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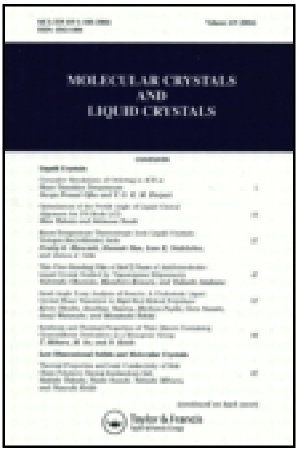

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Synthesis and Physical Properties of Tl-O Monolayer Superconductors: $T1Ba_{1+x}La_{1-x}CuO_5$ and $TlBa_2Y_{1-x}Ca_xCu_2O_7$

T. Manako [a], Y. Shimakawa [a], Y. Kubo [a], T. Satoh [b] & H. Igarashi [a]

[a] Fundamental Research Laboratories, NEC Corporation, 4-1-1, Miyazaki, Miyamae-ku, Kawasaki, 213, Japan

[b] Resources and Environment Protection Research Laboratories, NEC Corporation, 4-1-1, Miyazaki, Miyamae-ku, Kawasaki, 213, Japan

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SYNTHESIS AND PHYSICAL PROPERTIES OF Tl-O MONOLAYER SUPERCONDUCTORS: $TlBa_{1+x}La_{1-x}CuO_5$ AND $TlBa_2Y_{1-x}Ca_xCu_2O_7$

T. MANAKO, Y. SHIMAKAWA, Y. KUBO, T. SATOH* and
H. IGARASHI
Fundamental Research Laboratories, *Resources and Environment
Protection Research Laboratories, NEC Corporation, 4-1-1,
Miyazaki, Miyamae-ku, Kawasaki, 213, Japan

ABSTRACT Two systems of Tl-based copper oxides with a Tl-O monolayer structure, $TlBa_2Y_{1-x}Ca_xCu_2O_7$ (1212 phase) and $TlBa_{1+x}La_{1-x}CuO_5$ (1201 phase), have been synthesized. For $x=0$, where formal Cu valences in both systems were estimated to be just +2, samples exhibited semiconductive or insulating behaviors in the resistivity measurement. With increasing x, electrical properties of samples became more metallic and superconductivity appeared. For the 1201 phase, the maximum T_c value was about 40K at around $x=0.2$, and sample became a metallic nonsuperconductor for $x>=0.4$. For the 1212 phase, maximum T_c value was about 90K at around $x=0.8$ and metallic nonsuperconductivity was not observed.

1. INTRODUCTION

Tl-based superconductors with a general composition of $Tl_mBa_2Ca_{n-1}Cu_nO_{2+2n+m}$ were specified by the number of Tl-O sheets ($m=1,2$) and the number of CuO_2 planes ($n=1,2,3,4...$) in a formula unit. In the earliest stage, single phase samples which contained one to three CuO_2 planes between double Tl-O layers ($m=2$) were synthesized, and both electrical properties and crystal structures were closely examined[1]. Whereas, it was rather difficult to obtain a single phase sample with Tl-O monolayer sheets ($m=1$), especially for $n=$ 1 or 2. The difficulty in getting single phase samples of Tl-O monolayer compounds seems to be related to the high formal oxidization state of Cu. For example, the formal Cu valence in $TlBa_2CuO_5$ is as high as +3 which is much higher than that in the ordinary copper oxides.

In our previous study, we could have prepared easily a single phase sample of $TlBa_2YCu_2O_7$ by substituting trivalent Y for divalent Ca in $TlBa_2CaCu_2O_7$ (1212 phase)[2]. This means that the 1212 structure is stabilized by such substitution that decreases the formal copper valence. In the present study, we synthesized two substituted systems having Tl-O monolayer sheets, $TlBa_2Y_{1-x}Ca_xCu_2O_7$ (1212) and $TlBa_{1+x}La_{1-x}CuO_5$ (1201), in which the formal Cu valence was reduced to +2 for $x=0$. Electrical and superconducting properties and the phase stability will be discussed with respect to the composition x.

2. EXPERIMENTAL

Samples were prepared by a solid state reaction as described in [2,3]. DC resistivities and AC magnetic susceptibilities were measured using a conventional four probe method and a self inductance method, respectively. Crystal structures and chemical compositions were studied by the powder X-ray diffraction (XRD) and the electron-probe micro-analysis (EPMA).

3. RESULTS AND DISCUSSION

3.1 $TlBa_{1+x}La_{1-x}CuO_5$ system

According to XRD, no extra peaks due to impurity phases were found for $0<x<0.4$, while $(La,Ba)_2CuO_4$ phase and a trace of $Tl_2Ba_2CuO_6$ phase were observed for $x<0$ and for $x>0.4$, respectively. On the other hand, EPMA measurement revealed that the Ba contents were decreased to less than the nominal values for $x>0$ as shown in Table 1. This suggests the appearance of a small amount of second phases except for samples with $x=0$. However, the quantities of the second phases estimated from XRD measurement were no more than a few percents, so the samples could be regarded as close to single phase. In the following discussion, the real x value determined by EPMA will be used. Samples with negative x values could not have been obtained in the present experiment, which suggested that the solubility limit of La for $TlBa_2CuO_5$ was located at around $x=0$ where the formal Cu valence was just +2. The lattice parameters a_0 and c_0 are plotted against x in Fig.1(a). A positive correlation was observed between c_0 and x, whereas a_0 exhibited no obvious dependence on x. Similar tendencies were observed in $TlBa_2Y_{1-x}Ca_xCu_2O_7$ [Fig.1(b)] and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ [4].

$TlBaLaCuO_5$, $x=0$ sample, exhibites a semiconductor-like behavior in resistivity. Since the formal Cu valence of this compound is +2, the hole concentration was estimated to be 0. It was expected that the Ba substitution

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Table 1 Chemical compositions of samples determined by EPMA with mixing compositions of $TlBa_{1+x}La_{1-x}CuO_5$.

x	Tl	Ba	La	Cu
−0.2	0.93	1.00	1.00	1.02
0.0	0.91	1.01	0.99	1.09
0.1	0.94	1.06	0.94	1.06
0.2	0.98	1.11	0.89	1.05
0.3	0.96	1.12	0.88	1.04
0.4	0.99	1.19	0.81	1.06
0.5	0.98	1.36	0.64	1.04
0.6	1.00	1.40	0.60	1.04

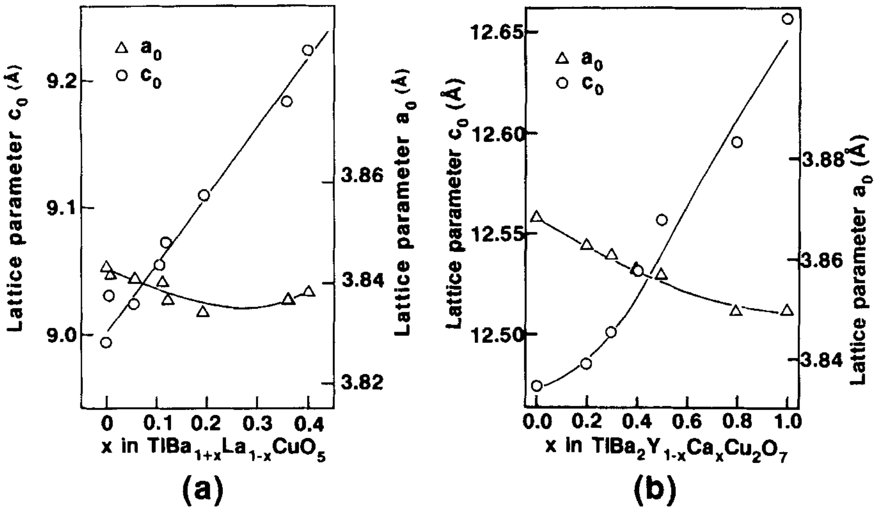

Fig. 1 The tetragonal lattice parameters a_0 and c_0 are plotted against x for (a) $TlBa_{1+x}La_{1-x}CuO_5$ and (b) $TlBa_2Y_{1-x}Ca_xCu_2O_7$

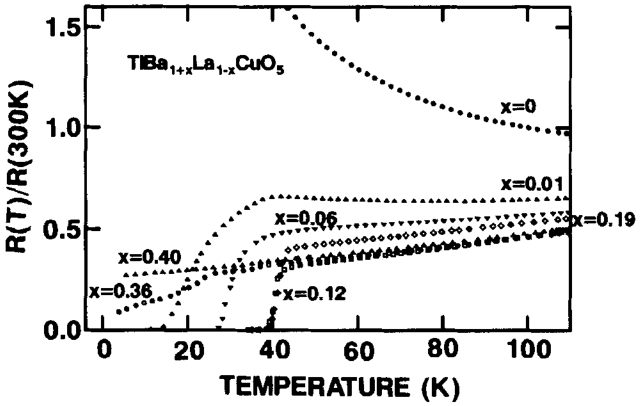

Fig. 2 Normalized resistivities plotted against temperature for $TlBa_{1+x}La_{1-x}CuO_5$.

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for La would dope hole carriers in the system. The temperature dependencies of normalized resistivities were shown in Fig.2. With increasing x, the temperature dependence of the resistivity became more metallic. For $0<x<0.4$, superconductivity appeared and the T_c showed a maximum value of 40K at around $x=0.2$. For $x \geqq 0.4$, the sample became a metallic nonsuperconductor. Such correlation between hole concentration and T_c was very similar to that observed in La-Sr-Cu-O system[5].

It should be noted that not only T_c but also the superconducting volume fraction changed with x. AC susceptibilities at 4.2K, which indicated the superconducting volume fraction, and the T_c's determined by resistivity measurement are plotted against x in Fig.3. It was clear that the change in T_c was accompanied by the change in the superconducting volume fraction. It was suggested that good superconductivity (T_c=40K) occured only in a very narrow range of composition around $x=0.2$.

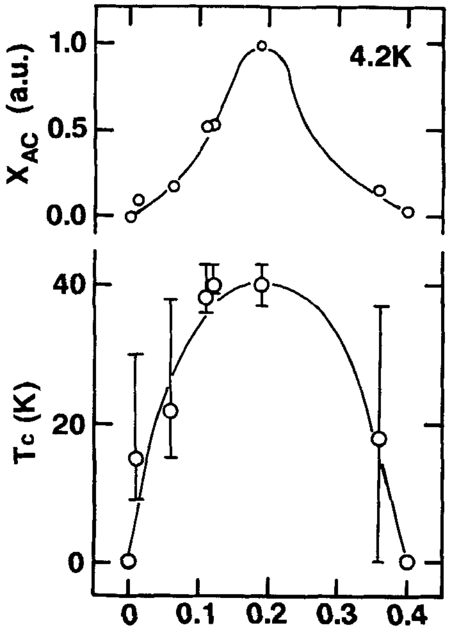

Fig. 3 AC susceptibilities at 4.2K and T_c determined by DC resistivities are plotted against x value. Upper bar, circle, lower bar represent onset, midpoint, zero resistivity temperature, respectively.

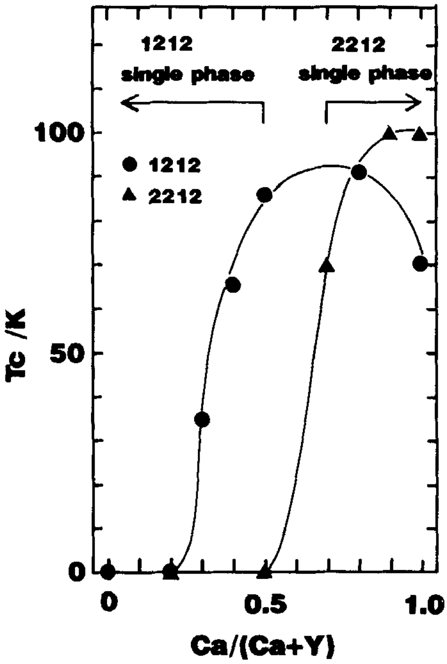

Fig. 4 T_c's and the single phase regions for samples with starting compositions of $TlBa_2Y_{1-x}Ca_xCu_2O_7$ (1212, circles) and $Tl_2Ba_2Y_{1-x}Ca_xCu_2O_8$ (2212, triangles).

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3.2 $TlBa_2Y_{1-x}Ca_xCu_2O_7$ system

When the starting composition was 1212, single phase samples with 1212 structure were obtained for $0<x<0.5$, while $BaCuO_2$ and a trace of 2212 phases appeared for $x \geqq 0.5$. This phase unstability for larger x values seems to be due to the highly oxidized Cu state, +2.5 for $x=1$. In contrast, when the starting composition was 2212, we obtained single phase 2212 samples only for $0.7<x<1.0$, and 1212 phase began to appeare for smaller x values. This suggested that the 2212 structure became unstable when the formal Cu valence was too much decreased from +2. Therefore, for all systems of the present study with 1201, 1212 and 2212 compositions, single phase samples were obtained only when the formal Cu valence was near +2.

Fig.4 shows T_c's and single phase regions for both cases where the samples were synthesized with starting compositions of 1212 and 2212, respectively. Although the samples were not single phase in the large x region for 1212 composition and the small x region for 2212 composition, the main impurity phase was $BaCuO_2$ which was an insulator. So the superconducting properties in Fig. 4 are considered to be very close to real behavior. For 1212 system, the $x=0$ sample ($TlBa_2YCu_2O_7$) was an insulator with an antiferromagnetic order[6]. As x increased, hole carriers were introduced and superconductivity appeared for $x>0.3$. T_c showed a maximum value of about 90K but metallic nonsuperconducting state was not achieved even for $x=1$. For 2212 system, the $x=1$ sample exhibited 100K superconductivity and the T_c decreased with x decreased.

In conclusion, We have prepared two series of Tl-based copper oxides with a Tl-O monolayer structure; $TlBa_{1+x}La_{1-x}CuO_5$ (1201 phase) and $TlBa_2Y_{1-x}Ca_xCu_2O_7$ (1212 phase). For 1201 phase superconductivity appeared for $0<x<0.4$, and maximum T_c value was about 40K at around $x=0.2$. For 1212 phase, superconductivity appeared for $x>0.3$, and maximum T_c value was about 40K at around $x=0.8$. It is concluded that superconductivity appears at compositions where the hole concentration becomes an optimum value.

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