Relationship between structural phase transition and carrier concentration in $La_{2-x-y}Sr_xR_yCuO_4$ (R = Ce or Tb)

T. Naito *, Y. Ueno, R. Takahashi, H. Fujishiro

Faculty of Engineering, Iwate University, Morioka 020-8551, Japan

ABSTRACT

We have studied the relationship between the crystal structure and the carrier concentration in $La_{2-x-y}Sr_xCe_yCuO_4$ by low-temperature X-ray diffraction method. The analysis for the $[110]_t$ peak of the tetragonal index confirms that the high-temperature tetragonal phase changes to the low-temperature orthorhombic one in both $La_{1.89}Sr_{0.11}CuO_4$ and $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$. We have also examined the effects of Tb substitution for La-site on the superconductivity and the structure in $La_{2-x-y}Sr_xTb_yCuO_4$. A dip of the critical temperature $T_c(x)$ due to the 1/8 anomaly and a maximum of $T_c(x)$ at the optimum carrier concentration do not depend on the Tb concentration. This result suggests the possibility that Tb is introduced as the trivalent ion for x = 0.07–0.18.

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1. Introduction

It is widely accepted that a structural phase transition from the high-temperature tetragonal (HTT) phase to the low-temperature orthorhombic (LTO) phase occurs in $La_{2-x}AE_xCuO_4$ (AE = Sr, Ba) with decreasing temperature. This HTT–LTO transition causes a buckling of the CuO_2 planes and a tilting of the CuO_6 octahedra, and then hides an intrinsic nature relating with superconductivity such as critical temperature T_c [1], spin fluctuation [2] and so on. The temperature at the structural phase transition T_{d1} decreases with increasing x, and finally reaches to zero at around x = 0.2 [3]. Therefore, the HTT phase only exists in an entire temperature range for the $x \geqslant 0.2$ region. Dabrowski et al. reported that the relaxation of the orthorhombic distortion of the CuO_2 planes with increasing x by observing the increase of the Cu–O(1)–Cu bond angle, where O(1) is in the CuO_2 plane [4]. If the distortion of the CuO_2 planes depends only on the x value, $La_{2-x}Sr_xCuO_4$ with the flatter CuO_2 planes can be obtained by the introduction of electrons by substituting tetravalent or higher valence ion for the La-site. In view of the so-called 1/8 problem, $La_{2-x-y}Ba_xCe_yCuO_4$ and $La_{2-x-y}Ba_xTb_yCuO_4$ were studied. As a result, Ce was tetravalent [5] and Tb took the average valence from 3.1 (x = 0.060) to 3.6 (x = 0.26) [6].

We studied the effects of the substitution of tetravalent Ce ion on the superconductivity and the HTT–LTO transition in $La_{2-x-y}Sr_xCe_yCuO_4$ by measuring the electrical resistivity and the thermal dilatation to detect the lattice anomaly [7]. $T_c(x)$ was shifted to the higher x region by the introduction of Ce, on the other hand, $T_{d1}(x)$ was not affected. This suggests that the struc-

tural phase transition is only affected by the Sr concentration. However, the single-phase of $La_{2-x-y}Sr_xCe_yCuO_4$ can be prepared only up to y = 0.01.

In this paper, we report the HTT–LTO transition in $La_{2-x-y}Sr_xCe_yCuO_4$ which is measured directly by a low-temperature X-ray diffraction method. We also report the effects of the Tb substitution on the superconductivity and the HTT–LTO transition.

2. Experimental

Polycrystalline samples of $La_{2-x-y}Sr_xR_yCuO_4$ (R = Ce, Tb; x = 0.07–0.21, y = 0–0.05) were prepared by a standard solid-state reaction method. Raw powders of La_2O_3, $SrCO_3$, CeO_2, Tb_4O_7 and CuO were weighted with an appropriate molar ratio and ground. The mixture was calcined at 900 °C for 24 h in air, and subsequently the calcined compound was pelletized and fired at 1150 °C for 72 h in air. As-sintered samples were annealed at 800 °C for 24 h in a 1 bar flowing oxygen gas. $La_{2-x-y}Sr_xCe_yCuO_4$ for y = 0 and 0.01 and all $La_{2-x-y}Sr_xTb_yCuO_4$ samples were confirmed to be the single-phase by a powder X-ray diffraction (XRD) pattern at room temperature. XRD at low temperatures below room temperature was performed using a hand-made cryostat with a Gifford–McMahon cycle helium refrigerator. Electrical resistivity, $\rho(T)$, was measured by a four-probe method.

3. Results and discussion

3.1. Effects of Ce substitution

Fig. 1a and b shows the x dependence of T_c and T_{d1} of $La_{2-x-y}Sr_xCe_yCuO_4$ for y = 0 and 0.01. The dip of $T_c(x)$ due to the

* Corresponding author. Tel.: +81 19 621 6362; fax: +81 19 621 6362.
 E-mail address: tnaito@iwate-u.ac.jp (T. Naito).
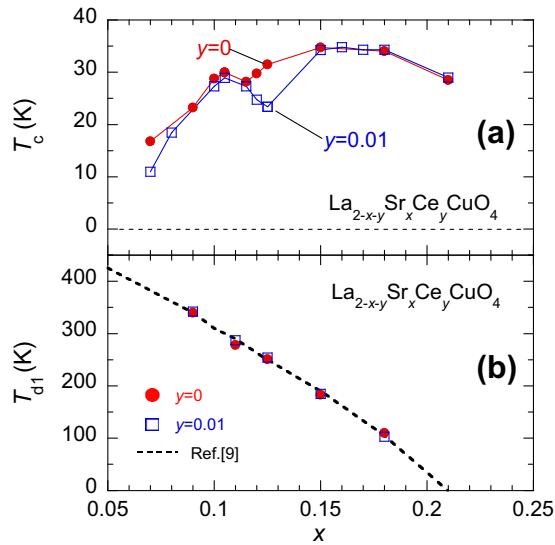
Fig. 1. (a) Sr-concentration x dependence of T_c for $La_{2-x-y}Sr_xCe_yCuO_4$ samples with $y = 0$ and 0.01. (b) $T_{d1}(x)$ for $La_{2-x-y}Sr_xCe_yCuO_4$ samples with $y = 0$ and 0.01. The broken line shows the reported $T_{d1}(x)$ [9].

1/8 problem shifts from $x = 0.115$ [8] for $y = 0$ to $x = 0.125$ for $y = 0.01$. The x value at the maximum of T_c also shifts from 0.15 ($y = 0$) to 0.16 ($y = 0.01$). The change in the x values are consistent with the Ce concentration. On the other hand, $T_{d1}(x)$ is not affected by the introduction of Ce. The T_{d1} values were determined by

measuring the thermal dilatation using a strain gage. To detect directly the HTT–LTO transition, we performed the X-ray diffraction at low temperatures.

Fig. 2a and b shows the XRD pattern around the $[110]_t$ peak of the tetragonal index for $La_{1.89}Sr_{0.11}CuO_4$ at 300 K and 182 K, respectively. The data were fitted using a Gaussian curve. The $[110]_t$ peak at 300 K and 182 K appears identical around $2\theta = 33.45°$ within an experimental error. The peak becomes broad with decreasing temperature; the full width at half maximum (FWHM) is about 0.24° and 0.33° at 300 K and 182 K, respectively. Since the $[110]_t$ peak of the tetragonal phase equivalent to the $[200]_o$ and $[020]_o$ peaks of the orthorhombic index, the orthorhombicity is evaluated by the separation of the $[110]_t$ peak. The difference of the peak angle, $\Delta(2\theta)$, between the $[200]_o$ and $[020]_o$ peaks changes from 0.01° at 300 K to 0.17° at 182 K, which clearly demonstrates that the crystal structure changes from the HTT phase at 300 K to the LTO one at 182 K. Fig. 2c and d represents the XRD pattern for $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$ at 300 K and 220 K, respectively. The shape of XRD pattern is quite similar to that of non Ce-substituted sample. The intensity of $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$ is about half of that of $La_{1.89}Sr_{0.11}CuO_4$. The similar analysis was adopted for both XRD patterns. $\Delta(2\theta)$ is approximately 0.015° at 300 K and 0.14° at 220 K, suggesting that the HTT–LTO transition occurs between both temperatures. T_{d1} could not be exactly determined but the HTT–LTO transition in $La_{1.89}Sr_{0.11}CuO_4$ and $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$ was confirmed directly by the low-temperature XRD method. Therefore, we can regard that the thermal dilatation anomaly reported in the previous paper [7] represents the HTT–LTO transition.
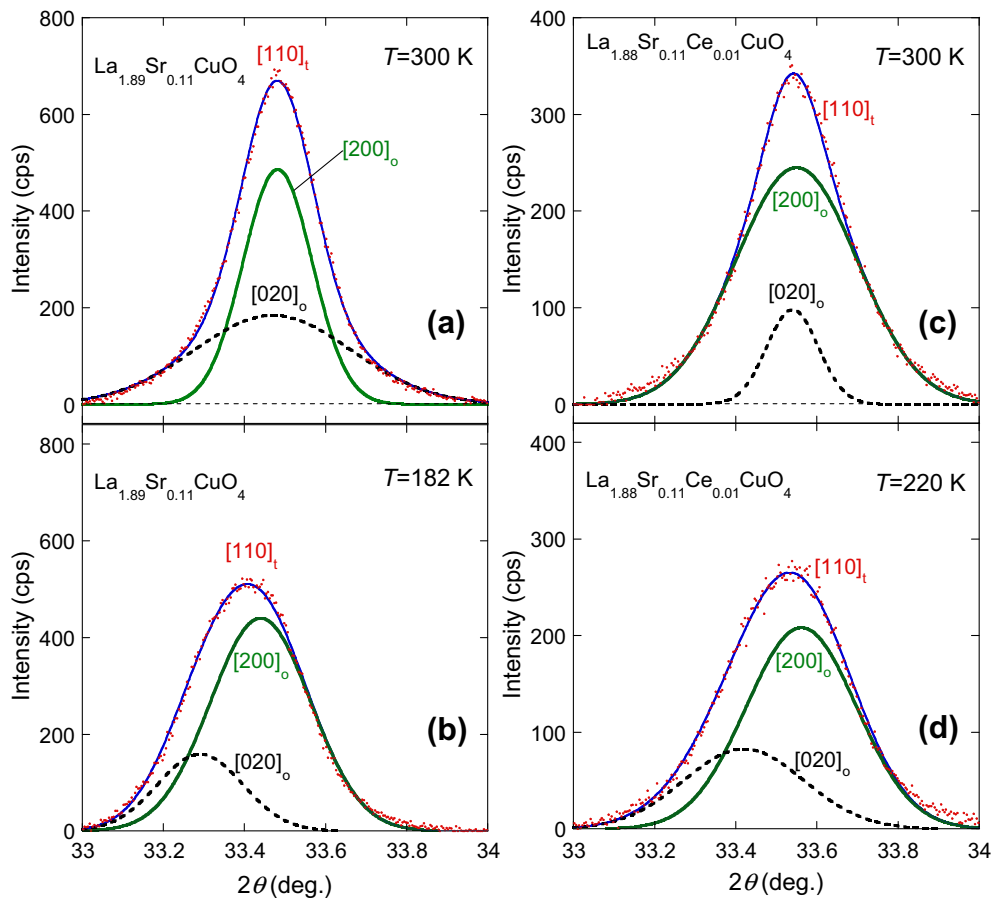
Fig. 2. X-ray diffraction patterns at around $[110]_t$ peak of the tetragonal index at (a) 300 K and (b) 182 K for $La_{1.89}Sr_{0.11}CuO_4$ and at (c) 300 K and 220 K for $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$.
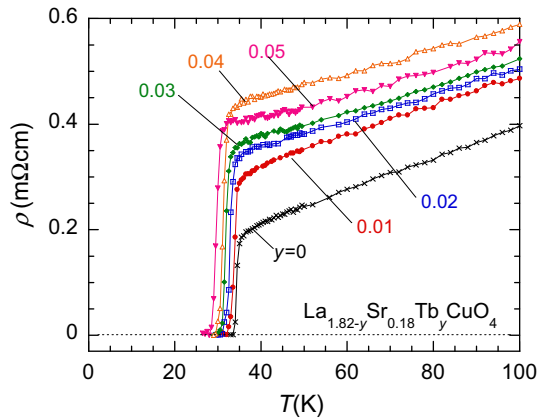
Fig. 3. Temperature dependence of the electrical resistivity of $La_{1.82-y}Sr_{0.18}Tb_yCuO_4$ samples for y = 0–0.05.

Fig. 5. Sr-concentration x dependence of T_c for $La_{2-x-y}Sr_xTb_yCuO_4$ samples with y = 0 and 0.01.

trivalent ion in $La_{2-x-y}Sr_xTb_yCuO_4$ for x = 0.07–0.18 and acts as an impurity which suppresses the superconductivity.

4. Summary

We have studied that the structural phase transition between the high-temperature tetragonal (HTT) and the low-temperature orthorhombic (LTO) phases by the temperature-variable X-ray diffraction method in $La_{1.89}Sr_{0.11}CuO_4$ and $La_{1.88}Sr_{0.11}Ce_{0.01}CuO_4$. The orthorhombicity was evaluated at the $[1\,1\,0]_t$ peak of the tetragonal index by the peak separation using the $[2\,0\,0]_o$ and $[0\,2\,0]_o$ of the orthorhombic index. We confirmed directly that the HTT phase changes to the LTO one passing through the structural phase transition temperature reported previously for both samples. This suggests that the thermal dilatation can detect the HTT–LTO transition.

The effects of Tb-substitution on the superconductivity and the structural phase transition in $La_{2-x-y}Sr_xTb_yCuO_4$ were also studied. The dip due to the 1/8 problem and the maximum at the optimum carrier concentration in $T_c(x)$ are not affected by the Tb-substitution. The monotonic decrease in $T_c(x = 0.18, y)$ was observed. These results suggest that Tb is not introduced as tetravalent or higher valence ion in $La_{2-x-y}Sr_xTb_yCuO_4$ for x = 0.07–0.18.
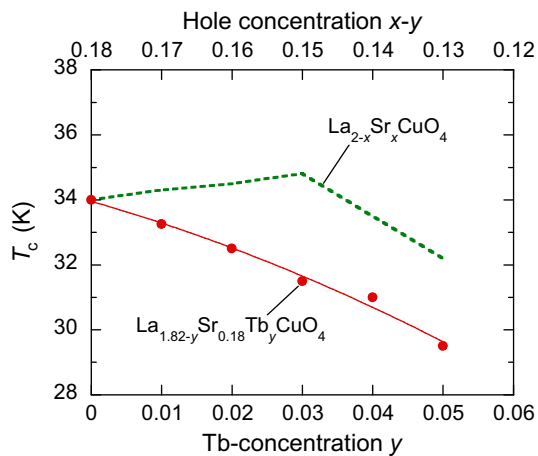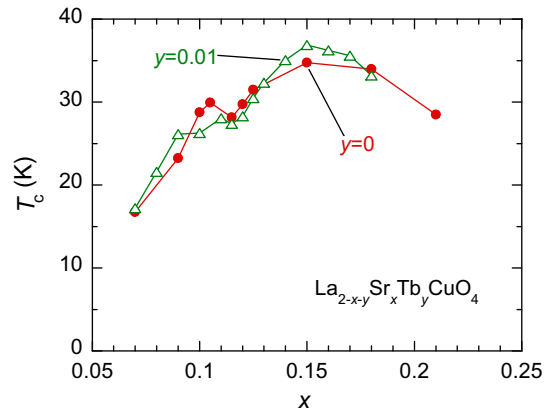
Acknowledgments

Fig. 4. Tb-concentration y dependence of T_c of $La_{1.82-y}Sr_{0.18}Tb_yCuO_4$. Upper horizontal axis represents the expected hole concentration $x - y$. The dotted line represents $T_c(x)$ of $La_{2-x}Sr_xCuO_4$.

3.2. Effects of Tb substitution

Fig. 3 shows the temperature dependence of the resistivity of $La_{1.82-y}Sr_{0.18}Tb_yCuO_4$ for y = 0–0.05. $\rho(T)$ decreases monotonically with decreasing temperature and shows a sharp zero-resistivity transition for all samples. Fig. 4 shows the Tb-concentration y dependence of T_c of $La_{1.82-y}Sr_{0.18}Tb_yCuO_4$. Upper horizontal-axis represents the expected hole concentration, $x - y$. $T_c(y)$ decreases monotonically with increasing y. This suppression of the superconductivity suggests that Tb ion acts as an impurity. If Tb-substitution introduces the electrons, $T_c(y)$ is expected to increase initially up to y = 0.03 which corresponds to the optimum hole concentration 0.15, and subsequently to decrease with increasing y, as the dotted line which is $T_c(x)$ of $La_{2-x}Sr_xCuO_4$. Fig. 5 shows the Sr-concentration x dependence of T_c of $La_{2-x-y}Sr_xTb_yCuO_4$ for y = 0 and 0.01. $T_c(x)$ for y = 0 is the same as that in Fig. 1. The dip due to the 1/8 problem appears at around x = 0.115 for y = 0.01 samples, although the dip structure is not so clear. On the other hand, the maximum of T_c appears at x = 0.15. Tb-substitution seems not to affect the structure of $T_c(x)$. Bao et al. reported that the average valence of Tb changes from 3.1 at x = 0.060 to 3.6 in x = 0.26 in $La_{2-x-y}Ba_xTb_yCuO_4$ [6]. Our results suggest that Tb is

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