THE FABRICATION AND CHARACTERIZATION OF SUPERCONDUCTING TI–Pb–Ca–Pr–Sr–Cu–O COMPOUNDS WITH Y₁Ba₂Cu₃O₇-LIKE STRUCTURE AND Tc (ZERO) UP TO 106 K

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Bulk superconductivity with Tc (zero) up to 106 K in a Tl₀.₅Pb₀.₅Ca₀.₅Pr₀.₂Sr₂Cu₂ oxide with Y₁Ba₂Cu₃O₇-like structure was observed. A single phase, tetragonal structure with a = 0.382 ± 0.001 and c = 1.200 ± 0.001 nm and space group P4/mmm, was found in Tl₀.₅Pb₀.₅CaₓPr₂Sr₂Cu₂ oxide samples by X-ray diffraction. Tc (zero)'s were found to be 78, 96, 106, 98, 45 and 25 K for Tl₀.₅Pb₀.₅CaₓPr₂Sr₂Cu₂ oxide samples with x = 0, 0.1, 0.2, 0.3, 0.5 and 0.7, respectively. For x = 1, the samples exhibited semiconducting behavior.

All sintered samples were found to be remarkably homogeneous both in composition and structure. They were also exceptionally regular in microstructure and highly reproducible and stable. Although the six-metal blend makes the system appear to be rather complicated composition-wise, it is compensated by the relatively simple crystal structure. Furthermore, the preparation conditions are much less stringent than those for other copper-based high-Tc superconductors.

1. Introduction

Bulk superconductivity above 100 K was first realized in the Bi–Sr–Ca–Cu–O (BSCCO) system [1] then in the Ti–Ca–Ba–Cu–O (TCBCO) system [2]. The development not only broadened the materials base of high-Tc superconductors but also provided significant insight on the amazing phenomenon of high-Tc superconductivity. For the BSCCO system, partial substitution of Bi by Pb was able to substantially increase the volume fraction of the phase with higher Tc (zero) [3]. Substitution of Sr and Ca by K was also attempted [4]. A study of Y substitution for Ca in Bi₂Sr₂CaCu₂O₈ revealed that Tc decreased and the lattice parameters changed with the substitution [5,6]. For Ti-containing oxides, superconductivity in the Ti–Sr–Ca–Cu–O system was reported to occur unambiguously at 20 K and possibly at 40–70 K [7,8]. A sample with nominal composition of Ti₂Sr₂CaCu₂O₆ was reported to be superconducting at 44 K [9]. A paper cited by ref. [7] reported 119- and 79-K superconductivity onset in the Ti–Sr–Cu–O system contaminated by 7% of Ca [10]. Manako et al. observed a decrease in Tc with substitution of Ca by Y in the Ti–(Ca, Y)–Ba–Cu–O system [11]. Hermann et al. found superconductivity at 80–90 K in the Ti–(Ca, Y)–Sr–Cu–O system [12]. Bulk superconductivity was observed up to 122 K with approximately 30% Meissner fractions in the Ti–Pb–Ca–Sr–Cu–O (TPCSCO) system. The phase was identified to be Tl₀.₅Pb₀.₅Ca₂Sr₂Cu₃O₇ [13]. A major advance was made recently with the successful fabrication of a single-phase Tl₀.₅Pb₀.₅Ca₀.₈Y₀.₂Sr₂Cu₂O₆ compound with Tc (zero) = 108 K with consistent magnetization data [14]. The structure bears close similarity to the now-famous Y₁Ba₂Cu₃O₇ structure [15]. We note that superconductivity above 100 K was never achieved previously for any superconductor with Y₁Ba₂Cu₃O₇-like structure. In the Ti–Ca–Ba–Cu–O system, compounds with Y₁Ba₂Cu₃O₇-like structure were called “1122” phase, named after its cation ratio. The superconducting temperature was found to be only about 80 K [16]. Subsequent study found the sub-
stitution of Y by twelve other rare-earth elements (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) in the Tl0.3Pb0.5Ca0.8Y0.2Sr2Cu2Ox compound could yield superconductors with \( T_c \) (zero) above 105 K [17]. In an attempt to further optimize the superconducting properties of the new class of septenary compounds, the compositions of (Tl,Pb) and (Ca,R) were selectively varied. In this paper, we report the fabrication and characterization of Tl-Pb-Ca-Pr-Sr-Cu-O compounds. It is worthwhile to note that superconducting phases with “1122” structure were also reported for Tl\(_{1-x}\)Pb\(_x\)Ca\(_1\)Sr\(_2\)Cu\(_2\)O\(_7\) with \( x = 0.25 \) and 0.5 as well as for Tl\(_{1-x}\)Bi\(_x\)Ca\(_3\)Sr\(_2\)Cu\(_2\)O\(_7\)+\(_y\) with \( x \) less than 0.5. However, the highest \( T_c \) (onset) reported was only 92 K [18,19].

2. Experimental procedures

Appropriate amounts of high purity CaCO\(_3\), Pr\(_6\)O\(_{11}\), SrCO\(_3\) and CuO powders were weighed stoichiometrically and ground in an agate mortar. The well-mixed oxides were calcined at 920 °C in air for 12 h to obtain a mixture of Ca–Pr–Sr–Cu–O powders. The Ca–Pr–Sr–Cu–O powders were then mixed with an appropriate amount of PbO and Tl\(_2\)O\(_3\) to yield mixtures with nominal compositions of Tl\(_{0.3}\)Pb\(_{0.5}\)Ca\(_{1-x}\)Pr\(_x\)Sr\(_2\)Cu\(_2\)O\(_7\) oxides with \( x = 0.025 \) and 0.5 as well as for Tl\(_{0.75}\)Pb\(_{0.25}\)Ca\(_{1-x}\)Pr\(_x\)Sr\(_2\)Cu\(_2\)O\(_7\)+\(_y\) with \( x \) less than 0.5. However, the highest \( T_c \) (onset) reported was only 92 K [18,19].

3. Results and discussion

Fig. 1 shows normalized resistance versus temperature curves for Tl\(_{0.3}\)Pb\(_{0.5}\)Ca\(_{1-x}\)Pr\(_x\)Sr\(_2\)Cu\(_2\) oxide samples with \( x = 0, 0.1, 0.2, 0.3, 0.5, 0.7 \) and 1. The superconducting temperatures were found to be 78, 96, 106, 98, 45 and 25 K for samples with \( x = 0, 0.1, 0.2, 0.3, 0.5, 0.7 \) and 1, respectively. For \( x = 1 \), the samples exhibited semiconducting behavior. SQUID magnetometer measurement data for \( x = 0.2 \) samples were found to be consistent with the resistance data as shown in fig. 2. The fractions of superconducting phase from ZFC and FC measurements were found...
Fig. 2. Magnetization versus temperature curves for Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.4}$Pr$_0$.Sr$_2$.Cu$_2$ oxide samples.

to be 52 and 22%, respectively. For Tl$_{0.25}$Pb$_{0.75}$Ca$_{0.8}$
Pr$_{0.2}$Sr$_2$.Cu$_2$ and Tl$_{0.75}$Pb$_{0.25}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$ oxide
samples $T_c$ (zero)'s were found to be 102 and 84 K,
respectively.

A single phase, tetragonal in structure with
$a=0.382 \pm 0.001$, $c=1.200 \pm 0.001$ nm and of P4/
mmm space group, was found in Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Pr$_{0.2}$
Sr$_2$.Cu$_2$ oxide samples by XRD. The XRD peaks are
almost identical to those of the semiconductor phase
reported by Manako et al. and are very close to those
of Y$_1$Ba$_2$.Cu$_3$.O$_y$ phase [11,21].

For Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$.Sr$_2$.Cu$_2$ oxide samples with
$x=0$, 0.1 and varying from 0.3 to 1 as well as in
Tl$_{0.25}$Pb$_{0.75}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$ and Tl$_{0.75}$Pb$_{0.25}$Ca$_{0.8}$
Pr$_{0.2}$Sr$_2$.Cu$_2$ oxides, a phase with the same structure
was found to be predominant. A small amount of a
yet unidentified phase was also present.

The series of XRD spectra for Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$
Pr$_x$.Sr$_2$.Cu$_2$ oxide samples with $x$ varying from 0.1 to
1 are shown in fig. 3. The lattice parameters of the
Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$.Sr$_2$.Cu$_2$ oxide samples with $x$ varying
from 0 to 0.3 were found to increase slightly with
Pr concentration. For Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$.Sr$_2$.Cu$_2$
oxides samples with $x$ varying from 0.5 to 1, the length
of the $c$-axis was increased considerably from
1.200 nm for $x=0.2$ to about 1.240 nm, whereas the
length of the $a$-axis was increased only slightly with
Pr concentration.

Fig. 3. XRD spectra of Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$.Sr$_2$.Cu$_2$ oxide samples
with $x=0$, 0.1, 0.2, 0.3, 0.5, 0.7 and 1.

No significant change in lattice parameters was
found for Tl$_{0.25}$Pb$_{0.75}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$ and
Tl$_{0.75}$Pb$_{0.25}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$ oxides compared to those
of Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$ oxide samples. The
samples were found to be highly reproducible. They
were also found to be very stable since supercon-
ductivity persisted after one month.

In addition, the samples were found to be re-
markably homogeneous both in composition and
structure. EDS revealed that the compositions of the
sintered samples were almost identical to their start-
ing compositions for the series of
Tl$_{0.5}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$.Sr$_2$.Cu$_2$ oxide samples with $x$ varying
from 0 to 1 as well as for Tl$_{0.25}$Pb$_{0.75}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$.Cu$_2$
Tl$_{0.75}$Pb$_{0.25}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxides.

Less than 20% deviation from the average cation composition of each component was found for each of the twenty-seven grains as well as for ten surface areas of about 1 mm$^2$ each measured.

Electron diffraction data and high resolution images also revealed that the crystal structure of the single phase in Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxides samples is of P4/mmm symmetry with lattice parameters close to those of Y$_1$Ba$_2$Cu$_3$O$_7$ phase. An example of high resolution image of Tl$_{0.3}$Pb$_{0.3}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxide sample is shown in fig. 4. The schematic diagram of a probable structure of the phase with two Cu-O layers interposed between (Tl,Pb)-O layers is also highlighted in fig. 4. The diagram was drawn with the assumption that dark dots correspond to metal atoms. We note that identification of the exact positions of metal atoms by lattice imagings requires extensive image simulation with known electron-optical and specimen parameters, which has not been carried out in the present work.

Manako et al. found that the structure of Tl$_1$Y$_1$Ba$_2$Cu$_3$O$_7$ resembles the Y$_1$Ba$_2$Cu$_3$O$_7$ structure with Tl occupying the corners of the modified perovskite structure [11]. Y sites in the Y$_1$Ba$_2$Cu$_3$O$_7$ structure are occupied by Ca and Y atoms. Sr is thought to replace Ba from a symmetry consideration. The crystal structure of Tl$_{0.3}$Pb$_{0.3}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxide can be seen as a further variation of the Tl$_1$Y$_1$Ba$_2$Cu$_3$O$_7$ structure. Pb is most likely substituting Tl in its atomic locations based on the closeness of valence (+4 and +3 for Pb and Tl, respectively) [22].

For Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Sr$_2$Cu$_3$ oxide, Pb and Tl were previously found to share the corner positions of the unit cell [13]. A structure model is shown in fig. 5. Substantial increase in the length of the c-axis in Tl$_{0.2}$Pb$_{0.8}$Ca$_1$$_x$Pr$_x$Sr$_2$Cu$_2$ oxide samples when $x$ increases from 0.3 to 0.5 may be related to the partial substitution of ions by Pr at sites other than the "Y" site. However, a more elaborate structure study is needed to clarify this point. Structural variations in Tl-Ca-Ba-Cu-O samples with T$_c$ above 100 K were previously reported. A multiple layer structure of (CuO$_2$-Ca-CuO$_2$) $\times$ $n$ with $n$ = 1 to 6 was observed [23]. On the other hand, a high density of twins was found to be always present in Y$_1$Ba$_2$Cu$_3$O$_7$ samples [24]. Neither twins nor intergrowths were observed in "1122" compounds in the present study. The structure of the phase appeared to be extraordinarily regular.

For both BSCCO and TCBCO systems, sintering of samples with an overall composition always failed
to produce a large amount of the phase with the same composition [16,25–30]. It is therefore rather remarkable that single phase with almost identical stoichiometry to that of the starting material was formed in the present septenary Tl-containing samples. The addition of Pb appeared to stabilize the compounds formed. Since Ca and Pr ions are divalent and tri- or tetravalent, respectively, the average Cu valence is expected to change with the substitution of Ca by Pr [22]. For Y substitution of Ca in both Bi$_2$Sr$_2$CaCu$_2$O$_8$ and TlCaBa$_2$Cu$_2$O$_y$, the decrease of $T_c$ was considered to be caused by the decrease of the average Cu valence [3,11]. In the YBCO system, incorporation of Pr in YBa$_2$Cu$_3$O$_{7-x}$ showed a monotonic decrease in $T_c$ and eventually a metal–insulator transition with increasing Pr concentration. The monotonic decrease in $T_c$ with Pr concentration was attributed to the reduction of the Cu oxidation state by incorporation of Pr in its tetravalent state of the Y site [31].

For the YBCO system and its derivatives, $T_c$ (zero) was found to be up to the 90-K-range but never above 100 K. Controlled cooling in O$_2$ was found to be essential to control the oxygen content and possibly the distribution in the compound. In contrast, the cooling rate did not seem to affect the superconducting properties of the Tl$_{1.2}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$Sr$_2$Cu$_2$ oxide [14]. Similar behavior is expected for the Pr-containing septenary compounds. In this context, it is likely that the oxygen content and location were not significantly varied by changing the cooling rate for the septenary system. In addition, the tetragonal symmetry of the structure also discounts the possibility that oxygen ordering in the a–b plane plays an important role for high-$T_c$ superconducting properties as been suggested for the Y$_x$Ba$_2$Cu$_3$O$_y$ compound.

A comparison with the results on the Tl$_1$Ca$_{1-x}$Y$_x$Sr$_2$Cu$_2$ oxide system indicated that substitution of Tl by Pb was essential to achieve superconductivity above 100 K [14]. Although the six-metal blend makes the system appear to be complicated composition-wise, it is compensated by the relatively simple crystal structure. Furthermore, the preparative conditions are much less stringent than those of other high-$T_c$ superconducting compounds. The new compound is highly reproducible, stable, homogeneous in both composition and structure with exceptional regularity in microstructure. The stability of the compounds may be enhanced by the elimination of Ba since Ba is notorious for its poor resistance to moisture. The successful fabrication of the septenary compound is believed to provide valuable insights on the high-$T_c$ superconductivity and point to the new routes to be explored. The ease in process control may also lead to practical applications.

4. Summary and conclusions

Bulk superconductivity with $T_c$ (zero) up to 106 K in a Tl$_{1.2}$Pb$_{0.5}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxide with Y$_x$Ba$_2$Cu$_3$O$_y$-like structure was observed. A single phase, tetragonal in structure with $a=0.382\pm0.001$, $c=1.200\pm0.001$ nm and of P4/mmm space group, was found in Tl$_{1.2}$Pb$_{0.5}$Ca$_{0.8}$Pr$_{0.2}$Sr$_2$Cu$_2$ oxide samples by XRD. The single-phase samples were prepared with the starting materials with the same cation stoichiometry and annealed at 950°C in O$_2$ for 3h. The lattice parameters of the Tl$_{1.2}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$Sr$_2$Cu$_2$ oxide samples with $x$ varying from 0 to 0.3 were found to increase slightly with Pr concentration. For Tl$_{1.2}$Pb$_{0.5}$Ca$_{1-x}$Pr$_x$Sr$_2$Cu$_2$ oxide samples with $x$ varying from 0.5 to 1, the length of the c-axis was increased considerably from 1.200 nm for $x=0.2$ to about 1.240 nm, whereas the length of the a-axis was increased only slightly with Pr concentration. No significant change in the lattice...
parameters was found for Tl₀.25Pb₀.75Ca₀.8Pr₀.3Sr₂Cu₂
and Tl₀.75Pb₀.25Ca₀.8Pr₀.2Sr₂Cu₂ oxides compared to
that of Tl₀.5Pb₀.5Ca₀.5Pr₀.2Sr₂Cu₂ oxide samples. The
samples were found to be remarkably homogeneous
both in composition and structure. Neither twins nor
intergrowths were observed in the “1122” com-
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phase appeared to be extraordinary regular. In ad-
dition, they were highly reproducible and stable. The
superconducting temperatures were found to be 78,
96, 106, 98, 45 and 25 K for samples with x = 0, 0.1,
0.2, 0.3, 0.5 and 0.7, respectively. For x = 1, the sam-
ple exhibited semiconducting behavior.

The addition of Pb appeared to stabilize the com-
ponents formed. A comparison with the results on
Tl₁Ca₁₋ₓYₓSr₂Cu₂ oxide system indicated that sub-
stitution of Tl by Pb was essential to achieve super-
conductivity above 100 K. Although the six-metal
blend made the system appear to be rather compli-
cated composition-wise, it was compensated by the
relatively simple crystal structure. Furthermore, the
preparation conditions were much less stringent than
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