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High-T_c Superconducting Oxide Solid Solutions $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$

Kohji KISHIO,* Koichi KITAZAWA,* Nobuyuki SUGII, Shinsaku KANBE, Kazuo FUEKI,*
Hidenori TAKAGI,† and Shoji TANAKA†
Department of Industrial Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113
†Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113

The system $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$ with x=0.1 has been found to be a high temperature superconducting phase in the entire compositional range of the three alkali earth cations. $(La_{0.9}Sr_{0.1})_2CuO_{4-\delta}$, displayed the highest critical temperature and the shortest distance for Cu-O bonds within the basal layer plane of the K_2NiF_4-type crystal structure, suggesting the two-dimensional nature of the conduction mechanism.

The first report by Bednorz and Müller1) on the possible superconductivity in La-Ba-Cu-O system has prompted the recent susceptibility and resistivity studies by their group2) and Uchida and Takagi et al.3-5) The superconducting phase has now been identified2,4) to be of a composition designated as $(La_{1-x}Ba_x)_2CuO_{4-\delta}$, where δ represents some deficiency of oxygen. More recently, the present authors have found6) that $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $(La_{1-x}Ca_x)_2CuO_{4-\delta}$ are also superconducting oxides, the former with x=0.1 exhibiting the onset critical temperature, T_c=37 K, the highest among all the materials reported. They have further examined the compositional dependence of T_c and lattice parameters of the strontium system and discussed the close correlation among them, in terms of a schematic two-dimensional band, in a separate paper.7) Cava, Dover, Batlogg and Rietman, more recently, have also reported the high T_c of the Sr system.8)

Since the superconducting phases in all of these oxides2,4,6) adopt the same crystal structure, tetragonal K_2NiF_4-type, it is of particular interest to find out whether these oxides are soluble into each other, and whether a composition with still higher T_c can be obtained in such a quasi-ternary system. In this letter, we report the superconductivity of the oxide solid solution system $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$ with x=0.1.

The details of sample preparation and susceptibility measurements were described previously.6) A total of 15 oxide samples was prepared, covering the whole triangle range of the quasi-ternary composition. More specifically, in chemical formula $(La_{1-x}(Ba,Sr,Ca)_x)_2CuO_{4-\delta}$, La was fixed at 0.9 and Ba, Sr, and Ca were introduced in intervals of 0.025 so that the total fraction, x, of these alkali earths was 0.1.

The powder X-ray diffraction analysis revealed that all of these samples had a distinct main phase of K_2NiF_4 structure accompanied by a trace amount of a cubic perovskite phase. All of the main diffraction peaks could be assigned for indices of a tetragonal system, and lattice parameters, a_0 and c_0 were determined by a least square fitting procedure.[7)] The obtained lattice parameters were found to vary smoothly as a function of composition, leading to the conclusion that this quasi-ternary system, at least for x=0.1 examined, is a homogeneous oxide solid solution in the entire compositional range of the three alkali earth cations. The formation of the present solid solution system is presumably related to the stability of K_2NiF_4-type crystal structure which closely resembles the well-known perovskite-type.

The results of the a.c. susceptibility measurements revealed that all the samples examined were, in fact, high T_c superconductors. In Fig. 1, the observed onset critical temperatures are indicated on a contour diagram for each data point measured. The onset T_c here has been defined[6)] as the intersection point of the flat line above T_c and the sharply dropping curve of the inductance signal on the lower temperature side. It is evident in Fig. 1 that T_c changes smoothly with composition. The maximum T_c is 37.0 K and the minimum is 18.2 K, both of which are found at the corner compositions of Sr and Ca, respectively.

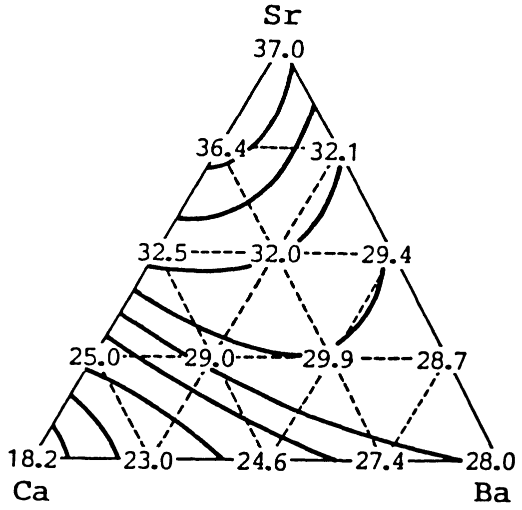

Fig. 1. Contour diagram of superconductivity onset T_c (in K) as determined from a. c. susceptibility measurement as a function of composition for solid solution $(La_{0.9}(Ba,Sr,Ca)_{0.1})_2CuO_{4-\delta}$.

In order to find out the factors which determine the superconducting properties, the lattice parameters, a_0 and c_0 have been plotted as a function of T_c in Fig. 2. As can be seen, a_0 seems to monotonically decrease with T_c, while c_0 does not behave in a simple manner. A maximum c_0 corresponds to the composition pure Ba(ionic radius r_i=1.35 Å) and a minimum to pure Ca(r_i=0.99 Å), while that of pure Sr(r_i=1.13 Å) is located in the middle. This suggests that c_0 is determined mainly by the ionic size of alkali earth ions but T_c is not directly related to this parameter. On the other hand, a_0 thus seems to be the vital parameter which controls the superconductivity in this system.

In the previous report,[7)] based on the change of the lattice parameters with x in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$, the authors proposed a two-dimensional band scheme derived from a significant overlapping of the Cu:$3d_{x^2-y^2}$ and O:$2p_\sigma$ orbitals on the basal plane of the interconnected networks of CuO_6 octahedra. This model has further been supported by our recent observation that the substitution of 4f magnetic ions for the La sites[9]) exerts much less effect on destructing superconductivity than the substitution of 3d ions for the Cu sites.[10]) This means that Cu site contributes to form the conduction paths while La site is rather isolated from them.

The present results can be understood under the same model, because the lattice parameter a_0, i.e., the length of O-Cu-O bonds in the basal plane, is the key factor to determine T_c but the change in c_0, does not seem to be directly related to T_c. All of this suggest the two-dimensional character of the band. The reason that a shorter Cu-O bond is favored for the higher T_c is probably due to the increased itinerancy of carriers in the two-dimensional conduction path. This will result in decrease both in the tendency of localization of the carriers and hence in the effective coulomb repulsion coefficient μ^*. It is known that a two-dimensional thin metal tends to exhibit the Anderson localization.

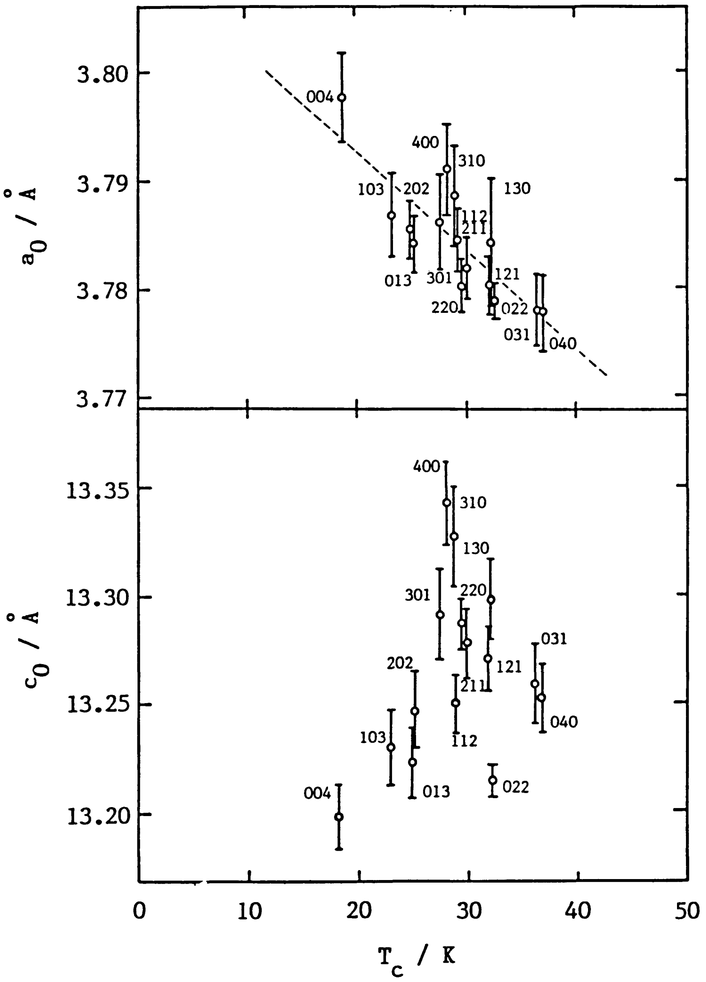

Fig. 2. Tetragonal lattice parameters a_0 and c_0 as a function of onset T_c for solid solution $(La_{0.9}(Ba,Sr,Ca)_{0.1})_2CuO_{4-\delta}$. Indices attached to each data point express the ratio of alkali earth ion compositions in the order of Ba, Sr, Ca ; e.g. [013] represents $(La_{0.9}Sr_{0.025}Ca_{0.075})_2CuO_{4-\delta}$.

In the present material system, Nguyen et al.[11]) has reported the presence of oxygen deficient sites on the basal plane. The material system $(La_{1-x}M_x)_2CuO_4$ has been known to exhibit either metallic or semiconductive temperature dependence of resistivity depending on the annealing in oxidizing or reducing atmosphere, respectively. As the content of M ions increases, an increase in the oxygen deficiency is also expected.[11]) This should give an adverse effect on superconductivity. However, we presume that this tendency towards localization of carriers is overcompensated by the decrease in the Cu-O bond which is expected to intensify the itinerancy of the two-dimensional Cu:$d_{x^2-y^2}$-O:p_σ band. Hence a rise in T_c is expected with increase in x. Also, the observation of the semiconductive nature in resistivity is understandable when the specimen is slightly reduced.

Moreover, it is notable that T_c is relatively insensitive to the mass of alkali earth ions. It is well known that T_c varies with isotopic masses of the constituent atoms. Therefore if the phonons involving the displacement of ions on the La sites contributed mainly to the electron-phonon interaction in this material system, the effect of difference in ionic masses of Ba, Sr, and Ca should have been reflected in the variation of T_c. This is not, however, the case as is seen in Fig. 1. Since the breathing mode phonon is considered to give an exceptionally strong elctron-phonon interaction in another superconducting oxide $BaPb_{1-x}Bi_xO_3$ of a perovskite structure,12-13) a similar mechanism of strong electron-phonon interaction is likely to play a role in the present perovskite-derived structure. Furthermore, the density of states at the Fermi level could be much higher in this two-dimensional band system than in the three-dimensional $BaPb_{1-x}Bi_xO_3$, and the extraordinary high T_c may be understood in this context.

Further investigation is undertaken to elucidate how oxygen ions on the basal plane relative to those not within the basal plane are involved in the superconductivity.

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