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SYNTHESIS AND ELECTRICAL PROPERTIES OF $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$

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Abstract We have synthesized $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$ ($0 \leqq x \leqq 0.3$) which was an iso-structural Ba version of the superconducting $Pb_2Sr_2ACu_3O_{8+y}$ (where A is a rare earth metal + Sr or Ca). Single crystalline ($x=0$) and polycrystalline ($0.05 \leqq x \leqq 0.3$) samples were obtained. Ca substitution for Y decreased the resistivity and a filamentary superconducting transition at around 70K was observed for samples with $x=0.3$.

INTRODUCTION

The discovery of a new class of high-T_c superconductors with the formula $Pb_2Sr_2ACu_3O_{8+y}$ (where A is a rate earth metal + Sr or Ca) offers the possibility of better understanding the superconducting phenomenon[1,2]. For further understanding the superconductivity of the $Pb_2Sr_2ACu_3O_8$ structure, a study of $Pb_2Ba_2YCu_3O_8$ should be fruitful, because it has the same local structure of BaO-CuO_2-Y-CuO_2-BaO as in the well characterized $Ba_2YCu_3O_7$. It is also expected that the Ca substitution for Y will create hole carriers and give rise to superconductivity. We have synthesized single crystals ($x=0$) and polycrystals ($0.05 \leqq x \leqq 0.3$) of the $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$. Crystal structures and electrical properties were studied.

SAMPLE PREPARATION

Polycrystalline samples were prepared by a two-step solid phase reaction. At first, mixed powders of $BaCO_3$, Y_2O_3, CuO and $CaCO_3$ with nominal compositions of $Ba_2(Y_{1-x}Ca_x)Cu_3O_z$ ($0 \leqq x \leqq 0.7$) were calcined at 930°C for 20 h in oxygen atmosphere with one intermediate grinding. The obtained precursor was single phase ($0 \leqq x \leqq 0.2$) or a phase mixture with $BaCuO_2$ and unknown impurities ($0.2 < x < 0.7$). The precursor was reduced at 700°C in flowing nitrogen. Then a PbO powder was added so as to obtain a nominal composition

of $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$. The mixed powder was then pelleted, and sintered in nitrogen for 20 h with one intermediate grinding. The sintering temperatures (700°C-800°C) were chosen to obtain the best result depending on the Ca content. Single phase $Pb_2Ba_2(Y_{1-x}Ca_x)\ Cu_3O_{8+y}$ ($0.05 \leqq x \leqq 0.1$) was obtained using this technique. Samples with starting Ca-compositions of $0.1 < x \leqq 0.5$ contained a small amount of impurity phases. According to a powder X-ray diffraction and an electron-probe micro-analysis (EPMA), the impurity phases were $BaPbO_3$, $CaCuO_2$ and a trace of $BaCuO_2$, but $Ba_2YCu_3O_7$ type phase was not observed at all. Samples with starting Ca-composition more than 0.5 were showed a significant phase separation, and the main phase was $BaPbO_3$. So, we could not get any structural and electrical data from these samples. The real compositions in the $Pb_2Ba_2(Y_{1-x}Ca_x)\ Cu_3O_8$ phase determined by EPMA are listed in table 1. The Ca-free ($x=0$) sample also contained impurity phases such as $BaPbO_3$.

Table 1 Atomic ratio of each element in $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$ determined by EPMA. Starting Ca compositions of samples A,B and C are 10%, 30% and 50%, respectively.

	Pb	Ba	Y	Ca	Cu	Y+Ca	Ca/(Y+Ca)%
A	1.91(2)	2.00(6)	0.82(7)	0.080(2)	3.2(1)	0.90(7)	9.0(4)%
B	2.03(7)	2.04(2)	0.77(2)	0.16(2)	2.99(2)	0.94(4)	17.(1)%
C	1.92(2)	2.01(1)	0.69(2)	0.30(1)	3.08(1)	0.99(1)	30.(1)%

Single crystal samples with $x=0$ were grown using a self flux method in an alumina crucible. The detailed process is described in ref.3.

RESULTS AND DISCUSSION

The crystal structure of the single crystal ($x=0$) was determined using RIGAKU AFC-5R. Figure 1 and table 1 show the obtained crystal structure and its crystallographic data. The space group was assumed to be orthorhombic(C4mmm). This crystal structure has PbO-Cu-PbO triple layers instead of a CuO chain layer in $Ba_2YCu_3O_7$. The distances between each layers were almost same as those in $Ba_2YCu_3O_7$. The c-axis was slightly longer than that of $Pb_2Sr_2YCu_3O_8$, which seemed to be due to the difference in size between Sr and Ba ions. Oxygen ions on the PbO layer showed a small shift from the original position approximately to the [110] direction. It is now

Table 2 Crystallographic data of $Pb_2Ba_2YCu_3O_8$ single crystal
orthorhombic cell
$a_0=5.471$Å(1) $b_0=5.5078(6)$Å $c_0=16.194(2)$Å
space group Cmmm, $z=2$
observed reflections 405, $Rw=0.060$

atom	position	x	y	z	B(eq)[Å^2]
Pb	41	1/2	0	0.38934(5)	0.81(3)
Ba	4k	0	0	0.22306(7)	0.60(5)
Y	2a	0	0	0	0.6(1)
Cu1	2d	0	0	1/2	1.1(1)
Cu2	41	1/2	0	0.1013(2)	0.55(9)
O1	41	1/2	0	0.256(1)	1.2(3)
O2	16r	0.071(6)	0.090(6)	0.392(2)	1.0(5)
O3	8m	1/4	1/4	0.0876(7)	0.9(2)

uncertain whether this shift causes any long range order as is found in $Pb_2Sr_2YCu_3O_8$[4]. Crystal structures of the polycrystalline samples studied by the Rietveld refinement of x-ray diffraction were essentially the same as that of the single crystal. As x increased, c-axis smoothly elongated to 16.28A ($x=0.3$) while a- and b-axis were unchanged or slightly shortened for $x<0.2$. For $x>0.2$, a_0 and b_0 values gradually approached each other, converging at $x\sim0.35$.

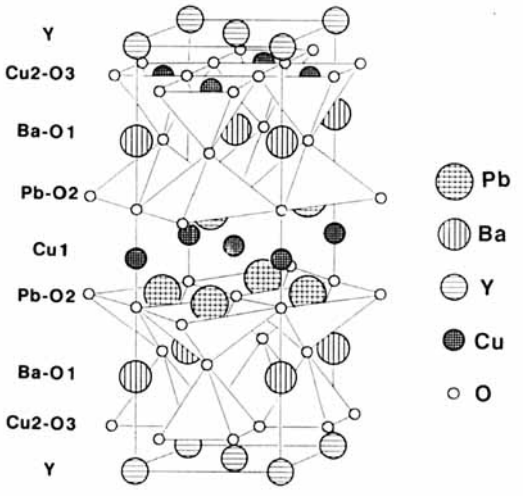

Figure 1 Crystal structure of $Pb_2Ba_2YCu_3O_8$

Annealing effects on the oxygen content and electrical properties were investigated using polycrystalline samples with $x=0.1$ because they showed no impurity phases in the X-ray diffraction patterns. The absolute oxygen content of a sample synthesized in N_2 atmosphere were 8.1 ± 0.1, which was determined by Horiba EMGA-2800. Figure 2 shows the resistance-temperature curves for oxygen-annealed samples with $x=0.1$. The annealing temperature must be below 300°C, because oxygen annealing at temperatures higher than 300°C easily oxidized Pb^{2+} to Pb^{4+} and resulted in formation of

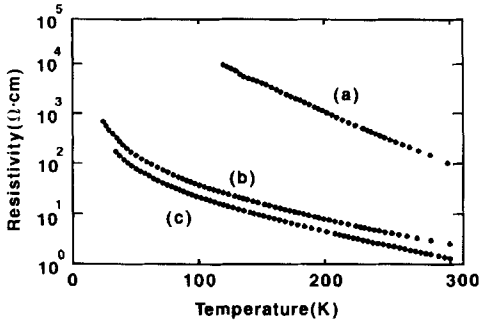

Figure 2 Resistance-temperature curves of $Pb_2Ba_2(Y_{0.9}Ca_{0.1})Cu_3O_{8+y}$. (a) as prepared, (b) oxygen-annealed at 270°C for 2h, (c) oxygen-annealed at 270°C for 49h.

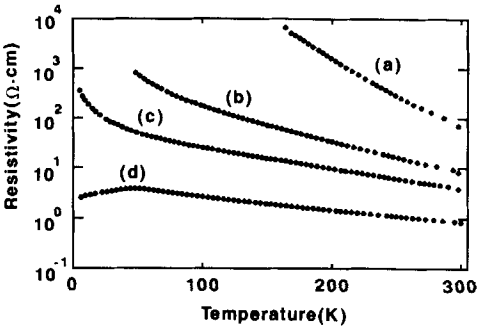

Figure 3 Resistance-temperature curves for $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$ with various Ca contents. Each samples was synthesized in a pure nitrogen stream. (a), (b), (c) and (d) correspond to the Ca contents of 5%, 10%, 17% and 30%, respectively.

$PbBaO_3$ based perovskite. It is noted that the annealing condition is much more critical as compared with that for the Sr version[1]. The oxygen annealing at 270° C for 29h.increased the oxygen content up to 8.25 and decreased the reisistivity by two orders, but no superconductivity was observed.

Figure 3 shows the temperature dependence of the resistivity for samples with various Ca contents. Ca doping reduced the resistivity, and the sample with $x=0.3$ showed a slight drop in resistivity at around 50K. Meissner volume fraction at 5K was 0.23%. Considering that the sample was synthesized in a pure nitrogen stream, this superconductivity should not be originated from $Ba_2YCu_3O_7$. Oxygen annealing at 270°C for 5 h slightly improved the Meissner fraction to 1.4% and the resistive onset temperature to 70K, but additional annealing for 5h reduced the Meissner fraction to 1.2%. On the other hand, following annealing in vacuum at 300°C enhanced the Meissner fraction to 2.1% as shown in fig.4, and made the resistive transition sharper as shown in fig.5. These facts strongly suggest that the observed superconductivity is not originate in an impurity phase of $Ba_2YCu_3O_7$, which would not be superconducting any more after the reduction. Since the temperature dependence of the normal resistivity is still semiconducting, further Ca-doping over 0.3 would increase the hole concentration and improve the superconductivity. It was also reported for the Sr version that bulk superconeuctivity appeared at $x\sim0.5$[1]. However, the present study revealed

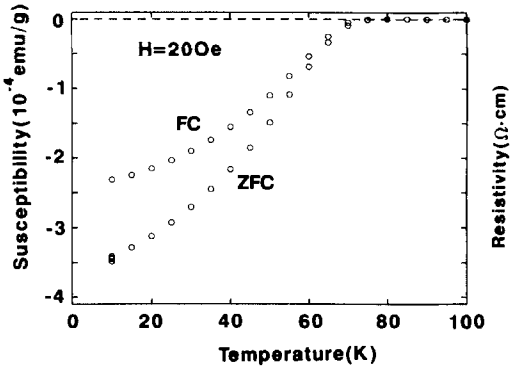

Figure 4 Magnetic susceptibility of $Pb_2Ba_2(Y_{0.7}Ca_{0.3})Cu_3O_{8+y}$. Annealing condition are described in the text.

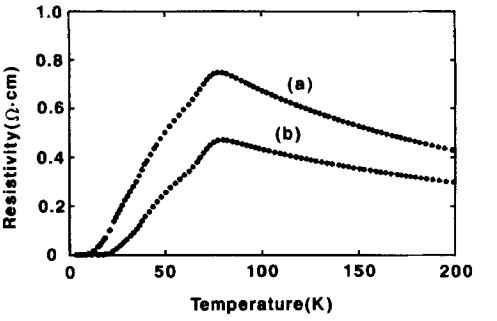

Figure 5 resistance-temperature curves of $Pb_2Ba_2(Y_{0.7}Ca_{0.3})Cu_3O_{8+y}$. (a) annealed sample in O_2 at 270°C for 5h, (b) further annealed in vacuum at 300°C for 3h.

that the solubility limit of Ca in the Ba version was about 0.3, which suggested the difficulty of the appearance of bulk superconductivity in this system.

CONCLUSION

We have successfully synthesized $Pb_2Ba_2(Y_{1-x}Ca_x)Cu_3O_{8+y}$ ($0<x<0.3$) which was a Ba version of the superconducting $Pb_2Sr_2ACu_3O_{8+y}$. As x increased, the electrical resistivity decreased and filamentary superconductivity appeared at around 70K for $x=0.3$. Further Ca doping (hole doping) might improve the superconductivity. However, it was quit difficult to prepare samples with $x>0.3$ because significant amounts of second phases appeared.

REFERENCES

[1] R.J. Cava, B. Batlogg, J.J. Krajewski, L.W. Rupp, L.F. Schneemeyer, T. Siegrist, R.B. Van Dover, P. Marsh, W.F. Peck Jr., P.K. Gallagher, S.H. Glarrum, J.H. Marshall, R.C. Fallow, J.V. Waszczak, R. Hull and P. Trever, Nature 336(1988)211.

[2] R.J. Cava, M. Marezio, J.J. Krajewski, W.F. Peck Jr, A. Santoro and F. Beech, Physica C 157(1989)272.

[3] T. Hibiya, S. Imoto, T. Satoh, Y. Nakabayashi and M. Sakonjyu, J. Cryst. Growth., (in Press).

[4] R. Hull, J.M. Bonar, L.F. Schneemeyer, R.J. Cava, J.J. Krajewski and J.V. Waszczak, Phys. Rev. B 39(1989)9685.