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Crystallographic evolution and superconductivity in the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ system ($0 \leq x \leq 1.85$)

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Abstract

In our comprehensive crystallographic investigation of the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ system ($0 \leq x \leq 1.85$), we observe the structural phase evolution $T \rightarrow T+T' \rightarrow T'$ with increasing Pr substitution. In the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ system, the suppression of the superconductivity is not related to the interaction of the Pr ions with the O ions in the CuO_2 plane which leads to the localization of hole carriers. It is the removal of apical oxygen from the (La, Pr)–O plane that is responsible for the suppression of the superconductivity.

1. Introduction

The 2:1:4 cuprate superconductors are known to crystallize with three structures: the K_2NiF_4 -type, the RE_2CuO_4 -type ($\text{RE} = \text{Pr}, \text{Nd}, \text{Sm}$), and the $(\text{RE}, \text{Sr}, \text{Ce})_2\text{CuO}_4$ -type [1, 2] structures. For brevity they will be referred to as the T, T', and T* phases, respectively.

Since it was reported that Pr_2CuO_4 doped with Ce is an electron-doped metal that becomes a superconductor, there has been considerable interest in this and related materials [3]. $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ has the T' structure which is closely related to the T structure found in hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductors. A remarkable difference between the above-mentioned phases is as regards whether there is apical oxygen above or below the copper site. Müller has reminded us that the apical oxygen of the CuO_6 octahedron plays an important role in the superconductivity in high- T_c superconductors [4]. Many experimental results suggest that in $\text{Y}(\text{Pr})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, Pr ions interact with the in-plane oxygen, which leads to localization of holes in the CuO_2 plane. Thus, light Pr doping results in strong suppression of the superconductivity in p-type superconductors [5–7]. It seems that in p-type $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductors too, light Pr doping would suppress the superconductivity. In this paper we perform a comprehensive crystallographic study of the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ ($0 \leq x \leq 1.85$) system and find the structural evolution $T \rightarrow T+T' \rightarrow T'$ phase with increasing Pr substitution.

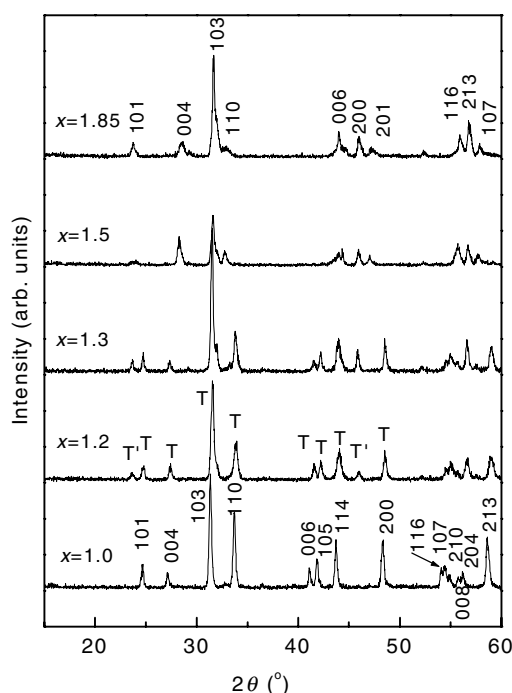


Figure 1. Powder XRD patterns of polycrystalline samples of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ ($1.0 \leq x \leq 1.85$).

A similar phase transition has been found in the $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ system and the $\text{Na}_{2-x}\text{Sr}_x\text{CuO}_4$ system [8, 9]. We also investigated the transport properties and the superconductivity of this compound. We consider the suppression of superconductivity as being a result of the removal of apical oxygen and the structural phase transition.

2. Experiments

Polycrystalline samples of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ ($0 \leq x \leq 1.85$) were prepared by means of a conventional solid-state reaction method using high-purity powders of La_2O_3 , Pr_6O_{11} , SrCO_3 , and CuO . The mixed powders, pressed into pellets, were then reacted at 1150–1200 °C for 48 h under oxygen.

X-ray diffraction (XRD) analysis was carried out by a Rigaku-D/max- γ A diffractometer using high-intensity $\text{Cu K}\alpha$ radiation to screen for the presence of an impurity phase and the changes in structure. The lattice parameters were determined from the d -values of the XRD peaks by a standard least-squares refinement method. The measurements of infrared (IR) transmission spectra (Nicolet 700) were carried out at room temperature with powder samples in which KBr is used as a carrier. The resistivity was measured using a standard four-probe method in a closed-cycle helium cryostat.

3. Results and discussion

Figure 1 shows a section of the x-ray powder diffraction in the 2θ range between 15° and 60°. The analysis of the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ ($0 \leq x \leq 1.85$) compounds by means of x-ray powder diffraction reveals the existence of three domains:

Table 1. Unit-cell parameters of samples of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$, obtained by Rietveld analysis of the XRD patterns.

x	Phase	a (Å)	c (Å)
0	T	3.771	13.241
0.1	T	3.764	13.240
0.5	T	3.746	13.012
1.0	T	3.718	12.763
1.2	T	3.710	12.746
	T'	3.925	12.292
1.3	T	3.706	12.741
	T'	3.925	12.286
1.5	T'	3.925	12.286
1.85	T'	3.925	12.282

- (i) For $0 \leq x \leq 1.0$ a single phase is obtained and the corresponding powder pattern is fully indexed using a T-type cell. All the diffraction peaks can be assigned to T-type structures.
- (ii) For $1.2 \leq x \leq 1.3$ a mixture of T phase and T' phase is obtained.
- (iii) For $x \geq 1.5$ there is mainly T' phase, because of the higher praseodymium concentration.

The diffraction peaks for the $x = 1.85$ sample correspond to T'-type structure.

The unit-cell parameters of the samples of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ obtained by Rietveld analysis of the experimental XRD patterns are summarized in table 1. In the composition range $0 \leq x \leq 1.0$, the unit-cell parameters a and c decrease linearly with increasing praseodymium content. Such behaviour is in agreement with the effects of replacement of lanthanum ions ($r(\text{La}^{3+}) = 1.06$ Å) by smaller praseodymium ions ($r(\text{Pr}^{3+}) = 1.03$ and $r(\text{Pr}^{4+}) = 0.90$ Å). The substitution does not induce any structural transition at room temperature at doping contents in the range $0 \leq x \leq 1.0$. This is dissimilar to the results for other $\text{La}_{2-x-y}\text{RE}_x\text{Sr}_y\text{CuO}_4$ systems (RE = rare earth), where there is an increase in the bond length mismatch between the CuO_2 layers and the (La, RE, Sr)O layers when La^{3+} ions are replaced by smaller RE^{3+} ions [10, 11]. Pr^{4+} ions are smaller than La^{3+} ions, while $r(\text{Pr}^{3+})$ is similar to $r(\text{La}^{3+})$. Since doping with smaller Pr^{4+} ions would lead to lattice mismatch and valence mismatch, we suggest that praseodymium substitutes for lanthanum at the valence of +3. This valence is consistent with that in the Pr_2CuO_4 system. For the range $1.2 \leq x \leq 1.3$, there is a mixture of T phase and T' phase. This can be considered as coexistence of two compounds, $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ and Pr_2CuO_4 . The existence of the CuO_4 planes would be responsible for the superstructure of the T'-type compound. When $x \geq 1.5$, there is mainly T' phase while a little T phase is still present. For the $x = 1.85$ sample in particular, where the nominal component is $\text{Pr}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, doping with bivalent Sr ions leads to the appearance of a T phase. This indicates that it is hard to dope holes into the Pr_2CuO_4 system. Thus, even when lanthanum is completely replaced by praseodymium, a pure T'-phase sample cannot be obtained. Similar results can be obtained for Sm or Nd doping of systems [8, 12]. Mombrú *et al* [8] have studied the T–T' transition in the $\text{La}_{2-x}\text{Nd}_x\text{CuO}_4$ system in which there is competition between lanthanide and copper ions for bonding with apical oxide in La_2CuO_4 . In the T' phase the Cu–O bond length elongates with respect to the equatorial Cu–O one in the T phase, and the RE–O (RE = Nd, Pr, etc) bond lengths are shorter than the La–O ones. This evidence suggests that the RE–O layer is the primary driving force in this T–T' transition.

In order to explore further the doping effects of praseodymium, vibration modes of the CuO_6 octahedron (CuO_5 pyramid and CuO_4 plane) have been investigated by means of IR absorption measurements, because the vibration modes are effective in reflecting the changes

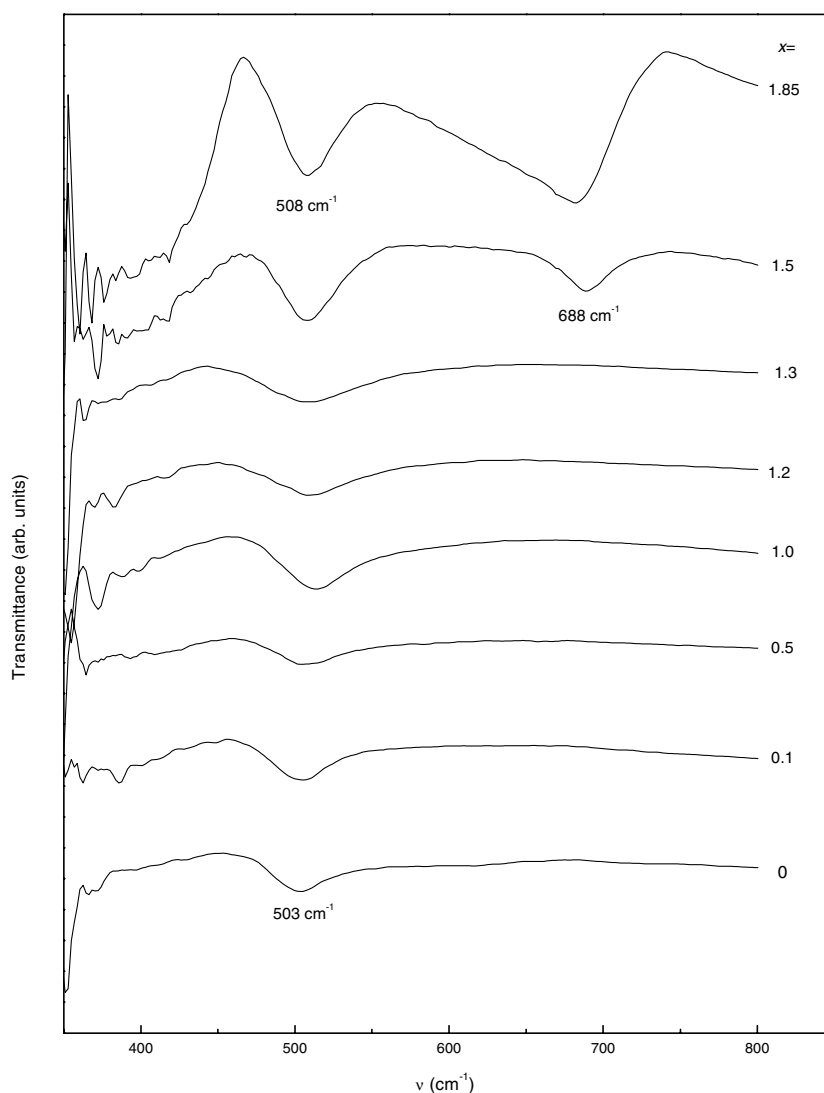


Figure 2. IR transmission spectra of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ samples.

of structure and other properties induced by Pr doping. Figure 2 shows the IR transmission spectra of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ samples. In these samples, an IR transmission peak ν_1 located at 503 cm^{-1} can be clearly observed within the frequency range of $350\text{--}800\text{ cm}^{-1}$. The IR measurement results confirm that these samples are crystallized in the K_2NiF_4 tetragonal symmetry phase. Henn and co-workers [13, 14] have studied the IR-active modes with D_{4h} symmetries A_{2u} and E_u ($B_{2u} + B_{3u}$) in the tetragonal La–Cu–O system. Using the assignment of the IR modes made by them, the ν_1 band corresponds to the E_u stretching mode of in-plane O–Cu bond along a axis. For samples with $x < 1.5$, only the ν_1 line is present, while for samples with $x \geq 1.5$, another peak, ν_2 , located at about 688 cm^{-1} appears. It seems that this peak is related to the appearance of T' phase. However, this line cannot be observed for $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ systems [15], while it was observed by Napolitano *et al* [16] for the La–Sr–Cu–O system. This

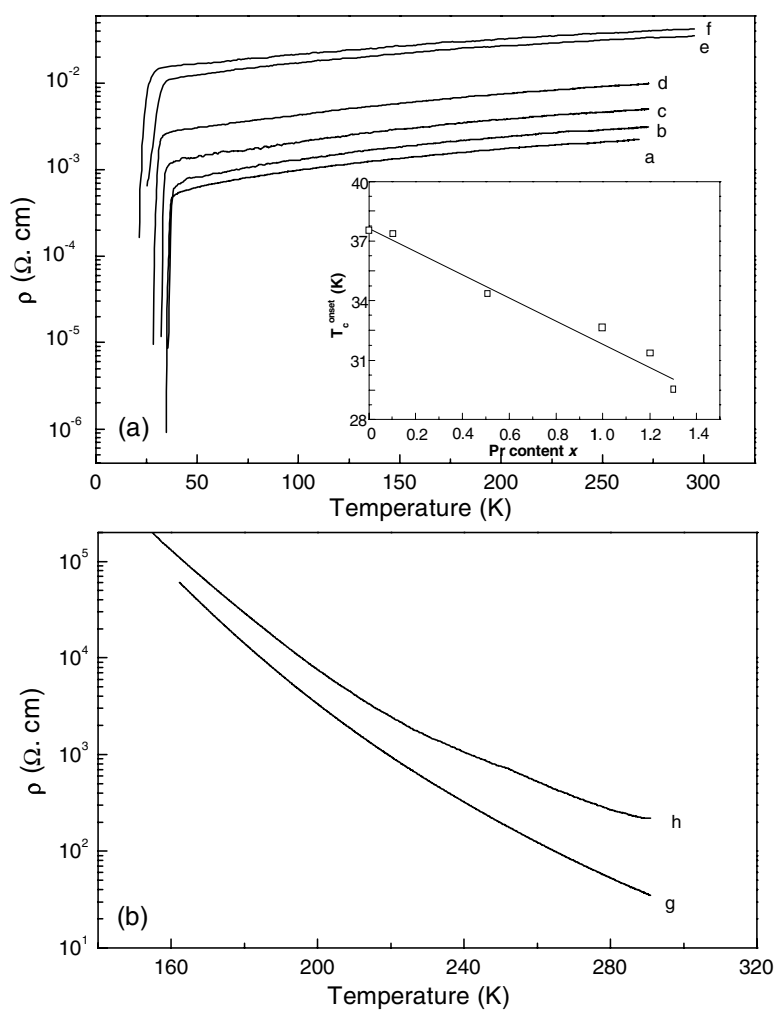


Figure 3. The temperature dependence of the resistivity for samples of $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$: (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.5$; (d) $x = 1.0$; (e) $x = 1.2$; (f) $x = 1.3$; (g) $x = 1.5$; (h) $x = 1.85$.

mode should be assigned to another component in the structure for the in-plane O–Cu breathing mode. In La-based systems, the conclusion that there is electron–phonon interaction suggests that the emergence of the ν_2 peak is associated with the metal–insulator transition [17]. The resistivity measurement results confirm this suggestion for $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ compounds.

The temperature dependence of the electrical resistivity for these samples is given in figure 3. A remarkable phenomenon is that superconductivity is exhibited by both the single-T-phase samples and the two-phase (T and T') samples even when the doping content is increased to $x = 1.3$. The T_c -value gradually decreases from 37.6 K ($x = 0$) to 29.1 K ($x = 1.3$), while at higher doping levels, when the T' phase is present, the superconductivity is suppressed and the resistivity at room temperature is about three orders of magnitude larger than the resistivity in superconducting samples.

Samples with $x \leq 1.3$ show metallic behaviour over the whole temperature range and exhibit a superconducting transition. The T_c^{onset} -values of the samples are given in figure 3(a). The T_c -value decreases gradually with increasing praseodymium doping. And the room temperature resistivity gradually increases with increasing Pr doping from $2 \times 10^{-3} \Omega \text{ cm}$ ($x = 0$) to $3 \times 10^{-2} \Omega \text{ cm}$ ($x = 1.3$), while when the Pr doping content increases from $x = 1.3$ to 1.5, the room temperature resistivity sharply increases by up to three orders of magnitude and the metal–insulator transition occurs. The resistivity for the samples with $x = 1.5$ and 1.85 increases sharply with decrease in temperature (see figure 3(b)).

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor, light Pr doping at the Y site leads to strong suppression of superconductivity due to the interaction of Pr ions with in-plane oxygen ions, which leads to the localization of holes in the CuO_2 plane [3–5]; while in $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ samples, the exhibiting of superconductivity for the doping region $0 \leq x \leq 1.3$ indicates that the interaction of Pr ions with in-plane oxygen is not a significant factor in the suppression of the superconductivity. The suppression of the superconductivity in samples with $x \geq 1.5$ is related to the change in structure.

A remarkable difference among the three phases of 2:1:4 cuprates concerns the CuO_2 plane and the adjacent carrier-reservoir layer: according to whether there is apical oxygen above or below the Cu site or not, there can be CuO_6 octahedra, CuO_5 pyramids, and CuO_4 planes in the bodies of T, T*, and T' phases. We know that the so-called carrier-reservoir layer provides hole carriers to the CuO_2 conductivity layer in p-type superconductors. Thus the apical oxygen would play an important role in the superconductivity. In addition, there are some reports that T_c^{onset} rises under high pressure in materials with octahedron or pyramid structure, while T_c^{onset} does not depend on the pressure at all in the Nd–Ce–Cu–O compound where is no apical oxygen [18]. These reports also indicate the important role of the apical oxygen in p-type superconductors.

In $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ systems, there exist CuO_6 octahedra and CuO_4 planes at various doping contents. Samples with $x \leq 1.0$ are all crystallized in the T-type structure where only CuO_6 octahedra exist. The carrier-reservoir (La, Pr)–O layer provides hole carriers to the CuO_2 conductivity layer. And superconductivity is present in these samples, logically. For the $1.2 \leq x \leq 1.3$ samples, the CuO_6 octahedra and CuO_4 planes coexist in the bodies of the samples. Although a certain number of apical oxygen atoms are removed from their former positions, there is a carrier-reservoir (La, Pr)–O layer which provides hole carriers to the CuO_2 conductivity layer. The T-phase part dominates the superconductivity in $1.2 \leq x \leq 1.3$ samples, naturally. In T' samples where there are no apical oxygen atoms above or below Cu atoms, there is no oxygen in the La (Pr) layer near the CuO_2 plane. The oxygen atoms in (La, Pr) $_2\text{O}_2$ double layers are inserted into the middle of the two La (Pr) layers. Thus the (La, Pr) $_2\text{O}_2$ layers do not provide hole carriers to the conduction CuO_2 layer. The hole carrier concentration in the CuO_2 plane decreases sharply at the structural transition from the T (T + T') phase to the T' phase. Thus the superconductivity is suppressed and the room temperature resistivity sharply increases until it is about three orders of magnitude larger than the resistivity of the superconducting samples. From the above analyses, we suggest that in the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ system, the suppression of superconductivity is not related to the interaction of Pr ions with in-plane oxygen, which leads to hole localization in the CuO_2 plane as in $\text{Y}(\text{Pr})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The disappearance of the superconductivity and the changes of the transport properties mainly originate from the removal of the apical oxygen induced by the change of structure.

4. Conclusions

In the $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ system ($0 \leq x \leq 1.85$), we observe the structural evolution $T \rightarrow T+T' \rightarrow T'$ phase with increasing Pr substitution. The apical oxygen atoms are removed from the (La, Pr)–O layer with this structural evolution. The exhibiting of superconductivity for the doping region $0 \leq x \leq 1.3$ indicates that the interaction of Pr ions with in-plane oxygen is not significant in the suppression of superconductivity in $\text{La}_{1.85-x}\text{Pr}_x\text{Sr}_{0.15}\text{CuO}_4$ superconductors. The disappearance of the superconductivity and the changes in transport properties mainly originate from the removal of the apical oxygen induced by the change of structure.

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