results for $Sr_{0.15-x}Ba_xLa_{1.85}CuO_{4-y}$, in which the crystal lattice was varied by the difference between the ionic radii of Sr^{2+} and Ba^{2+} ions at constant hole concentration.

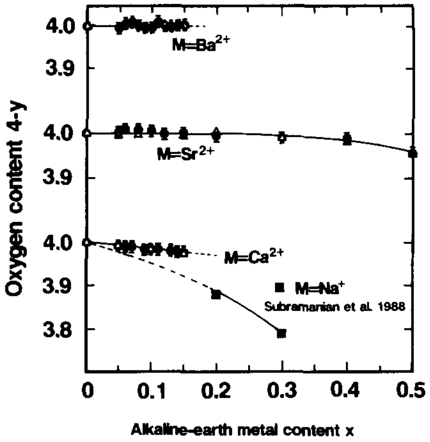

FIG. 1. The dependence of the oxygen content, $4 - y$ on the alkaline-earth metal content, x, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca, Na). Solid circles, thermogravimetry and open triangles, iodometry. Data of the Na series were extracted from those of Subramanian *et al.* (*9*).

2. Experimental Procedures

Samples of $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) oxides were synthesized from appropriate amounts of MCO_3 (M = Ba, Sr, Ca), La_2O_3, and CuO powders, each 99.99% pure. The powders were thoroughly mixed, pressed into pellets, prefired at 950°C for 12 hr, and then furnace cooled in air. Prefired materials were ground, pressed into pellets, sintered at 1100°C for 12 hr, and then furnace cooled in air. Sintered materials were given the same sintering cycle again.

The samples were examined by X-ray powder diffraction analysis using monochromatized Cu*K*α radiation with a Rigaku diffractometer. The following measurements were only performed on single-phase samples.

The lattice parameters of a sample were refined from measured *d*-spacings by the least-squares method to better than 0.01% accuracy.

Oxygen content, $4 - y$, of the sample was measured by both thermogravimetry and iodometry. The details of the measurements have been described elsewhere (*7*, *8*). The hole concentration, P, of the sample was estimated by $P = x - 2y$ from the measured y value and nominal alkaline-earth metal content, x, on the basis of charge neutrality.

Superconductivity of the sample was examined by electrical resistivity measurements using the usual four-probe method and ac magnetic susceptibility measurements. In the latter, the measurement was performed from 12 K to room temperature. T_c was defined as the midpoint temperature of the resistivity transition and/or the temperature where the measured voltage of a secondary coil began to decrease in the ac method.

3. Results

The samples of $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) oxides were found to be single phase, having the K_2NiF_4 structure in the range $x \leqq 0.15$ for the Ba series, $x \leqq 0.5$ for the Sr series, and $x \leqq 0.15$ for the Ca series. The dependence of the oxygen content on the alkaline-earth metal content, x, is shown in Fig. 1. No oxygen deficiency was de-

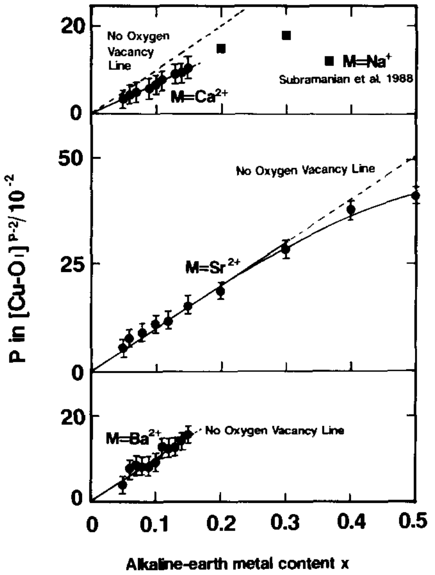

FIG. 2. The dependence of the hole concentration, P, on the alkaline-earth metal content, x, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca, Na) by using the data from thermogravimetry, except the Na-series, which is from Subramanian *et al.* (9).

tected in the range $0 \leqq x \leqq 0.15$ for both the Ba series and the Sr series. The oxygen content began to decrease with increasing Sr content, x, for $x \geqq 0.3$. For the Ca series, the oxygen content decreased linearly with increasing Ca content, x, and as a result, the oxygen defect was found to increase by $y = 0.15x$ with increasing x. A large quantity of oxygen defects with increasing Na content, x, were found for $Na_xLa_{2-x}CuO_{4-y}$ (Na series) by Subramanian *et al.* (9). A tendency for the oxygen content to decrease with decreasing cation valence was shown. The hole concentration, P, was estimated by $P = x - 2y$ using the measured oxygen content. The dependence of P on the alkaline-earth metal and/or alkaline metal content, x, is shown in Fig. 2. P increased linearly by $P = x$ in the interval $0 \leqq x \leqq 0.15$ for both the Ba and the Sr series. The rate of increase of P with x reduced in the region $x > 0.2$ for the Sr series. For the Ca series, P increased linearly by $P = 0.7x$, and the rate of increase was smaller than those of the Ba and Sr series.

The dependences of the lattice parameters a, b, c and unit cell volume, V, on the alkaline-earth metal content, x, are shown in Fig. 3. For the orthorhombic phase having a distorted K_2NiF_4 structure, $a/\sqrt{2}$ and $b/\sqrt{2}$ are plotted in the figure. For all the series, a and b approached each other and the unit cell distortion was gradually mitigated with increasing x; that is, there was a symmetry change from orthorhombic to tetragonal. A trend that $(a + b)/2$ is shortened and c expanded with increasing x was found for all the series. The shortening of $(a + b)/2$ or a for the Sr series and the expansion of c for the Ba series was remark-

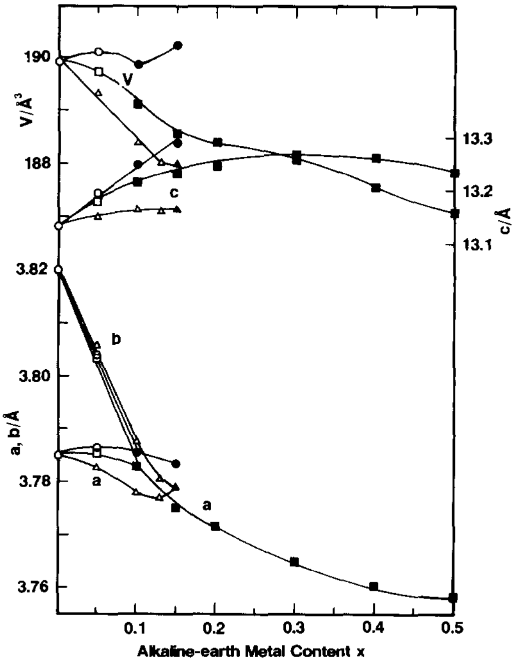

FIG. 3. The dependence of the lattice parameters a and c and the unit cell volume, V, on the alkaline-earth metal content, x, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). Circles, Ba series; squares, Sr series; and triangles, Ca series. Solid and open symbols correspond to those of the orthorhombic and tetragonal phases.

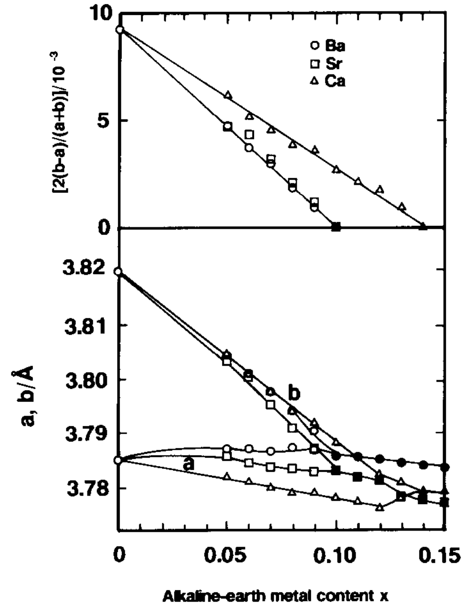

FIG. 4. The dependence of the lattice parameters *a* and *b* and the orthorhombicity, which was defined by $\{2(b-a)/(a+b)\}$ on the alkaline-earth metal content, *x*, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). Circles, Ba series; squares, Sr series; and triangles, Ca series. Solid and open symbols correspond to those of the orthorhombic and tetragonal phases.

able. A remarkable decrease in volume with increasing x was found for the Sr and Ca series. The dependences of the lattice parameters a, b and orthorhombicity on the alkaline-earth metal content, x, are shown in Fig. 4. The orthorhombicity, which is a measure of the orthorhombic distortion from tetragonal symmetry, was defined by $\{2(b-a)/(a+b)\}$ with the lattice parameters a and b. The orthorhombicity decreased linearly with increasing x and disappeared at $x = 0.1$ for both the Ba and the Sr series; for the Ca series it disappeared at $x = 0.14$ though the linearity still held.

The dependence of T_c on the alkaline-earth metal content, x, is shown in Fig. 5. The dependences of the Ba and Sr series were consistent with the results of Axe *et al.* (*5*), Suzuki and Fujita (*6*), and Torrance *et al.* (*4*). A tendency for saturation of T_c with x was found for the Ca series. A superconducting state appeared at $x = 0.07$ for both the Ba and Sr series, while at $x = 0.1$ for the Ca series.

Lattice parameters a and c, unit cell volume V, oxygen content, $4 - y$, hole concentration, P, and T_c of $Sr_{0.15-x}Ba_xLa_{1.85}CuO_{4-y}$ samples are plotted against Ba content, x, in Fig. 6. It was found that a, c, and V increased linearly with x, while $4 - y$ and P were independent of x. Therefore, the unit cell was expanded only due to the difference between the ionic radii of Ba^{2+}

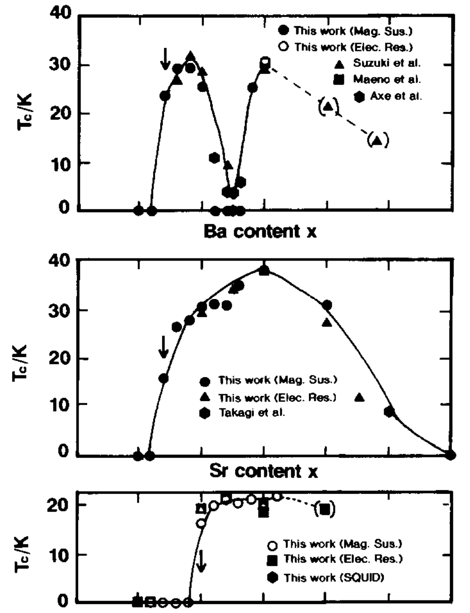

FIG. 5. The dependence of T_c on the alkaline-earth metal content, x, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). For the Ba series, solid and open circles, ac magnetic susceptibility and electrical resistivity measurements, respectively. Solid triangles, squares, and hexagons, data by Suzuki *et al.*, Maeno *et al.*, and Axe *et al.*, respectively. For the Sr series, solid circles and triangles, ac magnetic susceptibility and electrical resistivity measurements, respectively. Solid hexagons, Takagi *et al.*

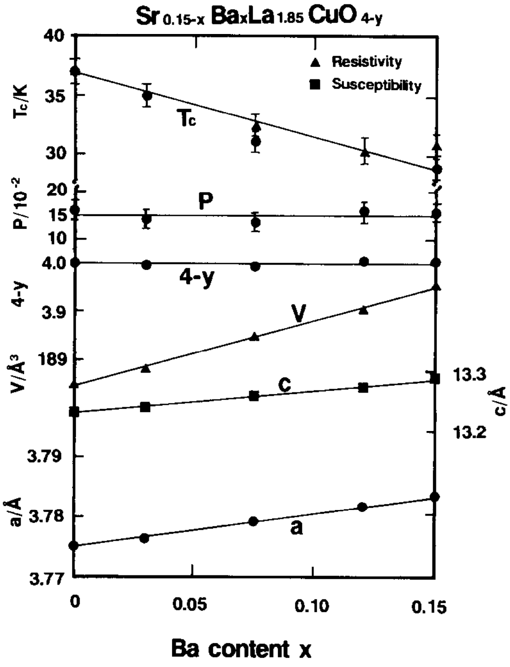

FIG. 6. The dependence of the lattice parameters, unit cell volume, oxygen content, hole concentration, and T_c on the Ba content, x, for $Sr_{0.15-x}Ba_xLa_{1.85}CuO_{4-y}$.

and Sr^{2+} at constant hole concentration. T_c dropped linearly with increasing x, that is, expanding the unit cell at constant hole concentration.

Discussion

Oxygen Content

According to the results of the oxygen content measurement, substitution of La^{3+} by Ba^{2+} and/or Sr^{2+} having larger ionic radii than that of La^{3+} suppresses the appearance of oxygen vacancies, while substitution of La^{3+} by Na^+ having a smaller cation valence than that of La^{3+} facilitates the appearance of oxygen vacancies. In La_2CuO_4 with the K_2NiF_4 structure, La^{3+} is located in the site coordinated by nine oxygen ions. The stability of the coordinating oxygen ions in the structure seems to depend on the attractive force between the cations and the oxygen ions and also on the repulsive force between the oxygen ions on the basis of Coulombic force. The average ionic radius of a La^{3+} site, r_{LaM} defined by $\{(2 - x)r_{La^{3+}} + xr_{M^{2+}}\}/2$ using the ionic radii of La^{3+} and the alkaline-earth metals ($r_{La^{3+}} = 1.20$, $r_{Ba^{2+}} = 1.47$, $r_{Sr^{2+}} = 1.28$, and $r_{Ca^{2+}} = 1.18$ Å) (*10*) increases with the substitutions by Ba^{2+} and Sr^{2+}, while it decreases with that by Ca^{2+}. In this case, a decrease in the cation ionic radius (r_{LaM}) makes the oxygens approach each other, the repulsion increase, and the stability decrease. Similarly, a decrease in the cation valence makes the attraction decrease and the stability decrease. In contrast, increases in the ionic radius (r_{LaM}) and valence make the stability increase.

By this reasoning, the stability of the oxygens depends on both the cation ionic radius (r_{LaM}) and the valence, and the change in the oxygen content with x for all the series can be explained.

Lattice Parameters

The shortening of the lattice parameter, a, with x for the Ba and Sr series is not consistent with the simple view of the ionic radius because r_{LaM} increases with x for both series. Therefore, the shortening with x seems to depend on other factors. The dependence of a on the hole concentration is shown in Fig. 7. According to Ref. (*4*), the hole carrier exists in the Cu–O_2 plane or the CuO_I bond. It is found that a shortens with increasing P. In Cu $3d$ orbitals of La_2CuO_4, the highest energy level is the Cu $3d_{x^2-y^2}$ orbital having one electron due to Jahn–Teller effect of CuO_6 octahedron. This orbital forms the Cu–O_I ($=a/2$) bond within the basal plane with the O $2p$ orbital. If the increase in P would relate to loss of the electron from the Cu $3d_{x^2-y^2}$ orbital, the Cu–O_I bond would shorten with increasing P. Hence, the shortening of a seems to be

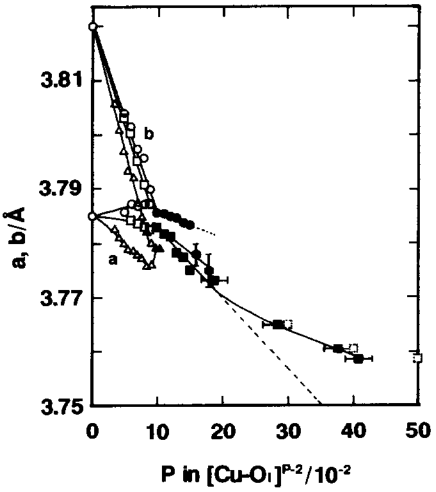

FIG. 7. The dependence of the lattice parameter *a* on the hole concentration for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). Circles, Ba series; squares, Sr series; triangles, Ca series; and hexagons, the Na series from Subramanian *et al.* (9). Open and solid symbols correspond to the orthorhombic and tetragonal phases. For the Sr series, squares with broken lines show the case without the oxygen vacancy.

due to the increase in P. At the same time, it is found that a shortens with a decrease in the ionic radius of the alkaline-earth metal at the same hole concentration; that is, a shortens rather strongly with x for the Ca and Sr series, while a shortens more weakly with x for the Ba series at the same hole concentration. Thus, a depends on both the hole concentration, P (electronic factor), and the average ionic radius of the La^{3+} site (structural factor).

The lattice parameter c is plotted against r_{LaM} in Fig. 8. First, linearities between c and r_{LaM} are found in the range $0 \leqq x \leqq 0.15$ for the Ba and Sr series having no oxygen defect. Second, the rate of expansion of c with r_{LaM} becomes negligible for the Na series having a large concentration of oxygen defects and Sr series. Third, expansion of c with r_{LaM} for the Ca series is not consistent with the decrease of r_{LaM}. Moreover, it is not consistent with the fact that the increasing rate of c with r_{LaM} for the Sr series is higher than that of the Ba series. According to the discussion about the lattice parameters, a shortens rapidly with x for the Ca and Sr series. In fact, the decrease in V with x is observed despite the increase of r_{LaM} for the Sr series. If there is a volume compensation effect against the large shortening of a, a large expansion of c is expected for the Ca and Sr series. Thus, the lattice parameter c depends on three factors, the average ionic radius of the La^{3+} site, the oxygen defect, and the volume compensation.

Orthorhombicity

The tolerance factor, t, defined by $t = \{(La\text{-}O_{II})/\{\sqrt{2}(Cu\text{-}O_I)\}$ in La_2CuO_4 represents a mismatch of ionic sizes between La^{3+} and Cu^{2+} ions and relates to the distortion of the orthorhombic phase. The distortion of the orthorhombic phase depends on both r_{LaM} (denominator of t) and the Cu–O_I

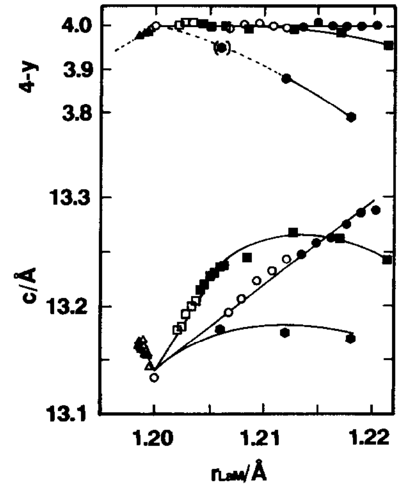

FIG. 8. The dependence of the lattice parameter c and the oxygen content $4 - y$ on the average ionic radius, r_{LaM}, for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca, Na). Circles, Ba series; squares, Sr series; triangles, Ca series; and hexagons, Na series from Subramanian *et al.* (9). Open and solid symbols correspond to the orthorhombic and tetragonal phases.

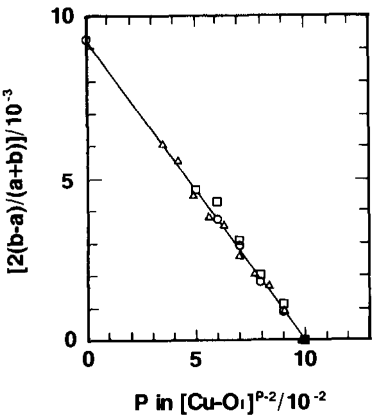

FIG. 9. The dependence of the orthorhombicity on the hole concentration for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). Circles, Ba series; squares, Sr series; and triangles, Ca series. Open and solid symbols correspond to the orthorhombic and tetragonal phases.

bond (numerator of t) which depends on the r_{LaM} and P. The dependence of the orthorhombicity on the hole concentration is shown in Fig. 9. It is found that the orthorhombicity decreases linearly with P and disappears at $P = 0.1$ despite the kind of alkaline-earth metal. This universal linear relationship would be due to the fact that the Cu–O_I bond depends on both r_{LaM} and P, because the increase of r_{LaM} obstructs the shortening of the Cu–O_I bond at the same hole concentration, and the effect of r_{LaM} on t is compensated by the effect of the Cu–O_I bond on t. On the other hand, the mitigation of the distortion would electronically relate to the increase in conductivity with increasing x and/or P, as well (*11*).

Superconductivity, T_c*, and Hole Concentration, P*

The dependence of T_c on the hole concentration is shown in Fig. 10. Though the dependence resembles the alkaline-earth metal dependence of T_c, it is found that the superconducting state appears at the same hole concentration, $P = 0.07$, regardless of the alkaline-earth metal used, and T_c of the Ca series having the oxygen defect is lower than T_c of the Ba and Sr series at the same hole concentration. The appearance of the superconducting state is found to be normalized by P and the oxygen defect seems to reduce T_c. On the other hand, the hole-concentration dependence of T_c is consistent with the results of Torrance *et al.* (*4*) for the Sr series.

T_c *and the Cu–*O_I *Bond*

The dependence of T_c on the Cu–O_I bond length at the variable hole concentration, P, is shown in Fig. 11. Though there is no essential difference between this dependence and the hole-concentration dependence of T_c, it is found that the supercon-

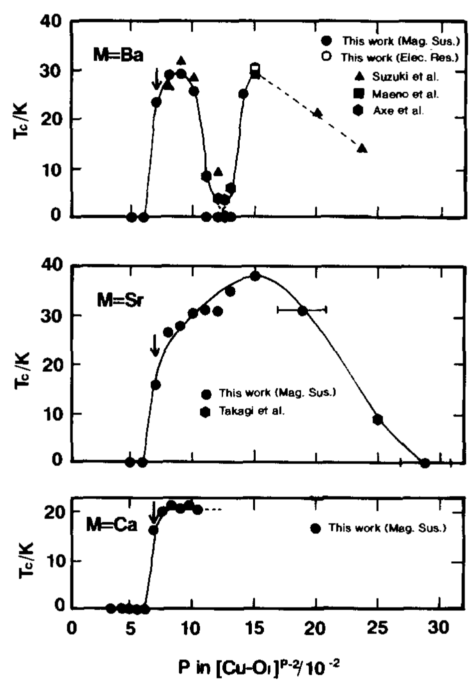

FIG. 10. The dependence of T_c on the hole concentration for $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca). Meanings of symbols are consistent with those in Fig. 5, a proviso; data for the Sr and Ca series were those from the magnetic susceptibility measurement.

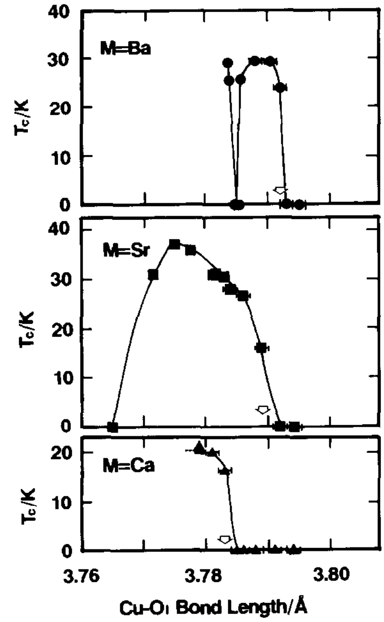

FIG. 11. The dependence of T_c on the Cu–O_I bond length at variable hole concentration. Data for T_c were those from the magnetic susceptibility measurement.

ducting states for each series appear at a different Cu–O_I bond length. Therefore, the appearance of the superconducting state is not found to be normalized by the Cu–O_I bond length, which is dissimilar to the case of the hole concentration. This is caused by the fact that the Cu–O_I bond depends on both the hole concentration, P, and the average ionic radius of La^{3+}, r_{LaM}.

The dependence of T_c on the Cu–O_I bond length at constant hole concentration is shown in Fig. 12. It is found that T_c decreases linearly with expanding Cu–O_I bond length. Therefore, the relation between T_c and the Cu–O_I bond length is only intrinsic at constant hole concentration. A similar result has been reported in the N-type $Ce_{0.15}Nd_{1.85-x}La_xCuO_{4-y}$ system (*12*). Though Kishio *et al.* (*2*) have revealed a linear relation between T_c and the Cu–O_I bond length from results of (Ba, Sr, $Ca)_{0.2}La_{1.8}CuO_{4-y}$-sintered samples, the oxygen content has not been measured. On the basis of our discussion, it is predicted that those samples have almost the same oxygen content.

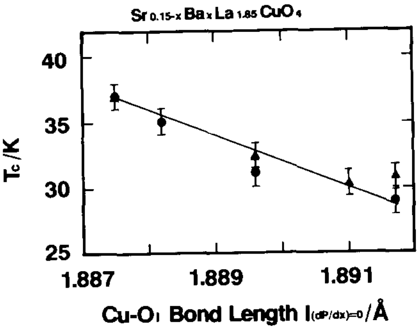

FIG. 12. The dependence of T_c on the Cu–O_I bond length at constant hole concentration for $Sr_{0.15-x}Ba_xLa_{1.85}CuO_4$. Solid circles and triangles, magnetic susceptibility and electrical resistivity measurements, respectively.

Summary

For $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca) with the K_2NiF_4 structure, the oxygen content varies with both the average ionic radius and the valence of the La^{3+} site. The lattice parameter a varies with both the hole concentration, P, and the average ionic radius of the La^{3+} site. The lattice parameter c varies with the average ionic radius of the La^{3+} site, the oxygen content, and the volume compensation. The orthorhombicity depends on only the hole concentration. The relation between the superconducting transition temperature, T_c, and the hole concentration is essential, while the relation between T_c and the Cu–O_I bond is only intrinsic at a constant hole concentration.

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