An enhancement of $T_c$, from 45 K to 70 K, via Cd substitution in (Pb, Cu)Sr$_2$(Ca, Y)Cu$_2$O$_{7-d}$

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An enhancement in the superconducting transition temperature, $T_c$, from 45 K to 70 K, has been discovered during the course of our investigation of Cd-doping of the Pb-based 1212 superconductors. Specifically, we have attempted to synthesize a material with nominal composition (Pb$_{0.6}$Cd$_{0.2}$)Sr$_2$(Ca$_{0.4}$Y$_{0.6}$)Cu$_2$O$_{7-d}$ derived from the lead cuprate superconductor (Pb$_{0.7}$Cu$_{0.3}$)Sr$_2$(Ca$_{0.5}$Y$_{0.5}$)Cu$_2$O$_{7-d}$. From X-ray and electron diffraction, coupled with energy-dispersive X-ray spectrometry, we can identify the phase responsible for the 70 K superconductivity to be (Pb$_{0.67}$Cd$_{0.33}$)Sr$_2$(Ca$_{0.4}$Y$_{0.6}$)Cu$_2$O$_{7-d}$. Thus, we propose substitution of Cd both for Cu, in the rock salt-type (Pb, Cu)O layers, and Ca, in the Ca$_{0.4}$Y$_{0.6}$ lattice sites. No superlattice spots or streaks were observed in the electron diffraction experiments along the $a^*$, $b^*$ and $c^*$ directions in the Cd-substituted material.

1. Introduction

The discovery of high-temperature superconductivity in La-Ba-Cu-O [1], Y-Ba-Cu-O [2], Bi-Sr-Ca-Cu-O [3,4] and Tl-Ba-Ca-Cu-O [5,6] systems has stimulated intense interest in the substitutional chemistry of both superconducting and non-superconducting cuprate materials. Cadmium, the Cd$^{2+}$ ion, is particularly interesting for investigation since its intrinsic chemical reactivity, ionic size and position in the periodic table do not allow one, a priori, to predict its substitutional chemistry. For example, the ionic radius of Cd$^{2+}$ is 1.10 Å (CN = 8), similar to both Ca$^{2+}$ (1.12 Å, CN = 8) and Y$^{3+}$ (1.019 Å, CN = 8) [7]. Andreas et al. [8] propose that ~30 mol.% Cd can substitute for Y in (Y$_{1-x}$Cd$_x$)Ba$_2$Cu$_3$O$_{7-d}$; here $T_c$ remains unchanged for $x \approx 0.3-0.6$. These same workers find an increase in the $a$ and $c$ lattice constants, which they attribute to the effects of the slightly larger ionic radius of Cd$^{2+}$, as compared to that of Y$^{3+}$. Niu et al. [9] have also reported the substitution of cadmium for lanthanum in La$_2$CuO$_4$. The substitution of the A-site cation La$^{3+}$, having a radius 1.216 Å (CN = 9) [7] also illustrates the ability of Cd$^{2+}$ to substitute in ionic sites having larger characteristic radii. The enhancement of $T_c$ (from 80 K to 100 K) has been reported for the incorporation of Cd into the Bi-Sr-Ca-Cu-O phase [10,11]. Parise et al. [12] have investigated (Tl$_{1.5}$Cd$_{0.5}$)Ba$_2$CuO$_{6+d}$ and, from a variety of structural investigations, have confirmed that Ca$^{2+}$ substitutes exclusively within the rock salt-type layers incorporating Tl$^{3+}$. Finally, a detrimental effect on $T_c$ was observed with CdTi$_2$BaCuO$_{4.5}$ [13] and Tl$_2$Cd$_{0.2}$Ba$_2$Cu$_2$O$_y$ [14]. Given the ubiquity of Cd$^{2+}$ ion substitution in this range of systems, we have investigated its substitutional chemistry in the Pb-based 1212 cuprate materials, which possess a range of (potential) substitution sites, encompassing pre-transition elements (Ca and Sr), a transition element (Cu) and post-transition elements (Y and Pb). Superconductivity up to 90 K in this structure was discovered for the first time for the cuprates (Pb$_{0.5}$Sr$_{0.5}$)Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{7-d}$.
The replacement of strontium by calcium allowed one also to obtain superconductivity in the phase (Pb, Ca)Sr2(Ca, Y)Cu2O7−δ with a lower value of $T_c$ close to 80 K [17]. Following the discovery of the nonsuperconducting Pb-based 1212 cuprate, (Pb, Cu)Sr2(Ca, Y)Cu2O7−δ [18,19], investigations involving a careful heat-treatment (via high-temperature quenching [20–23] and high-pressure oxygen annealing [24,25]) and optimization of the Ca2+ and Y3+ ratio [26] have served to induce superconductivity. The 1212 compound (Pb, Cu)Sr2(Ca, Y)Cu2O7 has a P4/mmm space group (a ≈ 3.8 Å and c ≈ 11.8 Å) and the structure is characterized by an intergrowth of double rock salt-type layers ((Pb, Cu)O(SrO)) with double (Sr(Ca, Y)Cu2O4) oxygen-deficient perovskite layers formed by sheets of corner-sharing CuO4 pyramids interleaved with calcium and yttrium ions. We have previously reported that In3+ doping into the Pb4+ sites in (In,Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7−δ results in an increase in $T_c$ from 45 K for $x=0$ to 60 K for $x=0.2$ [27].

Here we demonstrate that the substitution of Cd2+ into the phase (Pb, Cu)Sr2(Ca, Y)Cu2O7−δ can increase the superconducting temperature significantly, from 45 K to 70 K.

2. Experimental

Samples with the nominal compositions of (Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7 and (Pb0.3Cd0.7)Sr2(Ca0.5Y0.5)Cu2O7 were prepared by mixing the oxides PbO/CdO, SrO2, Sr2CuO3, CaO, Y2O3 and CuO in the appropriate molar ratios. The mixtures were intimately ground in an agate mortar and pressed under 1 ton/cm2 in the form of bars of dimensions 12×2×2 mm3. The bars were placed in alumina crucibles and heated in evacuated quartz tubes at 880°C for 12 h. The samples were then quenched to room temperature. The as-synthesized (Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7 sample was a semiconductor. However, the as-synthesized (Pb0.3Cd0.7)Sr2(Ca0.5Y0.5)Cu2O7 sample was superconducting below 20 K and exhibited a semiconducting behaviour in the normal state. Both samples were then wrapped in Au foil, returned to the furnace and annealed at 970°C for 3 h in oxygen. Subsequently, the furnace was cooled down to room temperature by a cooling rate of 2°C/min. After this annealing, superconductivity was induced in (Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7 and enhanced in (Pb0.3Cd0.7)Sr2(Ca0.5Y0.5)Cu2O7.

X-ray diffraction (XRD) analysis was performed using an Inel counter and Philips diffractometer, with Cu Kα radiation. The chemical compositions of individual microcrystallites of the specimens were examined by energy-dispersive X-ray spectrometry (EDS) using a JEOL-2100 electron microscope operating at 200 kV. Gold specimen grids were used and background spectra were recorded to ensure that no copper signals were detected from the sample-free area. The (Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7−δ compound [26] has been used as a standard material. Electron diffraction patterns of the sample were obtained from the same electron microscope as that used for EDS. A standard four-point-probe was used to measure the electrical resistivity of the samples. The electrical contacts to the sample were made by fine copper wires with a conductive silver paint; the applied current was 1 mA. The temperature was recorded using a calibrated silicon diode sensor located close to the sample. A Lake Shore 7000 AC susceptometer with a frequency of 333.3 Hz and an applied magnetic field of 1 Oe was used to measure the susceptibility.

3. Results and discussion

In fig. 1 we show the powder XRD pattern of the sample with nominal composition of (Pb0.7Cd0.3)Sr2(Ca0.5Y0.5)Cu2O7−δ. The majority of lines from the XRD pattern can be fitted using a space group of P4/mmm with tetragonal unit cell of $a=3.8195(2)$ Å and $c=11.9543(1)$ Å except for a small amount of unidentified impurity phase (marked by “•” in fig. 1). A detailed comparison of the XRD pattern of (Pb0.7Cd0.3)Sr2(Ca0.5Y0.5)Cu2O7−δ with that of (Pb0.7Cu0.3)Sr2(Ca0.5Y0.5)Cu2O7−δ revealed that an expansion of ±0.8% in the $c$ lattice parameter for the Cd-substituted sample occurred. This effect may arise because of the larger Cd2+ (0.95 Å, CN = 6) [7] ion substitution into the Cu2+ (0.73 Å, CN = 6)
Fig. 1. Powder XRD pattern of the sample with nominal composition of \((\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\). A small amount of unidentified impurity phase was marked by ‘*’.

[7] sites in the rock salt-type \((\text{Pb}, \text{Cu})\text{O}\) layers. On the other hand, if the \(\text{Cd}^{2+}\) ions are substituted into the \(\text{Ca}^{2+}\) sites, one would anticipate a slight decrease in the \(c\) lattice constant due to the presence of the \(\text{Cd}^{2+}\) (1.10 Å) ions in place of the \(\text{Ca}^{2+}\) (1.12 Å) ions. However, the difference between the sizes of the \(\text{Cd}^{2+}\) and \(\text{Ca}^{2+}\) ions is much less than the difference between the \(\text{Cd}^{2+}\) and \(\text{Cu}^{2+}\) ions. Therefore, even if EDS results (see below) reveal that \(\text{Cd}\) substituted for both \(\text{Cu}\) and \(\text{Ca}\), we would expect that the effect of \(\text{Cd}\) substitution for \(\text{Cu}\) would predominate and an increase in the \(c\) lattice parameter would be observed. Moreover, a small (\(<0.1\%\)) decrease in the \(a\) lattice parameter in the \(\text{Cd}\)-substituted sample was found. We propose that this contraction in the \(a\) lattice constant can be attributed to an increase in the average copper oxidation state, leading to a shorter \(\text{Cu}â€“\text{O}\) distance in the superconducting \(\text{CuO}_2\) sheets (see later).

For chemical analysis, the compositions of twenty individual microanalyses in the specimens with nominal compositions \((\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\) and \((\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\) were determined by EDS. These yielded experimental \(\text{Pb}/\text{Cu}\), \(\text{Sr}/\text{Cu}\), \(\text{Ca}/\text{Cu}\) and \(\text{Y}/\text{Cu}\) ratios. Comparison with the values from the standard compound \((\text{Pb}_{0.75}\text{Cu}_{0.25})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\) then allowed the former to be converted to true values. As no standard compound containing \(\text{Cd}\) was available, the \(\text{Cd}/\text{Cu}\) ratio could not be determined.

For the sample with nominal composition \((\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\), this procedure, coupled with the requirement that \(N_{\text{Cu}} + N_{\text{Pb}} = 3\), where \(N_{\text{Cu}}\) and \(N_{\text{Pb}}\) are the numbers of copper and lead atoms in the formula unit, lead to an experimental composition of \((\text{Pb}_{0.70(2)}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.50(6)}\text{Y}_{0.50(3)})\text{Cu}_2\text{O}_{7-\delta}\). A typical EDS spectrum from this phase is shown in fig. 2(a). For the sample with nominal composition \((\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}\) certain assumptions were necessary before the data could be interpreted. The first of these was that the X-ray emission of the \(\text{Cd}\) lines did not affect the measurement of the \(\text{Ca} \text{K}\alpha\) line. As may be seen in a typical EDS spectrum of this compound (fig. 2(b)), these lines are adjacent, and overlap of \(\text{Ca} \text{K}\alpha\) and \(\text{Cd} \text{L}\beta\) is a possibility. However, comparison of the relative intensities of \(\text{Ca} \text{K}\alpha\) and \(\text{Ca} \text{K}\beta\) lines between fig. 2(a), where no \(\text{Cd}\) is present, and fig. 2(b), indicates little significant difference, owing to the very low intensity of the \(\text{Cd} \text{L}\gamma\) line, and hence, within the limits of experimental error this assumption was justified.
The second assumption was that no chemical substitution occurred in the copper-oxygen sheets, implying a minimum value for $N_{Cu}$ of 2. The justification for this was that substitution of Cd for Cu in the (Pb, Cu) sites produced an increase in $T_c$. In all previous cases where substitution of copper in the Cu–O sheets is proven a corresponding decrease in $T_c$ is found. Given this assumption, a trial stoichiometry can be evaluated using $N_{Cu}$=2; this was $(Pb_{0.67(2)}Cd_{0.33(5)})Sr_{2.1(1)}(Cd_{0.20(3)}Ca_{0.33(3)}Y_{0.48(4)})Cu_{2}O_{7-\delta}$. An increase of $N_{Cu}$ much above 2 necessitated a corresponding increase in the numbers of all other elements. This will be the cause of an increase in the number of strontium atoms, and these must be accommodated in the rock salt layer. However, the additional copper atoms must also be placed in this layer, and consequently there will be excess atoms for this layer. Therefore, the total number of copper atoms present cannot exceed 2.

In fig. 3 we show (a) the [001] and (b) the [010] electron diffraction patterns of the $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ sample. The space group and lattice constants deduced from both patterns are consistent with the XRD results. Moreover, neither a superlattice nor streaks along the $a^*$, $b^*$ and $c^*$ directions were observed in the $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ sample, which is unlike the well-known Pb-based material which exhibits satellite diffraction maxima along both these directions [15,17]. One possible reason for this absence is that the larger Cd$^{2+}$ ions prefer to remain in the rock salt-type layers, coexisting with Pb$^{4+}$ ions. However, the Cu$^{2+}$ ions in (Pb, Cu)O layers of the Pb-based 1212 materials prefer perovskite-type sites, in association with rock salt-type-like Pb$^{4+}$ ions. This type of combination (perhaps incompatible) would cause a disordering of the oxygen ions within the (Pb, Cu)O layers, and could result in a superstructure which could be detected by electron diffraction. Therefore, the absence of any superstructure in the Cd-substitution sample demonstrates that the structural stability of the Pb-based materials can be improved via Cd doping.

In fig. 4 we show the temperature dependence of the normalized electrical resistance of the (a) $(Pb_{0.7}Cu_{0.3})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ and (b) $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ samples. Both samples, $(Pb_{0.7}Cu_{0.3})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ and $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$, exhibit metallic behaviour in their normal states and have room temperature resistivities of 27.8 and 14.6 m$\Omega$ cm, respectively. The $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$

![Fig. 3. The (a) [001] and (b) [010] electron diffraction patterns of the $(Pb_{0.5}Cd_{0.5})Sr_{2}(Ca_{0.5}Y_{0.5})Cu_{2}O_{7-\delta}$ (nominal) sample.](image-url)
sample has superconducting transition temperatures of $T_c^{\text{onset}} = 78$ K, $T_c^{\text{midpoint}} = 65$ K and $T_c^{\text{zero}} = 58$ K which are higher than the corresponding $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ sample ($T_c^{\text{onset}} = 55$ K, $T_c^{\text{midpoint}} = 40$ K and $T_c^{\text{zero}} = 34$ K).

In fig. 5 we show the temperature dependence of the susceptibility of the (a) $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ and (b) $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ samples. The onset of diamagnetism, $T_c^{\text{mag}}$, appears at temperatures of 45 K and 70 K for $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ and (b) $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ samples, respectively. We estimate the superconducting (Meissner) volume fraction to be more than 50% at 5 K for those two samples which indicates that bulk superconductivity exists.

Both the electrical resistivity (fig. 4) and magnetic susceptibility (fig. 5) measurements confirmed that the $T_c$ can be effectively increased from 45 K in $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ to 70 K in $(\text{Pb}_{0.7}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$. The precise origin for this large enhancement in $T_c$ via Cd-doping is still unclear. However, both the slope of the temperature dependence of the electrical resistivity in the normal state (fig. 4) and the absolute values of room temperature resistivity revealed that the $(\text{Pb}_{0.7}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ material has an enhanced metallic behaviour and lower room temperature resistivity than those of $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$. One possibility, therefore, is that the $(\text{Pb}_{0.7}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ sample has a higher hole concentration than the $(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ sample, resulting in the higher $T_c$ for the Cd-substituted sample.

Further support for this suggestion arises from the observed contraction in the $a$ lattice parameter, implying a shorter Cu-O bond distance in a Cd-substituted sample which may be attributed to the removal of an antibonding electron from the $\sigma_{x^2-y^2}$ band; this gives rise to an increase in the hole concentration within the CuO$_2$ sheets. Moreover, the oxygen content and cation ratio (e.g. Ca/Y or Ca/Sr) in the Cd-substituted Pb-based 1212 compound may also have a strong influence on the superconductivity. More details of the crystal structure, the effects of oxygen content and cation ratio, and physical properties will shed further light on this discovery.

In summary, we have demonstrated that the substitution of Cd in the phase (Pb, Cu)Sr$_2$(Ca, Y)Cu$_2$O$_{7-\delta}$ can lead to an increase in $T_c$ from 45 K to 70 K.

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