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Effect of Barium Doping on High-T_c Superconductor $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$

(high-T_c superconductor/$Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$/Ba doping)

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The effect of replacement of the Sr ions by Ba or Ca ions has been studied in the high-T_c superconductor $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$. With increasing the amount of Ba, the lattice expands and $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ shows an orthorhombic-to-tetragonal transition. A superconducting transition has been observed in the sample of the nominal composition $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$. Magnetization measurements have shown that the superconducting transition is not of bulk nature. The doping of Ca ions has been unfavorable for the formation of the $Pb_2Sr_2YCu_3O_8$-type phase.

1. INTRODUCTION

A superconducting oxide $Pb_2Sr_2ACu_3O_{8+\delta}$, where A is a rare earth or a mixture of rare earth and Ca or Sr, was discovered by Cava *et al.* [1] and has a superconducting transition temperature T_c of about 70 K. The crystal structure contains double CuO_2 pyramidical layers commonly included in high-T_c superconductors: $YBa_2Cu_3O_{7-\delta}$ [2], the $Bi_2Sr_2CaCu_2O_{8+\delta}$ phase in the Bi-Sr-Ca-Cu-O system [3], and the $Tl_2Ba_2CaCu_2O_8$ or $TlBa_2CaCu_2O_7$ phase in the Tl-Ba-Ca-Cu-O system [4]. The layer sequence along the c-axis in $Pb_2Sr_2ACu_3O_{8+\delta}$ is -A-CuO_2-SrO-PbO-CuO_δ-PbO-SrO-CuO_2-, which may be derived by replacing the CuO chains in the $YBa_2Cu_3O_{7-\delta}$-type structure with PbO-CuO_δ-PbO triple layers. A neutron powder diffraction study showed that $Pb_2Sr_2YCu_3O_{8+\delta}$ is orthorhombic with the lattice parameters; a = 5.3933(2), b = 5.4311(2) and c =15.7334(6) Å [5].

The compound $Pb_2Sr_2ACu_3O_{8+\delta}$ is to be compared with $YBa_2Cu_3O_{7-\delta}$ from the chemical point of view. First, in case of $Pb_2Sr_2ACu_3O_{8+\delta}$, the Sr sites can accommodate divalent atoms having a wider range of ion radius compared with the $YBa_2Cu_3O_{7-\delta}$-type oxides. A semiconducting oxide $Pb_2Ba_2YCu_3O_{8+\delta}$, which is comparable with $YBa_2Cu_3O_{7-\delta}$, was successfully synthesized [6]. In contrast, it is difficult to synthesize $YSr_2Cu_3O_{7-\delta}$ by replacing the Ba ions in $YBa_2Cu_3O_{7-\delta}$ with smaller Sr ions. Secondly, the A atoms in $Pb_2Sr_2ACu_3O_{8+\delta}$ can be partly occupied with divalent Ca or Sr atoms. This chemical doping changes $Pb_2Sr_2ACu_3O_{8+\delta}$ from semiconductor to superconductor.

In this paper, we study the effect of replacement of the Sr ions in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ ($y=8+\delta$) with larger Ba or smaller Ca ions on the crystal structure and superconducting transition by X-ray diffraction, resistivity and magnetization measurements.

2. EXPERIMENTAL

Samples were synthesized by a two-step solid-state reaction method. First, the precursor was prepared by heating well-mixed powders of appropriate amounts of $SrCO_3$, $BaCO_3$, Y_2O_3, $CaCO_3$ and CuO in air at 900°C. Then the precursor was pulverized, mixed with PbO, pressed into pellets and sintered in flowing nitrogen gas at 725°C for 2-3 h. The pellets were furnace-cooled in nitrogen gas. The products were examined by powder X-ray diffraction with Cu-K$_\alpha$ and Co-K$_\alpha$ radiation. The lattice parameters were determined by use of Co-K$_\alpha$ radiation. Electrical resistivity measurements were

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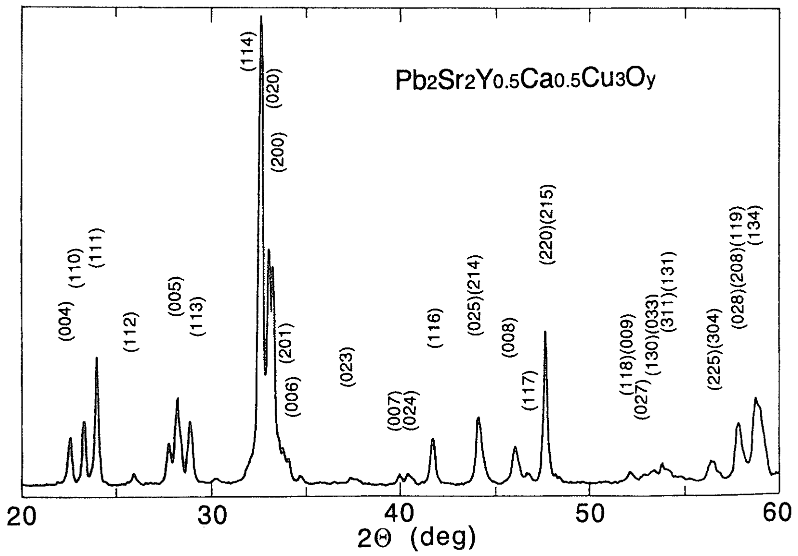

Fig.1. Powder X-ray (Cu-K$_\alpha$) diffraction pattern for a $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ sample.

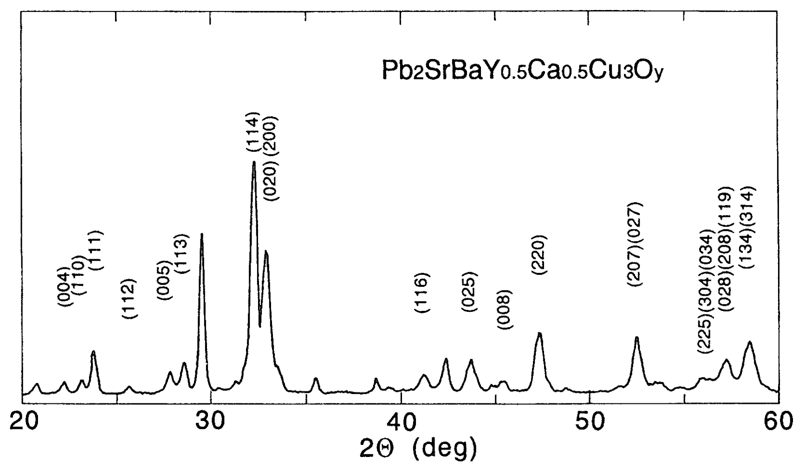

Fig.2. Powder X-ray (Cu-K$_\alpha$) diffraction pattern for a $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ sample.

done on bar samples cut from the pellets by a standard d.c. four-terminal method. Leads were attached to the samples with silver paint. The temperature of the sample was measured by a Au+0.07%Fe-chromel thermocouple.

Magnetization measurements were carried out using a d.c. SQUID magnetometer in an applied field of 3 Oe under field-cooled conditions.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern for a sample with the nominal composition $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ is shown in Fig.1. The sample is in single phase and the peaks can be indexed in terms of the orthorhombic crystal structure reported by Cava *et al.* [1,5]

Figure 2 represents the X-ray pattern for a sample prepared from the starting composition $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$. In comparison with Fig.1, the splitting between the (200) and (020) peaks is found to vanish. In addition, a relatively strong peak is seen around 30° which appears to be due to an impurity phase of $BaCuO_2$.

The lattice parameters determined by X-ray analysis using Co-K$_\alpha$ radiation are listed in Table I together with the data on $Pb_2Ba_2YCu_3O_y$ by Fu *et al.* [6] The crystal structure is orthorhombic for both $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ and $Pb_2Ba_2YCu_3O_y$ (semiconductor). Table I shows that the unit cell expands by introducing Ba into $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$. The lattice constant a increases approximately linearly with the amount of Ba. However, the

Table I. Lattice parameters for samples with the nominal compositions $Pb_2Sr_{2-x}Ba_xY_{0.5}Ca_{0.5}Cu_3O_y$ (x=0,1) and $Pb_2Sr_{2-x}Ca_xY_{0.5}Ca_{0.5}Cu_3O_y$ (x=0.5). The data on $Pb_2Ba_2YCu_3O_y$ are taken from ref. 6.

Nominal composition	a (Å)	b (Å)	c (Å)
$Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$	5.37(9)	5.41(3)	15.79(6)
$Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$	5.42(4)	5.42(4)	15.97(5)
$Pb_2Sr_{1.5}Ca_{0.5}Y_{0.5}Ca_{0.5}Cu_3O_y$	5.39(7)	5.41(7)	15.74(0)
$Pb_2Ba_2YCu_3O_y$	5.4654	5.4973	16.1729

degree of the change for b is smaller between $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ and $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ than between $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ and $Pb_2Ba_2YCu_3O_y$. The orthorhombic-tetragonal transition induced by Ba doping can be explained by this difference.

On the basis of neutron powder diffraction study, Cava *et al.* [5] reported that the orthorhombic distortion in $Pb_2Sr_2YCu_3O_8$ is induced by disorders of the oxygen atoms in the PbO layers perpendicular to the c-axis. The crystal structure of $Pb_2Ba_2YCu_3O_y$ was studied by Fu *et al.* [6] using electron diffraction and neutron powder diffraction. They concluded that, in contrast to $Pb_2Sr_2YCu_3O_8$, the orthorhombic deviation from the tetragonal symmetry in $Pb_2Ba_2YCu_3O_y$ is due to the ordering of the oxygen atoms in the PbO layers. In $Pb_2Sr_2YCu_3O_8$ or $Pb_2Ba_2YCu_3O_y$, the Sr or Ba atoms are located just above the oxygen atoms in the PbO plane. Therefore, the partial replacement of the Sr with Ba atoms influences the shift of the oxygen atoms in the PbO planes, leading to the orthorhombic-to-tetragonal transition.

The temperature dependence of the resistivity for a sample with the nominal composition $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ is plotted in Fig.3. For comparison, we have measured the temperature dependence of the resistivity for a $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ sample. (see Fig.4) Figure 3 shows that a superconducting transition appears in the $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ sample around 80 K which nearly agrees with $T_c \sim$ 82 K for $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$. The transition width is rather broad for both samples. In Figs. 3 and 4, the temperature coefficient of the resistivity is negative above T_c. A similar behavior was reported earlier and was attributed to inhomogeneity in the metal and/or oxygen distribution [1].

Figure 5 shows the static magnetization data for

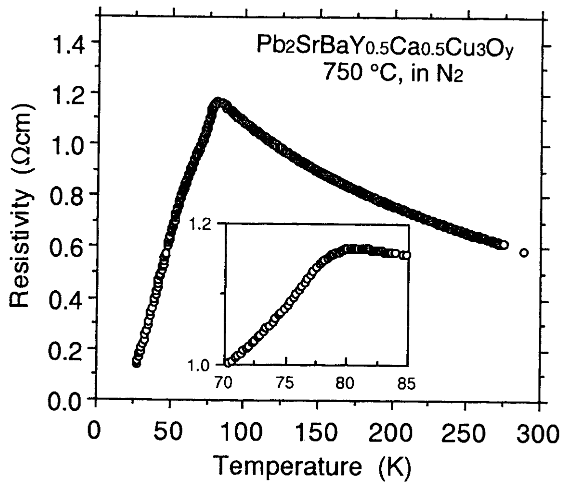

Fig.3. Temperature dependence of the resistivity for the $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ sample.

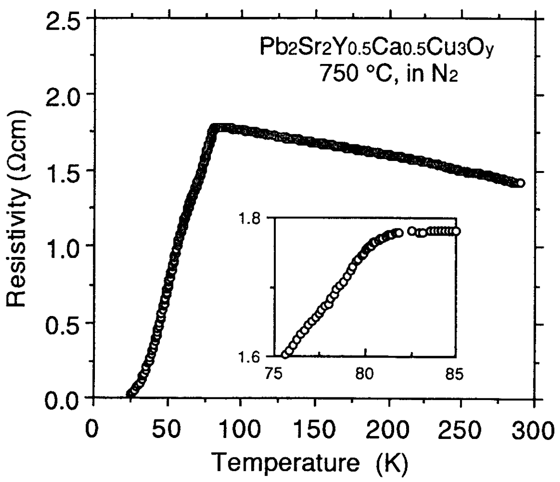

Fig.4. Temperature dependence of the resistivity for the $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ sample.

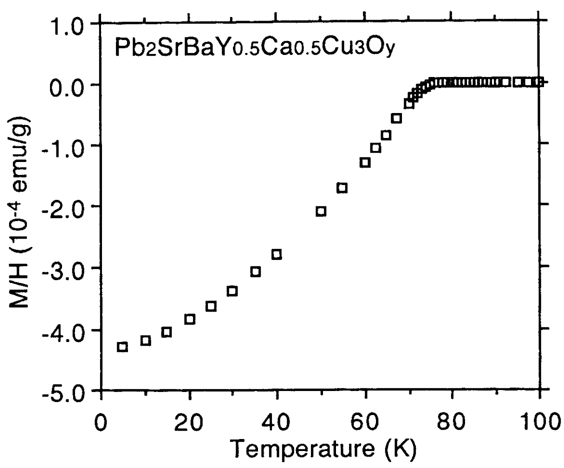

Fig.5. Temperature dependence of magnetization for the $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ sample (d.c. field-cooled at 3 Oe).

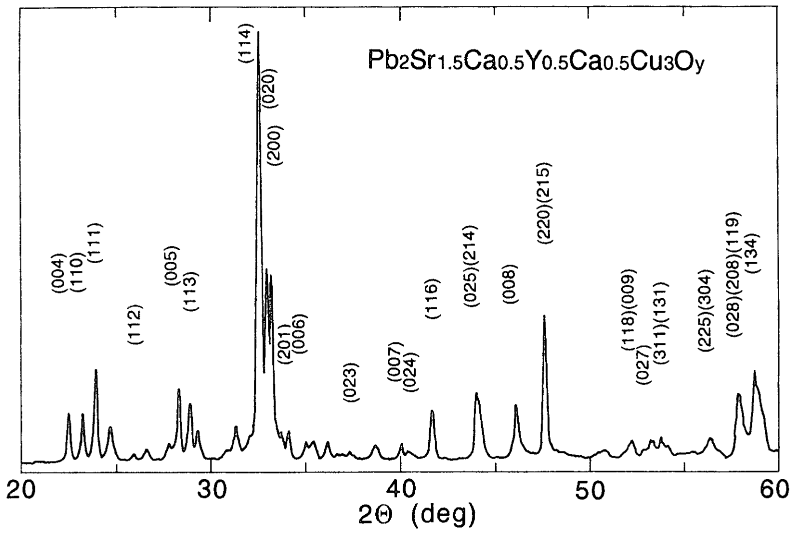

Fig.6. Powder X-ray (Cu-K$_\alpha$) diffraction pattern for a sample with the starting composition $Pb_2(Sr_{1.5}Ca_{0.5})Y_{0.5}Ca_{0.5}Cu_3O_y$.

the sample of the nominal composition $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$. Using the data at 5 K and a density $\rho \sim 4$ g/cm^3, the Meissner fraction is estimated to be about 2 %. The value suggests that a very small fraction of phase-separated orthorhombic phase becomes superconducting, which may not be easy to detect. Tokiwa *et al.* [7] found superconductivity in a related compound $PbBaSrY_{1-x}Ca_xCu_3O_7$ which has a tetragonal structure. However, an intergrowth of this structure in the host of the tetragonal phase of $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ is probably not the present case judging from that T_c onset at 65 K in $PbBaSrY_{1-x}Ca_xCu_3O_7$ is fairly low.

It is also possible that the small grain size responds to the small amount of flux expulsion if it is comparable to the superconducting penetration depth. The low-temperature heat treatment for the sample normally leads to the small grain size; the present samples were sintered at 725 °C for a short period. In addition, we cannot disregard the porous nature of the samples because the products are observed to swell up after sintering. Magnetic flux trapped in the pores of the low-density ceramic samples gives a small value of flux expulsion. Thus, at present, we cannot conclude that the tetragonal compound of $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ is superconducting.

We have also studied the substitution effect of Ca for Sr. Figure 6 shows the X-ray diffraction pattern for a sample with the starting composition $Pb_2Sr_{1.5}Ca_{0.5}Y_{0.5}Ca_{0.5}Cu_3O_y$. The pattern is almost characterized in terms of the crystal structure of $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$. However, it includes some unknown peaks from a second phase. As is expected, the parameter c is small compared with $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$. The measured value of the room-temperature resistivity is great compared with $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ or $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$. The temperature dependence of the resistivity, which is plotted in Fig. 7, shows a large increase of the resistivity at low temperatures with no drop. Small structures are noticed near 84 and 81 K. The agreement of the temperatures with T_c in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ suggests that the structures are related to the superconducting transition of the major phase. A further increase of the amount of Ca in the starting composition $Pb_2Sr_{2-x}Ca_xY_{0.5}Ca_{0.5}$

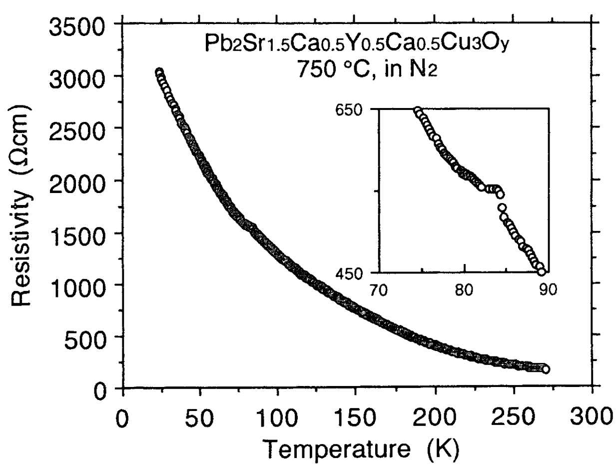

Fig.7. Temperature dependence of the resistivity for the sample with the starting composition $Pb_2(Sr_{1.5}Ca_{0.5})Y_{0.5}Ca_{0.5}Cu_3O_y$.

Cu_3O_y resulted in the growth of secondary phases and is against the formation of the $Pb_2Sr_2YCu_3O_y$ phase.

4. CONCLUSIONS

The Ba doping in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_y$ influenced the arrangement of the oxygen atoms in the PbO planes. The crystal structure of $Pb_2SrBaY_{0.5}Ca_{0.5}Cu_3O_y$ was found to change from orthorhombic to tetragonal. The sample showed a superconducting transition. The magnetization measurements revealed that the Meissner fraction of the superconductivity was very low. This suggests that the superconductivity does not originate from the tetragonal phase but from an unknown phase which could not be detected by X-ray diffractions.

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