Incorporation of sulfur ions into La$_{2-x}$Sr$_x$CuO$_4$ superconducting cuprate

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ABSTRACT

The superconductivity of La$_2$CuO$_4$-based materials is known to be achievable by doping holes in Cu ions. In this study, the hole content was tuned by mixing anion sites with oxygen and sulfur. The substitution of La$_{1.75}$Sr$_{0.3}$CuO$_4$ with sulfur led to the recovery of superconductivity from overdoped regions, a result indicative of decreased hole content. Precise structural analysis revealed that the majority of sulfur is incorporated into impurities in the SrSO$_x$ phase, which decreases the hole content of Cu ions via a decrease in the Sr content; however, the superconductivity cannot be interpreted by this mechanism alone. Supporting evidence for the incorporation of sulfur into the La$_{1.75}$Sr$_{0.3}$CuO$_4$SO$_x$ phase was obtained by an investigation of the composition dependence of the lattice parameters and X-ray photoelectron spectroscopy. Substitution of oxygen with sulfur, which served to decrease the hole content, as a means of recovering superconductivity was shown to act.

1. Introduction

In 1985, a high-temperature superconducting oxide with a K$_2$NiF$_4$ structure, i.e. La$_{2-x}$M$_x$CuO$_4$ (M = Ba, Sr, and Ca), was discovered. Several experimental and theoretical studies of this material have been reported [1–3]. Such systems are classified as hole-doped superconductors. The substitution of La$^{3+}$ by divalent cations such as Ba$^{2+}$, Sr$^{2+}$, and Ca$^{2+}$ leads to a change in the valence of Cu from 2+ to $(2+x)$+ for maintaining electronic neutrality. The doped hole in Cu$^{2+}$ serves as an electron carrier, leading to superconductivity. The composition dependence of the critical temperature ($T_C$) of this system has been reported to exhibit a dome-shaped phase diagram [4]. For a La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) system, superconductivity is observed at $x > 0.07$ and the maximum $T_C$ is found at 38 K when $x = 0.15$. Further substitution leads to an overdoped state, where $T_C$ decreases with increases in the hole content, and superconductivity eventually disappears at $x > 0.3$.

In addition, formation of doping holes (or electrons) in Cu$^{2+}$ of superconducting cuprates can be achieved by mixing heteroanions with different valences [5]. Hole- and electron-doped superconductivities have been reported for Sr$_x$Cu$_{2-2x}$O$_{x}$F$_{2+x}$ [6] and Nd$_3$Cu$_{2-3x}$O$_{4-x}$F$_x$ [7] oxyfluorides which are isostructural with LSCO, respectively. Among mixed anion systems, oxysulfide, in which anion sites are occupied by oxygen and sulfur, is a possible candidate for cuprate superconductors, and some studies of this have been reported. Kozuka et al. have reported the effect of sulfur doping on the structure and superconductivity of La$_{1.84}$Sr$_{0.16}$CuO$_4$-$y$S$_y$ [8]. La$_{1.84}$Sr$_{0.16}$CuO$_4$ adopts the tetragonal structure, and substitution of oxygen with sulfur induces structural distortion, leading to an orthorhombic phase at $y > 0.09$. A single phase of the K$_2$NiF$_4$ structure is obtained at $y < 0.12$, and further substitution leads to the formation of impurity phases, indicating that the substitution limit has been attained. With increases in the sulfur content, $T_C$ decreases from 38 K ($y = 0$) to 35 K ($y = 0.07$) and eventually disappears at $y = 0.12$. In addition, Palmer et al. have reported a decrease in $T_C$ and the superconducting volume fraction with the substitution of sulfur for oxygen in a La$_{1.85}$Sr$_{0.15}$CuO$_{1-y}$S$_y$ system at $y = 0.05$ and 0.1 [9]. X-ray emission spectroscopy results revealed the presence of the SO$_{2-}$ species in the La$_{1.85}$Sr$_{0.15}$CuO$_{2-x}$S$_x$ samples. As no SrSO$_x$ impurity was observed in the X-ray diffraction (XRD) patterns, they concluded that the incorporated sulfur could be confirmed to be situated on the copper site as $S^{2-}$, affording SO$_{2-}$. Based on these results, the substitution of sulfur in the oxygen site is thought to decrease the hole content of Cu ions.

The determination of substitution behavior is indispensable to interpreting superconducting properties. Machida et al. have reported the presence of a SO$_{2-}$ species by X-ray photoelectron spectroscopy (XPS) data for La$_{1-x}$Sr$_x$Cu(O/S)$_{1-4}$; this result is in agreement with those reported previously. They concluded that sulfur does not act as a substitution in the oxygen and copper sites but occupies the interstitial sites, affording SO$_{2-}$ [10]. By evaluating the intensities of the peaks in the XRD patterns, they confirmed that half the sulfur content was SrSO$_x$, and the other half was incorporated into the crystal structure. Although these experimental results...
have been reported, the reduction of the hole content by the substitution of sulfur for oxygen in LSCO is not conclusive, because the decay of superconductivity can be induced by factors of extrinsic origin, such as the presence of the impurity phase and loss of crystallinity.

In this study, the crystal structures and phase fractions of $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4\text{S}_x$ samples were precisely investigated by synchrotron XRD (SXRD). We chose $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4$ as the mother compound for sulfur substitution. Because $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4$ is positioned just above the overdoped region in the phase diagram, which does not exhibit superconductivity, this composition reveals sensitivity to decreases in the hole content by showing the recovery of superconductivity. SXRD can afford high-resolution, reliable XRD patterns, which permit accurate analysis of the crystal structure and phase composition for investigating the morphology of sulfur. X-ray photoelectron spectroscopy (XPS) was employed to examine the electronic state of sulfur. In addition, the effect of sulfur incorporated into $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4\text{S}_x$ on superconductivity was described.

2. Experimental details

$\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4\text{S}_x$ was prepared by solid-state reaction according to the method used in previously reported studies [8]. A mixture of $\text{La}_2\text{O}_3$ (99.9%; Rare Metallic Co., Chiyoda-ku, Tokyo, Japan), $\text{SrCO}_3$ (99.9%; Rare Metallic Co., Japan), $\text{CuO}$ (99.9%; Rare Metallic Co., Japan), and $\text{CuS}$ (99%; Rare Metallic Co., Japan) powders was used. First, $\text{La}_2\text{O}_3$ powder was precalcined at 1173 K, while $\text{SrCO}_3$ and $\text{CuO}$ powders were calcined at 873 K. Second, the powders were weighed to nominal stoichiometric ratios with $x = 0.025, 0.075, 0.125, 0.15, \text{ and } 0.30$; hereafter, these samples are denoted as 0025, 0075, 0125, 015, and 030, respectively. Finally, the mixtures were pelletized and treated at 1273 K for 12 h in air.

SXRD patterns were recorded using a solid-state detector with a large Debye–Scherrer camera installed at the BL02B2 beamline of SPring-8 [11] and refined by the Rietveld method using the RIETAN-FP program [12]. The wavelengths were set to $\lambda = 0.41975$ Å for 0025, 0075, 0125, and 015, and to 0.42045 Å for 030. Magnetic susceptibility was measured with a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL; Quantum Design, San Diego, CA, USA) with zero-field cooling. XPS spectra were recorded on a spectrometer (ESCA-3400; Shimadzu, Kyoto, Japan) with Mg-K radiation. The obtained XPS spectra were calibrated using the C 1s peak position (284.8 eV). The particle morphology of the samples was investigated using a scanning electron microscope (JCM-500; JEOL, Akishima, Tokyo, Japan).

3. Results and discussion

Figure 1 shows the room-temperature SXRD patterns and results of Rietveld refinement for the 0075, 015, and 030 samples. A $\text{K}_2\text{NiF}_4$-type LSCO phase was observed for all samples, and the crystal structure changed from the tetragonal ($I4/mmm$) to the orthorhombic ($Bmab$) phase with increases in sulfur content above 0075. This behavior is in agreement with that reported previously [8–10]. Table 1 summarizes the refined phase fractions. At a low sulfur content, impurity phases such as $\text{SrSO}_4$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CuO}_{2.5}$ [13], were observed as broad peaks in the SXRD patterns, and further increases in the sulfur...

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content afforded peaks corresponding to CuO and La$_2$O$_3$SO$_4$. Notably, the refined phase fractions of SrSO$_4$ were comparable to a nominal sulfur content of less than 0.15, indicating that the majority of sulfur is incorporated into the impurity phase. This indicates the presence of a strontium deficiency in the LSCO phase caused by formation of SrSO$_4$ as an external impurity phase. For the 0.30 sample, CuO became dominant in the phase fractions, indicating that the decrease in the Sr content from the LSCO phase had reached its limit, leading to phase decomposition. To confirm the independence of the sulfur content from the LSCO phase, the lattice parameters of the obtained samples, La$_{2-x}$Sr$_x$CuO$_4$ system [14] and Sr-deficient samples without sulfur, were compared. Sr-deficient samples with compositions of La$_{1.7}$Sr$_{0.3-x}$CuO$_4$ (La$_{1.7}$Sr$_{0.3-0.03}$CuO$_4$) and La$_{1.7}$Sr$_{0.22}$CuO$_4$ (La$_{1.7}$Sr$_{0.3-0.07}$CuO$_4$) were prepared as counter compounds for the 0.025 and 0.075 samples, respectively. Figure 2 summarizes their lattice parameters, where the data for La$_{1.7}$Sr$_{0.3-x}$CuO$_4$S$_x$ and La$_{1.7}$Sr$_{0.3-0.05}$CuO$_4$ are plotted on the corresponding c axis lengths of the La$_{2-x}$Sr$_x$CuO$_4$ system. With increases in sulfur content, the a and b axes lengthened, while the c axis contracted, a result that is in agreement with those reported previously [8,9]. Notably, the changes in lattice parameters were greater for La$_{1.7}$Sr$_{0.3-x}$CuO$_4$S$_x$ than for the Sr-deficient counterparts. Larger a and b lattice parameters suggested a decrease in the valence of the Cu ion leading to an increase in the Cu–O bond length. This decrease of the valence of the Cu ion, in addition to the Sr deficiency, can presumably occur in two ways, i.e. oxygen deficiency and substitution of sulfur for oxygen, respectively. Nevertheless, oxygen deficiency in the La$_{1.7}$Sr$_{0.3-x}$CuO$_4$S$_x$ samples was not plausible, as these samples were treated at 1273 K in air. These findings suggested that the sulfur content is not independent of the LSCO phase, but that it is incorporated into the crystal structure, leading to decreased hole content of the Cu ion in addition to a Sr deficiency. The large deviation between the lattice parameters of La$_{1.7}$Sr$_{0.3-x}$CuO$_4$S$_x$ and La$_{2-x}$Sr$_x$CuO$_4$ in a high-sulfur-content region can be explained by the large Sr deficiency.

Superconducting characteristics were investigated using a SQUID magnetometer. Figure 3 shows the temperature dependence of magnetic susceptibility of the samples. Superconductivity was not observed for La$_{1.7}$Sr$_{0.3}$CuO$_4$ because this composition is positioned just above the overdoped region in the superconducting

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**Table 1.** Refined phase fractions obtained through Rietveld refinement.

| Sample | Nominal x in La$_{1.7}$Sr$_x$CuO$_4$–S$_x$ | LSCO (mol%) | SrSO$_4$ (mol%) | La$_{2.5}$Sr$_{2.5}$CuO$_4$ (mol%) | CuO (mol%) | La$_2$O$_3$SO$_4$ (mol%) |
|--------|---------------------------------|-------------|----------------|-------------------------------|-------------|--------------------------|
| 0025   | 0.25                            | 96.90       | 2.44           | 0.66                          | 0           | 0                        |
| 0075   | 0.75                            | 91.83       | 7.15           | 1.02                          | 0           | 0                        |
| 0125   | 0.125                           | 85.92       | 11.35          | 0.1                           | 2.63        | 0                        |
| 015    | 0.15                            | 83.37       | 13.54          | 0.42                          | 2.67        | 0                        |
| 030    | 0.30                            | 66.70       | 20.20          | 0.8                           | 12.89       | 0.21                     |

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**Figure 2.** Composition dependence of the lattice parameters. Blue symbols denote the lattice parameters previously reported for La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [14]. Lattice parameters for the La$_{1.7}$Sr$_{0.3}$CuO$_4$S$_x$ samples are located at the corresponding c axis length of LSCO denoted by red symbols, while those for Sr-deficient La$_{1.7}$Sr$_{0.22}$CuO$_4$ and La$_{1.7}$Sr$_{0.22}$CuO$_4$ are denoted by green symbols in the same manner.

**Figure 3.** Temperature dependence of magnetic susceptibility for La$_{1.7}$Sr$_{0.3}$CuO$_4$S$_x$ (filled symbols) and for Sr-deficient La$_{1.7}$Sr$_{0.22}$CuO$_4$ and La$_{1.7}$Sr$_{0.22}$CuO$_4$ (open symbols) samples. Magnetic susceptibility was measured under magnetic fields of 20 and 5 Oe for La$_{1.7}$Sr$_{0.3}$CuO$_4$S$_x$ and Sr-deficient La$_{1.7}$Sr$_{0.22}$CuO$_4$ and La$_{1.7}$Sr$_{0.22}$CuO$_4$, respectively.
phase diagram [4]; however, the addition of sulfur led to the recovery of superconductivity from the 0025 sample. For the 030 sample, it was deduced that a much lower hole content of the Cu ion was required to exhibit superconductivity. Table 2 shows the $T_C$ values observed for each sample. Judging from the superconducting volume fractions at 2 K (27% for 0025 and 21% for 0075), superconductivity originated from the major phase rather than from the minor phase. This behavior is related to the reduced hole content of the Cu ion, which was attributed to the decrease in Sr content resulting from the formation of SrSO$_4$ impurity. However, the observed $T_C$ values for the 0025 and 0075 samples were 37 and 38 K, respectively; these values are considerably higher than the values, i.e. $T_C = 17$ and 18 K, observed for the sulfur-free counterparts La$_{1.70}$Sr$_{0.27}$CuO$_4$ and La$_{1.70}$Sr$_{0.27}$CuO$_4$, respectively. These results indicate that some of the sulfur is incorporated into the LSCO phase in agreement with the composition dependence of lattice parameters.

The electronic state was further investigated to interpret the superconductivity. Hence, the S 2p XPS spectra of sulfur were investigated (Figure 4). Because of the limited amount of sulfur, the resolution was insufficient to separate S 2p$_{3/2}$ and 2p$_{1/2}$. The component corresponding to the SO$_4^{2-}$ species was clearly observed for all samples, which was in agreement with the previous report [15]. For the 0125 and 015 samples, however, additional peaks corresponding to S$^{2-}$ and S$_2^{2-}$ were observed, suggesting the possibility that sulfur is incorporated into the LSCO phase [16,17]. In the 030 sample, the S$^{2-}$ and S$_2^{2-}$ components disappeared again. This behavior can be interpreted as meaning that the LSCO phase particles were covered by the SrSO$_4$ impurity, as is clear from the particle morphology (Figure 5). When comparing with the particle morphology of sulfur-free La$_{1.7}$Sr$_{0.3}$CuO$_4$, that of the La$_{1.5}$Sr$_{0.3}$CuO$_4$S$_x$ samples indicates that grain growth was inhibited by the

Table 2. $T_C$ measured by zero-field cooling for La$_{1.7}$Sr$_{0.3}$CuO$_{4-x}$S$_x$ and Sr-deficient La$_{1.7}$Sr$_{0.3-x}$CuO$_4$.

| Sample          | $T_C$ (K) |
|-----------------|-----------|
| 0025            | 37        |
| 0075            | 38        |
| 0125            | 30        |
| 015             | 25        |
| 030             | 0         |
| La$_{1.7}$Sr$_{0.3}$CuO$_4$ | 17       |
| La$_{1.5}$Sr$_{0.3}$CuO$_4$ | 18       |

Figure 4. S 2p XPS spectra of La$_{1.7}$Sr$_{0.3}$CuO$_4$. Red and black lines denote the presence and absence of superconductivity, respectively.

Figure 5. Scanning electron microscope (SEM) images of the La$_{1.7}$Sr$_{0.3}$CuO$_4$, 0075, 015, and 030 powder samples with 5000× magnification.
increases in sulfur content. The limited sulfur content makes it difficult to perform elemental analysis to determine the dispersion of SrSO$_4$ and other impurity species on the particle surfaces. We can speculate, however, that this change in morphology can be understood by considering the presence of the impurity phase on the LSCO phase surface to inhibit grain growth.

At this stage, the sulfur incorporated into the LSCO phase cannot be directly observed; some supporting evidence for its presence has been provided, however, by the lattice parameters and superconducting properties. If the sulfur content is independent of the LSCO phase and simply reduces the Sr content of the LSCO phase by forming SrSO$_4$, we cannot explain the higher $T_C$ observed for the La$_{1-x}$Sr$_{0.3}$CuO$_4$$_x$$_y$ samples than for their Sr-deficient La$_{1-x}$Sr$_{0.3}$CuO$_4$$_y$ counterparts. The difference in the lattice parameters (longer $a$ and $b$ axes and a shorter $c$ axis for the La$_{1-x}$Sr$_{0.3}$CuO$_4$$_y$$_x$ samples) also indicates the presence of reduced hole content by substitution of sulfur for oxygen, in addition to a Sr deficiency caused by the formation of SrSO$_4$.

4. Conclusion

The substitution of oxygen with sulfur in La$_{1-x}$Sr$_{0.3}$CuO$_4$ was examined in this study. Structural analysis by SXRD revealed the incorporation of a majority of the sulfur into the SrSO$_4$ phase rather than LSCO phase. The superconducting properties of this La$_{1-x}$Sr$_{0.3}$CuO$_4$$_y$$_x$ system revealed, however, that the LSCO phase is dependent on sulfur content because no consideration of the Sr deficiency based on the formation of SrSO$_4$ can sufficiently explain the superconductivity. The changes in lattice parameters and XPS spectra provide supporting evidence for the incorporation of sulfur into the LSCO phase, leading to decreased hole content in the Cu ion.

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Disclosure statement

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References

[1] Dagotto E. Correlated electrons in high-temperature superconductors. Rev Mod Phys. 1994;66(3):763–840.
[2] Lee PA, Nagaosa N, Wen X-G. Doping a Mott insulator: physics of high-temperature superconductivity. Rev Mod Phys. 2006;78:17–85.
[3] Hashimoto M, Vishik IM, He R-H, et al. Energy gaps in high-transition-temperature cuprate superconductors. Nat Phys. 2014;10:483–495.
[4] Ohishi K, Syono Y. Dependence of lattice-parameters and Tc on the hole concentration determined by precise measurement of the oxygen-content of M$_x$La$_{2-x}$Sr$_x$CuO$_4$$_y$ ($M = Ba, Sr, Ca$). J Solid State Chem. 1991;95:136–144.
[5] Kageyama H, Hayashi K, Maeda K, et al. Expanding frontiers in materials chemistry and physics with multiple anions. Nat Commun. 2018;9:772.
[6] Almamouri M, Edwards PP, Greaves C, et al. Synthesis and superconducting properties of the strontium copper oxy-fluoride Sr$_x$CuOF$_2$$_x$. Nature. 1994;369:382–384.
[7] James ACWP, Murphy DW, Zahrak SM. Superconductivity at 27 K in fluorine-doped Nd$_3$CuO$_4$. Nature. 1989;338:240.
[8] Kozuka H, Fujihara S, Yoko T, et al. Effect of sulfur doping on the structure and properties of La$_{2-x}$Sr$_x$CuO$_4$ superconductor. Jpn J Appl Phys. 1999;29:1608–1611.
[9] Palmer HM, Greaves C, Slaski M, et al. Substitution of SO$_4$ anions in La$_{1.85}$Sr$_{0.15}$CuO$_4$: structure and superconductivity. Physica C. 1997;291:104–112.
[10] Machida M, Ochiai K, Ito K, et al. Synthesis, crystal structure and catalytic activity for C$_2$H$_4$ combustion of La–Sr–Cu–O–S with K$_2$NiF$_4$-type perovskite structure. J Catal. 2006;238:58–66.
[11] Kawaguchi S, Takemoto M, Osaka K, et al. High-throughput powder diffraction measurement system consisting of multiple MYTHEN detectors at beamline BL02B2 of SPring-8. Rev Sci Instrum. 2017;88:085111.
[12] Izumi F, Momma K. Three-dimensional visualization in powder diffraction. Solid State Phenom. 2007;130:15–20.
[13] Hiroi Z, Takano M. Absence of superconductivity in the doped antiferromagnetic spin-ladder compound (La$_x$Sr)CuO$_2$. Nature. 1995;377:41.
[14] Radaelli PG, Hinks DG, Mitchell AW, et al. Structural and superconducting properties of La$_{2-x}$Sr$_x$CuO$_4$ as a function of Sr content. Phys Rev B. 1994;49:4163–4175.
[15] Krylova V, Andrulevicius M, Optical, XPS and XRD studies of semiconducting copper sulfide layers on a polycrystalline film. Int J Photonenergy. 2009;2009:1–8.
[16] Schaufuss AG, Nesbitt HW, Karito I, et al. Incipient oxidation of fractured pyrite surfaces in air. J Electron Spectrosc Relat Phenom. 1998;96:69–82.
[17] Park MS, Yu JS, Kim KJ, et al. One-step synthesis of a sulfur-impregnated graphene cathode for lithium-sulfur batteries. Phys Chem Chem Phys. 2012;14:6796–6804.