Synthesis and Characterization of "Infinite Layer" Compounds Doped with p-Type Carriers

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Abstract

The p-type carrier doping in infinite-layer structural $CaCuO_2$ thin films was successfully done by substituting Li ions into the Ca site using a laser deposition technique. The lattice constants and X-ray diffraction patterns strongly indicated that the film samples had an infinite layer structure. However, they did not exhibit superconductivity.

1. Introduction

The infinite-layer structural compounds which consist of infinite stacking of alkaline-earth elements and CuO_2 planes are thought to be parent materials of all the high Tc cuprates. Some researchers have predicted that they could exhibit Tc's higher than 130 K because of their unique structure. It is known that there exists an anti-ferromagnetic insulating parent compound, La_2CuO_4, $Bi_2Sr_2YCu_2O_z$ etc., for each of the high Tc cuprates. In fact, $Ca_{0.86}Sr_{0.14}CuO_2$ was reported to be an anti-ferromagnetic material whose transition temperature is very high[1]. This suggests that strong magnetic interactions exist among the electrons in this material. It has been reported that n-type charge carriers were successfully doped into infinite layer compounds to become superconducting with Tc's as high as that known for an n-type superconducting cuprate. These facts make us to anticipate that if p-type carriers were doped into infinite layer compounds, they may become very high-Tc superconductors. Some researchers tried to dope p-type carriers into infinite layer compounds by creating defects in the (Ca,Sr) site[2]. Different groups found superconductivity in such materials that were synthesized using a high pressure method. Surprisingly, the Tc's for these materials were reported to be as high as 110 K[3], in spite of the fact that there are only alkaline earth ions besides copper and oxygen in these compounds. We tried to partially substitute the alkaline earth element by an alkali metal element, in order to realize p-type doping into an infinite layer structural compound without destruction of the crystallographic structure or without introducing stacking faults and some other lattice defects.

Li was chosen to be a suitable element for such constitution. This is because Li has an electronegativity strong enough to form an infinite layer structure and its spherical electron orbital may not favour the square planar 4-fold coordination such as that for Cu in the infinite layer structure.

2. Experimental

Thin films of (Ca,Li)CuO_2 were grown on a $SrTiO_3$ (100) substrate by laser ablation. This technique was thought to be much superior to any other methods, and enable us to form some phases metastable such as films of the infinite-layer compounds $Ca_{1-x}Li_xCuO_2$ with x=0.2 to 0.45 which, to date, have not been successfully synthesized. One of the major reasons may be that the synthesis of these materials requires extremely high oxidizing atmosphere. Therefore an O_2 gas jet containing 5% ozone, which was collimated towards the substrate with a nozzle, was used as the deposition atmosphere. The target was prepared by a solid-state reaction method with calcination and sintering at 850 to 900 °C for powder mixtures of CuO and carbonates of Ca and Li. The sputtering conditions employed are listed in table 1.

3. Characterization

We have characterized samples using following 3 probes. (i) X-ray diffraction pattern (single axis) (ii) 4-axis X-ray diffraction to determine lattice constants (iii) resistivity vs. temperature (4 probe method)

Table 1. Ablation conditions

substrate	SrTiO$_3$ (100)
target	powder mixture sintered at 900 °C (1-x)CaCO$_3$+(x/2)Li$_2$CO$_3$+CuO
gas	O2 gas contained 5 % ozone (through stainless nozzle)
gas pressure	1.2 mTorr
substrate temperature	600 ~ 700 °C
laser	ArF eximer laser (λ=193nm, repetition rate=20Hz)

3.1. X-ray diffraction patterns

We have successfully synthesized Ca$_{1-x}$Li$_x$CuO$_2$ for the range of x = 0.2 ~ 0.45.

Figure 1 (a) and (b) are the typical diffraction patterns from Ca$_{1-x}$Li$_x$CuO$_2$ on SrTiO$_3$(100). There are no peaks other than those for the reflections of Ca$_{0.7}$Li$_{0.3}$CuO$_2$ or Ca$_{0.6}$Li$_{0.4}$CuO$_2$ and of substrate. The peak width is narrow and the intensity is strong as compared to the background intensity. Around the (001) reflection, there can be seen a Laue function oscillation. These results suggested that the film had a smooth surface and the film thickness was very thin to be about 180 Å, as calculated from the period of oscillation.

We compared the experimental diffraction pattern with a calculated one based on an ideal model, in order to confirm whether Li ions entered in the Ca site. The intensity ratio of the (002) / (001) peaks has been compared with the calculated values for the range of x = 0 to 0.5 as shown in Fig. 2.
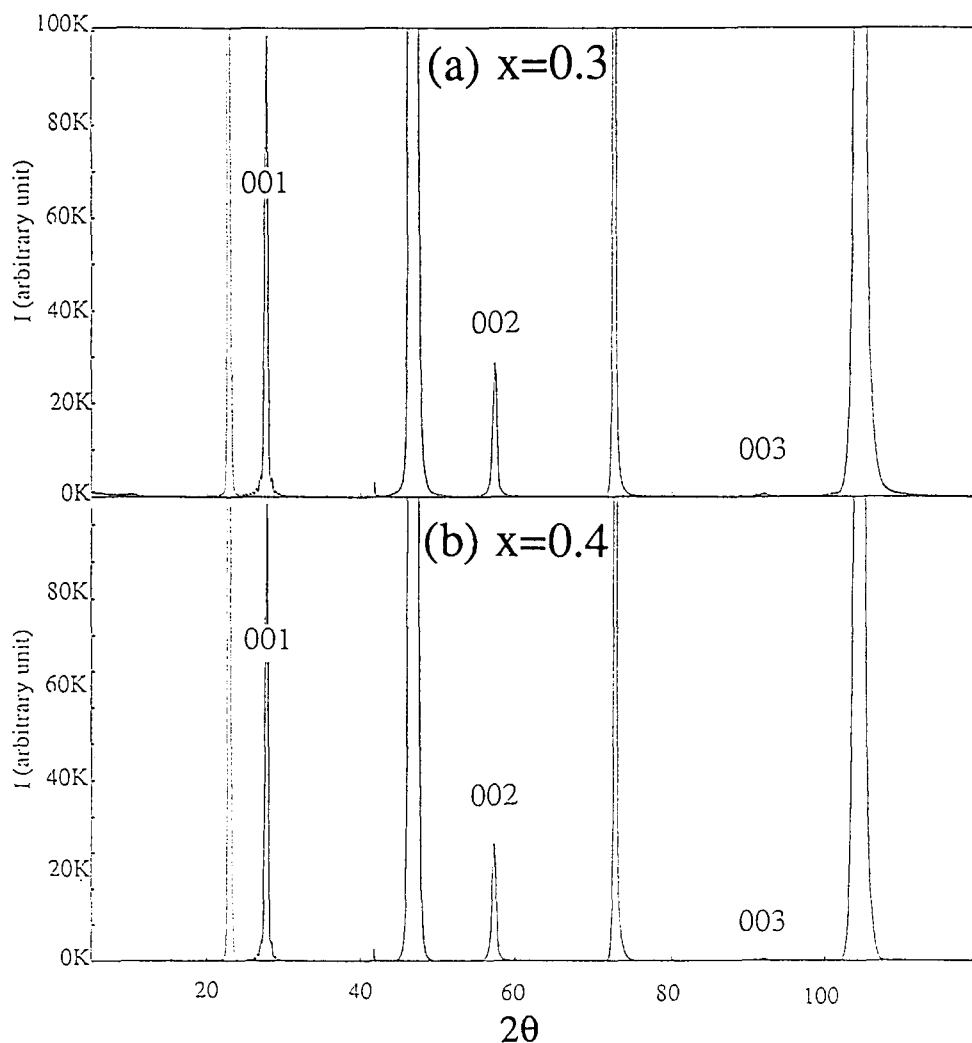

Fig.1　X-ray diffraction patterns for Ca$_{1-x}$Li$_x$CuO$_2$ on SrTiO$_3$ (100) substrates
(a) x=0.3, (b) x=0.4

The solid line shows the calculated results for $Ca_{1-x}Li_xCuO_2$ with an infinite layer structure. The broken line represents hypothetical compounds of $CaCu_{1-x}Li_xO_2$ whose Cu ions are substituted by Li ions. The open circles are the experimental results, which agree quite well with the case of $Ca_{1-x}Li_xCuO_2$.

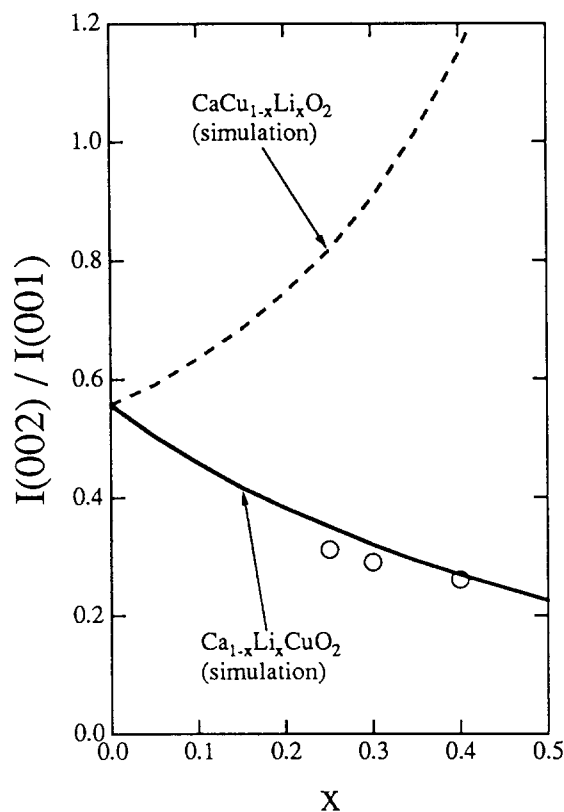Fig.2 Intensity ratio of Bragg reflection spots I(002) / I(001) v.s. Li content. Open circles are results of our experiment.

3.2. Lattice constants

The lattice constants were determined from 20 reflection spots using a 4-axis X-ray diffractometer. As shown in Fig.3, the a and c parameters were about 3.82 Å and 3.23 Å, respectively. These values are reasonable compared with those for the known phase of $Ca_{0.91}Sr_{0.09}CuO_2$[4]. Unfortunately, the data points were scattered and the error bar was considerably large (0.02 Å). These lattice constants may be affected by the substrate crystal which has the lattice constant larger than those for the film when the film thickness is as thin as the present film. Nevertheless, in Fig.3, the lattice parameter a seems to decrease and c seems to increase with doping of holes. This result corresponds to Smiths' data[5] for the case of electron doping.
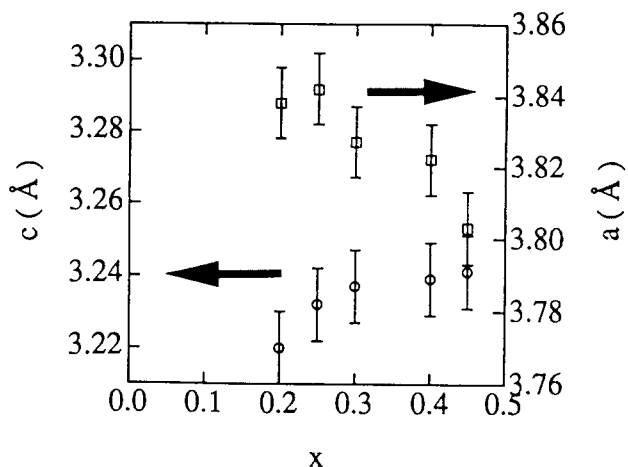

Fig.3 Lattice constants of $Ca_{1-x}Li_xCuO_2$ determined by the least square method from 20 reflection spots obtained using 4-axis X-ray diffractometer.

3.3. Resistivity vs. Temperature

The resistivity of all the samples increased as the temperature decreased, despite of heavy doping to the range of x=0.2 to 0.45, and no superconductivity was observed at any temperatures down to 4.2 K. Figure.4 shows the results of the samples with x=0.25, 0.35 and 0.4.
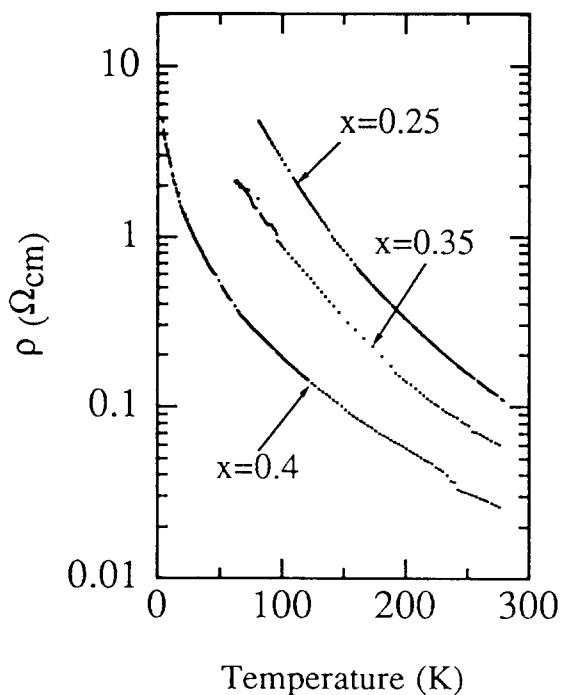

Fig.4 Temperature dependence of resistivity for $Ca_{1-x}Li_xCuO_2$.

4. Discussion

So far no superconductivity was obtained for the presently synthesized $Ca_{1-x}Li_xCuO_2$. However, some important information on the high Tc superconductivity mechanism was obtained. Possible reasons why no superconductivity was observed are as follows : (i) charge carriers were not doped due to oxygen deficiency and (ii) charge carriers were doped but the amount was not enough to shift the Fermi level which rather remained being located in the semiconducting gap. In order to discuss the electronic structure concerning Cu ions we have to take account not only the valence but also the coordination. A band picture for $(La,Sr)_2CuO_4$ has been proposed by a couple of groups[6,7], as shown on the left hand side of Fig.5. where H.G. and J.G. mean Hubbard and Jahn-Teller gap respectively. The metallization of the Hubbard insulator results in one of the two cases. One is the annihilation of the Hubbard gap and another is that the lower portion of one of the Hubbard bands becomes overlapped to the upper portion of the other Hubbard band as shown on the left hand side of Fig.5. The larger the distance between the apex oxygen atom and Cu is, the larger is the Jahn-Teller gap, while the heavier the hole doping is, the larger the Hubbard gap as reported for $(La,Sr)_2CuO_4$[6]. Then the square planer 4-fold coordination, as shown on the right hand side of Fig.5, can be regard as the limit for the long distance between the apex oxygen and Cu. Therefore the dz^2 level still remains lower than the lower Hubbard band for dx^2-y^2 in spite of the heavy hole doping. That is, the dz^2 band is not split to yield a Hubbard gap. As a result, only a single Hubbard gap exists in the electronic system in the 4-fold coordination case. For the infinite layer structure, the energy band structure satisfies neither of the above conditions. Because of this, the metallization of the infinite-layer structural compounds is thought to be difficult.

Conclusion

i) We successfully synthesized the infinite layer structural $Ca_{1-x}Li_xCuO_2$. ii) The temperature dependence of resistivity shows a semiconducting behaviour for all the samples.

Acknowledgments

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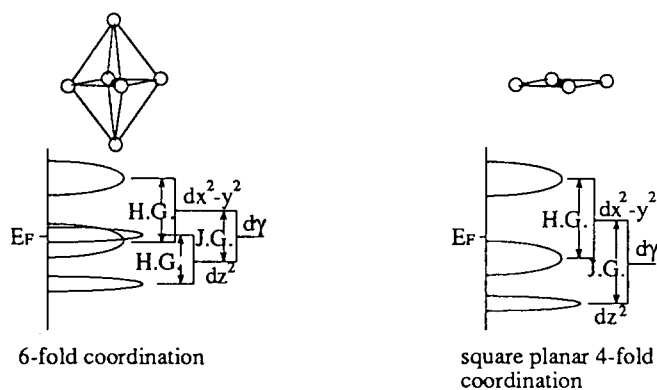7 J.B.Goodenough, J-S.Zhou and K.Allan, J. Mater. Chem., (1991), Vol 1, 715

Fig. 5   Energy band picture for 6-fold coordination of La1.85Sr0.15CuO2 (left hand side) and 4-fold coordination of Ca0.75Li0.25CuO2 (right hand side)