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Influence of structural changes induced by co-doping in YBCO on superconductivity

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Abstract
The single-phase samples of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ (YCBLCO) were synthesized with $x < 0.2$ and characterized by DC magnetization measurement and x-ray diffraction (XRD). The structure of the samples was refined by the Rietveld method. Although the carrier concentration in the samples is constant for different dopant levels, the superconductivity evidently changes. We attribute the decrease in T_c to charge redistribution in the crystalline lattice. Comparing the change of the T_c value caused by structural influences and carrier concentration, it is suggested that the influence of structural changes on the superconductivity is independent of that induced by carrier concentration.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The cuprate high temperature superconductor comes from doping in the Mott insulator with an antiferromagnetic background. The unit cell is formed by stacking oxygen-deficient perovskite units in some way in the c-axis direction [1]. No high temperature superconductivity (HTSC) has been found yet in any other system to date. The structural character should play an important role in the formation of HTSC. Previous work mostly focused on the effect of carrier concentration on superconductivity, which is indeed an important part of superconductivity. There are some systematic results, with the representation of the electronic phase diagram [2]. But so far, no uniform theory can explain the mechanism of HTSC. Its structural study deserves more attention. We have been doing some work on the influence of the structure on superconductivity, including the influences of combinative energy [3, 4] and phase transition [5], and have obtained some interesting results.

For cuprates, doping makes the changes in carrier concentration and crystalline structure simultaneous. We cannot distinguish how much change in the superconductivity is induced by

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the change of carrier concentration and how much by the structure. This obscurity may mask many intrinsic effects of the structural changes on the superconductivity and lead to complexity in our understanding of the mechanism of HTSC. To study the single influence of structural changes, the co-doping in $YBa_2Cu_3O_y$ is adopted for charge compensation, i.e. keeping the carrier concentration constant. The substitution of Ca^{2+} for Y^{3+} and La^{3+} for Ba^{2+} forms the compound $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$. According to the result of Tokura [6], the carrier concentration was constant when y was invariant. There has been some work on double-site doping in the $YBa_2Cu_3O_y$ superconductor, including the $Y_{1-x}Ca_xBa_{2-y}La_yCu_3O_z$ [7, 8], $Ca_xLa_{1-x}Ba_{1.75-x}La_{0.25+x}Cu_3O_y$ [9, 10] (CLBLCO) and $R_{1-x}Ca_xBa_2Cu_{3-y}Co_yO_z$ [11–13] (R is lanthanide) series. Most of these works explained the change in superconductivity from the point of view of the change in hole concentration [7–9, 11] or band structural changes [9]. Few works concerned the effects of structural changes on superconductivity. The aim of our work is to make clear whether the changes in the carrier concentration and structure influence the superconductivity dependently or independently. Our results suggest that the influence of structural changes on superconductivity is independent of that induced by the carrier concentration.

2. Experimental details

Samples of the series of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ with x from 0 to 0.2 in intervals of 0.025 were synthesized through a solid-state reaction method. The ingredients Y_2O_3, $CaCO_3$, $BaCO_3$, La_2O_3 and CuO were mixed completely in the proper proportions and calcined at $870\,°C$ for 24 h in air. The exercise was repeated at $910\,°C$ with intermediate grinding. The calcinates were pressed into rectangular pellets and sintered at $930\,°C$ for 24 h, followed by an annealing at $450\,°C$ for 24 h. The last two procedures were done in an oxygen atmosphere.

The samples were analysed by x-ray diffraction (XRD) on a Philips X'pert Pro MPD diffractometer using Cu Kα radiation. The results show that all the samples are single phase within the resolution of the diffractometer. All the peaks in each pattern can be indexed with the symmetry of *Pmmm*. Detailed structural characteristics were obtained by Rietveld refinement [14] using the X'pert Plus software whose core program is LHPM1, which is the successor to the program DBW3.2 [15]. The goodness of fit (GOF $= R_{wp}/R_{exp}$) of all samples is about 1.5 (see table 1), demonstrating the samples are good single phases and the refinement results are reliable. T_c was determined by DC magnetization measurement at 10 Oe field in the temperature range of 20–120 K, using the Quantum Design MPMS system.

3. Results and discussion

DC magnetization measurements show that the superconducting transition is sharp and has no phase separation phenomena in all the nine samples. Figure 1 shows the T_c–x relation. It is evident that T_c decreases monotonically as the dopant increases. Slater *et al* [7] studied the same system with x from 0.05–0.7 and demonstrated that T_c decreased with increasing dopant and the oxygen content kept invariant. From Tokura's formula [6]

$$p_{sh} = \tfrac{1}{2}(y - Q + \tfrac{1}{2})$$

p_{sh} is the mobile hole amount per Cu atom in the CuO_2 plane; y and Q are the oxygen content and total charge of noncopper cations in the unit cell, respectively. Q and y are constant in our system and the hole number p_{sh} is constant, too. Figure 1 has demonstrated that T_c decreases even if the hole concentration is not changed. The normal T_c–p_{sh} relation cannot explain this result. We must find new approaches in order to understand this phenomenon. The structural change may be a reasonable explanation.
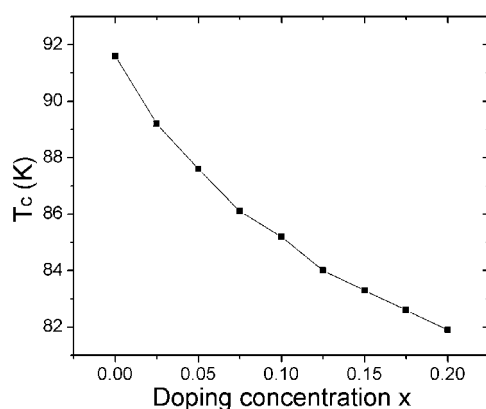
Figure 1. T_c versus doping concentration x in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$, x from 0–0.2.

Table 1. Refined structural parameters in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$. The symmetry is $Pmmm$. The atomic position was defined as follows: Y/Ca (1/2, 1/2, 1/2), Ba/La (1/2, 1/2, z), Cu(2) (0, 0, z), O(4) (0, 0, z), Cu(1) (0, 0, 0), O(2) (1/2, 0, z), O(3) (0, 1/2, z), the same as defined in figure 4. The values of z_{Ba}, $z_{Cu(2)}$ and $z_{O(4)}$ in the table are the ratios of the positions of Ba, Cu(2) and O(4) to the corresponding parameter c.

x	0	0.025	0.05	0.075	0.10	0.125	0.15	0.175	0.20
a (Å)	3.8828	3.8830	3.8805	3.8799	3.8772	3.8740	3.8725	3.8706	3.8696
b (Å)	3.821 13	3.821 73	3.8249	3.8241	3.8243	3.8274	3.8253	3.8268	3.8260
c (Å)	11.6741	11.6745	11.6682	11.6665	11.6643	11.6612	11.6581	11.6569	11.6523
z_{Ba}	0.183 66	0.183 87	0.184 07	0.1842	0.184 27	0.183 95	0.184 64	0.1846	0.185 32
$z_{Cu(2)}$	0.3546	0.3538	0.3545	0.3539	0.3537	0.3543	0.3543	0.3534	0.3544
$z_{O(4)}$	0.160	0.159	0.158	0.158	0.158	0.155	0.155	0.156	0.1551
R_{wp} (%)	6.2725	6.1912	6.1873	6.5532	6.2833	6.4564	6.4261	6.4733	6.5385
R_{exp} (%)	4.3085	4.3342	4.3005	4.3347	4.3356	4.3558	4.3581	4.3427	4.4361
GOF	1.4558	1.4285	1.4387	1.5118	1.4492	1.4823	1.4745	1.4906	1.4739

Rietveld refinement was carried out with the atom proportion constraints of Y, Ca, Ba and La the same as the proportion of ingredients. Refining the results show that all of the GOFs are rather good, showing that the constraints are reasonable and doping is successful. Refinement profiles of $YBa_2Cu_3O_y$ and $Y_{0.8}Ca_{0.2}Ba_{1.8}La_{0.2}Cu_3O_y$ are shown in figures 2(a) and (b). The structural parameters determined by Rietveld refinement are summarized in table 1. The a, b and c versus x are plotted in figure 3. The definitions of a, b, c and atoms in the unit cell are identified in figure 4. The changing trends of these three crystalline parameters are consistent with previous results [7, 8, 16], getting from neutron diffraction or XRD, showing that our refinement results from the XRD pattern are reliable. The obvious reduction in the c axis comes from the substitution of La for Ba, because La has an ionic radius of 1.28 Å for 10-fold coordination, compared with 1.52 Å for Ba. Figure 3 shows that, as the dopant increases, the structure tends towards tetragonal. In fact, previous results [7, 8] showed the lattice was tetragonal when x was greater than 0.4.

A rather interesting phenomenon is the changes of the Ba/La's z coordinate. As shown in figure 5, when the dopant increases, the T_c decreases with the increase in the coordinate of Ba/La in the c direction. La_{Ba} (La atom in the Ba position) is believed to play an important role as a bridge atom when oxygen tends to accumulate in the basal plane [9, 17, 18]. But
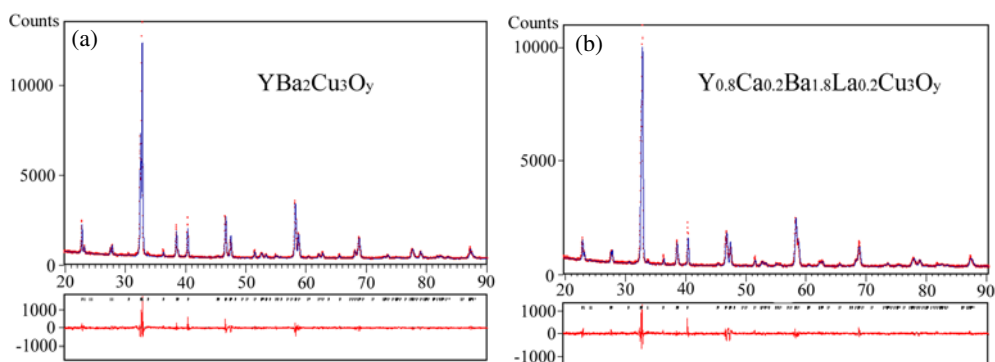
Figure 2. Refinement profiles of $YBa_2Cu_3O_y$ (a) and $Y_{0.8}Ca_{0.2}Ba_{1.8}La_{0.2}Cu_3O_y$ (b). The dotted line is the measurement results and the full line is the calculated profile. The vertical short line represents the position of the Bragg reflection. The difference curves were plotted at the bottom.
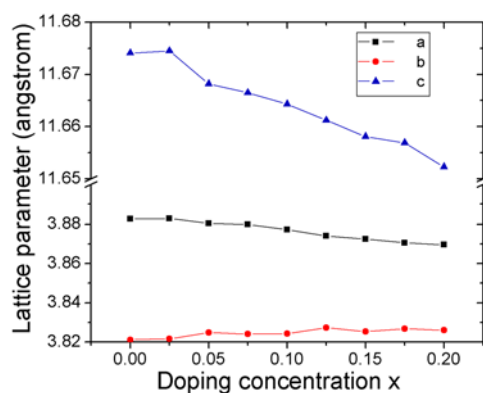
Figure 3. Lattice parameters a, b and c versus doping concentration x.

as has been said before, the oxygen amount of the current series is constant and the carrier concentration is constant. We suggest that, as Ba is substituted by La, the distribution of the charge through the bridge atom to the basal plane is changed, and therefore influences the superconductivity, although the carrier concentration is not changed.

Other parameters, such as the bond lengths between different atoms, were also calculated by the Rietveld refinement method. The bond lengths of Cu(1)–O(4) and Cu(2)–O(4) show a close correlation with the superconductivity. As shown in figures 6(a) and (b), T_c decreases with the reduction of the Cu(1)–O(4) and the increase of the Cu(2)–O(4) bond lengths. Comparing these changes with undoped $YBa_2Cu_3O_{7-\delta}$ and other related systems, we get an important result. In Jorgensen's work [19], the T_c changed with the variation in the oxygen content. As the oxygen content is changed, the structure and hole amount change simultaneously. In this case, the influences of the carrier concentration and structure could not be distinguished, and most people attributed the change in T_c to the change of the carrier concentration. It is obvious that the hole amount weighs strongly with the superconductivity, but the role of structure in this case could not be excluded. In the YCBLCO system, the carrier concentration is constant; the crystalline structure, including some bond lengths, is the most likely factor to determine the changes in superconductivity.
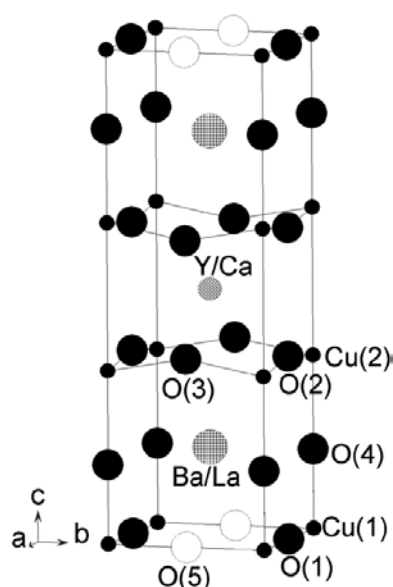
Figure 4. The orthorhombic structure of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$. The space group is *Pmmm*.
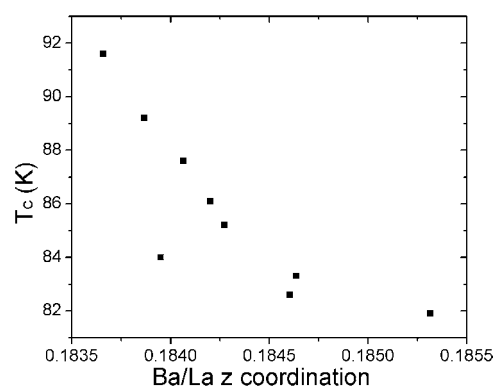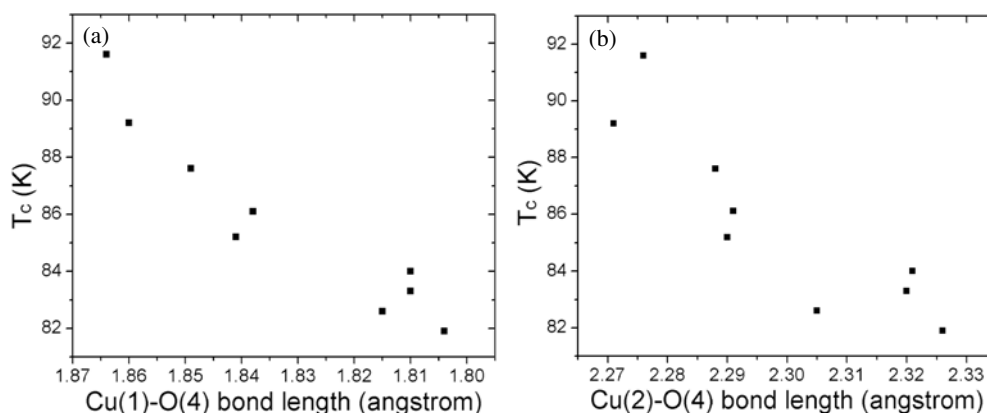

Figure 5. The correlation between the T_c and the Ba/La z coordinate.

In fact, T_c decreases by about 10 K in YCBLCO when the Cu(1)–O(4) bond length is reduced by 0.06 Å, while in Jorgensen's work [19] the sample becomes non-superconducting when the Cu(1)–O(4) bond length is reduced by about 0.06 Å as well. Comparing these two results, it is reasonable to attribute the change of T_c to the joint influence of the structure and amount of holes. The influence of the carrier concentration on T_c may be stronger than that of the structure, but they are independent.

4. Conclusion

In summary, the superconductivity and structural parameters in the Ca, La co-doped $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ system with x from 0–0.2 were investigated. The superconductivity was suppressed because of charge redistribution in the unit cell although the hole concentration

Figure 6. The correlation between the T_c and the Cu(1)–O(4) (a) and Cu(2)–O(4) (b) bond lengths.

is invariant. The results demonstrate that the influence of the structural change on superconductivity is independent of the carrier concentration. To understand the mechanism of HTSC, not only the carrier concentration, but also the structural change, should be taken into account.

Acknowledgments

References

[1] Park C and Snyder R L 1995 *J. Am. Ceram. Soc.* **78** 3171
[2] Orenstein J and Millis A J 2000 *Science* **288** 468
[3] Zhang H, Cheng L L, Qin X C and Zhao Y 2000 *Phys. Rev.* B **61** 1618
[4] Zhang H, Cheng L L and Zhao Y 2000 *Phys. Rev.* B **62** 13907
[5] Zhang H, Feng Q R, Wang S G, Zhao Y, Ritter F and Assmus W 1996 *J. Phys.: Condens. Matter* **8** 3653
[6] Tokura Y, Torrance J B, Huang T C and Nazzal A I 1988 *Phys. Rev.* B **38** 7156
[7] Slater P R and Greaves C 1992 *Supercond. Sci. Technol.* **5** 205
[8] Rajagopal H, Sequeira A, Ganguly R and Yakhmi J V 1996 *J. Supercond.* **9** 615
[9] Goldschmidt D, Knizhnik A, Direktovitch Y, Reinser G M and Eckstein Y 1994 *Phys. Rev.* B **49** 15928
[10] Goldschmidt D, Reinser G M, Direktovitch Y, Knizhnik A, Gartstein E, Kimmel G and Eckstein Y 1993 *Phys. Rev.* B **48** 532
[11] Kuberkar D G, Shah N A, Thampi R S, Rayaprol S, Gonal M R, Ram Prasad and Kulkarni R G 2001 *Int. J. Inorg. Mater.* **3** 59
[12] Pansuria K M, Joshi U S, Kuberkar D G, Baldha G J and Kulkarni R G 1996 *Solid State Commun.* **98** 1095
[13] Suard E, Maignan A, Caignaert V and Raveau B 1992 *Physica* C **200** 43
[14] Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65
[15] Wiles D B and Young R A 1981 *J. Appl. Crystallogr.* **14** 149
[16] Wu X S, Wang F Z, Liu J S, Jiang S S and Gao J 1999 *Physica* C **320** 206
[17] Wagener D, Buchgeister M, Hiller W, Hosseini S M and Kopitzki K 1991 *Supercond. Sci. Technol.* **4** S211
[18] Mitzi D B, Feffer P T, Newsam J M, Webb D J, Klavins P, Jacobson A J and Kapitulnik A 1988 *Phys. Rev.* B **38** 6667
[19] Jorgensen J D, Veal B W, Paulikas A P, Nowicki L J, Crabtree G W, Claus H and Kwok W K 1990 *Phys. Rev.* B **41** 1863