Bulk Superconductivity up to 60 K in the In-Pb-Ca-Y-Sr-Cu-O System

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The discovery of superconductivity in the Pb,Sr,Cu,Ln,-,Cu,O system (Ln = Y, rare earth) by Iizuka et al. [1] with a maximum T$_c$ of 70 K for x $\sim$ 0.5, has led to intensive research on lead-based high-T$_c$ superconductors. The crystal structures of these lead-containing superconductors are characterized by slabs of two planes of square pyramidal CuO$_2$, with a Cu valence of $+2.25$, separated by calcium and/or rare earth ions (i.e. Ca,Ln$_{1-x}$). Each copper slab is separated by slabs of PbO-CuO$_2$-PbO triple layers with $+1$ valence for Cu.

Reducing conditions (e.g. 1% O$_2$ in N$_2$) are usually used to synthesize these new materials which exhibit superconductivity. [1] Synthetic conditions which are generally considered necessary to produce Pb$^{2+}$, and the concomitant layered structure arising from the presence of the 6$s^2$ ion pair. [2] We have attempted to prepare this new material under oxidizing conditions, air or oxygen, but generally obtained semiconducting materials.

Here, we report a new high-$T_c$ superconducting material in the In-Pb-Ca-Y-Sr-Cu-O system with a $T_c$ up to 60 K which is synthesized at one atmosphere of oxygen. X-ray diffraction as well as energy dispersive spectrometric studies were carried out to determine the probable composition and crystal structure of the superconducting phase.

Samples with the nominal composition of In$_{1-x}$Pb$_x$Ca$_y$Y$_{0.2}$Sr$_2$Cu$_4$O$_{8+y}$ were prepared as described previously. [3] Briefly, high purity CaCO$_3$, Y$_2$O$_3$, SrCO$_3$, and CuO powders were calcined in stoichiometric proportions at 970°C for 12 h in air to form a precursor with a nominal composition of Ca$_{0.8}$Y$_{0.2}$Sr$_2$Cu$_4$O$_8$. The precursor was then mixed with In$_2$O$_3$ and PbO, ground and pressed into a cylindrical pellet, 10 mm in diameter and 2 mm in thickness, under a pressure of 2 ton/cm$^2$. The pellets were wrapped in gold foil to prevent loss of indium and lead during the heating. The samples were then sintered at 970°C for 3 h in flowing oxygen, followed by cooling to room temperature at a rate of 2°C/min.

We also tried various combinations of starting materials to form the nominal composition In$_{1-x}$Pb$_x$Ca$_y$Y$_{0.2}$Sr$_2$Cu$_4$O$_{8+y}$: 1) Directly mixed In$_2$O$_3$, PbO, CaCO$_3$, Y$_2$O$_3$, SrCO$_3$, and CuO powders and then calcined and sintered as the previous process. However, this method always resulted in semiconducting phases. 2) To prevent loss of In$_2$O$_3$ during the high-temperature preparation, a stable precursor of In$_2$Cu$_{0.8}$O$_{8+y}$ was mixed with Ca-Y-Sr-Cu-O (well-calcined) powders and then sintered. This method resulted in a superconducting material but the $T_c$ of the material was usually lower than that obtained from calcined Ca-Y-Sr-Cu-O/In$_2$O$_3$ + PbO.

A standard four-point probe method was used for electrical resistivity measurements. Electrical contacts to the samples were made through 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). Field-cooled (FC) DC magnetization was measured from 120 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 CuK$_\alpha$ radiation was used to obtain the powder X-ray diffraction (XRD) patterns. The chemical compositions of the specimens were determined by energy dispersive X-ray spectrometry (EDS). Molybdenum specimen grids were used and background spectra were studied to ensure that no copper signals were detected from the sample-free area.

Figure 1 shows the temperature dependence of resistivity for a sample with the nominal composition In$_{0.3}$Pb$_{0.7}$.
The superconductivity transition was found to have $T_{\text{onset}} = 80$ K, $T_{\text{mid-point}} = 65$ K and $T_{\text{zero}} = 54$ K. This behavior is comparable with that of the $65-70$ K and $T_c(\text{mid-point}) = 32-55$ K. Figure 1 also shows the temperature dependence of the field-cooled magnetization for the same sample as the resistivity measurement in a field of 100-gauss. The diamagnetic signal (Meissner effect) is observed at 60 K which is consistent with the result of the resistivity measurement. Excluding any correction for demagnetization effects or size effects, we calculate a diamagnetic volume of about 35 to 40% of $-1/4 \pi$ which indicates that bulk superconductivity exists in the sample.

Figure 2a shows the powder diffraction pattern for a sample with a nominal composition $\text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.5}\text{Y}_{0.5}\text{Sr}_{2}\text{Cu}_2\text{O}_8$. Most of the lines of this phase, which we believe to be responsible for the superconductivity, can be fitted by using the space group $P4/mmm$ with unit cell dimensions $a = 3.82$ Å, $c = 11.88$ Å and $V = 173.4$ Å$^3$; this phase could not be indexed with that from a $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_8$ material. Additional, a semiconducting phase, $(\text{Sr}_{0.8}\text{Ca}_{0.2})\text{Sr}_{2}\text{Cu}_2\text{O}_8$ labeled * in Fig. 2a) with an $(\text{Sr, Ca})(\text{Pb, Cu})_2\text{O}_3$-type structure, together with a trace of an unidentified phase are also present in the sample.

Figure 2b shows the XRD pattern of the $(\text{In}_{0.5}\text{Pb}_{0.5})\text{(Ca}_{0.5}\text{Y}_{0.5})\text{Sr}_{2}\text{Cu}_2\text{O}_8$ compound which has the space group $P4/mmm$ and unit cell dimensions $a = 3.80$ Å, $c = 12.07$ Å and $V = 174.3$ Å$^3$. This material has the highest $T_c$ (110 K) among the thallium cuprate systems with the TlCaBa$_2$Cu$_2$O$_y$-type structure (typical $T_c$ about 80 K), e.g. TlCaBa$_2$Cu$_2$O$_{17}$, (Tl$_{0.5}$Pb$_{0.5}$) CaSr$_2$Cu$_2$O$_y$ and Tl (Ca,Y)- Sr$_2$Cu$_2$O$_y$. The XRD pattern of this thallium-based material is similar to that of the $\text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.5}\text{Y}_{0.5}\text{Sr}_{2}\text{Cu}_2\text{O}_8$ sample, but the latter has a smaller cell volume.

In Figure 3, we show the EDS analysis for a sample with a nominal composition of $\text{In}_{0.3}\text{Pb}_{0.7}\text{Ca}_{0.5}\text{Y}_{0.5}\text{Sr}_{2}\text{Cu}_2\text{O}_8$, for a phase based on the 1122 structure (Fig. 3a), which has the actual chemical composition of $(\text{In}_{0.03}\text{Pb}_{0.70}\text{Cu}_{0.25})\text{(Ca}_{0.5}\text{Y}_{0.5})\text{Sr}_{2}\text{Cu}_2\text{O}_8$. The corresponding EDS spectrum from (monophasic) $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{(Ca}_{0.4}\text{Y}_{0.6})\text{Sr}_{2}\text{Cu}_2\text{O}_8$ (Fig. 3b) is shown in Figure 3b.

Combining both the XRD and EDS results, we propose that the superconducting phase in the In-Pb-Ca-Y-Sr-Cu-O system has the chemical composition of $(\text{In}_{0.05}\text{Pb}_{0.70}\text{Cu}_{0.25})\text{(Ca}_{0.5}\text{Y}_{0.5})\text{Sr}_{2}\text{Cu}_2\text{O}_8$ and that it is isostructural with the $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{(Ca}_{0.8}\text{Y}_{0.2})\text{Sr}_{2}\text{Cu}_2\text{O}_8$ system. This thallium-based TlCaBa$_2$Cu$_2$O$_y$-type structure can be described in terms of an intergrowth of double rocksalt-type layers $(\text{TI}/...$
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Pb]O(SrO)] with double [Sr(Ca, Y)Cu2O4] oxygen deficient perovskite layers, formed by sheets of corner-sharing CuO4 pyramids interleaved with calcium and/or yttrium ions. The structure of (T1,Pb)O layers in (Ca0.5Y0.5)Sr2CuO4 resembles that of YBa2Cu3O7-δ: the (T1,Pb)-O layers replacing the Cu-O chains, Sr atoms replacing Ba atoms and Ca atoms partially substituting for the Y atoms. However, it is important to note that the replacement of Cu-O chains in YBa2Cu3O7-δ by (T1,Pb)-O layers in (T1,Pb)-O layers in (Ca0.5Y0.5)Sr2CuO4 branches a major change in the electronic structure. It is well known that both (T1,Pb)-O planes and Cu-O chains play a crucial role as a “hole reservoir” for the copper oxide system. We propose that the (In, Pb, Cu)-O layers in the chemical composition (In0.05Pb0.70Cu0.25)(Ca0.5Y0.5)Sr2CuO4 compound will also be important in controlling the copper valence and superconductivity. Subramanian et al.[2] and Lee et al.[12] have reported a semiconducting phase with the chemical composition of (Pb0.25Cu0.75)(Ca0.15Y0.85)Sr2CuO4 which has the P4/mmm space group and unit cell dimensions of a = 3.818 Å, c = 11.820 Å and V = 172.4 Å3. This compound contains a (Pb,Cu)-O layer which is comparable to the (In,Pb,Cu)-O layer in the (In0.05Pb0.70Cu0.25)(Ca0.5Y0.5)Sr2CuO4 superconductor. For the (In1-Pb) (Ca0.88Y0.2)(Ca0.88Y0.2)Sr2CuO4 system synthesized at 950 °C, we find semiconducting behavior down to 4 K for x = 1, and superconducting behavior for 0.9 ≤ x ≤ 0.4 with Tc ranging from 45 K (x = 0.9) to 20 K (x = 0.4), and the maximum Tc (51 K) occurring at x = 0.7.[14] It should be noted that samples prepared with the same nominal compositions and firing conditions, but without the complete combination of indium, lead, calcium and yttrium, showed no evidence of superconductivity down to 10 K. Thus, the coexistence of indium, lead, calcium and yttrium ions in the sample is necessary for the appearance of superconductivity in the In-Pb-Ca-Y-Sr-Cu-O system.

Recently, Rouillon et al.[13, 14] reported a new superconductor, (Pb0.25Sr0.75) (Ca0.5Y0.5)Sr2Cu4Oy which exhibits a Tc (onset) = 100 K and Tc ranging from 45 K to 53 K. It should be noted that superconductivity in the (Pb0.25Sr0.75) (Ca0.5Y0.5)Sr2Cu4Oy material was correlated with the presence of the 6s2 lone pair on Pb2+; this ion effectively stabilizing oxygen vacancies in the material. Hence, the synthesis of this compound in an evacuated silica tube, in order to control the partial pressure of oxygen and therefore the PbO2/PbO ratio, is generally necessary. Our attempts to prepare (Pb0.25Sr0.75) (Ca0.5Y0.5)Sr2Cu4Oy in air or oxygen always produced semiconducting material. Therefore, the synthetic conditions (in oxygen) and the EDS analysis of the superconducting In-Pb-Ca-Y-Sr-Cu-O system lead us to conclude that the material responsible for superconductivity is not the (Pb0.25Sr0.75) (Ca0.5Y0.5)Sr2Cu4Oy phase.

In summary, we have synthesized a new superconducting phase with Tc (mid.) up to 65 K in the In-Pb-Ca-Y-Sr-Cu-O system. The structure of the superconducting phase with the chemical composition (In0.05Pb0.70Cu0.25) (Ca0.5Y0.5)Sr2CuO4 appears to be similar to that found in thallium-based materials.

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