COMPLEXITY AND SIMPLICITY OF THE METAL-SUPERCONDUCTOR-INSULATOR TRANSITION IN THE 
(Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ} SYSTEM

R. S. LIU and P. P. EDWARDS

IRC in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.

The (Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ} system exhibits the highest superconducting transition temperature, \( T_c = 110 \) K, at \( x = 0.5 \) and \( y = 0.2 \), yet observed in the TIBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7-δ} (1212) structure type. This complex, six-blend combination of metallic elements which make up the material is, however, compensated by a relatively simple crystal structure, which bears many similarities to that of 90 K superconductor YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ}. Here, we report some of the important features of the cation-substitution chemistry of the title compound, drawing attention to fundamental changes in the electronic properties and the Metal-Superconductor-Insulator transition of the (Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ} system as Ti\textsuperscript{3+} and Ca\textsuperscript{2+} is replaced by Pb\textsuperscript{4+} and Y\textsuperscript{3+}, respectively. In addition, we also report preliminary results concerning the effects of the chemical substitution in the (Tl,Pb)O layers.

1. INTRODUCTION

The occurrence of superconductivity - possibly high temperature superconductivity - adjacent to a metal-insulator boundary is a characteristic feature of many new high-\( T_c \) superconducting copper oxide systems.\(^1\) The variation of chemical composition within a compound to adjust the optimum carrier concentration may play a crucial role in inducing, and controlling, high temperature superconductivity. In general, the "parent" compound in such systems is an antiferromagnetic insulator as a consequence of strong (on-site) Coulomb interactions. An increase in the hole concentration in the CuO\textsubscript{2} layers via chemical substitution can lead to the transition from insulator to superconductor. While the mechanism of the superconductivity in the cuprates system is not yet fully understood, it is of great interest to study a system having a Metal-Superconductor-Insulator transition. Here we demonstrate such "chemical" control of superconductivity in the system (Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ}, which exhibits a Metal-Superconductor-Insulator transition when Ti\textsuperscript{3+} and Ca\textsuperscript{2+} is replaced by Pb\textsuperscript{4+} and Y\textsuperscript{3+}, respectively. In addition we also report the effects of the substitution of hole reservoir layers, e.g. (Tl,Pb)O is replaced by (Tl,M)O (M= transition metal elements), (Pb,Cu) and (In,Pb,Cu)O.

2. EXPERIMENTAL

The detailed processes relating to the preparation of the series (Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ} are described in elsewhere.\(^2\) Based on X-ray and neutron diffraction studies, the structure of this system is similar to TIBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7-δ} having a p4/mmm space group (a=3.8Å and c=12 Å) with an intergrowth of double rock salt-type layers[ ([Tl/Pb]O)(SrO)] with double [Sr(Ca,Y)Cu\textsubscript{2}O\textsubscript{5}] oxygen-deficient perovskite layers formed by sheets of corner-sharing CuO\textsubscript{5} pyramids interleaved with calcium and/or yttrium ions. A schematic comparison of the structure of the title compound, and YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} is shown in Fig. 1.

Fig. 1 An idealized structural model for (Tl\textsubscript{1-x}Pb\textsubscript{x})Sr\textsubscript{2}(Ca\textsubscript{1-y}Y\textsubscript{y})Cu\textsubscript{2}O\textsubscript{7-δ} and YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ}.

3. RESULTS AND DISCUSSION

The compound TISr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7} is a metal having no superconductivity at temperatures down to 4 K.\(^4\) The nominal Cu valency of this compound is 2.5+, which...
indicates an excess of hole carriers present in the conducting CuO$_2$ layers, which give rise to a so-called "over-doped" state. Such over-doping can be reduced by stepwise substitution of Tl$^{3+}$ by Pb$^{4+}$, by substitution of Ca$^{2+}$ by Y$^{3+}$, or, indeed, both substitutions. Interestingly, a chemical compositional induced Metal-Superconductor-Insulator transition was observed$^2$ in the system (Tl$_{1-x}$Pb$_x$)$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.8}$ as shown in Fig. 2.

![Fig. 2. Metal-Superconductor-Insulator phase diagram for the system (Tl$_{1-x}$Pb$_x$)$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.8}$. (Ref. 2)](image)

Both the (Tl$_{1-x}$Pb$_x$)$_2$CaCu$_2$O$_{7.5}$ and TISr$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.8}$ systems have the highest $T_c$(zer0) of 78 K for $x=0.5$ or $y=0.6$. However, the (Tl$_{0.5}$Pb$_{0.5}$)$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.8}$ system has superconductivity over the homogeneity range $y=0$--0.5, with the superconducting transition temperature showing a maximum (108 K) at $y=0.2$. Across the homogeneity range $y=0.6$--1.0, the material undergoes a metal-semiconductor transition. We propose that substitution of Y$^{3+}$ for Ca$^{2+}$ in the system (Tl$_{1-x}$Pb$_x$)$_2$CaCu$_2$O$_{7.8}$ effectively reduces the hole concentration in the CuO$_2$ sheets. We have some support for this suggestion. With increasing concentration of Y$^{3+}$ in the Ca$^{2+}$ sites, the following effects have been observed: (1) an increase in the room temperature resistivity, (2) a decrease in the number of carriers per unit cell, (3) the sign of the thermopower changing from negative to positive at the maximum $T_c$, (4) an increase of the a lattice constant across the series which is attributed to a decrease in the average copper oxidation state, leading to longer Cu-O distances within the copper oxygen plane.

Hybertsen and Mattheiss$^5$ have suggested on the basis of band structure calculations that the TlO sheets may act as a hole reservoir providing mobile hole carriers to the coupled CuO$_2$ layers in the Tl-based material. Thus, a chemical modification of the (Tl,Pb)O layers is expected to affect the superconducting properties of this material. The substitutional chemistry of the hole reservoir (Tl,Pb)O layers in (Tl$_{1-x}$Pb$_x$)$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.8}$ is rich and varied (Table 1). For example, the (Pb$_{0.75}$Cu$_{0.25}$)$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{7.5}$ system will only tolerate ca. 50% substitution of Ca$^{2+}$ into the Y$^{3+}$ sites. This may be the reason that the Pb-based material has a natural limit to increase its hole concentration. However, replacement of the IVA and VA elements for Pb do not decrease $T_c$ greatly. There may yet be scope for other chemical substitutions into the hole reservoir layer in this system.

### Table 1. Examples of the replacement of the (Tl,Pb)O layers in (Tl$_{1-x}$Pb$_x$)$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{7.5}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Tl$<em>{0.8}$V$</em>{0.2}$)$<em>2$(Ca$</em>{0.8}$Y$_{0.2}$)Cu$<em>2$O$</em>{1.5}$</td>
<td>100 K</td>
<td>6</td>
</tr>
<tr>
<td>(Pb$<em>{0.75}$Cu$</em>{0.25}$)$<em>2$(Ca$</em>{0.8}$Y$_{0.2}$)Cu$<em>2$O$</em>{7.5}$</td>
<td>45 K</td>
<td>7</td>
</tr>
<tr>
<td>(In$<em>{0.2}$Pb$</em>{0.8}$)$<em>2$(Ca$</em>{0.8}$Y$_{0.2}$)Cu$<em>2$O$</em>{7.5}$</td>
<td>60 K</td>
<td>8</td>
</tr>
</tbody>
</table>

*"V" can be also replaced by IVA and VA elements.

ACKNOWLEDGEMENTS

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

REFERENCES