

Superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with high strontium concentration by sulphur doping

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The effects of sulphur substitution for oxygen on the structure and properties of non-superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, where $x = 0.26$ and 0.30 , have been studied. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$, the sulphur-doped samples exhibit superconducting transition at 37–39 K and a larger Meissner effect than undoped samples. It was found that the superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ is apparently determined by the value of $x - y$ and the strontium concentration region in which $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shows superconductivity shifts to higher strontium concentrations with sulphur doping.

1. Introduction

Because the first-discovered high- T_c superconductors, $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Ba}, \text{Sr}, \text{Ca}$) [1–5], have the relatively simple structure of K_2NiF_4 type, they are suitable for the investigation of the mechanism of high-temperature oxide superconductivity. In particular, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ has been extensively studied because a single-phase material can be obtained over a wide range of strontium concentration [6].

It has been reported that the electrical properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ vary with strontium concentration, x , from insulating for $0 \leq x \leq 0.06$ to superconducting for $0.06 \leq x \leq 0.26$ to normal metal for $0.26 \leq x$ [7]. This variety of electrical behaviour is considered to be related to the change of the electronic interaction between the Cu 3d band and the O 2p band with varying hole concentration in the CuO_2 plane. Adachi and Takano [8] have estimated the electronic state of CuO_4^{6-} and CuS_4^{6-} clusters by the quantum mechanical calculation DV-X α method and concluded that the overlap of S 3p and Cu 3d bands is larger than that of O 2p and Cu 3d bands. Therefore, it is expected in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ that the substitution of sulphur for oxygen may change the electronic structure in the vicinity of copper and may affect the electrical and magnetic properties.

We have reported that in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$, which shows the highest T_c in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, sulphur substitution for oxygen leads to changes of crystal structure and electrical properties; that is, the in-plane lattice constants increase and the lattice constant c decreases monotonically and the superconducting transition temperature decreases with increasing sulphur content [9]. In the present study, the effects of sulphur doping on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been investigated for $x = 0.26$ and 0.30 at which the superconductivity disappears and metallic behaviour is observed.

2. Experimental procedure

Samples of the nominal composition of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$, where $x = 0.26, 0.30$ and $y = 0, 0.10, 0.20$,

were prepared from high-purity reagent-grade La_2O_3 , SrCO_3 , CuO and CuS by solid-state reaction. The chemicals were mixed and calcined by heating at 900°C for 5 or 10 h in air. A heating rate of 5°C min^{-1} was adopted. The calcined powder was ground and pressed into pellets of 20 mm diameter and 1–1.5 mm thick. The pellets were sintered at 1000 or 1100°C for 10 h in air and cooled slowly in the furnace to room temperature.

X-ray diffraction patterns of the samples were taken for identification of the crystalline phases with a Rigaku Denki Company model RAD-IIA using $\text{CuK}\alpha$ radiation. Lattice constants of the crystal were determined for the samples of $x = 0.26$ by the internal standard method using the least squares method. The sulphur content in the samples was determined by X-ray fluorescence analysis with a Rigaku Denki Company model KG-4. The d.c. electrical resistance of the samples was measured at temperatures from 300–28 K by the four-probe method. The a.c. magnetic susceptibility of the samples was also measured from 300–28 K by the Hartshorn bridge method with a frequency of 270 Hz and an amplitude of 100 mV. The d.c. magnetic susceptibility of several samples was measured from 50–5 K with a Quantum Design MPMS SQUID magnetometer in a static magnetic field of 20 Oe ($1 \text{ Oe} \approx 79.58 \text{ A m}^{-1}$).

3. Results

The analysed sulphur contents, y , of all the samples are plotted against the calculated sulphur contents of the starting composition in Fig. 1. It is shown that more than 70% of the sulphur in the starting mixture remains in the sintered products. In order to prepare $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with high strontium concentration, heat treatment in oxygen is more suitable than that in air. Nevertheless, in this work, heat treatment had to be conducted in air, otherwise sulphur may be oxidized and may not remain in the solid solution as S^{2-} . Hereafter, y represents the analysed sulphur content.

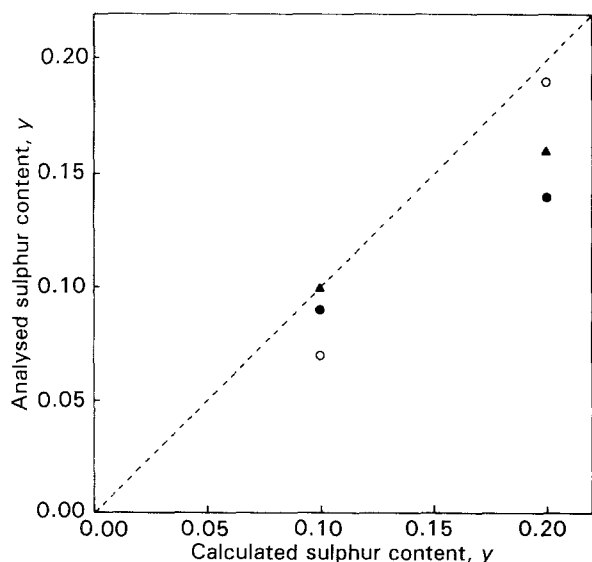


Figure 1 Relation between the analysed sulphur content, y , and the calculated sulphur content, y , in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$. x : (\blacktriangle) 0.26 (1000°C), (\bullet) 0.30 (1000°C), (\circ) 0.30 (1100°C).

Fig. 2 shows the X-ray diffraction patterns of the sintered pellets. For $x = 0.26$, all the samples, whose y values are 0, 0.10 and 0.16, were obtained as single phase of the K_2NiF_4 -type structure by heating at 1000°C for 10 h. For $x = 0.30$, the single-phase material was obtained for $y = 0.09$ and 0.14 but could not be obtained for $y = 0$ by heating at 1000°C for 10 h.

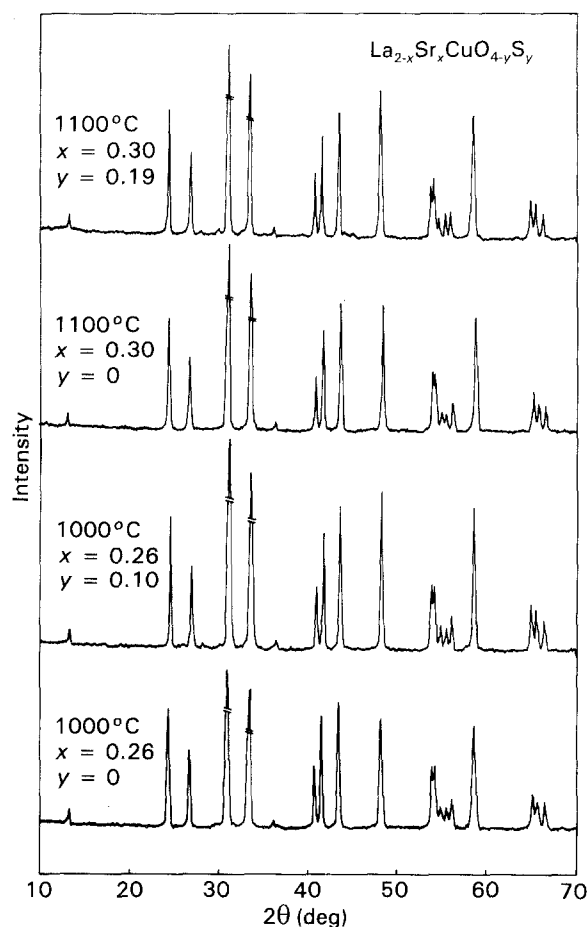


Figure 2 X-ray diffraction patterns of the samples with and without sulphur doping. Each pattern shows the single phase of the K_2NiF_4 -type structure.

TABLE I Lattice constants a and c of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$.

Sulphur content, y	Lattice constants (nm)	
	a	c
0	0.377	1.324
0.10	0.377	1.324
0.16	0.378	1.322

sulphur-free sample of $x = 0.30$ could be obtained as single phase by heating at 1100°C for 10 h. With this heating condition, sulphur-containing samples of $x = 0.30$ and $y = 0.07$ and 0.19 were also obtained as single phase. All the single-phase materials had a tetragonal K_2NiF_4 -type structure at room temperature.

The values of lattice constants a and c of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ are given in Table I. No change in values was observed with sulphur content y . The c -axis value is smaller than that of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ prepared by Torrance *et al.* [7].

The temperature dependence of d.c. electrical resistance of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ is shown in Fig. 3. The sample with no sulphur, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$, shows metallic conduction and superconducting transition at 37 K. The sulphur-containing sample of $y = 0.10$, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.90}\text{S}_{0.10}$, also shows metallic conduction and T_c (onset) at 39 K and T_c (end) at 35 K. The sample of $y = 0.16$, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.84}\text{S}_{0.16}$, shows semiconducting behaviour in the lower temperature range and T_c (onset) at 38 K, but zero resistance is not observed, at least above 28 K. Fig. 4 shows the temperature-resistance curve of $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{4-y}\text{S}_y$. It is seen that all three samples with $y = 0, 0.09$ and 0.14 show metallic conduction at higher temperatures and superconducting transition at 38 K.

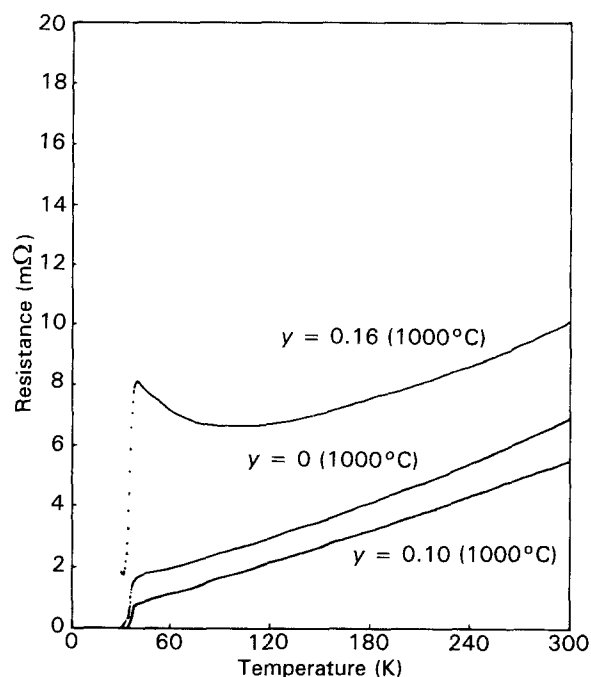


Figure 3 Temperature dependence of d.c. electrical resistance of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$.

TABLE II Composition, heating temperature and T_c of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$.

x	y	Heating temp. (°C)	Resistance		Susceptibility T_c (K)
			T_c (onset) (K)	T_c (end) (K)	
0.26	0	1000	37	32	a
0.26	0.10	1000	39	35	32
0.26	0.16	1000	38	a	34
0.30	0	1100	38	34	a
0.30	0.07	1100	37	a	a
0.30	0.09	1000	38	a	a
0.30	0.14	1000	38	35	35
0.30	0.19	1100	37	a	30

^a T_c not observed at least above 30 K.

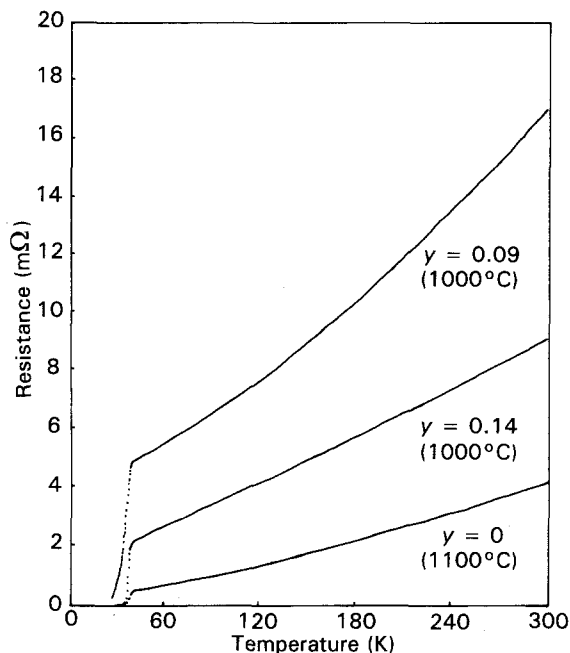


Figure 4 Temperature dependence of d.c. electrical resistance of $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{4-y}\text{S}_y$.

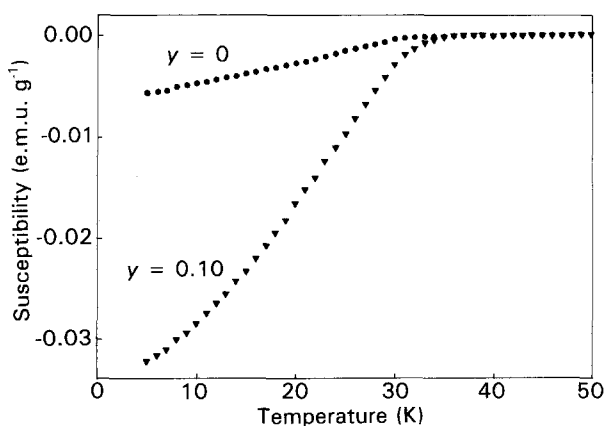


Figure 5 Temperature dependence of d.c. magnetic susceptibility of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$.

The temperature dependence of d.c. magnetic susceptibility of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ measured by SQUID is shown in Fig. 5. The Meissner volume fraction of the sulphur-doped material of $y = 0.10$ at 5 K is much larger than that of the material containing no sulphur. This result indicates that the sample with

no sulphur, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$, contains a relatively small amount of superconducting phase, while the sulphur-doped sample contains a larger amount of superconducting phase. The larger Meissner volume fraction of the latter sample is considered to result from the substitution of sulphur for oxygen, as discussed below.

The composition and superconducting transition temperature of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ are summarized in Table II. All the samples show T_c (onset) at temperatures between 37 and 39 K according to the resistance data, whereas only the sulphur-doped samples show superconducting transition above 30 K according to the a.c. magnetic susceptibility data. Fig. 6 shows the range of strontium concentration, x , and the sulphur concentration, y , in which the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions exhibit the superconducting transition above 30 K in susceptibility. It is seen that the superconducting range shifts to the higher strontium concentration region with increasing sulphur content, y .

4. Discussion

4.1. Presence of superconductivity in the nominal composition $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$
It is reported by Torrance *et al.* [7] that the superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ disappears at the

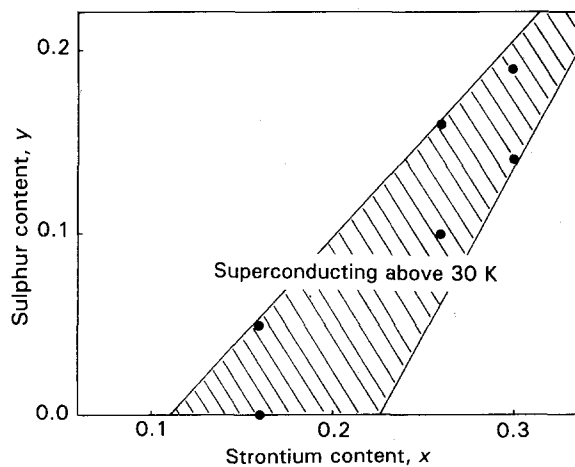


Figure 6 Relation between the strontium concentration, x , and the sulphur concentration, y , in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ which shows superconducting transition above 30 K. The data at $x = 0.16$ are cited from our previous work [9].

strontium content, x , equalling 0.26. In the present work, however, the $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ composition corresponding to $x = 0.26$ has shown a superconducting transition at 38 K according to the resistance data. This discrepancy may be assumed to arise from the difference in the heating atmosphere in the preparation process and the resulting absence or presence of oxygen vacancies in the products. It is plausible to assume that the product of Torrance *et al.* prepared in pure oxygen gas has an exact composition of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ with regard to the oxygen content and accordingly has no oxygen vacancies, whereas in the present product prepared in air, a loss of some oxygens occurs, creating some oxygen vacancies which causes the phase inhomogeneity. It is considered that the inhomogeneous distribution of oxygen vacancies may result in the phase separation of the product into phases of different oxygen contents [7].

The formation of oxygen vacancies may result in a decrease in the hole concentration. According to Shafer *et al.* [10] and Torrance *et al.* [7], the occurrence of superconductivity in the range $0.06 \leq x \leq 0.26$ in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system is attributed to the presence of suitable concentrations of holes and the disappearance of superconductivity at $x = 0.26$ for their products may be caused by the presence of excessive holes. In other words, there are upper and lower limits of hole concentration at CuO_2 plane for the occurrence of superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds. Then, it can be assumed that in our work, the heating of the composition of $x = 0.26$ in air causes the formation of oxygen vacancies and accordingly the phase inhomogeneity, which leads to the formation of the phase whose hole concentration is lower than the upper limit for the occurrence of superconductivity.

Consideration of the lattice constants also seems to support the formation of oxygen vacancies in our $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$. According to Torrance *et al.* [7], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shows superconductivity in the composition range $0.06 \leq x \leq 0.26$, and the lattice constant a decreases and c increases with increasing strontium content, x , until about $x = 0.28$. Above $x = 0.28$, however, the lattice constant a increases and c decreases with increasing x , which is accompanied by an increase in the number of oxygen vacancies. Our superconducting material of composition $x = 0.26$ prepared in air has a smaller c value than the material of composition of $x = 0.26$ prepared by Torrance *et al.* [6, 7] in pure oxygen, which may imply that our material has a higher number of oxygen vacancies.

4.2. The effect of sulphur on the superconductivity of

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions

Our previous work [9] on sulphur substitution in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ showed that the lattice constant a increases and c decreases with increasing sulphur content, y , in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$, which might have few oxygen vacancies because of the low strontium content. On the contrary, for $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$, the composition of $y = 0.10$ has the same a and c values as those of the composition of y

$= 0$, which contains no sulphur, as shown in Table I. If we take account of the increase in the lattice constant a and decrease in c with increasing number of oxygen vacancies for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ of $x \geq 0.28$ found by Torrance *et al.*, very little change observed in the lattice constants of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ provided by the sulphur substitution seems to reveal that the expected changes in the lattice constants with increasing sulphur content are cancelled by the effect of the decrease in the number of oxygen vacancies.

Reduction of the number of oxygen vacancies with increasing sulphur content is thought to be caused by a change in the electronic structure of the CuO_2 plane. Copper atoms in the immediate neighbourhood of sulphur atoms have a larger electronic density than other copper atoms coordinated only by oxygens, because the electronegativity of sulphur is lower than that of oxygen and, therefore, the covalency of the Cu-S bond is larger than that of the Cu-O bond. It is expected, then, that some of the holes may be trapped and localized in the Cu 3d orbital with the higher electronic density due to the Cu-S bond. It is reasonable to think that the number of oxygen vacancies would be decreased as the fraction of localized holes trapped around sulphur atoms increases.

In addition, the change in the electronic structure of the CuO_2 plane mentioned above can explain the change in superconductivity by sulphur substitution. Because localized holes at the higher electronic density region around sulphur atoms cannot contribute to superconductivity, the excessive, superconductivity-relating holes introduced by the higher content of strontium might be decreased, leading to increased superconductivity of the system. Therefore, we propose the explanation that the incorporation of sulphur may change the electronic structure of the CuO_2 plane so that the concentration of holes related to superconductivity (delocalized holes) might be decreased.

Based on the above discussion, a concept is proposed that in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions, the electrical and magnetic properties related to superconductivity may be determined by $x - y$, that is, the difference of strontium content, x , and sulphur content, y , and the system loses superconductivity when $x - y$ is too large (x is large and the sulphur content is small) or too small (sulphur content is too large). Application of this assumption to the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions having $x = 0.26$ and $x = 0.30$ can explain the presence or absence of superconductivity of the compositions as follows. The too large $x - y$ value for $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.93}\text{S}_{0.07}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.91}\text{S}_{0.09}$ implies insufficient suppression of the hole concentration to reach the upper limit for the appearance of superconductivity. The too small $x - y$ value for $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.84}\text{S}_{0.16}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.81}\text{S}_{0.19}$ leads to excessive lowering of the hole concentration, resulting in the occurrence of superconductivity only in the lower temperature region. Only the compositions $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.90}\text{S}_{0.10}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.84}\text{S}_{0.16}$ have moderate hole concentrations at which the superconducting transition is observed at 30–40 K, as shown in Fig. 6.

5. Conclusions

The effects of sulphur doping on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.26, 0.30$) have been studied. The sulphur-doped materials exhibit superconducting transition at 37–39 K and a larger Meissner volume fraction than materials with no sulphur doping. It was also found that the region in which $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shows superconductivity shifts to higher strontium concentrations with increasing sulphur content, y . It is considered that the sulphur doping increases the fraction of the localized holes, by which the excessive holes introduced by higher strontium content might be decreased, resulting in the appearance of superconductivity. The lattice constants of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ hardly change in the range from $y = 0$ –0.16, which indicates that sulphur doping causes the change in electronic state rather than in structure.

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