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Mori, De.; Asai, S.; Terasaki, I.; Okazaki, R.; Yasui, Y.; Parkkima, Outi; Karppinen, Maarit An origin of good electrical conduction in La4BaCu5O13+δ

Published in: Journal of Applied Physics

DOI: 10.1063/1.4926482

Published: 01/01/2015

Document Version Publisher's PDF, also known as Version of record

Please cite the original version:

Mori, D., Asai, S., Terasaki, I., Okazaki, R., Yasui, Y., Parkkima, O., & Karppinen, M. (2015). An origin of good electrical conduction in La4BaCu5O13+δ. *Journal of Applied Physics*, *118*(3), 1-6. Article 035104. https://doi.org/10.1063/1.4926482

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Citation: Journal of Applied Physics **118**, 035104 (2015); doi: 10.1063/1.4926482 View online: http://dx.doi.org/10.1063/1.4926482 View Table of Contents: http://aip.scitation.org/toc/jap/118/3 Published by the American Institute of Physics

AIP | Journal of Applied Physics

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An origin of good electrical conduction in $La_4BaCu_5O_{13+\delta}$

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(Received 23 March 2015; accepted 27 June 2015; published online 16 July 2015)

We have prepared a set of polycrystalline samples of the metallic copper oxide $La_4BaCu_{5-x}Co_xO_{13+\delta}$ ($0 \le x \le 0.35$) and have measured the resistivity from 4 to 800 K. All the resistivities show metallic temperature dependence with a small magnitude less than 2 m Ω cm at 800 K, indicating that the metallic conduction is robust against impurities. The robust metallic conduction further suggests that this class of oxide is a promising candidate for electrical leads at high temperature, which might replace platinum. A detailed measurement and analysis on the Hall resistivity have revealed that at least two components are responsible for the electrical conduction, in which a large number of electrons of moderate mobility coexist with a much smaller number of holes of extremely high mobility. This large electron density well screens the impurity potential and retains the metallic conduction against 7% impurity doping. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4926482]

[Intp://dx.doi.org/10.1005/1.492048

I. INTRODUCTION

The electroceramics is a huge area of ceramic engineering and materials science, inspired by application and technology.¹ It includes electronics, ferroelectrics, magnetism, thermoelectrics, and even superconductivity engineering, which is equipped with a vast range of outputs such sensors, filters, memories, solid oxide fuel cells, MEMS devices, energy devices, etc.^{2,3} Electrical leads are indispensable for all those applications and have been made of various elemental metals. In particular, platinum has been used for high temperature application because of the chemical stability at high temperature in air. Owing to the poor natural abundance, postplatinum materials have been sought for electrical leads.

Oxides are most promising ceramic materials, because they are mostly stable at high temperatures. In addition to natural abundance and high-temperature stability, ceramic materials are superior to metals for the contacts to functional ceramics, because of good matching of the expansion coefficients. We have searched for good metallic oxides, which can replace platinum as an electrical contact material,⁴ and have arrived at the perovskite-related oxide $La_4BaCu_5O_{13+\delta}$.

La₄BaCu₅O_{13+ δ} was first synthesized by Michel *et al.*,⁵ the crystal structure of which is schematically drawn in Fig. 1 (using VENUS).⁶ This oxide belongs to *P*4/*m* with an *a* -axis length of 8.65 Å and a *c*-axis length of 3.87 Å.⁷ The basic structure is an ordered perovskite of ABO₃, where the Cu ions occupy the B site and the La and Ba ions occupy the A site. The four La ions and the one Ba ion order in the *ab* plane and form columns along the *c* axis. Michel *et al.*⁵ further found that this material is highly metallic with a magnitude of 1.5 m Ω cm at 673 K. Neglecting the excess oxygen δ , we estimate

the formal valence of Cu to be +2.4, which is close to the value corresponding to quarter filling (+2.5). This unusually high value is rarely seen in air-sintered copper oxides.⁸ Such a high valence is described in terms of "*p*-hole" (hole on oxygen ion), which can often be a cause of metallic oxides.⁹ Yet, the nature of the metallic conduction of this oxide is not well understood.¹⁰ Shivakumara *et al.*¹¹ found that this metallic conduction is robust at high temperature against impurity substitution, and such robustness is also rare in conducting oxides.

In order to clarify the mechanism of the good metallic conduction in La₄BaCu₅O_{13+ δ}, we have prepared a set of polycrystalline samples of La₄BaCu_{5-x}Co_xO_{13+ δ} ($0 \le x \le 0.35$) and have measured the resistivity, Hall resistivity, and thermopower. We have found that the good metallic conduction is responsible for a large number of electrons with moderate mobility, and the impurity potential seems to be screened by the high electron density. On the other hand, we have also detected a tiny amount of holes with extremely high mobility, which dominates the complicated x dependence of the thermopower. We discuss a possible microscopic picture of the electronic states by comparing the band structure calculation.

II. EXPERIMENTAL

Polycrystalline samples of La₄BaCu_{5-x}Co_xO_{13+ δ} ($0 \le x \le 0.35$) were prepared by solid state reaction. Stoichiometric amounts of La₂O₃, BaCO₃, CuO, and Co₃O₄ were mixed, and the mixture was calcined at 900 °C for 24 h in air. The calcined powder was ground, pressed into a pellet, and sintered at 1000 °C for 48 h in air. These conditions were similar to those for high-temperature superconducting (HTSC) copper oxides,^{12,13} and all the pellets were well sintered with a typical density of 87%. Excess oxygen δ was evaluated to be

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FIG. 1. Schematic crystal structure of La₄BaCu₅O₁₃.

between 0.04 and 0.20 (with an uncertainty of ± 0.04) from iodometric titration and showed no systematic change with *x*.

X-ray diffraction was measured with an x-ray diffractometer with CuK_{α} radiation (Rigaku RINT2000). Resistivity was measured using a four-probe method in a liquid helium cryostat from 4.2 to 300 K and in a cylinder furnace in air from 300 to 800 K. Thermopower was measured with a steady-state method using a copper-constantan differential thermo-couple from 4.2 to 300 K in a liquid helium cryostat. Hall resistivity was measured up to 7 T from 10 to 150 K in a Quantum Design Physical Property Measurement System using an ac resistance bridge (Linear Research LR700).



FIG. 2. Typical x-ray diffraction patterns of La₄BaCu_{5-x}Co_xO_{13+ δ}. (a) x = 0 and (b) x = 0.15. CuK_x is used as an x-ray source.



FIG. 3. Resistivity of La₄BaCu_{5-x}Co_xO_{13+ δ} plotted as a function of temperature. The data below and above 300 K were taken with different measurement setup. The magnitude of the high-temperature data were properly normalized within an uncertainty of ±15% to connect at the low temperature data smoothly.

III. RESULTS AND DISCUSSION

Figure 2 shows typical x-ray patterns of the prepared samples, in which all the observed diffraction peaks are indexed without any trace of impurity phases. In addition, the diffraction patterns are almost identical between Figs. 2(a) and 2(b), meaning that the lattice parameters are not changed appreciably with the Co concentration *x*. A detailed structure analysis reveals a slight decrease in the *a* axis length (a = 8.644 Å for x = 0 and 8.639 Å for x = 0.15) with remaining the *c*-axis length (3.862 Å) unchanged. As is shown in Fig. 1, there are two Cu sites in the title compound, i.e., four pyramidal sites and one octahedral site in the unit cell. Within experimental resolution, the site occupancy of the substituted Co ion was unable to be determined from the x-ray diffraction patterns.

The resistivity ρ of the prepared samples is plotted as a function of temperature in Fig. 3. Since we used two different measurement systems below and above 300 K, the magnitude of the resistivity slightly differed at 300 K for the two measurements. Thus, we multiplied a normalized constant to the high temperature data to connect smoothly at the low-temperature data within an uncertainty of $\pm 15\%$. Namely, the normalized constant, we used ranges from 0.85 to 1.15.

First, all the data exhibit metallic conduction for all the temperatures measured. The magnitude of the resistivity is less than 2 m Ω cm at 800 K, which is almost the lowest resistivity among the oxide materials¹⁴ except for noble-metal oxides such as RuO₂, IrO₂,¹⁵ PdCoO₂,¹⁶ and ReO₃.¹⁷ Since the resistivity of platinum is around 25 $\mu\Omega$ cm at 600 K, the observed ρ is nearly 40 times larger. Yet, we think an application to printable conducting paste possible, for the sheet resistance can be controlled by properly choosing solvent and particle size. Second, the Co substitution does not change the metallic temperature dependence of $\rho(T) - \rho(0)$ very much but increases the residual resistance $\rho(0)$. This is what one can see in the resistivity of conventional metals

and alloys where the impurity scattering is simply added as a temperature-independent component. This further implies that the impurity potential is weak in the title compound.

One may notice that there is significant difference between the two samples of x = 0 (#1 and #2). We made several samples of x = 0 and found that the resistivity differed from sample to sample; #1 and #2 showed the highest and lowest values at 300 K, respectively. We have measured δ in six samples for x = 0 and found it to be 0.04 (#2), 0.08, 0.08, 0.12, 0.18, and 0.19 (#1), where no correlation between δ and ρ is detected. The x-ray diffraction patterns are also identical among the six samples. From these results, we think that the main phase is identical, but oxygen content at the grain boundary may vary from sample to sample. Three phases (tetragonal, orthorhombic, and monoclinic) are known for La₄BaCu₅O_v, depending on the oxygen content y.^{18–20} Since oxygen ions easily pass through the grain boundaries, different minor phases may be stabilized at the grain boundaries, which can affect the resistivity significantly. As we will see later, such a small fraction of the minor phases at the grain boundary does not affect the thermopower,²¹ which is actually found in the thermopower measurement (see Fig. 7). We find that the Co substitution suppresses the resistivity variation probably owing to the suppression of oxygen variation at the grain boundary, and that the resistivity data for x > 0 are reproducible within experimental uncertainties. Thus, we conclude that the Co substitution is technically effective to stabilize a low resistivity above room temperature, being useful for high temperature application, although the residual resistance worsens the low-temperature conduction.

In order to understand the robust metallic nature against impurities, we have measured the Hall resistivity, as shown in Fig. 4. Compared with the resistivity, the Hall effect is known to be insensitive against grain boundaries in the HTSC copper oxides.²¹ It predominantly probes the contribution from the conducting CuO₂ planes, where in the ceramic samples and the c-axis oriented thin-film samples give quantitatively the same values.¹³ Although the anisotropic ratio of the resistivity $(\rho_{\parallel}/\rho_{\perp})$ is more than 100 for the HTSC copper oxides, the Hall coefficient is essentially the same as that along the in-plane direction in single crystals. Unfortunately, single-crystal samples of La₄BaCu₅O_{13+ δ} are not available at present, and the anisotropic ratio is unknown. Instead, we can estimate this value from $\rho_{\parallel}/\rho_{\perp}$ of the related oxide $La_{8-x}Sr_xCu_8O_{20}$ known as $La_5SrCu_6O_{15-\delta}^{10}$ and find $\rho_{\parallel}/\rho_{\perp} = 5$ for thin film samples²² and 10 for single-crystal samples.²³ These values are around one-order of magnitude smaller than the anisotropy of the HTSC copper oxides, and use of ceramic samples is well justified in the title compound for quantitative discussion on the Hall effect.

Obviously, the Hall resistivity is superlinear in external fields, which implies multiple components of charge carriers with different mobilities. The sign is negative for all the temperature measured, and the superlinear dependence tends to be more remarkable at lower temperatures. These features suggest that the majority of carrier is electron, and a small fraction of hole conduction with high mobility is responsible for the superlinear behavior.



FIG. 4. Hall resistivity of La₄BaCu₅O_{13+ δ} (sample #2) plotted as a function of magnetic field. The solid curves are the calculation by Eq. (2) (see text).

Let us analyze the Hall resistivity ρ_{xy} in terms of a two component model. Just for simplicity, we employ the mobility μ_i and the Hall coefficient component R_H^i as transport parameters, where i = e and h represent the electron and hole components, respectively. Then, the resistivity ρ is written as

$$\rho = \left(\frac{\mu_h}{R_H^h} + \frac{\mu_e}{R_H^e}\right)^{-1}.$$
 (1)

Similarly, the Hall resistivity $\rho_{xy}(H)$ is expressed by

$$\rho_{xy}(H) = \frac{a + bH^2}{1 + cH^2}H,$$
(2)

where *a*, *b*, and *c* are the field-independent parameters. They are further expressed in terms of μ_i and R_H^i as

$$a = \left(\frac{\mu_h^2}{R_H^h} - \frac{\mu_e^2}{R_H^e}\right)\rho^2,\tag{3}$$

$$b = \mu_h^2 \mu_e^2 \left(\frac{1}{R_H^h} - \frac{1}{R_H^e} \right) \rho^2, \tag{4}$$

$$c = \mu_h^2 \mu_e^2 \left(\frac{1}{R_H^h} - \frac{1}{R_H^e} \right)^2 \rho^2.$$
 (5)

Thus, Eqs. (1)–(5) mean that the four unknown parameters of μ_e , μ_h , R_H^e , and R_H^h can be experimentally determined by fitting ρ_{xy} with Eq. (2) and by using the observed values of ρ . The solid curves representing results of the fitting excellently explain the measurement data, and the fitting parameters thus obtained are listed in Table I. We should note that the fitting is reasonably unique in the sense that *a* is determined at the low-field data, whereas c/b is determined at the high-field data. We should note here again that the Hall coefficient of ceramic samples is a kind of average of anisotropic Hall coefficients along various crystallographic directions of single crystal. Yet, this two-carrier model is meaningful in

TABLE I. Parameters obtained through the fitting the Hall resistivity with Eq. (2).

T (K)	$A (10^{-4} \text{cm}^3/\text{C})$	$b (10^{-5} \text{cm}^3/\text{CT}^2)$	$c (10^{-2}/\mathrm{T}^2)$
10	-2.7	-7.3	13.0
50	-2.1	-3.9	7.8
100	-1.2	-1.2	3.0
150	-1.4	-0.4	1.1

the sense that the two carrier components correspond to the two independent features of the Hall resistivity, i.e., the sign and the field dependence. The negative sign indicates an average of majority electron component, and the superlinear field dependence indicates an average of high-mobility minority hole component.

Figure 5 shows the transport parameters obtained through fitting. The electron- and hole-components show nearly identical temperature dependence; the Hall coefficient components are roughly independent of temperature (Fig. 5(a)), whereas the mobility components increase with decreasing temperature (Fig. 5(b)). These temperature dependences are what one expects in a simple two-carrier model and strongly suggest that the transport properties can be understood with a band picture. In other words, the electron correlation plays a secondary role in a remarkable contrast to the HTSC copper oxides. When the carrier density exceeds 0.3 per Cu ion in HTSC copper oxides, the system loses superconductivity and is in the so-called overdoped region.¹² It is generally agreed that the electronic states of the overdoped HTSC copper oxides are understood with the Fermi liquid theory, where the electron correlation is effectively weakened by a large amount of carriers.^{24–26} Owing to the high Cu valence of 2.4, the title compound can be compared with the overdoped HTSC copper oxides.

Contrary to the temperature dependence, the magnitudes of the two components are remarkably different. The Hall coefficient component for electron is of the order of 10^{-4} cm³/C, and this value is quantitatively consistent with a previous measurement reported by Tamegai and Iye²⁷ in which the Hall coefficient was evaluated by the values at ± 5 T. This value is too small to calculate the carrier density by $-1/eR_{H}^{e}$ but roughly corresponds to $10^{21}-10^{22}$ cm⁻³. The Hall coefficient component for hole is 10⁶ times larger than that for electron, indicating that the carrier density for the hole component $(10^{16} \text{ cm}^{-3})$ is much smaller than that for the electron component. Compensating the carrier density difference, the mobility of the hole component is 10^3 times higher than that of the electron component. As a result, the conductivity component $\sigma_i = \mu_i / R_H^i$ is 10³ times higher for the electron component than for the hole component (Fig. 5(c)). This means that the resistivity is almost equal to $1/\sigma_e$, while the Hall effect is affected by the small fraction of the hole component, for the first term of the right hand side of Eq. (3) is comparable to the second term. Kaplan *et al.*²⁸ measured the optical reflectivity of the title compound, and found a large Drude like contribution with a plasma frequency of $38\,000\,\mathrm{cm}^{-1}$. Such a large value is consistent with the small value of R_{H}^{e} .



FIG. 5. The transport parameters for the electron and hole components obtained from the fitting of the Hall resistivity. (a) The Hall coefficient component R_H^i , (b) mobility μ_i , and (c) conductivity for each component $\sigma_i = \mu_i/R_H^i$. The electron and hole components are plotted along the left and right axes, respectively.

The Co substitution significantly modifies the Hall effect, while it only acts as an impurity scattering center in the resistivity as already shown in Fig. 3. Figure 6 shows the Hall resistivity for the x = 0.25 sample at 10 K. Clearly, the Hall resistivity is positive and sublinear against magnetic fields, which indicates that the high-mobility hole component is dominant at 10 K, as was analyzed in Figs. 4 and 5. The resistivity at 10 K increases from 0.06 m Ω cm for x = 0 (#2) to 0.48 m Ω cm for x = 0.25 as was already shown in ρ in Fig. 3. We assign this increase in ρ to the decrease in μ_e , causing the sign change in the parameter *a* in Eq. (2). The solid curve represents the calculation by Eq. (2), where $\mu_e = 1 \text{ cm}^2/\text{Vs}$, $\mu_h = 700 \text{ cm}^2/\text{Vs}$, $R_H^h = 120 \text{ cm}^3/\text{C}$, and $R_H^e = 6 \times 10^{-4} \text{ cm}^3/\text{C}$ are used. The curve excellently reproduces the experimental results, and the parameters are consistent with what we discussed for x=0 (i.e., $\mu_e \ll \mu_h$ and $R_H^e \ll R_H^h$).

A small fraction of the hole component is also expected to appear in the thermopower S. The magnitude of the thermopower is larger for smaller carrier density, and thus, the hole component is expected to show a large positive value of S. In the present two-component model, the thermopower is described by



FIG. 6. Hall resistivity of the x = 0.25 sample in La₄BaCu_{5-x}Co_xO_{13+ δ} plotted as a function of magnetic field. The solid curve represents the calculation with Eq. (2).

$$S = \left(S_h \frac{\mu_h}{R_H^h} - S_e \frac{\mu_e}{R_H^e}\right)\rho \tag{6}$$

$$= pS_h - (1 - p)S_e, (7)$$

where $p = \sigma_h / (\sigma_h + \sigma_e)$ is the fraction of the hole component to the total conductivity. Since *p* is of the order of 10^{-3} for x = 0, the hole component pS_h is difficult to observe. However, it can be detected in the Co-substituted samples at low temperatures, because σ_e decreases by a factor of 10 from x = 0 to 0.35 at 4 K, which increases *p* up to 0.01.

Figure 7(a) shows the temperature dependence of the thermopower of La₄BaCu_{5-x}Co_xO_{13+ δ}. The magnitude of the thermopower is of the order of $10^0 \mu$ V/K, meaning that the electron component of $10^{21} - 10^{22}$ cm⁻³ is dominant. With increasing *x*, the thermopower systematically changes as if a positive component linearly increased with *x*. We can understand this behaviour by assuming that the hole component remains intact against the Co substitution, while $\sigma_e = 1/\rho$ decreases with *x* as shown in Fig. 3. On such assumptions, the electron component of $(1-p)S_e$ is almost equal to S_e , for $p \ll 1$. Thus, the difference in the thermopower (ΔS) from x = 0 to x = 0.35 roughly equals ΔpS_h .

As shown in Fig. 7(b), the temperature dependence of ΔS is similar to that for a non-degenerate semiconductor with a carrier density of *n* given as²⁹

$$S_{\rm nd} = \pm \frac{k_B}{e} \left[\ln \left(\frac{n}{N(T)} \right) - \left(r + \frac{5}{2} \right) \right],\tag{8}$$

where *r* is the scattering parameter. N(T) is the thermal carrier density given by $N(T) = 2(2\pi mk_BT/h^2)^{3/2}$, where *m* is the effective mass. Then, ΔpS_h is roughly approximated as ΔpS_{nd} . Taking reasonable values of $\Delta p = 0.013$, $n = 10^{16}$ cm⁻³, and r = -1/2, we plot ΔpS_{nd} by the dotted curve. For the sake of simplicity, we assumed that the effective mass is the bare electron mass. Although the temperature dependence of *p* is neglected, the curve qualitatively explains the lowtemperature part of ΔS .

The room-temperature thermopower has been regarded as a measure of hole concentration per Cu in the HTSC



FIG. 7. (a) Thermopower of $La_4BaCu_{5-x}Co_xO_{13+\delta}$ plotted as a function of temperature. (b) The increment in the thermopower for x = 0.35 from x = 0 (#2). The broken curve represents the calculation by Eq. (7) with a carrier density of 10^{16} cm⁻³ and a hole conductivity fraction of 0.013.

copper oxides. According to Obertelli et al.,30 a value of $4 \mu V/K$ for x = 0 corresponds to 0.2 holes per Cu, which corresponds to around half estimated from the formal Cu valence (2.4) in La₄BaCu₅O₁₃. However, the temperature dependence of the thermopower is even qualitatively different from that of HTSC, and it is nontrivial whether Ref. 30 is applicable to this less anisotropic oxide. A negative value of -3μ V/K at 150 K suggests that electrons are majority carriers as in "overdoped" HTSC, which is consistent with the negative and small Hall resistivity. The Zn-substitution in YBa₂Cu₃O_y leaves the room-temperature thermopower intact³¹ and only increases the residual resistance.³² In contrast, the Co substitution in $La_4BaCu_5O_{13+\delta}$ similarly increases the residual resistance, but changes the roomtemperature thermopower. This should be ascribed to the two conductive components, rather than a single conductive component as was done for the HTSC copper oxides.

Let us discuss the electronic states of $La_4BaCu_5O_{13}$ from the measured results. According to the band calculation by Herman *et al.*,³³ the unit cell of this compound can be viewed as four CuO chains and one CuO₆ chain along the *c* axis. The four CuO chains form four quarter-filled onedimensional bands with a large energy dispersion of 2 eV, which are responsible for the electron component in the transport parameters. They are interconnected via the edgeshared network along the *ab* plane, and concomitantly, the one-dimensional bands acquire a significant dispersion along the *ab* plane. We think this feature is important for the robust metallic nature, because quasi-one-dimensional conductor is quite susceptible against impurities. In this sense, this oxide is essentially a three dimensional material, in which $pd\sigma$ anti-bonding bands are spread in three dimension. Although we cannot clearly specify the origin of the hole component in the band structure from the present experiments, but one can see a hole-like dispersion along the Γ -Z direction and a valence band maximum at the Γ point.

IV. SUMMARY

We have prepared a set of polycrystalline samples of the metallic copper oxide La₄BaCu_{5-x}Co_xO_{13+ δ} (0 < x < 0.35) and have measured the resistivity, Hall resistivity, and thermopower. The field dependence of the Hall resistivity has been analyzed with a conventional two-carrier model. Based on the model, we find that the resistivity of this oxide is understood by an electron component of moderate mobility with a metallic carrier density of 10^{21} – 10^{22} cm⁻³, while a small fraction $(10^{16} \text{ cm}^{-3})$ of hole component of high mobility affects the Hall effect and the thermopower. Such a large electron density screens the impurity potential, and the resistivity remains metallic from 4 to 800K for the 7% Cosubstituted sample. The Co substitution seems to stabilize the nonstoichiometry and/or arrangements of the oxygen ions and gives rise to reproducible resistivity. The low resistivity obtained in the present study may be applied to contact material for future electroceramics.

ACKNOWLEDGMENTS

This work was partially supported by the Joint Research Project between Nagoya University and AIST, and by the Program for Leading Graduate Schools "Integrative Graduate Education and Research in Green Natural Sciences," by MEXT, Japan. We would like to thank W. Shin and H. Taniguchi for close collaboration and appreciate N. Murayama for initially motivating us to study conducting electroceramics.

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