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The influence of fluorine on the structures and properties of $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ ($x = 0.0, 0.4, 1.0$)

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Abstract. Introducing F into the lattices of the copper oxides Pr_2CuO_4 , $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ and PrSrCuO_{4-y} is accomplished via a low-temperature fluorination reaction using CuF_2 as the fluorinating reagent. The oxyfluorides retain the structures of their precursors, but striking lattice expansions are observed. No trace of SrF_2 was detected in the fluorinated products. F doping was successfully used to induce superconductivity in the oxyfluoride $\text{PrSrCu}(\text{O}, \text{F})_{4-\delta}$ ($T_c = 15$ K) with a reduced CuO_2 plane and in the presence of apical anions, but failed to optimize the carrier density and induce superconductivity in $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ and $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$.

1. Introduction

The fluorination reaction, as an effective preparation route, has been successfully applied, either to introduce F into the lattices of copper oxides, improving their superconductivity via doping, such as in $\text{La}_2\text{CuO}_4\text{F}_\delta$ [1], $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ [2] and in the Y system [3, 4] as well as in the Bi system [5], or to create structural features favouring superconductivity, such as in $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ [6]. Several fluorinating routes have been developed that use different fluorinating reagents: F_2 , NH_4F , NdF_3 , NH_4HF_2 , XeF_2 or MF_2 ($M = \text{Cu}, \text{Zn}, \text{Ni}, \text{Ag}$) [3–10]. Of these routes, the reaction with MF_2 is considered as the simplest and most effective fluorination process, since it eliminates the toxicity problem and restriction on sample size associated with elemental F_2 , and it reduces the amount of the impurity SrF_2 in relation to that of the impurity NH_4F . In our experiment, it is confirmed that fluorination treatment using CuF_2 as the fluorinating reagent is a general and workable method, which can fluorinate a wide range of cuprates.

Hwang *et al* [11] reported a comprehensive crystallographic study on the Pr_2CuO_4 – Sr_2CuO_3 system and found the structural evolution $T' \longrightarrow T^* \longrightarrow T \longrightarrow \text{Sr}_2\text{CuO}_3$ phase with increasing Sr substitution in $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$. Single-phase samples of the three structures in the system were successfully synthesized: Pr_2CuO_4 , $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ and PrSrCuO_{4-y} with the T' , T^* and T structures, respectively. Schematic representations of the crystal structures of the T' , T^* and T phases are shown in figure 1. However, neither metallic conductivity nor superconductivity has been observed in the three compounds.

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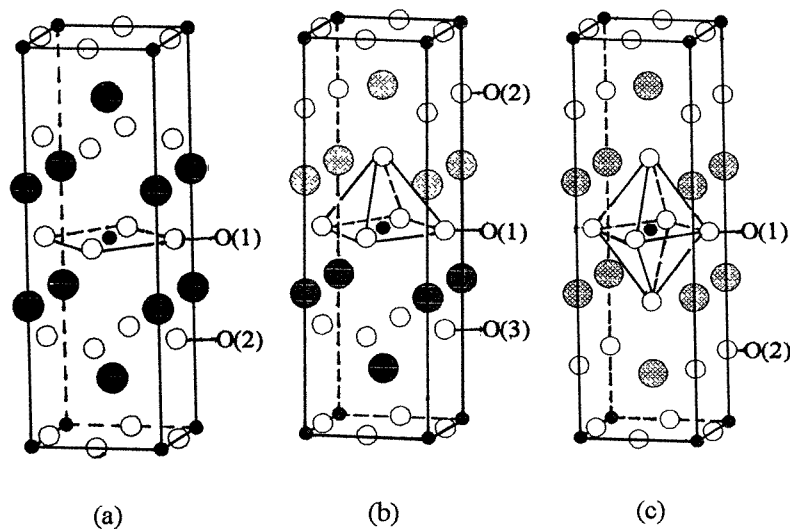


Figure 1. Schematic representations of the crystal structures of the (a) T' , (b) T^* and (c) T phases. The small solid circles denote Cu ions; the large solid circles denote Pr ions in the T' structure and Pr/Sr ions in the T^* structure; and the large cross-hatched circles denote Sr/Pr ions in the T^* and T structures.

Pr_2CuO_4 is a semiconductor, isostructural with Nd_2CuO_4 . James *et al* [2], using solid-state reaction of Nd_2O_3 , CuO and NdF_2 , followed by a reduction annealing in N_2 , successfully prepared $\text{Nd}_2\text{CuO}_{3.6}\text{F}_{0.4}$ with the superconducting transition temperature $T_c = 27$ K. This route also proved to be effective for obtaining $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ ($0 < x < 0.4$) with $T_c = 13$ K. These results indicated the possibility that anion substitution worked in parallel with cation substitution for controlling the carrier density. Examination of the effect of F doping and reduction on the electronic structure of $\text{Nd}_2\text{CuO}_{4-y}\text{F}_y$ by x-ray-emission spectroscopy and photoemission spectroscopy [12, 13] revealed that, in the T' structure, F substituted for the O atom in the Nd_2O_2 slab (see the O(2) site in figure 1(a)), affecting the charge density. However, $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ obtained using this solid-state reaction easily decomposes under N_2 gas above 900°C . So, in our experiment, we attempt to prepare $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ by low-temperature fluorination reaction, using CuF_2 as the fluorinating reagent.

For the case of $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ with the T^* structure, Hwang *et al* [11] have estimated the number of Pr^{4+} ions in this structure to be 30% of the total number of Pr ions using Pr L_3 x-ray absorption, and they inferred that tetravalent Pr ions in the T^* phase reduced the number of hole carriers in the CuO_2 layers introduced by Sr substitution, leading to non-metallic conductivity. Therefore, it is anticipated that incorporation of F in this structure would change the nature or concentration of the carriers, and induce superconductivity.

In the case of the T phase, PrSrCuO_{4-y} , the structure refinement by Hwang *et al* suggested that oxygen deficiency occurred primarily in the CuO_2 layers (not at the apical oxygen sites); that is, about a fifth of the oxygen sites in the CuO_2 layers are vacant. A similar structure is also found for the T phase in the La_2CuO_4 , Nd_2CuO_4 – Sr_2CuO_3 systems for a high level of Sr doping [14, 15]. The large number of oxygen vacancies in the T structure cause the hole localization, and lead to the absence of superconductivity. However, such a structure is suitable for F insertion, which could give rise to a structural rearrangement

favourable to the appearance of superconductivity. The oxyfluoride $\text{La}_{0.7}\text{Sr}_{1.3}\text{Cu}(\text{O},\text{F})_{4+\delta}$, in the $\text{La}_2\text{CuO}_4\text{--Sr}_2\text{CuO}_3$ system, has been synthesized by Chen *et al* [16]. In a previous paper, we have reported on the oxyfluoride $\text{Nd}_{0.7}\text{Sr}_{1.3}\text{Cu}(\text{O},\text{F})_{4-\delta}$ with $T_c = 44$ K [17]. Hence, inducing superconductivity in the fluorinated product of PrSrCuO_{4-y} appears quite possible.

Taking advantage of the instability of CuF_2 , we have examined the possibility of fluorinating the three compounds at low temperature and ambient pressure using CuF_2 as the fluorinating reagent, and successfully synthesized the superconducting copper oxyfluoride $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$ with $T_c = 15$ K.

2. Experimental details

Samples with the nominal compositions Pr_2CuO_4 , $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ and PrSrCuO_{4-y} were prepared by the solid-state reaction method using high-purity dried Pr_6O_{11} , SrCO_3 and CuO as starting materials. The powders were thoroughly mixed in an agate mortar, and calcined at 950°C in air for 12 h. The prereacted materials were reground and pelletized. The pellets were sintered at 1000°C or so for 24 h. The precursor powder was finally mixed with an appropriate amount of freshly prepared CuF_2 and subsequently heated in air. High-temperature heating ($\geq 400^\circ\text{C}$) and an excess amount of CuF_2 will yield predominantly SrF_2 owing to its high-thermodynamic stability. However, low-temperature heating ($\leq 200^\circ\text{C}$) will lead to insufficient reaction. Typical synthesis conditions are a mixture of the precursor and CuF_2 with molar ratio 1.0:1.0–1.2 and heating at $200\text{--}300^\circ\text{C}$ for 1–5 h. The phase identification and the measurement of the lattice parameters were performed on a MAC Science automatic diffractometer using $\text{Cu K}\alpha$ radiation with a graphite monochromator. The lattice parameters were then calculated using a standard least-squares refinement. A dc superconducting quantum interference device (SQUID) magnetometer was used to investigate the superconducting properties of the samples.

3. Results and discussion

3.1. $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$

Figure 2 shows the x-ray powder diffraction patterns of the precursor Pr_2CuO_4 and its fluorinated products obtained by heating the mixture for 3 h at 270°C , 286°C and 310°C . The precursor has a tetragonal lattice with $a = 3.9615(2)$ Å and $c = 12.2212(1)$ Å; these values are similar to the reported ones [11]. The tetragonal structure is retained in the samples fluorinated at the different temperatures. The lack of distinct change in the diffraction patterns of the different fluorinated products suggests that fluorine has substituted for oxygen in the lattice, causing no gross change in the crystal structure. For the oxyfluorides obtained at 270°C and 286°C , the slight broadening of the reflection lines indicates inhomogeneous F insertion into the lattice of the precursor and a reduction in particle size. In addition, several admixture phases (CuO and the unknown phase marked by asterisks in figures 2(b), 2(c) and 2(d)) are present in different minor proportions. The presence of amorphous CuO cannot be excluded due to the fluorination process. The unknown phase was not identified, as the peaks were too few and were weak. Sugiyama *et al* [18] reported that several impurities, NdOF , CuO and an unidentified phase, appeared in the $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ samples with $x > 0.3$. In the present samples, it is certain that the unknown phase is not PrOF , PrF_x or CuF_2 , nor the unidentified phase reported to appear in $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$. When the annealing temperature is elevated (see figure 2(d) for

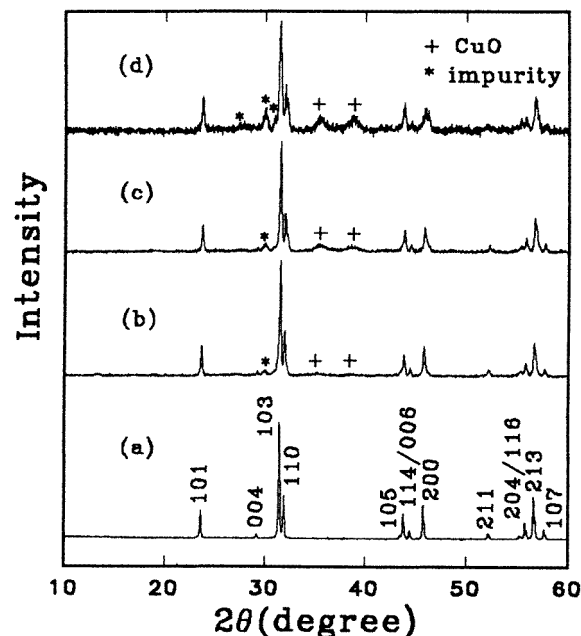


Figure 2. X-ray powder diffraction patterns: (a) the precursor Pr_2CuO_4 ; (b) the oxyfluoride obtained at 270 °C; (c) the oxyfluoride obtained at 286 °C; and (d) the oxyfluoride obtained at 310 °C.

$T_f = 310$ °C), the amount of the two impurities increases, and the broadening of the diffraction peak becomes more distinct. When the annealing temperature (T_f) is above 400 °C, the T' structure is substantially destroyed, and the impurity becomes the main phase, whereas when $T_f \leq 230$ °C, no noticeable change in the x-ray diffraction pattern of the fluorinated product, compared with that of the precursor, is observed. These results are comparable to those of Chevalier *et al* [19]. They synthesized the superconducting compound $\text{La}_2\text{CuO}_{4-x}\text{F}_x$ by low-temperature fluorination, and found that the La_2CuO_4 structure is completely destroyed when $T_f \geq 300$ °C, the result being a mixture of LaF_3 and CuF_2 , whereas when $T_f \leq 100$ °C, neither a significant change in the x-ray diffraction spectra nor a noticeable weight increase are detected.

Table 1. A list of lattice constants a , c and V for Pr_2CuO_4 and its fluorinated products synthesized at 270 °C, 286 °C and 310 °C.

Sample	a (Å)	c (Å)	V (Å ³)
Precursor	3.9615(2)	12.2210(1)	191.7921(4)
270 °C	3.9619(2)	12.2206(4)	191.8250(6)
286 °C	3.9628(4)	12.2157(3)	191.8370(5)
310 °C	3.9644(3)	12.2126(4)	191.9424(6)

The variations of the lattice constants a , c and V with the fluorination temperatures T_f are listed in table 1. The value of a slightly increases with T_f , while the value of c

decreases with T_f . This result suggests that, in this temperature range $T_f = 270\text{--}310\text{ }^\circ\text{C}$, the fluorination reaction proceeds more completely at elevated temperature, i.e. a larger number of F ions are incorporated in the lattice of the sample treated at higher temperature. Since the ionic radius of the F ion ($r = 1.333\text{ \AA}$) is smaller than that of the O ion ($r = 1.400\text{ \AA}$), the increase in a due to F substitution may indicate that F ions do not enter the O(1) sites in the CuO_2 plane, but enter the O(2) sites around the Pr^{3+} ions (see figure 1(a)). The substitution of F for O will inject electrons into the CuO_2 sheet and reduce the valence state of the Cu ions. These results are comparable to the reported ones [18]. As regards the occupation of F ions in the T' structure, James *et al* [2] inferred that fluorine was located at the O(2) site in $\text{Nd}_2\text{CuO}_{3.6}\text{F}_{0.4}$. This inference was experimentally confirmed using XES and XPS [12, 13]. These results are also consistent with our preliminary XRD analysis result.

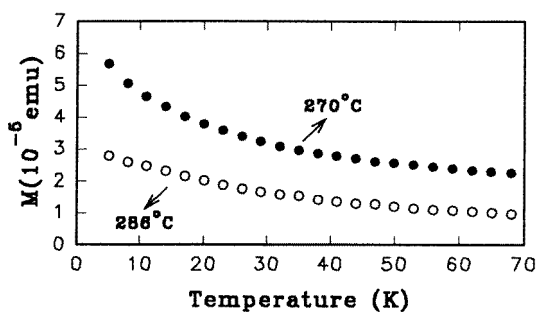


Figure 3. The magnetization M versus temperature for an applied field of $H = 10$ Oe for field-cooled $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ synthesized at $270\text{ }^\circ\text{C}$ and $286\text{ }^\circ\text{C}$.

Because of the instability of the oxyfluoride at moderate temperature ($400\text{ }^\circ\text{C}$), pellets were not calcined and resistance measurements were not attempted. The superconductivities were examined magnetically in the temperature range of $4.5\text{--}70\text{ K}$ with a dc SQUID magnetometer at a field of 10 Oe. Figure 3 shows the magnetization M versus temperature for field-cooled $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ synthesized at $270\text{ }^\circ\text{C}$ and $286\text{ }^\circ\text{C}$. No superconductivity was observed, which might be attributed to the unsuitable doping concentration. At present, we are trying to optimize the fluorinating temperature in combination with a reduction treatment in order to adjust the carrier concentration to one suitable for superconductivity.

Table 2. A list of the lattice constants a , c and V for $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ and its fluorinated products synthesized at $250\text{ }^\circ\text{C}$ and $270\text{ }^\circ\text{C}$.

Sample	a (\AA)	c (\AA)	V (\AA^3)
Precursor	3.8639(3)	12.4980(2)	186.5948(7)
$250\text{ }^\circ\text{C}$	3.9208(4)	12.5352(3)	192.7039(2)
$270\text{ }^\circ\text{C}$	3.9245(3)	12.5377(5)	193.1056(2)

3.2. $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$

As shown in figure 4(a), the precursor $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ exhibited a tetragonal symmetry with the unit-cell constants $a = 3.8639(3)\text{ \AA}$ and $c = 12.4981(2)\text{ \AA}$, values in good agreement

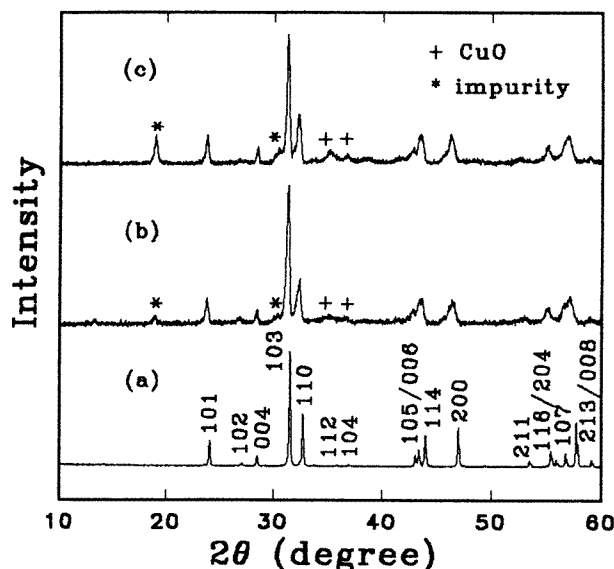


Figure 4. X-ray powder diffraction patterns: (a) the precursor $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$; (b) the oxyfluoride obtained at 250 °C; and (c) the oxyfluoride obtained at 270 °C.

with those previously reported [11]. For this T^* phase, an optimum fluorination treatment was performed at 240–280 °C for 3 h. Beyond this temperature range, either a large amount of SrF_2 appears or too few F insertions take place. Figures 4(b) and 4(c) show the x-ray powder diffraction patterns for the oxyfluorides $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$ synthesized at 250 °C and 270 °C, respectively. The indexing results reveal that the oxyfluorides retain the tetragonal lattices of their precursors, but a noticeable broadening of the diffraction peaks occurs, indicating that F enters the lattice and distributes inhomogeneously, and that F insertion could also arise from the reduction in particle size. It is noted that no trace of SrF_2 is detected. In addition, as is the case for $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$, CuO and an unknown phase appear accompanying the oxyfluoride.

The variations of the lattice parameters a , c and V with fluorinating temperature are listed in table 2. Unlike in the case for $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$, both a and c distinctly increase with T_f , which indicates that, in the temperature range 240–280 °C, more F ions enter the lattice of the precursor when it is fluorinated at a higher temperature. The enlargement of a after fluorination treatment suggests that fluorine does not enter the O(1) sites in the CuO_2 sheet, but enters the O(3) sites around Pr ions or at the apical O(2) site of the CuO_5 pyramid (see figure 1(b)), while the enlargement of c might be attributed to a reduction of the number of tetravalent Pr ions. It is well known that both x-ray and neutron diffraction techniques are unsuitable for distinguishing oxygen and fluorine atoms in a crystal lattice due to their close scattering powers for x-ray and neutron diffraction. So, at this stage, we cannot give direct proof regarding the occupation of F and O ions. The distribution of F and O ions in the T^* structure still remains to be ascertained by XES and XPS.

Though F doping in the T^* structure has been accomplished, the carrier concentration of the oxyfluoride has not yet been adjusted to make conditions suitable for superconductivity. Figure 5 depicts the magnetization measurement result at an applied field of $H = 10$ Oe in

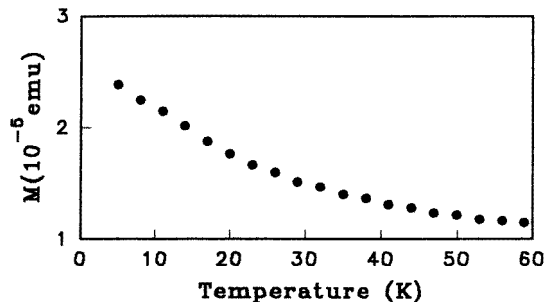


Figure 5. The magnetization M versus temperature for an applied field of $H = 10$ Oe for field-cooled $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$ synthesized at 250°C .

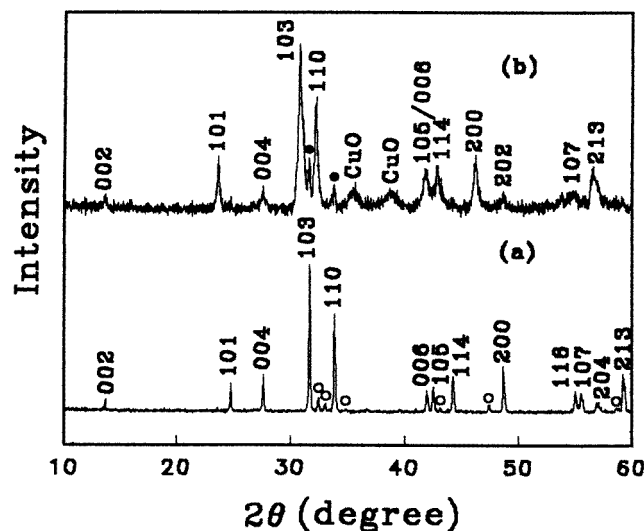


Figure 6. X-ray powder diffraction patterns: (a) the precursor PrSrCuO_{4-y} (\circ denotes the superstructure); and (b) the oxyfluoride obtained at 240°C (\bullet denotes the initial phase).

the temperature range 4–70 K for field-cooled $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$ synthesized at 250°C for 3 h. F doping essentially compensates the reduction of the number of Pr^{4+} ions, does not provide a proper carrier concentration, and therefore does not give rise to superconductivity. Hwang *et al* [11] argued that the stabilization of the T^* structure in the Pr_2CuO_4 – Sr_2CuO_3 system was due to the presence of small tetravalent Pr ions. Kito *et al* [20] also reported that $\text{Pr}_{1.4}\text{Ce}_{0.2}\text{Sr}_{0.4}\text{CuO}_4$ crystallized in the T^* structure, but did not show superconductivity, probably due to the presence of a significant number of tetravalent Pr ions that strongly affect the carrier concentration. On the basis of the discussions above, we believe that the number of Pr^{4+} ions is a crucial factor for both the stabilization of the T^* structure and the appearance of superconductivity. Therefore, further work should focus on optimizing the number of Pr^{4+} ions.

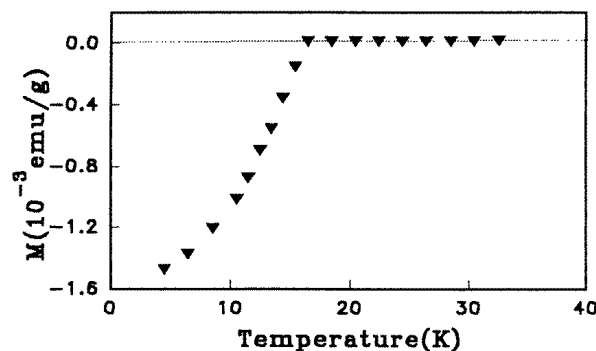


Figure 7. The magnetization M versus temperature for an applied field of $H = 5$ Oe for zero-field-cooled $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$ synthesized at 240°C .

3.3. $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$

Fluorination of PrSrCuO_{4-y} with the T structure was also attempted. Figure 6 shows the x-ray diffraction patterns of the precursor and fluorinated products synthesized at 240°C for 3 h. A substantial enlargement of the lattice constants was observed: $a = 3.7415(5)$ Å, $c = 12.9154(2)$ Å for the precursor and $a = 3.9372(3)$ Å, $c = 12.9496(2)$ Å for the oxyfluoride. The weak peaks (marked as hollow circles in figure 6(a)) were due to superstructure as was the case for $\text{Nd}_{0.7}\text{Sr}_{1.3}\text{CuO}_{4-y}$. No Sr_2CuO_3 was detected. As shown in figure 6(b), CuO and the initial phase coexist with the main phase $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$. The broadening of the diffraction peaks might be attributed to inhomogeneous fluorination and reduction of the particle size. No trace of SrF_2 was observed. Magnetization measurement revealed that the oxyfluoride exhibited a superconducting transition at about 15 K with a Meissner fraction of 3% estimated at 4.5 K. The small superconductivity volume fraction might be attributed to the particle size effect and the imperfect anion distribution in the structure. The zero-field-cooled magnetization versus temperature for the sample prepared at 240°C for 3 h in air is shown in figure 7. Combining the XRD analysis and magnetic measurement, we could deduce that the superconductivity originates from the main phase. The non-metallic behaviour of PrSrCuO_{4-y} and CuO also indicates that the impurity phases in the sample are not responsible for the superconductivity at 15 K. The fact that the transition temperature ($T_c = 15$ K) for the present sample is much lower than those of the superconducting phases possibly occurring in the fluorinated product, i.e. the series $\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+\delta}\text{F}_{2+y}$ (>40 K) [21], provides further evidence for this deduction. This result is also in good agreement with that of the XRD examination, in which no trace of the series $\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+\delta}\text{F}_{2+y}$ was detected.

The T structure of PrSrCuO_{4-y} with a great number of oxygen vacancies at the equatorial sites is suitable for F insertion. However, it is difficult to determine accurately the distribution of F and O in this structure by XRD. Therefore, at this stage, we can only estimate the occupation of F and O atoms from indirect results. For $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$, structure refinement and the Madelung energy calculation [22] suggested that F ions preferably occupied the apical sites, and excess F ions could also enter the interstitial sites. However, we think that the interstitial occupation of F ions is impossible because there are no interstitial sites in the closely stacked T structure large enough for F ions with large ionic

radii. In a previous paper, we inferred the distribution of F and O ions in terms of the different lattice expansions for two samples of $\text{Nd}_{0.7}\text{Sr}_{1.3}\text{Cu}(\text{O},\text{F})_{4-\delta}$ fluorinated at 200 °C and 240 °C. For the sample fluorinated at 200 °C, a larger number of F ions enter the CuO_2 sheets. For the sample prepared at the higher temperature, 240 °C, F ions primarily occupy the apical positions. So, in the oxyfluoride $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$, with similar lattice expansions to those of $\text{Nd}_{0.7}\text{Sr}_{1.3}\text{Cu}(\text{O},\text{F})_{4-\delta}$ synthesized at 240 °C, F ions could preferentially occupy the apical sites, but the possibility of a few F ions entering the vacancies at the equatorial sites is not completely ruled out. The accurate determination of the oxygen and fluorine contents, which is important for the understanding of the ideal chemical formulae, is currently ongoing. At present, we tentatively adopt $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$ as the chemical formula of the oxyfluoride on the basis of the discussions above. In the light of the valence neutrality, the Cu oxidation state in the oxyfluoride should be lower than 2+, indicating that the CuO_2 plane of these compounds is reduced. In addition, from the structural point of view, the oxyfluoride seems to be an electron-type superconductor with apical fluorine or oxygen. Firstly, it has a large lattice parameter: $a = 3.9372(2)$ Å. It is well known that the known n-type superconductors have lattice parameters $a \geq 3.90$ Å and $c \leq 12.3$ Å, and that the known p-type superconductors have lattice parameters $a \leq 3.87$ Å and $c \geq 12.5$ Å. In particular, all hole-type superconductors with the La-214 structure have lattice parameters a less than 3.87 Å, which is distinguishably different from the large a -parameter of $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$. Secondly, the substitution of Pr^{3+} for Sr^{2+} in $\text{PrSrCu}(\text{O},\text{F})_{4-\delta}$ would introduce more electrons and lead to a -parameter enlargement, having the same effect as F doping, whereas the c -parameter being enlarged from 12.9154(2) Å to 12.9494(3) Å—larger than the values for usual n-type superconductors—suggests the existence of apical oxygen or fluorine.

Figure 8 depicts the dependences of the lattice constants (a , c and V) on the Sr content for the precursors $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ and their fluorinated products. For the three single-phase precursors, the values of a and V decrease with Sr content, while the value of c increases. The contraction—not expansion—of a and V after replacing the smaller Pr ions by the larger Sr ions may be attributed to the compensating effect exerted by the presence of Pr^{4+} in the T^* structure or by the occurrence of oxygen vacancies in the T structure. Furthermore, this contraction also probably results from the different stacking densities for the three structures. The increase of the c -parameter with the Sr content is due to the appearance of the apical sites in the T^* and T structures. When the precursors were fluorinated, different changes in the lattice constants were observed (see figure 8). For the T' structure, Pr_2CuO_4 , F insertion gives rise to slight changes for a , c and V . This may be attributed to F substitution into the O(2) site in the Nd_2O_2 slab, resulting in the appearance of the low-valence Cu ions. However, the number of low-valence Cu ions is not high enough to induce superconductivity in this oxyfluoride. So, a greater number of the low-valence Cu ions, produced via more F insertion into the lattice of the precursor and a reduction reaction, are necessary. Unlike in the case of the T' structure, Sr doping introduces hole carriers into the T^* precursor $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ in spite of the compensating effect of the Pr^{4+} ions, resulting in a Cu-ion valence larger than 2+. The distinct enlargement of the a -parameter as well as the cell volume and a small enlargement of the c -parameter were induced by the fluorination reaction. The obvious enlargement of the a -parameter after fluorination treatment suggests that substitution of F for the oxygen atoms in the Pr–O and Sr–O sheets injects electrons into the CuO_2 plane, lowering the Cu-ion valence. So a larger amount of substitution of F for O should be examined as regards the possibility of inducing superconductivity in this compound by dint of retaining the T^* structure. For a high level of Sr doping, a great number of oxygen vacancies appear in the CuO_2 plane, which is the main origin of the

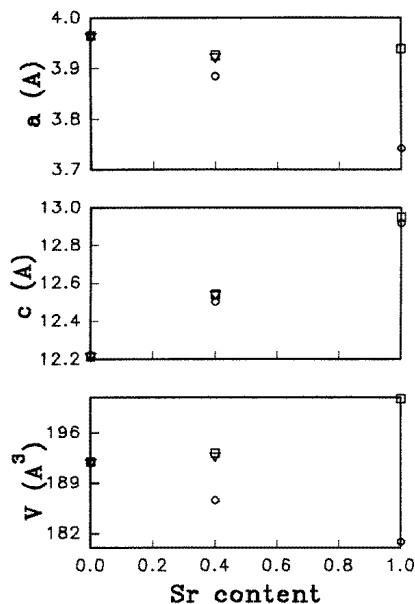


Figure 8. The dependences of the lattice constants (a , c and V) on the Sr content for the precursors $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ ($x = 0.0, 0.4, 1.0$) and their fluorinated products. ○: the values for the precursors; ▽: the values for the oxyfluorides of the T' and T* phases obtained at 286 °C and 250 °C, respectively; □: the values for the oxyfluorides of the T', T* and T phases obtained at 310 °C, 270 °C and 240 °C, respectively.

a -parameter being so small for the T structure. The striking enlargement of the a -parameter to such a size—comparable to the corresponding value for $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ —further indicates that a great number of Cu ions are reduced to the lower valence state by F insertion into the oxygen sites or vacancies.

4. Summary

We successfully incorporated F ions into the lattices of three cuprates, Pr_2CuO_4 , $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_4$ and PrSrCuO_{4-y} , via low-temperature fluorination reactions using CuF_2 as the fluorinating reagent. No trace of alkaline-earth fluoride was detected in the fluorinated products for the latter two cuprates. Insertion of F ions into PrSrCuO_{4-y} induces superconductivity in the oxyfluorides with a reduced CuO_2 plane and in the presence of apical anions. This provides further support for the assertion that apical anions are present in n-type superconductors. However, no superconductivity was induced by F doping in the oxyfluorides $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ and $\text{Pr}_{1.6}\text{Sr}_{0.4}\text{CuO}_{4-x}\text{F}_x$, probably due to the unsuitable carrier concentrations. Further work is ongoing to optimize these.

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