An investigation of the new high-$T_c$ TI-V-Sr-Ca-Cu-O and TI-V-Sr-Ca-Y-Cu-O superconductors

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
1991 Supercond. Sci. Technol. 4 S310
(http://iopscience.iop.org/0953-2048/4/1S/089)
View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 140.112.55.213
The article was downloaded on 07/02/2012 at 07:31

Please note that terms and conditions apply.
An investigation of the new high-\( T_c \) Tl-V-Sr-Ca-Cu-O and Tl-V-Sr-Ca-Y-Cu-O superconductors

R. S. Liu, W. Zhou, R. Janes and P. P. Edwards
IRC in superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

Abstract. Superconductivity up to 105K has been achieved in the Tl-V-Sr-Ca-Cu-O and Tl-V-Sr-Ca-Y-Cu-O systems. The partial substitution of vanadium for thallium in the crystal lattice stabilizes the Tl\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_7\) phase and enhances superconductivity up to 80K. Importantly, 20% of Y\(^{3+}\) replacement of Ca\(^{2+}\) sites in the (Tl,V)\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) compound reduces the excess hole concentration and increases superconductivity by about 20K.

1. Introduction

The discovery of a low volume fraction (<1%) superconductivity in the multiphase Tl-Sr-Ca-Cu-O (Nagashima et al. 1988; Sheng et al. 1988) system, with \( T_c \) ranging from 20K to 80K, has led to widespread research aimed both at identifying the superconducting phase, and stabilizing the superconducting transition temperature. The substitution of Pb\(^{4+}\) cations (Subramanian et al. 1988) or Bi\(^{3+}\rightarrow\)^{5+} cations (Halder et al. 1988) into the trivalent Tl sites in Tl\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_7\) compound results in the stabilization of the crystal structure and bulk superconductivity with \( T_c \) up to 80K. Similarly, introduction of trivalent rare earth ions (R) into (divalent) Ca sites leads to superconductivity around 80K in the Tl\(_2\)(Ca,R)\(_2\)O\(_7\)-\(\delta\) compounds (Sheng et al. 1989). Liu et al. (1990) have also found that the combined substitution of Pb and rare earth (e.g. Y) ions into the Tl and Ca sites, respectively, results in a monophasic, septenary compound (Tl\(_{1-x}\)Pb\(_x\))\(_2\)(Ca\(_{1-y}\)R\(_y\))\(_2\)O\(_7\)-\(\delta\) with a \( T_c \) up to 110K. All of these studies, therefore, lead one to conclude that inherent "over-doping" of the parent Tl\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_2\)O\(_7\) compound can be diminished by high valent element substitution into lower valent metal lattice sites. Vanadium is one such candidate; having a range of oxidation states, including V\(^{3+}\), V\(^{4+}\) and V\(^{5+}\), as found, for example, in the oxides V\(_2\)O\(_3\), VO\(_2\) and V\(_2\)O\(_5\). We report here the synthesis and investigation of a new high-\( T_c \) material containing vanadium with a superconducting transition temperature up to 105K.

2. Experimental

Samples with nominal compositions of \((\text{Tl}_{1-x}\text{V}_x)\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_{7-\delta}\) (0\( \leq \) \( x \) \leq 1 and 0\( \leq \) \( y \) \leq 1) were prepared by solid state reaction from stoichiometric mixtures of high purity Tl\(_2\)O\(_3\) and/or V\(_2\)O\(_3\), SrO, CaO and/or Y\(_2\)O\(_3\) and CuO powders. The powders were weighed, mixed and pressed into pellets with dimensions of 10mm diameter and 2mm thick using a pressure of 5 ton/cm\(^2\). The pellets were then wrapped with gold foil to alleviate loss of thallium during the heat treatment. The sample was then sintered at 950\(^\circ\)C for 3 hours in flowing oxygen, followed by cooling to room temperature at a rate of 5\(^\circ\)C/min.

A standard four point probe method was used for the electrical resistivity measurement. Magnetisation data was obtained using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). X-ray diffraction (XRD) studies were carried out with CuK\(\alpha\) radiation using a Spectrofab CPS-120 diffractometer. From the XRD measurements of the compounds with nominal compositions \((\text{Tl}_{1-x}\text{V}_1\text{Y}_x)\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_{7-\delta}\) (0\( \leq \) \( x \), \( y \) \leq 1), the majority of the peaks for each compound can be indexed on the basis of the...
tetragonal unit cell (P4/mmm) and lattice constants $a \approx 3.8\,\text{Å}$ and $c \approx 12\,\text{Å}$ except for small amounts of SrVO$_3$-type impurity phase. Varying chemical compositions were examined by energy dispersive X-ray spectrometry (EDS) in a Jeol JEM-200CX electron microscope. Electron spin resonance (ESR) spectra were recorded between ca.77K and room-temperature using a Bruker ER200D X-band spectrometer.

3. Results and discussion

Figure 1 shows the temperature dependence of the (normalised) electrical resistivity for samples with nominal compositions of TlSr$_2$CaCu$_2$O$_y$ (a), (Tl$_{0.5}$V$_{0.5}$)Sr$_2$CaCu$_2$O$_y$ (b) and (Tl$_{0.5}$V$_{0.5}$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ (c). The TlSr$_2$CaCu$_2$O$_y$ sample clearly exhibits a metallic behaviour [room temperature resistivity ($\rho$$_{300K}$) of 7.15 m$\Omega$cm], down to 4K except for a very small (but reproducible) resistivity drop around 84K, as shown in Fig. 1(a). This anomaly at 84K may arise from a small amount of the superconducting phase of the TlSr$_2$CaCu$_2$O$_y$ present in this sample. The (Tl$_{0.5}$V$_{0.5}$)Sr$_2$CaCu$_2$O$_y$ [the actual composition as determined by EDS is $[\text{Tl}_{0.72(4)}\text{V}_{0.28(4)}]\text{Sr}_{2.1(1)}\text{Ca}_{1.04(8)}\text{Cu}_2\text{O}_y$] sample [Fig. 1(b)] displayed metallic behaviour in the normal state ($\rho$$_{300K}$=3.2 m$\Omega$cm) and a two-step resistivity drop at 110K and 80K, and $T_c$(zero)=57K. Interestingly, the (Tl$_{0.5}$V$_{0.5}$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ [the actual composition as determined by EDS is $[\text{Tl}_{0.71(6)}\text{V}_{0.27(4)}]\text{Sr}_{1.95(9)}\text{[Ca}_{0.86(7)}\text{Y}_{0.14(3)}]\text{Cu}_2\text{O}_y$] sample possessed the largest room temperature resistivity ($\rho$$_{300K}$=17.4 m$\Omega$cm) but also has the highest superconducting transition temperature, with $T_c$(onset)=110K, $T_c$(mid-point)=100K and $T_c$(zero)=87K. All the transition temperatures were also observed by the dc magnetisation measurements for these samples.

![Fig. 1 Temperature dependence of the normalised resistivity for samples with nominal compositions of TlSr$_2$CaCu$_2$O$_y$ (a), (Tl$_{0.5}$V$_{0.5}$)Sr$_2$CaCu$_2$O$_y$ (b) and (Tl$_{0.5}$V$_{0.5}$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ (c).](image)

ESR spectra of the two vanadium containing superconducting phases with nominal compositions of (Tl$_{0.5}$V$_{0.5}$)Sr$_2$CaCu$_2$O$_y$ and (Tl$_{0.5}$V$_{0.5}$)Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$ were measured between room-temperature and 77K, with a view to probing the valence state of the vanadium ions. The synthetic conditions (see earlier), would almost certainly decompose V$_2$O$_5$ to produce V$_2$O$_3$ and/or VO$_2$. The ESR of localised V$^{4+}$ (3d$^1$), V$^{3+}$ (3d$^2$) and V$^{2+}$ (3d$^3$) have all been extensively investigated (Abragam et al. 1986). However, neither superconducting phase gave an ESR signal. The V$^{3+}$ ion has been previously detected as a dopant in Al$_2$O$_3$ (Abragam et al. 1986). It is characterised by a very large spin-lattice relaxation rate (a consequence of strong spin-orbit coupling and accessible, low-lying excited states) meaning the spectrum could only be observed at liquid helium temperatures. Clearly, low temperatures are required to probe the valence state of vanadium via ESR, and in this regard, we were hampered by the appearance of a intense low-field microwave absorption that appeared on cooling the sample through $T_c$. This response is characteristic of the superconducting state and has been widely studied (Sastry et al. 1989). Figure 2 shows the
low-field microwave absorption from both samples at 77K, the signal from (Tl0.5V0.5)Sr2(Ca0.8Y0.2)Cu2Oy (b) being significantly more intense and broader than that from (Tl0.5V0.5)Sr2CaCu2Oy (a), equivalent quantities of material being used in each case. The variation in the signal intensity of (Tl0.5V0.5)Sr2CaCu2Oy as a function of microwave power is also shown as inset in Fig. 2; the signal exhibits an initial enhancement followed by saturation as the microwave power is raised, the latter being accompanied by a significant detuning of the microwave bridge. This response is common to all cuprate superconductors (Janes et al 1990).

![Graph showing modulated low-field microwave absorption](image)

**Fig. 2** Modulated low-field microwave absorption measured at 77K for (Tl0.5V0.5)Sr2CaCu2Oy (a) and (Tl0.5V0.5)Sr2(Ca0.8Y0.2)Cu2Oy (b). Inset shows the variation of the signal intensity as a function of incident microwave power for (Tl0.5V0.5)Sr2CaCu2Oy.

Hence, we conclude that the partial replacement of vanadium for thallium in the crystal lattice stabilizes the (Tl,V)Sr2CaCu2Oy phase and enhances superconductivity up to 80K, which is comparable to the corresponding (Tl,Pb)Sr2CaCu2Oy phase, with Tc around 85K. Further substitution of 20% Y3+ in the Ca2+ sites, corresponding to (Tl,V)Sr2(Ca0.8Y0.2)Cu2Oy, effectively reduces the hole concentration and increases Tc to 105K. This is a similar effect to that found in the (Tl,Pb)Sr2(Ca0.8Y0.2)Cu2Oy system (Liu et al 1990). Pb, Bi and V, therefore, can stabilize the TlSr2CaCu2Oy structure even though their electronic configurations are quite different. Other 3d elements with accessible 3+ and or 4+ valence states may also be candidates for stabilizing the TlSr2CaCu2Oy phase.

We thank the SERC and British Petroleum for support. One of us (R. S. L.) thanks the Materials Research Laboratories, Industrial Technology Research Institute, Taiwan for the financial support to study in Cambridge.

**References**

Nagashima T et al 1988 Jpn. J. Appl. Phys. 27 L1077
Subramanian M A et al 1988 Science 242 249
Haldar P et al 1988 J. Supercond. 1 211
Abragam A and Bleaney B 1986 Electron Paramagnetic Resonance of Transition Ions (Dover Publications, New York)
Janes R et al 1990 Physica C 167 520