Bulk new high-\( T_c \) superconductors in the (Pb,Cu)Sr\(_2\)(Ca,Y)Cu\(_2\)O\(_7\)\(_{-\delta}\) and (In,Pb,Cu)Sr\(_2\)(Ca,Y)Cu\(_2\)O\(_7\)\(_{-\delta}\) systems

R.S. Liu \(^a\), S.F. Hu \(^b\), I. Gameson \(^a\), S.D. Obertelli \(^a\), P.P. Edwards \(^a\), D.A. Jefferson \(^b\), T. Rouillon \(^c\), M. Hervieu \(^c\), C. Michel \(^c\), D. Groult \(^c\), J. Provost \(^c\) and B. Raveau \(^c\)

\(^a\) IRC in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK
\(^b\) Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
\(^c\) Laboratoire CRISMAT, ISMRA, Boulevard du Maréchal Juin, 14050 Caen, France

Bulk superconductivity was observed in the systems (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_7\)\(_{-\delta}\) and (In\(_y\)Pb\(_{0.75-y}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\). With decreasing \( x \) in (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_7\)\(_{-\delta}\), \( T_c \) increases up to 55 K at \( x=0.1 \); however this specimen is multiphasic with a superconducting Meissner volume fraction of ca. 1.5%. In contrast, the sample with \( x=0.5 \) is nearly single phase and has a lower \( T_c \) (45 K) and a high superconducting Meissner volume fraction ca. 20.2%. An increase of the indium doping in (In\(_y\)Pb\(_{0.75-y}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\), \( 0 < y < 0.2 \), results in an increase in the superconducting transition temperature from 45 K for \( y=0 \), to 60 K for \( y=0.2 \).

1. Introduction

The Pb-based 1212 phase, (Pb,Cu)Sr\(_2\)(Ca,Y)Cu\(_2\)O\(_7\), has been reported to be a non-superconductor \([1,2]\). The compound is isostructural with the TI-based 1212 phase, e.g., (TI,Pb)Sr\(_2\)(Ca,Y)Cu\(_2\)O\(_7\) \((T_c=110\) K\) \([3]\), but contains (Pb,Cu)O layers instead of (TI,Pb)O layers. Subsequently, Ono et al. \([4]\) observed superconductivity at 20 K in a liquid nitrogen-quenched bulk sample of (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\) and Bush et al. \([5]\) found superconductivity at 40 K in a single crystal with a chemical composition of (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\). Soon after, Maeda et al. \([6]\) pointed out that a sample having a nominal chemical composition of (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\) exhibits a superconductivity onset (as measured by resistivity) at 52 K, when the material was prepared in an oxidizing atmosphere and subsequently quenched into liquid nitrogen. Tang et al. \([7]\) and Maignan et al. \([8]\) have also reported that samples with nominal compositions (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\) and (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\) become superconducting below 67 and 42 K, when prepared under a high oxygen pressure of 100–200 bar and 40–60 bar, respectively. Moreover, bulk superconductivity \((T_c<80\) K\) was also observed in the (Pb\(_{0.3}\)Mo\(_{0.7}\)Sr\(_2\)(Ca\(_{1-y}\)Y\(_y\))Cu\(_2\)O\(_7\)\(_{-\delta}\) \((M=\text{Sr} \ [9] \) and Ca \[10]\). It is very interesting to note that the rocksalt-type layer in the Pb-based 1212 compound always contains Pb and Cu, or Sr or Ca or Ti. Here we report the results for a series based on the substitutional chemistry in the new high-\( T_c \) systems (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_7\)\(_{-\delta}\) and (In\(_y\)Pb\(_{0.75-y}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\).

2. Experimental

Details of sample preparation will be published elsewhere \([11,12]\). The powder X-ray diffraction (XRD) patterns of samples with nominal compositions (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)(Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_7\)\(_{-\delta}\) and (In\(_y\)Pb\(_{0.75-y}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\) were performed by a Philips PW1710 X-ray diffractometer. Nearly single-phase samples were found in the region of \( 0.5 \leq x \leq 1.0 \) and \( 0 \leq y \leq 0.2 \). Most of the lines from the XRD pattern of the monophasic samples can be fitted by using a space group of p4/mmm with a tetragonal unit cell with \( a \sim 3.8 \) Å and \( c \sim 11.8 \) Å. Compositions of individual microcrystals in the as-prepared specimens, (Pb\(_{0.75}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\) and (In\(_y\)Pb\(_{0.75-y}\)Cu\(_{0.25}\)Sr\(_2\)Ca\(_{0.5}\)Y\(_{0.5}\))Cu\(_2\)O\(_7\)\(_{-\delta}\), have been examined using energy dispersive X-ray spectrometry from a JEM-200CX electron microscope operating at 200 kV. Monophasic (Ti\(_3\)Pb\(_{0.3}\)Sr\(_2\)(Ca\(_{0.7}\)Y\(_{0.3}\))Cu\(_2\)O\(_7\) \([3]\) has been used as a standard material. Twenty particles in each sample were chosen for investigation. The majority phases in both
samples were determined to be \[ \left[ \text{Pb}_{0.75} \left( \text{Cu}_{0.25} \right) \right] \left[ \text{Sr}_{1.99(7)} \left( \text{Ca}_{0.49(1)} \text{Y}_{0.51(2)} \right) \right] \text{Cu}_{2} \text{O}_{7-\delta} \] and \[ \left[ \text{In}_{0.06(1)} \left( \text{Pb}_{0.69(1)} \text{Cu}_{0.25} \right) \right] \left[ \text{Sr}_{1.99(7)} \left( \text{Ca}_{0.47(1)} \text{Y}_{0.53(2)} \right) \right] \text{Cu}_{2} \text{O}_{7-\delta} \] respectively. Both compositions fit the 1212 phase very well.

Measurements of thermoelectric power were made by a steady state technique, employing a small reversible temperature gradient of between 0.4 and 1 K. The data have been corrected for the contribution of the gold measurement leads.

3. Results and discussion

The compound \( \left( \text{Pb}_{0.75} \text{Cu}_{0.25} \right) \text{Sr}_{2} \text{YCu}_{2} \text{O}_{7-\delta} \) is a semiconductor. The nominal Cu valency of this compound is \( 1.75^+ \) (Assuming \( \delta = 0 \)), which indicates a deficiency of hole carriers present in the conducting \( \text{CuO}_2 \) layers, which give rise to a so-called “underdoped” state. Such underdoping can be alleviated by stepwise substitution of \( \text{Y}^{3+} \) by \( \text{Ca}^{2+} \). Across the homogeneity range phase \( 0.5 \leq x \leq 1.0 \), a compositionally induced semiconductor-to-superconductor transition in the system of \( \left( \text{Pb}_{0.75} \text{Cu}_{0.25} \right) \text{Sr}_2(\text{Ca}_{1-x} \text{Y}_x)\text{Cu}_2\text{O}_{7-\delta} \) has been found at \( x = 0.7 \). At \( x = 0.5 \), \( T_c \) is 45 K (as defined from the onset of the diamagnetism) as shown in fig. 1.

The \( \left( \text{Pb}_{0.75} \text{Cu}_{0.25} \right) \text{Sr}_2(\text{Ca}_{0.5} \text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta} \) system will only tolerate ca. 50% substitution of \( \text{Ca}^{2+} \) into the \( \text{Y}^{3+} \) sites. This may present a natural (system-dependent) limit to increasing the hole concentration via this type of chemical substitution. Hence, partial substitution of the \( \text{In}^{3+} \) ions into the \( \text{Pb}^{4+} \) sites in the “hole reservoir” layers of \( \left( \text{Pb}_{0.75} \text{Cu}_{0.25} \right) \text{O} \) may be another possible route which would lead to an increase in the effective hole concentration in the \( \text{CuO}_2 \) layers. Within the single-phase region, \( 0 \leq y \leq 0.2 \), an increase in indium doping in \( \left( \text{In}_{y}\text{Pb}_{0.75-y} \text{Cu}_{0.25} \right) \text{Sr}_2(\text{Ca}_{0.5} \text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta} \) results in an increase in \( T_c \) from 45 K for \( y = 0 \) to 60 K (as defined from the onset of the diamagnetism) for \( y = 0.2 \) as shown in fig. 1.

The variation of thermoelectric power (TEP) with temperature of the system \( \left( \text{In}_{y}\text{Pb}_{0.75-y} \text{Cu}_{0.25} \right) \text{Sr}_2(\text{Ca}_{0.5} \text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta} \) for the nominal compositions \( y = 0 \) and \( y = 0.2 \) is shown in fig. 2. The magnitude of the TEP is large and nonmetallic, and typical of “underdoped” high-\( T_c \) oxides [13]. It can be seen that the effect of indium substitution is to decrease the magnitude of the TEP slightly (by \( \sim 4 \mu \text{V/K} \) at room temperature), while the temperature dependence remains unchanged, and \( T_c \) is increased from \( \sim 40 \) to \( \sim 60 \) K (as defined from the point

![Fig. 1. Phase diagram for the systems (Pb0.75Cu0.25)Sr2(Ca1–xYx)Cu2O7–δ and (In,Pb,Cu)Sr2(Ca,Y)Cu2O7–δ.](image-url)
Fig. 2. Thermoelectric power vs. temperature of the system (In,Pb)$_{0.75-y}$Sr$_{2}$Ca$_{0.5}$Y$_{0.5}$Cu$_{2}$O$_{7-\delta}$ for the nominal compositions $y=0$ and $y=0.2$.

where the TEP falls to zero). This is consistent with a picture where the substitution of indium has marginally increased the hole concentration in the CuO$_2$ planes. Interestingly, the TEP of the equivalent (Tl,Pb)O layers system (Tl$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{0.5}$Y$_{0.5}$)Cu$_2$O$_{7-\delta}$ has a room temperature magnitude of $\sim$50 $\mu$V/K, though qualitatively the same temperature dependence. For the parent system (Tl$_{0.5}$Pb$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{7-\delta}$, we have shown that by varying the hole doping $x$, the thermopower magnitude changes monotonically from small negative values ($-4$ $\mu$V/K for $x=0$) up to large positive values ($\sim$400 $\mu$V/K for $x=1$) [14]; it is small and positive ($5$–$10$ $\mu$V/K) for the composition of maximum $T_c$ ($x=0.24$). This suggests that the magnitude of the TEP can in certain cases be a useful measure of carrier concentration in these oxide systems. In the present case, our data lead us to suggest that $T_c$ would be further enhanced if a higher level of hole doping could be introduced into the CuO$_2$ layers in this Pb-based 1212 system.

Acknowledgements

We would like to thank the Fellowship of Engineering, BICC, SERC and BP for support.

References