FIRST EXAMPLE OF INDIUM AS A PRACTICAL ALTERNATIVE TO THALLIUM IN HIGH-Τ$_{c}$ SUPERCONDUCTORS

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The substitution of indium for thallium in the material Tl$_{1-x}$Pb$_x$Ca$_{1-x}$Y$_x$Sr$_2$Cu$_2$O$_y$ has been carried out. A stable and reproducible $T_{c(mid-point)}$ of circa 60 K for the new material, In$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Y$_{0.2}$Sr$_2$Cu$_2$O$_y$ was observed in both electrical resistivity and magnetization measurements. The X-ray diffraction pattern shows that the superconducting phase can be indexed on the basis of the tetragonal thallium-based 1122-type compound.

1. Introduction

Since the discovery of superconductivity in rare-earth [1,2], bismuth [3,4] and thallium-based [5,6] cuprates, there has been much effort to find new materials which give rise to high-temperature superconductivity. Recently, a new family of compounds Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Sr$_2$Cu$_2$O$_y$ (A=Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) with superconducting transition temperatures ($T_c$) close to 110 K have been synthesized [7,8]. These materials have the highest $T_c$ amongst the thallium cuprate systems with the 1122 structure, e.g. TlCaBa$_2$Cu$_2$O$_y$ [9], Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Sr$_2$Cu$_2$O$_y$ [10] and Tl(Ca, Y)Sr$_2$Cu$_2$O$_y$ [11,12]. Unfortunately, a major limitation in the use of any thallium-based compounds is their extremely high toxicity [13]. Indium also possesses the atomic ns$^2$np$^1$ electronic structure and an ionic diameter (0.81 Å) in its trivalent state somewhat smaller than the corresponding thallic ion (0.95 Å). Although the redox chemistry of indium and thallium differ in detail, these two heaviest congeners of group IIIB are generally described in terms of accessible, and mixed, M(I) and M(III) valence states [14]. In addition, the toxicity levels for elemental indium and many of its compounds are higher than those for thallium and its oxides [13]. All of these factors suggest that indium may be a practical alternative candidate for replacing thallium as part of a “hole-reservoir” for copper oxide sheets [15] in new superconducting materials. As far as we are aware, this replacement has not yet led to new high temperature superconductors. In the present work, we demonstrate complete atomic substitution of indium for thallium in the material Tl$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Sr$_2$Cu$_2$O$_y$. A stable and reproducible $T_{c(mid-point)}$ of circa 60 K for the new material, In$_{0.5}$Pb$_{0.5}$Ca$_{0.8}$Y$_{0.2}$Sr$_2$Cu$_2$O$_y$ was observed in both electrical resistivity and magnetization measurements.

2. Experimental

Stoichiometric amounts of high purity CaCO$_3$, Y$_2$O$_3$, SrCO$_3$ and CuO powders (Merck Chemicals) were mixed and ground in an agate mortar. These mixtures were calcined in air at 970°C for 12 h. The Ca–Y–Sr–Cu–O precursor was then ground and mixed with an appropriate amount of In$_2$O$_3$ and PbO. The resulting mixtures were then pressed into a cylindrical pellet, approximately 2 mm in thickness and 10 mm in diameter, under a pressure of about 2 ton/cm$^2$. These pellets were then wrapped in gold foil. This procedure was found to be necessary to alleviate loss of indium and lead during the heat-treatment. The samples were then sintered between 950°C
and 970°C for 3 h in flowing oxygen, followed by cooling to room temperature at a rate of 2°C/min.

A standard four-point probe method was used for electrical resistance measurements. Electrical contacts to the samples were made by fine copper wires attached to the samples with a conductive silver paint. The measurement temperature was recorded with a calibrated platinum resistor located close to the sample. The resistance measurement system was fully automated for data acquisition. The detection limit for zero resistance was 10⁻⁶ Ω. Magnetization data were taken in an automatic superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Both zero field-cooled (ZFC) and field-cooled (FC) DC magnetization were measured from 130 K to 10 K. For the magnetization measurements, a 100-gauss magnetic field was applied. A microcomputer-controlled Philips diffractometer equipped with a copper target and graphite monochromator for CuKα radiation was used to obtain the powder X-ray diffraction (XRD) patterns.

3. Results and discussion

Table I shows the dependence of the zero resistance temperature ($T_0$) for various sintering temperatures (950°C, 970°C and 990°C) of samples having nominal compositions of $\text{In}_x\text{Pb}_{1-x}\text{Ca}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ with $x$=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 1.0. For materials sintered at 950°C the optimum substitution occurred at a nominal indium level of 30% resulting in a $T_0$ of 51 K. The complete substitution of lead by indium in the $\text{PbCa}_{0.5}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ compound led to a loss in superconducting properties. Increasing the sintering temperature from 950°C to 970°C gave rise to an increase in $T_0$ of about 2–4 K, but $T_0$ then decreased for sintering temperatures of 990°C.

Fig. 1 shows the temperature dependence of the normalized resistance for samples of $\text{In}_n\text{Ca}_{1-n}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ ($n$=0.2, 0.3 and 0.5) which had been sintered at 970°C. The highest superconducting transition temperature was found for $n=0.2$ with $T_{c\text{(onset)}}=65$ K, $T_{c\text{(mid-point)}}=60$ K and $T_0=54$ K. Importantly, it should be noted that the sample without the complete combination of indium, lead, calcium and yttrium together, i.e.: $\text{PbCa}_{0.5}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$, $\text{InCa}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$, $\text{In}_{0.3}\text{Pb}_{0.7}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ and $\text{In}_{0.5}\text{Pb}_{0.5}\text{Ca}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$, showed no evidence of superconductivity down to 10 K. Thus, the coexistence of indium lead, calcium and yttrium ions in the sample is important for the appearance of superconductivity in the In–Pb–Ca–Y–Sr–Cu–O system.

Fig. 2 shows the temperature dependence of the mass diamagnetic susceptibility ($\chi_m$) for both ZFC and FC situations for a sample of $\text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ which had been sintered at 970°C. The Meissner signal (FC) shows $T_{c\text{(onset)}}$ around 60 K which is consistent with the resistance measurement and $\chi_m=5.8\times10^{-3}$ cm³/g at 10 K. This $\chi_m$ value at 10 K is larger than the value obtained ($-2.2\times10^{-3}$ cm³/g) for bulk superconductivity in the $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Ca}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ system [8].

The powder X-ray diffraction pattern for an $\text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ sample (sintered at 970°C) is shown in fig. 3. Most of the lines arise from a phase which we believe to be responsible for the superconductivity; these can be indexed on the basis of the tetragonal thallium-based 1122-type phase [10]. In addition, a second phase is observed which is derived from $\text{Pb}_5\text{Ca}_{12}\text{Sr}_{25}\text{Cu}_{25}\text{O}_{80}$ (a semiconducting phase, labelled (●) in fig. 3) together with a trace of an unidentified phase. Relative line intensities for the new superconducting phase can be fitted by using the space group P4/mmm. The computed lattice parameters for (nominal) 30% indium substitution on the lead sites in $\text{PbCa}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_2\text{O}_y$ compounds were $a=0.382\pm0.0001$ nm and $c=1.188\pm0.001$ nm.
which was noticeably smaller than the corresponding value for 30% (nominal) thallium substitution on the lead sites viz, \( a = 0.380 \pm 0.001 \text{ nm} \) and \( c = 1.207 \pm 0.001 \text{ nm} \). This difference presumably arises from the smaller radius of the indium(III) ion. Preliminary high-resolution transmission electron microscopic studies on a sample \( \text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Y}_{0.3}\text{Sr}_{2}\text{Cu}_{2}\text{O}_{y} \) showed a pattern similar to that observed from the 1122 phase, \( \text{Tl}_{0.5}\text{Pb}_{0.5}\text{Ca}_{0.5}\text{Sr}_{2}\text{Cu}_{2}\text{O}_{y} \) [7,8]. Detailed compositional analyses are currently underway.

In summary, we have synthesized a new superconducting phase with \( T_c(\text{mid-point}) \) up to 60 K in the \( \text{In–Pb–Ca–Y–Sr–Cu–O} \) system. The structure of the superconducting phase appears to be similar to that found in thallium-based 1122 materials. From our recent studies [16], an increased yttrium substitution for calcium in the \( \text{PbCaSr}_{2}\text{Cu}_{2}\text{O}_{y} \) system enhances the growth of 1122 phase, but none of the resulting samples showed any evidence of superconductivity down to 10 K. However, partial substitution of thallium, and now indium, into the lead sites in \( \text{PbCa}_{0.8}\text{Y}_{0.2}\text{Sr}_{2}\text{Cu}_{2}\text{O}_{y} \) gives rise to superconducting behaviour. Studer et al. [17] have shown recently that the valence of thallium and lead are 3+ and 4+, respectively, in the \( \text{Tl–Pb–Ca–Sr–} \)
Cu–O compounds and these ions therefore clearly play a crucial role in controlling the copper valence and the superconductivity. Therefore, this suggests that the isovalent replacement of thallium and indium for lead with material PbCe0.8Y0.2Sr2Cu2Oy is an important factor in obtaining superconductivity up to 60 K. The present work illustrates the potential for utilising indium substitution, rather than thallium as a method of controlling the redox chemistry of high-$T_c$ superconducting cuprates.

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References