Enhancement of the Superconducting Transition Temperature of TlSr$_2$CaCu$_2$O$_7$ by Yttrium and Vanadium Substitutions

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Superconductivity at 105 K has recently been observed in a family of compounds (Tl$_{1-x}$M$_x$)$_2$(Sr$_{2-x}$Y$_x$)$_2$Cu$_{2+8/7}$O$_{7-8}$ (M = Ti, Zr, Hf, V, Nb, and Ta). An interesting feature is the enhancement of $T_c$ in the parent TlSr$_2$CaCu$_2$O$_7$ compound via substitution of high-valent 3$d$ transition metals; this is in contrast to other high-$T_c$ cuprates investigated so far. The effects on crystal structure and electronic properties of yttrium and vanadium doping in the metallic, but not superconducting, TlSr$_2$CaCu$_2$O$_7$ compound are described. The new high-$T_c$ superconductor, (Tl$_{0.5}$Y$_{0.5}$)$_2$(Sr$_{0.8}$Y$_{0.2}$)$_2$Cu$_{2+8/7}$, exhibits a current density of $1.5 \times 10^6$ A/cm$^2$ at 5 K and 1 T for the sintered material which is comparable to that observed in YBa$_2$Cu$_3$O$_{7-8}$ and YBa$_2$Cu$_3$O$_6$. © 1991 Academic Press, Inc.

1. Introduction

Since the discovery of superconductivity in the La–Ba–Cu–O and Y–Ba–Cu–O systems, there has been extensive research on the substitution of 3$d$ transition metals. Unfortunately, the incorporation of transition elements into these superconducting oxides always has a detrimental effect on the transition temperature, $T_c$. Recently, Doi et al. (2) have synthesized a monophasic TlSr$_2$CaCu$_2$O$_7$ compound, which has single Tl–O sheets and tetragonal symmetry ($a = 3.7859$ Å, $c = 12.104$ Å; space group $p4/mmm$), but the material is not superconducting for temperatures down to 4 K. The authors proposed that the introduction of lead into TlSr$_2$CaCu$_2$O$_7$ would optimize the hole concentration and lead to superconducting at high temperatures. In fact, Subramanian et al. (3) synthesized the compound (Tl$_{0.5}$Pb$_{0.5}$)$_2$Sr$_2$CaCu$_2$O$_7$, which is superconducting below 80 K. In the case of the TlSr$_2$CaCu$_2$O$_7$ compound, the Cu valence is $2.5^+$, which appears to be too high and the compound is unstable and/or difficult to prepare as a single phase. Interestingly, a large number of 3$d$ transition metal cations have accessible valencies of four and above. This aspect leads one to suggest that high-valent 3$d$ transition metals might play the same role as lead (4+)—if they substitute for the Tl (3+) sites in TlSr$_2$CaCu$_2$O$_7$, rather than substituting in the Cu–O framework. If this is possible, the substitution would reduce the “overdoping” of TlSr$_2$CaCu$_2$O$_7$ and give rise to a superconductor. This reasoning led to the synthesis of a new family of high-$T_c$ superconductors in the system (Tl$_{1-x}$, $M_x$)$_2$(Sr$_{2-x}$Y$_x$)$_2$Cu$_{2+8/7}$ (M = Ti, Zr, Hf, V, Nb, and Ta) (4–6).

Here, we report the results of an investigation of the substitution of thallium by vanadium in (Tl$_{1-x}$Y$_x$)$_2$(Sr$_{2-x}$Y$_x$)$_2$Cu$_{2+8/7}$ by a combination of electrical resistivity, magnetic, and X-ray diffraction measurements.
The aim is to obtain information on the role of vanadium in the Tl–V–Sr–Ca–Y–Cu–O system. In addition, we have measured the critical current density of this new high-$T_c$ superconductor, $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_7$.

2. Experimental

Samples with nominal compositions of $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ and $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ ($0 \leq x \leq 0.7$) were prepared by mixing suitable amounts of $\text{Tl}_2\text{O}_3$, $\text{V}_2\text{O}_5$, $\text{SrO}$, $\text{CaO}$, $\text{Y}_2\text{O}_3$, and $\text{CuO}$, and forming a pellet, 10 mm in diameter and 2 mm in thickness, of this mixture under an applied pressure of 5 tons/cm$^2$. The pellets were wrapped in gold foil to prevent the loss of thallium at high temperature, then put into a tube furnace at 950°C for 3 hr (in flowing oxygen atmosphere). The samples were then cooled to room temperature at a cooling rate of 5°C/min.

A standard four-point probe method was used for the electrical resistivity measurements. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded by a calibrated silicon diode sensor located close to the sample. Magnetization data were obtained using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). X-ray diffraction (XRD) studies were carried out with CuKα radiation using a Spectrolab CPS-120 diffractometer.

3. Results and Discussion

Using the preparation route described above, as-synthesized $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ is multiphasic (XRD pattern will be shown later). The sample exhibits metallic behavior from 300 to 4 K, except for a small electrical resistivity drop around 80 K, probably arising from a minority ($<1\%$) superconducting phase ($6, 7$). Superconductivity in $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ can be induced by the replacement of 20% of the Ca$^{2+}$ sites by Y$^{3+}$ to give the compound $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ ($8$). However, the superconducting transition in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ begins at 74 K, but zero resistance is not achieved until 15 K (see Fig. 1; $x = 0$).

The temperature dependence of the normalized resistivity for a series of samples of $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ is also shown in Fig. 1. Samples with nominal compositions $0 \leq x \leq 0.5$ exhibit metallic behavior in their normal state and an increasing $T_c$ up to a maximum value of $T_c(\text{onset}) = 105$ K, $T_c(\text{midpoint}) = 100$ K, and $T_c(\text{zero}) = 87$ K for the sample $(\text{Tl}_{0.5}\text{V}_{0.5})\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. For compositions above $x = 0.5$, the superconducting transition temperature decreases and the normal state resistivity appears to show semiconducting behavior.

In Fig. 2 we summarize the characteristic superconducting properties for samples of different vanadium composition in $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. The superconducting transition temperature [$T_c(\text{midpoint})$] increases from 47 K ($x = 0$) to 100 K ($x = 0.5$) and, at the same time, the transition width decreases. However, for $x$ values above 0.5, the superconducting transition temperature decreases. In Fig. 2 we also show the compositional variation of the room temperature resistivity in $(\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. It is interesting that the room temperature resistivity increases from $x = 0.1$ to 0.7, which may be related to an effective decrease in the "hole" concentration in $\text{TlSr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ via vanadium substitution (either $\text{V}^{4+}$ or $\text{V}^{5+}$, see below) of thallium cations. This effect is similar to that found in the $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_y$ system, where substitution of Y$^{3+}$ for Ca$^{2+}$ results in a decrease in the hole concentration and an increase in the room temperature resistivity ($9$). However, we cannot rule out the possibility that this effect may arise from the presence of pyrochlore-type impurity.
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100
150 200
Temperature (K)

Fig. 1. The temperature dependence of the normalized electrical resistivity for a series of samples 
(Tl\(_1-x\)V\(_x\))Sr\(_2(Ca_{0.8}Y_{0.2})Cu_2O_y\), (x = 0 up to x = 0.7)

phases when large amounts of vanadium are introduced into the (Tl\(_1-x\)V\(_x\))Sr\(_2(Ca_{0.8}Y_{0.2})Cu_2O_y\) system.

In Fig. 3 we show the Meissner signals (field-cooled) for powder samples of 
(Tl\(_1-x\)V\(_x\))Sr\(_2(Ca_{0.8}Y_{0.2})Cu_2O_y\) as measured by a SQUID magnetometer in an applied magnetic field of 10 Oe. The magnitude of the Meissner signals increases from x = 0 to x = 0.5. At a nominal stoichiometry of x = 0.5, the sharpest superconducting transition (beginning around 105 K) was observed. With further increases in x above the value 0.5, the magnitude of the Meissner signals begins to decrease (Fig. 3). These magnetic data are in good agreement with the electrical resistivity results (Fig. 2).

In Fig. 4 we show the hysteresis loop at 5 K up to 5.4 T of the (Tl\(_0.5\)V\(_0.5\))Sr\(_2(Ca_{0.8}Y_{0.2})Cu_2O_y\) sample. The intragrain critical current density, \(J_{c(\text{intra})}\), has been estimated using the Bean model (10) based on the magnetization measurements. Assuming the grains are spherical, \(J_{c(\text{intra})}\) values can be calculated by the formula (10):

\[J_{c(\text{intra})} (\text{A/cm}^2) = 30 \Delta M/d,\]

where \(\Delta M\) (emu/cm\(^3\)) is the magnetization difference for the increasing and decreasing field sweeps and \(d\) is the average diameter (cm) of the grains. The intragrain critical current density at 5 K and \(H = 1\) T for the (Tl\(_0.5\)V\(_0.5\))Sr\(_2(Ca_{0.8}Y_{0.2})Cu_2O_y\) material was
calculated to be $1.5 \times 10^7 \text{ A/cm}^2$ when a current loop size of 1 $\mu$m was used, which was estimated from a scanning electron microscope. This value is comparable with that of sintered YBa$_2$Cu$_3$O$_{7-\delta}$ and YBa$_2$Cu$_4$O$_8$ (11).

In Fig. 5 we show the XRD patterns of samples with nominal compositions of TlSr$_2$CaCu$_2$O$_y$ (a) and a series (Tl$_{1-x}$V$_x$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ ($x = 0, 0.2, 0.5,$ and 0.7 in samples b to e. Under our preparation conditions, the TlSr$_2$CaCu$_2$O$_y$
compound is multiphasic. One phase (indicated by •) can be indexed on the tetragonal TlSr$_2$CaCu$_2$O$_y$ phase (2). The concentration of the unidentified impurity phase (marked ▲ in Figs. 5a and 5b) in TlSr$_2$CaCu$_2$O$_y$ can be reduced by ca. 20% of yttrium substitution into calcium in TlSr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ [Fig. 5b]. Further substitution of 10–30% vanadium into the thallium sites results in a considerable reduction in the levels of the impurity phases in TlSr$_2$CaCu$_2$O$_y$ [Fig. 5c]. Unfortunately, in addition to the vanadium incorporation into the thallium sites in TlSr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$, we also have observed the formation of a pyrochlore SrVO$_4$-type impurity phase (6) (marked by × in Figs. 5c to 5e). This phase appears to always compete with the superconducting (Tl$_{1-x}$V$_x$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ phase for vanadium. This is illustrated in Figs. 5c, 5d, and 5e. From our previous electron energy dispersive X-ray spectrometry studies, it was shown that the actual chemical composition corresponding to a nominal composition (Tl$_{0.5}$V$_{0.5}$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ was, in fact, [Tl$_{0.71(6)}$V$_{0.27(4)}$]Sr$_{1.95(9)}$[Ca$_{0.86(7)}$Y$_{0.14(3)}$]Cu$_2$O$_y$ (6). Across the series of the (Tl$_{1-x}$V$_x$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ samples, the superconducting phase is based on the TlSr$_2$CaCu$_2$O$_y$-type structure and the c lattice parameters decreasing and the a lattice parameters expanding with increasing of vanadium concentration were also observed. These results suggest that the smaller V$^{4+}$ (0.63 Å) or V$^{5+}$ (0.59 Å) ions partially replace the larger Tl$^{3+}$ (0.95 Å) sites resulting in a decrease in the c lattice parameter. In contrast, we propose that the partial substitution of vanadium for the thallium leads to a decrease in the hole concentration in the Cu–O plane and a corresponding increase in the a lattice parameter. Measurements of the normal state magnetic susceptibility of this new high-T$_c$ oxide system may help to evaluate the valence state of the vanadium ion.

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References