

THERMAL CONDUCTIVITY OF T*-PHASE $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ OXIDE SUPERCONDUCTORS

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T*-phase (214) oxide superconductors, $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$) were fabricated in a single phase and the thermal conductivity κ were measured between 10K and 150K to investigate the role of the apical oxygen for phonon scattering. The T*-phase structure has one apical oxygen in a unit Cu-O square. Similarly to T-phase with two apical oxygen such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, T*-phase is found to have much smaller κ than that of T'-phase without apical oxygen such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. The existence of the apical oxygen seriously influences the phonon transport.

1. INTRODUCTION

In the so-called (214) oxide superconductors, there are three different but closely related tetragonal structures which are named as T-phase with Cu-O octahedra such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), T'-phase with Cu-O squares such as $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (NCCO) and T*-phase with Cu-O pyramids such as $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ (NCSCO). Contrary to several high- T_c cuprates such as YBCO, Bi2223, in which the thermal conductivity $\kappa(T)$ shows a characteristic enhancement below the transition temperature T_c , the (214) superconductors with T-phase and T'-phase structures do not clearly show the characteristic enhancement below T_c . There is now much argument about the origin of the $\kappa(T)$ enhancement, whether it is electronic or phononic.^{1,2} Even in a (214) family, the magnitude and the temperature dependence of κ are quite different between T-phase and T'-phase.³ The existence of apical oxygen atoms in a unit Cu-O square and the structural instability between the high temperature tetragonal (HTT) and the low temperature orthorhombic (LTO) phase seem to be the origin to reduce κ of the T-phase system. We have measured the thermal conductivity κ of $\text{YBa}_2\text{Cu}_3\text{O}_7$,⁴ $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$,⁵ $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$,⁶ $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M=\text{Ba}, \text{Sr}$)⁷ etc. and have analyzed the phonon thermal conductivity κ_{ph} based on the Tewordt and Wölkhausen (TW) theory.⁸ Although there are many investigations about the structure and superconductivity for T*-phase $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ system,^{9,10} there have been no reported data for thermal transport properties so far as we know. In this paper, we fabricated the single phase

sintered T*-phase (214) superconductors, $(\text{Nd}_{1-x}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$), and measured the thermal conductivity. T*-phase materials in which only one apical oxygen exists in a unit Cu-O square have an intermediate structure between T-phase and T'-phase and is a suitable system to investigate the role of the apical oxygen for the phonon scattering, that is, to investigate the origin of the considerably different κ behaviors between T-phase and T'-phase.

2. EXPERIMENTAL

$(\text{Nd}_{1-x}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$) sintered materials were prepared from stoichiometric mixtures of Nd_2O_3 , CeO_2 , SrCO_3 and CuO raw powders. The mixtures were calcined twice at 900°C for 12h in air. They were pressed into pellets and sintered at 1150°C for 18h in air and then furnace-cooled. Finally, the samples were heat-treated at various temperatures $T_{\text{H.T.}}$ from 1000°C to 1210°C for 24h in flowing oxygen and furnace-cooled. The density of the samples was higher than 80% of each ideal density. The thermal conductivity was measured between 10 ~ 150K by a continuous heat-flow method with an automated measuring system using a GM refrigerator.⁵ The Seebeck coefficient was also measured by an identical experimental setup with κ .

3. RESULTS

Figure 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ of $(\text{Nd}_{1-x}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$) sintered materials for various heat-treatment (H.T.) temperatures $T_{\text{H.T.}}$. The sample without H.T. (as-sinter) showed the semiconductive $\rho(T)$ behavior and the superconducting transition did not occur. For all the H.T. samples $\rho(T)$ decreased with increasing $T_{\text{H.T.}}$ and the trend of the superconducting transition was observed. However, except for the sample of $T_{\text{H.T.}}=1210^\circ\text{C}$, the zero resistance was not observed down to 10K. The samples which were heat-treated at the higher temperature than $T_{\text{H.T.}}=1220^\circ\text{C}$ did not show the superconducting transition either. $\rho(T)$ of $T_{\text{H.T.}}=1210^\circ\text{C}$ sample showed the low and metallic $\rho(T)$ and a clear superconductivity ($T_c(\text{onset})=23\text{K}$, $T_c(\text{end})=16\text{K}$) was confirmed which was the highest transition temperature in this study as shown in Fig. 2. The X-ray diffraction analyses confirmed that only the $T_{\text{H.T.}}=1210^\circ\text{C}$ sample showed a pure T*-phase structure without impurity phases. The observed T_c is as high as those of T*-phase which were reported by other authors.⁹⁻¹¹

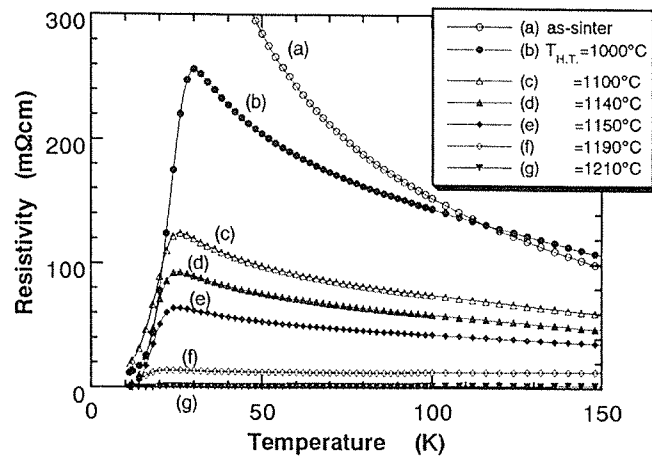


FIGURE 1 Temperature dependence of the electrical resistivity $\rho(T)$ of $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$) sintered materials for various heat-treatment temperatures $T_{\text{H.T.}}$.

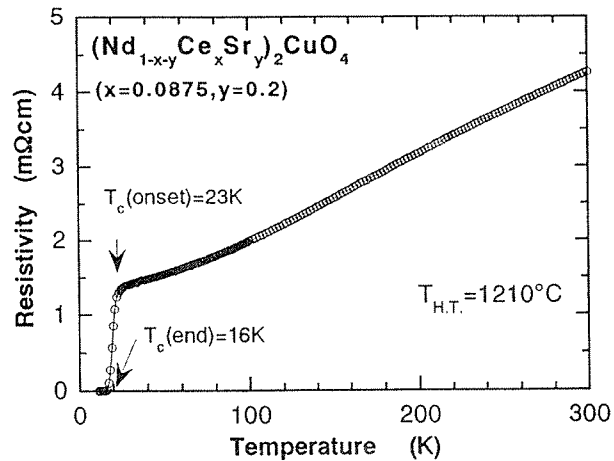


FIGURE 2 The electrical resistivity $\rho(T)$ of the best $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ ($x=0.0875$, $y=0.2$) samples ($T_{\text{H.T.}}=1210^\circ\text{C}$).

We characterized and analyzed the best sample ($T_{\text{HT}}=1210^\circ\text{C}$) as a standard T^* -phase material.

Figure 3 shows the temperature dependence of the magnetization $M(T)$ of the sample under the magnetic field of $H=50\text{G}$. T_c was determined also to be $T_c=16\text{K}$ from the magnetic measurement. Figure 4 shows the temperature dependence of the thermal

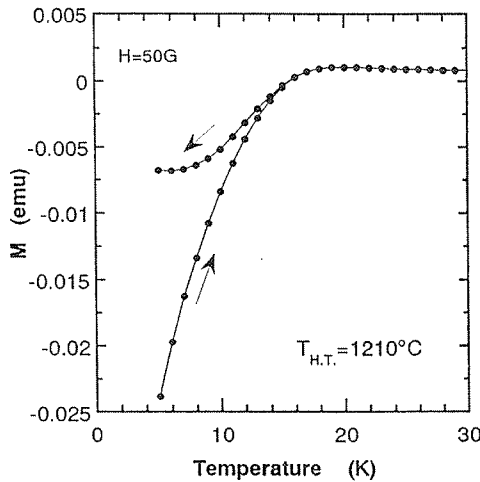


FIGURE 3
Magnetization $M(T)$ of the T^* -sample.

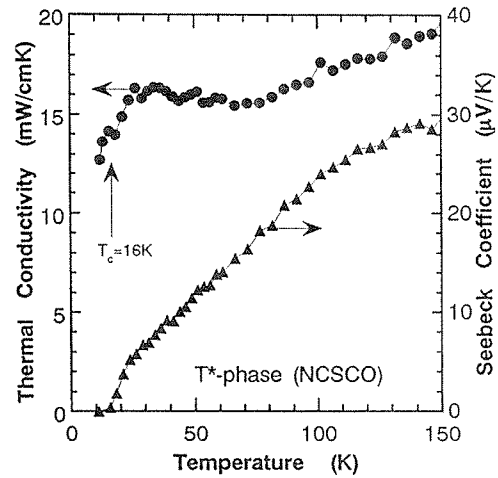


FIGURE 4
Temperature dependence of the thermal phase conductivity κ and the Seebeck coefficients.

conductivity κ and the Seebeck coefficient S . κ decreased monotonically with decreasing temperature and showed a slight local maximum at around $T=30\text{K}$ and then gradually decreased down to 10K . The anomaly of κ below T_c was not recognized similarly to κ of NCCO .⁶ The Seebeck coefficient S was positive and the decreased to zero below T_c . It was found that the charged carrier is a hole in this compound as pointed out in the other reported.¹⁰

4. DISCUSSION

In this subsection, we compare the thermal conductivity $\kappa(T)$ of the present $(\text{Nd}_{1-x-y}\text{Ce}_x\text{Sr}_y)_2\text{CuO}_4$ (T^* -phase) sample with those of other polycrystalline (214) superconductors, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (T -phase: $X=0.15$: $T_c=38\text{K}$)⁷ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (T' -phase: $X=0.15$: $T_c=20\text{K}$),⁶ both of which have already been investigated by us. Figure 5 shows the temperature dependence of the electrical resistivity $\rho(T)$ for three samples. $\rho(T)$ of the T' -phase sample shows the semiconductive behavior and those of T -phase and T^* -phase samples are metallic. The higher T_c and the lower $\rho(T)$ values indicate that these samples are good polycrystalline samples. Figure 6 shows the temperature dependence

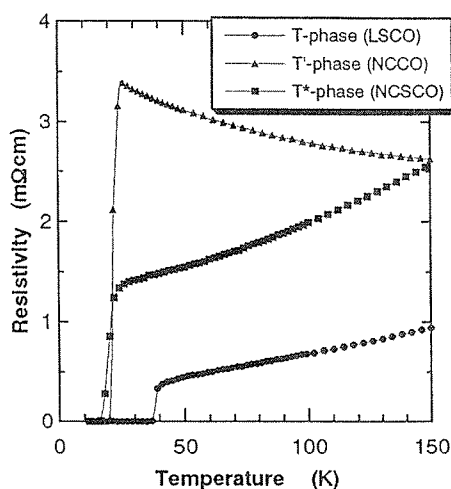


FIGURE 5
The electrical resistivity $\rho(T)$ of the T-, T'- and T*-phase samples.

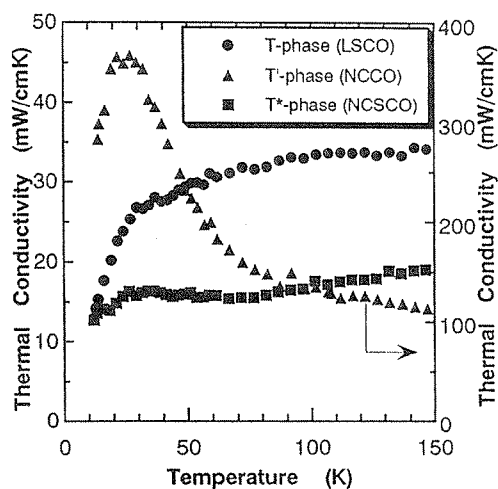


FIGURE 6
The thermal conductivity $\kappa(T)$ of the T-, T'- and T*-phase samples.

of the thermal conductivity $\kappa(T)$ of the same samples. In the T'-phase sample, $\kappa(T)$ exhibited a larger maximum value of ~ 370 mW/cmK at around 25K and then gradually decreased with further increase of temperatures. The peak is considered to come from phonon-phonon umklapp processes and the $\kappa(T)$ behavior is consistent with that of other reports.^{12,13} On the other hand, in T-phase and T*-phase, the magnitude of κ is very small and the $\kappa(T)$ peak related to umklapp processes does not exist, although the enhancement of $\kappa(T)$ below T_c is slightly observed in T-phase sample. There is some difference in $\kappa(T)$ behavior between T-phase and T*-phase. In T-phase, $\kappa(T)$ is reduced at lower temperatures more seriously than that in T*-phase. It may result from the difference of the crystal structure and the structural instability as discussed below.

In order to elucidate the difference of $\kappa(T)$ behaviors between T- and T*-phase, we analyzed the phonon thermal conductivity κ_{ph} based on the Tewordt and Wölkhausen (TW) theory.⁸ Since the heat transport in conductors is due to both electrons (κ_e) and phonons (κ_{ph}), we assume that the electron contribution in the normal state, κ_{en} follows the Wiedemann-Franz law, and the electron contribution in the superconducting state, κ_{es} follows the theory proposed by Kadanoff and Martin¹⁴ with the d-wave energy gap $\Delta = 2\Delta_{BCS} \cos 2\phi$.¹⁵ Taking account of the phonon scattering by various crystal defects and

electrons, the phonon thermal conductivity $\kappa_{ph} = \kappa - \kappa_e$ is given by⁸

$$\kappa_{ph} = \frac{3dnRv^2}{2\pi M} \left(\frac{T}{\Theta_D}\right)^3 \int_0^{2\pi} d\phi \int_0^{\Theta_D/T} \tau_{ph}(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where $n(=7)$ is the number of atoms composing these compounds, R the gas constant, $v(=5000\text{m/s})$ the average phonon velocity and x is the reduced phonon frequency, respectively. The phonon relaxation time τ_{ph} is given by

$$\begin{aligned} \tau_{ph}^{-1} &= \tau_b^{-1} + \tau_U^{-1} + \tau_{sh}^{-1} + \tau_p^{-1} + \tau_e^{-1} + \tau_k^{-1} \\ &= \tau_b^{-1} + U \exp\left(-\frac{\Theta_D}{aT}\right) + S(Tx)^2 + P(Tx)^4 + E(Tx)g(x, y) + K(Tx). \end{aligned} \quad (2)$$

Here, τ_b is the phonon relaxation time due to grain boundaries and P, S and E refer to the strength of the phonon scattering by point defects, sheet-like faults and electrons, respectively. The function $U \exp(-\Theta_D/aT)$ ($a=1.8$) is a standard form of phonon umklapp process at relatively low temperatures. Let us notice that KTx term, which usually corresponds to the phonon scattering by strain fields of dislocation, may also be regarded as standing for the scattering by two-level tunneling states familiar in amorphous solids. The KTx term results in T^2 dependence of $\kappa(T)$ at very low temperatures and gives the same results as $K'Tx \tanh(x/2)$ term which explicitly corresponds to the tunneling level scattering. The function $g(x, y) = \tau_{phn}/\tau_{phs}$ which depends on the energy gap through the parameter $y = \Delta(T)/k_B T$ stands for the ratio of the phonon-electron relaxation time in the normal and superconducting state.

Figure 7 shows the fitting curves for the phonon thermal conductivity κ_{ph} of T-phase and T*-phase samples. The parameters used and determined in the fitting process are summarized in Table I. The calculated $\kappa_{ph}(T)$ curves fully reproduce the experimental data. The phonon scattering strengths by point defects (P), sheet-like faults (S) and umklapp process (U) for T-phase are smaller than those for T*-phase. However, the $\kappa(T)$ curve for the T-phase sample, especially the steeper reduction at low temperatures, can only be reproduced by the large KTx term than that for T*-phase. We propose that the larger KTx term of T-phase comes from the local structural instability connected with the instability of the low temperature orthorhombic (LTO) phase against the high temperature tetragonal (HTT) phase. We infer that the tunneling state which is most directly related to apical oxygens is the origin of the K term, because the apical oxygen plays a key role at

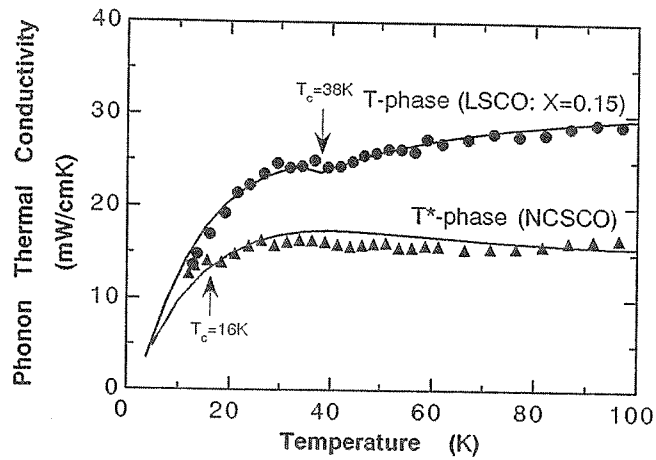


FIGURE 7 The phonon thermal conductivity κ_{ph} and fitting curves of the T-phase and T*-phase samples.

Table I. Fitting parameters determined by κ_{ph} analyses.

	T-phase (LSCO: X=0.15)	T*-phase (NCSCO: x=0.0875, y=0.2)
$\tau_b^{-1}(s^{-1})$	6.4×10^8	6.7×10^8
$U(K^1s^{-1})$	0	3.7×10^{11}
$S(K^2s^{-1})$	5.5×10^6	1.4×10^7
$P(K^4s^{-1})$	1.5×10^4	3.0×10^4
$E(K^1s^{-1})$	2.5×10^8	0
$K(K^1s^{-1})$	2.5×10^9	1.3×10^9
$T_c(K)$	38	16

LTO to HTT transition. For T*-phase, K term is about a half of that for T-phase. The local structural instability and the phonon scattering centers by two-level tunneling which result from the existence of apical oxygen may also influence the phonon transport in T*-phase NCSCO, though not so strongly as in T-phase LSCO.

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