DOPING EFFECT OF Sr OR Ca ON SINGLE PHASED YBa_{2}Cu_{3}O_{7-\delta}

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The relation between superconductivity and phase structure in YBa{sub 2}Cu{sub 3}O{sub 7-\delta} doped with Sr and Ca has been studied systematically by the measurements of superconductivity, phase structure and thermal analysis. It is found that, for series of YBa{sub 2-x}Ca{sub x}Cu{sub 3}O{sub 7-\delta}, as 0 \leq x \leq 0.25, the samples are of single phase, and their T{sub c} decrease linearly with content of Ca; for series of YBa{sub 2-x}Sr{sub x}Cu{sub 3}O{sub 7-\delta}, as 0 \leq x \leq 1.25, the samples are of single phase, but their T{sub c} can change with the content of Sr either monotonously or non-monotonously, depending on the preparation conditions. A strong correlation exists between T{sub c} and the crystal structure of the samples. The results obtained suggest strongly that the intensity of the coupling between Cu–O planes and Cu–O chains is very important to the high-T{sub c} superconductivity of YBa{sub 2}Cu{sub 3}O{sub 7-\delta}.

1. Introduction

In the current research of high-T{sub c} superconductors, the superconducting mechanism is one of the most concerned subjects. By elements substitution, some essential information has been obtained about the nature of the high-T{sub c} superconductivity of YBa{sub 2}Cu{sub 3}O{sub 7-\delta}. But up to now, most of these substitutions have been concentrated on Cu or Y sites, and those on Ba sites are rather limited. Since quite a lot of results [1–4] have suggested that the high-T{sub c} superconductivity of YBa{sub 2}Cu{sub 3}O{sub 7-\delta} arises from the Cu–O planes instead of Cu–O chains, the systematical study of the substitution on Ba sites will be helpful to investigate the role of the planes or chains (in high-T{sub c} superconductivity). We studied systematically the partial substitution of Sr and Ca for Ba and their effects on the superconductivity and crystal structure of YBa{sub 2}Cu{sub 3}O{sub 7-\delta}. It suggests that for the substitution of Ca, the solid state solubility is very small and only the samples with content of Ca lower than 12.5% are still single-phased. Both T{sub c} and the unit cell volume decrease with increasing content of Ca. This is consistent with the results of substitution of Sr for Ba by Veal et al. [5]. When Sr was used to substitute for Ba, the solid state solubility rises so much that the samples remain single phased until the content of Sr reaches 50–62.5%. But the variation of T{sub c} with the content of Sr is quite different among the samples prepared under different conditions. For the samples with conventional preparation for a single phase, T{sub c} decreases monotonously with increasing x, similar to that reported by Veal et al.; for the ones with extraordinary preparation (which will be described later), the variation of T{sub c} is different. T{sub c} decreases non-monotonously with a maximum in the vicinity of x = 1.0. Also a strong correlation was observed between T{sub c} and the crystal structure. All of these phenomena indicate that the effect of Sr-doping is very complicated, and it seems quite possible that the superconductivity of the system is affected by changing the coupling between the Cu–O planes and the Cu–O chains.

2. Experimental

The technique of solid state reaction is employed to prepare two series of samples: YBa{sub 2-x}Ca{sub x}Cu{sub 3}O{sub 7-\delta} (x = 0.05, 0.10, 0.15, 0.20, 0.25, 0.5, 0.75, 1.0 and 1.25) and YBa{sub 2-x}Sr{sub x}Cu{sub 3}O{sub 7-\delta} (x = 0, 0.10, 0.15, 0.25,
0.5, 0.75, 1.0, 1.25, 1.5 and 1.75). For the former series, the mixture of stoichiometric proportion of CaCO$_3$, BaCO$_3$, Y$_2$O$_3$ and CuO (all analytically pure) was fully ground and preheated at 900°C in air for 24 hours. Then, the reacted product was reground, pressed into strips, sintered at 920°C in flowing oxygen for 20 hours and then cooled down to room temperature within the furnace. For the latter series, two different preparing procedures were employed. The first one was the same as that mentioned above for Ca-doping samples (hereafter we refer to it as ordinary process); and the second one was as follows: the mixture of stoichiometric proportion of SrCO$_3$, BaCO$_3$, Y$_2$O$_3$ and CuO (all analytically pure) was fully ground, preheated at 850°C in air for 3 hours, 8–10 hours each time. Then the product was sintered at 930°C in air for 8 hours. After that the temperature was raised to 1010°C, kept for 10 minutes and finally cooled down to room temperature in the furnace (this process will be referred as extraordinary process).

The standard d.c. four-probe technique was adopted to measure the dependence of resistance on temperature. The voltage of the samples was taken by a 181 Nanovoltmeter. The temperature was determined by a calibrated Ge-resistance thermometer and Pt-resistance thermometer simultaneously. In the measurement of a.c. magnetic susceptibility, the mutual inductance bridge had a sensitivity better than 0.1 μH.

The X-ray analysis was carried out with a RIGaKuD-Max-2A rotating target X-ray diffractometer with a working voltage of Cu target of 40 kV. The indices of X-ray diffraction are normalized with a self-made program.

The thermogravimetric analysis was made by means of a DT-30 model thermoanalysis meter to estimate the oxygen stoichiometry. The temperature range of analysis was from room temperature to 1100°C.

3. Results and discussion

It is indicated by X-ray powder diffraction analysis that the Ca-doped series are of single-phase 1-2-3 compound only when $x \leq 0.25$. A second phase is observed in all the samples with $x > 0.5$. The variation of both $T_c$ (superconducting critical temperature) and $V$ (volume of crystal cell) with $x$ of YBa$_{2-x}$Ca$_x$Cu$_3$O$_{7-y}$ (0 ≤ $x$ ≤ 0.25) is shown in fig. 1. With increasing $x$, $V$ decreases gradually, while $T_c$ descends almost linearly. This is consistent with the results of the Sr-doped sample reported by Veal et al. [5] only with two slight differences. First, the composition range of the single phase for Ca-doped samples is much more narrow than that for Sr-doped ones. The former is $0 \leq x \leq 0.25$, while the latter is $0 \leq x \leq 1.0$. Second, the suppression of $T_c$ of Ca-doped samples is must more violent than that for Sr-doped ones. When the doping concentration is at about 12.5%, the suppression of $T_c$ is about 14% and 6.8%, respectively. We conclude that all these differences arise from the relatively smaller ion radius of Ca which makes it easier to produce vacancies around it. This is supported by the thermogravimetric analysis results which indicate that the oxygen stoichiometry is relatively lower for Ca-doped samples.

In the Sr-doped YBa$_2$Ca$_x$Cu$_3$O$_{7-y}$ samples, we find that the variation of $T_c$ with $x$ is not monotonous as reported by Veal et al. This phenomenon is first observed in multi-phased samples. For the multi-phase samples with nominal composition of Y$_{0.5}$(Ba$_{1-x}$Sr$_x$)$_{0.5}$CuO$_3$ and prepared under different sintering conditions within the temperature range of 1000–1100°C, the variation of $T_c$ with $x$ is shown in fig. 2. Even though there is a distribution of $T_c$ for the same composition due to the different preparing conditions, a general tendency of obvious non-mo-
notonousness can be obtained from the variation of \( T_c \) with \( x \). It is from this phenomenon that we get the hint for studying the Sr-doping effects on single phased \( \text{YBa}_2\text{Cu}_3\text{O}_{7-y} \) with different preparing procedures.

Similar to what we observed in multi-phased samples, the different preparing procedures have an important effect on the properties of single phased \( \text{YBa}_2\text{Sr}_x\text{Cu}_3\text{O}_{7-y} \) samples. For samples prepared by ordinary procedures, the composition range of the single phase is \( 0 \leq x \leq 1.0 \) and \( T_c \) decreases monotonously with increasing \( x \). All of these are consistent with the results of Veal et al. But for samples prepared by the extraordinary procedure, there are two obvious characteristics. First, the composition range of the single phase is widened from \( 0 \leq x \leq 1.0 \) to \( 0 \leq x \leq 1.25 \); second, the variation of \( T_c \) with \( x \) is not monotonous anymore (as shown in fig. 3). For the sample without doping, \( T_c = 89 \) K; as \( x \) increases, \( T_c \) decreases firstly and reaches its minimum at \( x = 0.25 \); then it increases gradually until it meets its maximum at \( x = 1.0 \). For \( x \geq 1.5 \), several other phases are observed in the samples. Although \( T_c \) decreases slowly within this range, the results of diamagnetism have shown that the effective component of superconductivity decreases drastically.

The analysis of oxygen stoichiometry indicates that the Sr-doped samples have less oxygen stoichiometry than the samples without doping. But we find also that there is no obvious difference in oxygen stoichiometry for the samples with \( x = 0.25 \) and 1.0, respectively. This means that the above non-monotinous anomaly in relation with \( T_c \) versus \( x \) does not come from the change of oxygen stoichiometry.

In order to obtain further information about the anomaly in the Sr-doped system, X-ray diffraction analysis was carried out on the single phased samples of various composition. The results (fig. 4) show that the degree of orthogonal distortion of the lattice (indicated by the crystal parameter difference \( b-a \))
varies non-monotonously corresponding to the non-
monotonous variation of $T_c$. This suggests that a
strong correlation exist between $T_c$ and crystal struc-
Akers cause by changing
ture, which is rather similar to that causa by chang-
ing of oxygen vacancies. This can easily be seen from
fig. 5 in which the relation of $T_c$ with $(b-a)$ is given.
The system of $\text{Yba}_2\text{Cu}_3\text{O}_{7-x}$, with changing oxygen
vacancies is rather similar to the Sr-doped system
$\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$.

It can be realized from the results above that the
doping on Ba sites has great influence on $T_c$, and that
the degree of influence is close related to the radii of
doping ions and the preparing conditions. According
to the analysis of Veal et al., when Ba ions are sub-
stituted by Sr ions, more oxygen vacancies emerge
on the Cu–O one-dimensional chains and induce
some local distortion, leading to a suppression of $T_c$.
So $T_c$ keeps decreasing when the content of Sr in-
creases. It seems that our results support this kind of
exploration in some respects, as all doped samples
have lower $T_c$ and less oxygen stoichiometry, and es-
pecially because the $T_c$ of the samples doped with Ca
decrease more rapidly than that doped with Sr. But
obviously these ideas only do not explain all our re-
sults, such as the non-monotonous variation of $T_c$
with the content of Sr and the absence of differences
in oxygen stoichiometry between the samples of $x=0.25$ and 1.0. In our opinion, except for the two
unfavourable effects proposed by Veal et al., the more
important influence of Sr-doping lies in weakening
the coupling between the Cu–O plane and the Cu–O
one-dimensional chain. In the Sr-doped samples it is
easier to remove the oxygen atoms between Cu1 and
Cu2 atoms, this induces more disorder, weakens the
coupling between Cu1 and Cu2 and leads to a
suppression of $T_c$. By some appropriate preparing
procedure, it is possible to keep the oxygen vacancies
somehow stable and to make the arrangement of Sr
and Ba atoms more ordered. This can enhance the
coupling between Cu–O planes and Cu–O chains and
improve $T_c$. Within this explanation, it is quite rea-
sonable to expect $T_c$ to exhibit a peak when the con-
tents of Sr and Ba are equal. As for the Cu–O one-
dimensional chain distortion itself, it seems not es-
Sential for the system.

Also it can be seen from our results that the or-
thogonal distortion varies greatly although no ob-
vious variation of oxygen stoichiometry is observed.
Such phenomena are also seen in the sample where
Fe or Ni are substituted for Cu [6,7]. This indicates
that in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the variation of $T_c$ caused by
the variation of electronic structure also induces a
change of the orthogonal distortion or even a struc-
tural transition from orthogonal to tetragonal. Thus,
fig. 5 shows that the variation of orthogonal distor-
tion is driven by electrons instead of the importance
of orthogonal distortion for the high-$T_c$
superconductivity.

Recently, more and more experiments have sug-
gested that the Cu–O one-dimensional chains are not
crucial for the superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$,
and this view is strongly supported by our results.
We propose that the coupling between the Cu–O
planes and Cu–O chains (strictly speaking they
should be called Cu2–O planes and Cu1–O planes)
plays an important role in the high-$T_c$
superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

Confined by measurement, no direct evidence for
the ordering of Ba and Sr has been nontained. But
the anomaly in $\text{YBaSrCu}_3\text{O}_{7-x}$, $(x=1.0)$ is not re-
ported for the first time. Traces of super-high-$T_c$
superconductivity at 65$ ^\circ C$ have previously been
observed by Ihara et al. [8]. Though the origin of
such a high temperature resistance anomaly is clearly
not known yet, the particularity of $\text{YBaSrCu}_3\text{O}_{7-x}$,
merits further attention.
References