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Semiconducting Properties of $(Ln_I, Ln_{II})CuO_4$ and of $(Ln, A)_2CuO_4$ (Ln = rare earth, A = alkaline earth)

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The ternary oxides, $(La,Pr)_2CuO_4$, $(Gd,Tb)_2CuO_4$, $(La,Tb)_2CuO_4$, $(La,Ca)_2CuO_4$ and $(La,Ba)_2CuO_4$, were prepared and their semiconducting properties were investigated. When the mean ionic radius of Ln^{3+} ($\bar{r}$) is increased, the $(La,Pr)_2CuO_4$ compounds transform from semiconductors to metals at a critical $\bar{r}$ value of 1.05 Å. The metal-semiconductor transition which accompanies the shrinkage of the a axis, is explained as being due to the π-bond formation of the Cu-O bond. Compounds in the composition range from $La_{1.3}Tb_{0.7}CuO_4$ to $La_{1.4}Tb_{0.6}CuO_4$ are peculiar to the $(La,Tb)_2CuO_4$ compounds. The crystal structure is the same as that of Ln_2CuO_4, but it is different from Ln_2CuO_4 as regards the *c*/*a* ratio and resistivity. The doping of 20 mol% CaO or 10 mol% BaO into La_2CuO_4 lowers the resistivity to tenth of that of La_2CuO_4.

In the $CuO\text{-}Ln_2O_3$ system (Ln = rare earth), there are three different types of compounds, the metallic La_2CuO_4 compound, the semiconductive Ln_2CuO_4 compounds (Ln = Pr—Gd) and the insulating $Ln_2Cu_2O_5$ compounds (Ln = Tb—Lu).[1-3] The resistivities of the Ln_2CuO_4 compounds decrease with increasing ionic radius of the Ln^{3+} ions continuously for Ln = Gd—Pr, but a semiconductor-metal transition takes place between Ln = Pr and La; the La_2CuO_4 compound is metallic.[3] The lattice parameters of these compounds vary with the size of the Ln^{3+} ions in accordance with the electrical behavior. The lattice parameters, both of the *a* and *c* axes, increase with increasing ionic radius of the Ln^{3+} ion continuously for Ln = Gd—Pr, but between Ln = Pr and La they change discontinuously; the *a* parameter for the La_2CuO_4 compound is smaller than that for the Pr_2CuO_4 compound although the La^{3+} ion is larger than the Pr^{3+} ion.[3] The ternary $(La,Pr)_2CuO_4$ compounds are expected to reveal how critically the resistivities and lattice parameters change with variations in the ionic radius between those of the Pr^{3+} and La^{3+} ions, because the ionic radii of the Ln^{3+} ions can be continuously varied by changing the La/Pr ratio.

The ternary $(La,Tb)_2CuO_4$ compounds would continuously cover ionic radii of the Ln^{3+} ion ranging from that of the La^{3+} ion to that of the Tb^{3+} ion, if the La^{3+} ion can freely be replaced by a Tb^{3+} ion. These ternary compounds would reveal how the resistivity and the lattice parameters of Ln_2CuO_4 compounds vary with the $\bar{r}$ value ($\bar{r}$ = mean ionic radius of rare earth ions) over the above range and will also reveal whether or not the ternary compounds containig two kinds of rare earth ions, the ionic radii of which are very different from each other, are the same as the binary compounds as regards the variation of structure and resistivity with the $\bar{r}$ value.

The resistivities of the Ln_2CuO_4 compounds decrease with increasing ionic radius of the Ln^{3+} ions.[3] If this trend could be extended to the region of the ionic radius beyond the La^{3+} ion, Ln_2CuO_4 compounds containing larger trivalent ions than La^{3+} ions would show a lower resistivity than that for La_2CuO_4. Such large trivalent ions are very difficult to obtain, but the less electronegative metals, such as alkaline earth metals, can be expected to give the same effect on the resistivity because this trend appears to be related to the electronegativity of atoms in the Ln^{3+} sites. Since the Gd^{3+} ions in the Gd_2CuO_4 compound are partially replaced by alkaline earth ions,[4] the La^{3+} ions in La_2CuO_4 can be expected to be replaced by some alkaline earth ions. CaO and BaO were added to the La_2CuO_4 compound to see if the resistivity decreased.

The composition of the Ln_2O_3–CuO compounds changes discontinuously between Ln = Gd and Tb; Gd_2CuO_4 and $Tb_2Cu_2O_5$ are known,[1,2] but $Gd_2Cu_2O_5$ and Tb_2CuO_4 are unknown. It is of interest to determine whether $Ln_2Cu_2O_5$ and Ln_2CuO_4 compounds coexist in a region of the ionic radius of the Ln^{3+} ion or the Ln_2CuO_4 compound changes into the $Ln_2Cu_2O_5$ compound at a certain critical Gd/Tb atomic ratio. Furthermore, these compounds also have different electrical properties. Gd_2CuO_4 is a semiconductor, while $Tb_2Cu_2O_5$ is an insulator. Since the mean ionic radius of the Ln^{3+} ion can be varied continuously by using ternay $(Gd,Tb)_2CuO_4$ compounds, these discontinuous compositional and electrical changes between Ln = Gd and Tb will be investigated in more detail.

Experimental

Reagents and Materials. Stock solutions of $Ln(NO_3)_3$, $Ba(NO_3)_2$, and $Ca(NO_3)_2$ were obtained by dissolving Ln_2O_3 (Nihon Yttrium Co., 99.9% pure), $BaCO_3$ and $CaCO_3$ (Wako Pure Chemical Co., Ltd., GR grade) into nitric acid (Wako Pure Chemical Co., Ltd., GR grade). A stock solution of $Cu(NO_3)_2$ was obtained by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ (Kanto Chemical Co., GR grade) into distilled water. The solutions were standardized by the EDTA chelatometric titration method.

Procedure. Samples were prepared using the same method as that described in a previous paper.[3] Aliquot portions of the solutions of $Ln(NO_3)_3$, $Cu(NO_3)_2$ (and an alkaline earth nitrate, when necessary) were mixed. A sodium hydroxide solution (1M) (and sodium carbonate solution (1M) for the addition of an alkaline earth nitrate) was added and the mixture was stirred. After the mixture had stood overnight, filtering and washing were repeated until no sodium ions were detected in the filtrate using the flame test. The mixtures of precipitates thus obtained were preheated to 750 °C in air. The dry powder of the oxide mixture thus obtained was milled, pressed into 15 mm diameter pellets and heated to 1000 °C for 15 h in air. The resistivity was measured using the 4-probe method in the same manner as described

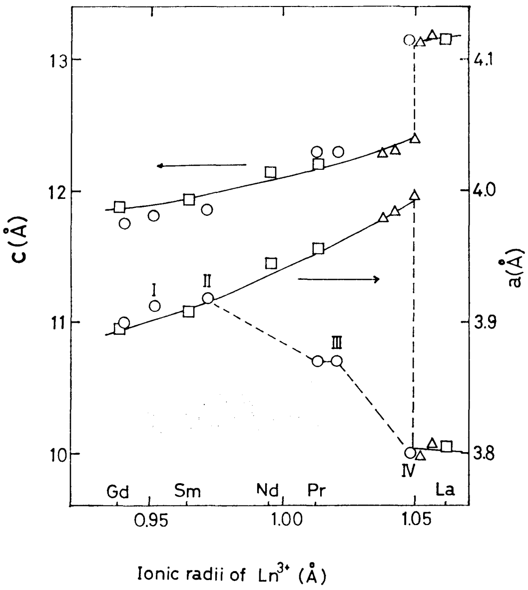

Fig. 1. Variation of lattice parameters of Ln_2CuO_4 with ionic radii or mean ionic radii of rare earth ions. □: Ln_2CuO_4, ○: $(La,Tb)_2CuO_4$, △: $(La,Pr)_2CuO_4$.

in a previous report.[3] An X-ray diffractometer was used for the measurement of lattice parameters and for the solid solubility determination in the ternary system.

Results and Discussion

Figure 1 gives the variation of the lattice parameters of binary Ln_2CuO_4 and ternary $(Ln_I,Ln_{II})_2CuO_4$ compounds with the ionic radius, or the mean ionic radius of the Ln^{3+} ion ($\bar{r}$). Both the a and c axes expand for an increase in the ionic radius of the Ln^{3+} ions for Ln=Gd—Pr. For Ln=La, the c axis expands more than the value estimated by extrapolating the data for Ln=Gd—Pr, and the a axis shortens (□). La_2CuO_4 is electrically metallic, while Pr_2CuO_4 is semiconductive.[3] This marked difference between Ln=La and Pr can be explained as a change in the nature of the Cu–O bond on the a axis ($(Cu\text{–}O)_a$) as described below.

The Cu^{2+} ions in the Ln_2CuO_4 lattice are octahedrally surrounded by six O^{2-} ions.[5] According to ligand field theory,[6] in the ground state with the Cu^{2+} ion coordinated octahedrally, the $3d_{z^2}$, $3d_{x^2-y^2}$, 4s and 4p orbitals of the Cu^{2+} ion are used for the σ-bonds. The $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$ orbitals (t_{2g}) can form π-bonds with the coordinating O^{2-} ions, but for Ln=Gd—Pr, they are essentially nonbonding. The upper edge of the valence band originates from the antibonding σ-orbitals ($e_g{}^*$). The conduction band is formed of the π-orbitals of higher energy levels, probably the 4d orbitals of the Cu^{2+} ions. For Ln=Gd—Pr the relatively long bond-length of the $(Cu\text{–}O)_a$ bond prevents any great overlapping in the π-bond so that the conduction band is located at a higher energy level than the $e_g{}^*$ orbitals, or the valence band. Therefore, the Ln_2CuO_4 compounds are semiconductive for Ln=Gd—Pr. When the effective change of the O^{2-} ions on the c axis is enhanced, the energy levels of the t_{2g} orbitals are elevated due to the electrostatic repulsive force. Since the less electronegative Ln atom or the atom with the smaller atomic number pushes more electrons toward the O^{2-} ions surrounding the Ln^{3+} ions, the effective charge of the O^{2-} ions increases with decreasing atomic number of the Ln atom so that the energy levels of the t_{2g} orbitals are elevated. For Ln=La, the t_{2g} energy level is maximum so that the La_2CuO_4 lattice becomes unstable. To stabilize it, the $(Cu\text{–}O)_c$ bond expands; this weakens the electrostatic repulsive force [$(Cu\text{–}O)_c$ is the Cu–O bond on the c axis]. This is the reason why the c axis of La_2CuO_4 expands more than expected from the size of the La^{3+} ion. The lengthening of the $(Cu\text{–}O)_c$ bond weakens it, that is, lowers its σ-bond energy but this energy lowering is compensated for by the π-bond formation in the $(Cu\text{–}O)_a$ bond composed of the $3d_{xz}$ and $3d_{yz}$ orbitals. This is the reason for the shortening of the a axis in La_2CuO_4. The shortening of the $(Cu\text{–}O)_a$ bond also enhances the electron overlap in the conduction band, lowering the energy level of the conduction band to that of the $e_g{}^*$ band. Thus, the upper edge of the $e_g{}^*$ band overlaps the lower edge of the conduction band and metallic conduction results. This is the reason why La_2CuO_4 is metallic.

The lattice parameters for the ternary $(La,Tb)_2CuO_4$ compounds are given in Fig. 1 (open circles). In the region of $\bar{r}$ from 0.94 to 0.97 Å, these increase with increasing $\bar{r}$ as do the lattice parameters of binary compounds. This phase is called phase 1. However, when the $\bar{r}$ value increases beyond 0.97 Å, another phase appears as a separated phase and the relative amount of the phase increases with increasing amount of the La^{3+} ions. The X-ray diffraction data reveal that this phase is a single phase in the composition range from $La_{1.3}Tb_{0.7}CuO_4$ to $La_{1.4}Tb_{0.6}CuO_4$ and that the X-ray diffraction patterns can be indexed as Ln_2CuO_4 structures. Since this phase exists as a phase separated from phase 1 and its *c*/*a* ratio is different from that of all binary Ln_2CuO_4 compounds, it should be considered to be a new phase which is peculiar to the $(La,Tb)_2CuO_4$ system. This phase is called phase 2.

When the $\bar{r}$ value increases beyond $\bar{r}=1.015$ Å, the La_2CuO_4 phase appears and coexists with phase 2. This fact indicates that phase 2 is different from both phase 1 and the La_2CuO_4 phase. Beyond $\bar{r}=1.05$ Å the La_2CuO_4 phase occurs as a single phase.

The semiconducting properties of this system correspond well to the structural behavior described above. Figure 2 gives the log ρ *vs.* $1000/T$ plots for the $(La,Tb)_2CuO_4$ compounds (ρ=resistivity). The roman numerals refer to the sample numbers given in Fig. 1. The ρ values at a given temperature for phase 1 decrease with increasing $\bar{r}$ value, but with slopes that are essentially the same (I and II). The plots for phase 2 (III) give a less steep slope than those for phase 1, indicating that the activation energy for the phase 2 sample is lower than that of phase 1.

The lowering of the activation energy in phase 2 can be explained as being due to π-bond formation in the $(Cu\text{–}O)_a$ bond. As described in the previous sec-

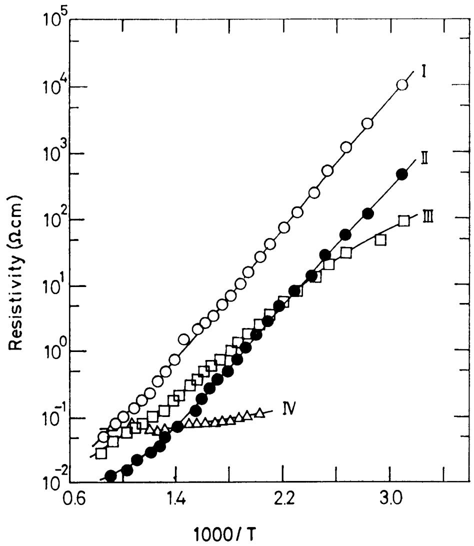

Fig. 2. Temperature dependence of resistivities of (La, $Tb)_2CuO_4$ compounds.
○(I): $La_{0.28}Tb_{1.72}CuO_4$, ●(II): $La_{0.6}Tb_{1.4}CuO_4$, □(III): $La_{1.4}Tb_{0.6}CuO_4$, △(IV): $La_{1.8}Tb_{0.2}CuO_4$.

tion, the shortening of the $(Cu–O)_a$ bond can be attributed to the π-bond formation of the t_{2g} orbitals of the Cu^{2+} ions and the degree of π-electron overlap increases with decreasing $(Cu–O)_a$ bond length. The $(Cu–O)_a$ bond length in phase 2 is between that of phase 1 and of La_2CuO_4 so that the $(Cu–O)_a$ bond in phase 2 can be expected to include π-bond characteristic although the electron overlap is not as great as for La_2CuO_4. The π-bond formation lowers the energy of the conduction band, resulting in a lower activation energy.

The fact that the composition range of phase 2 is very narrow and that the La/Tb ratio is two approximately suggests that the phase 2 compound is $La_4Tb_2Cu_3O_{12}$, although no super lattice lines due to ordering of the La^{3+} and Tb^{3+} ions were observed.

The triangles in Fig. 1 show the variation of the lattice parameters for the $(La,Pr)_2CuO_4$ compounds with $\bar{r}$. These lattice parameters change very critically at $\bar{r}=1.05$ Å. No stable specimens of compounds having $\bar{r}\simeq1.05$ Å could be obtained; the pellets spontaneously reduced to powder when removed from the furnace and cooled to room temperature. Therefore, it was not determined whether or not the critical change in lattice parameters is accompanied by a semiconductor-metal transition, although shortening of the a axis and the very great lengthening of the c axis strongly suggests the same semiconductor-metal transition as that between La_2CuO_4 and Pr_2CuO_4.

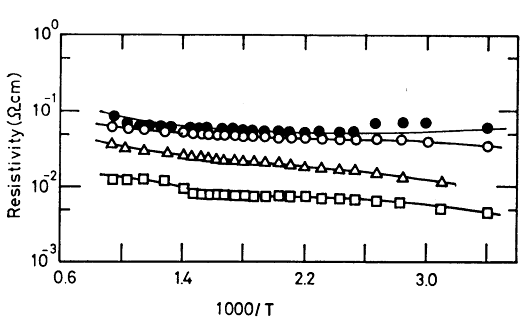

Fig. 3. Temperature dependence of resistivities of CaO-doped La_2CuO_4 compounds.
●: La_2CuO_4, ○: 2.5 mol% CaO-doped, △: 5 mol% CaO-doped, □: 20 mol% CaO-doped.

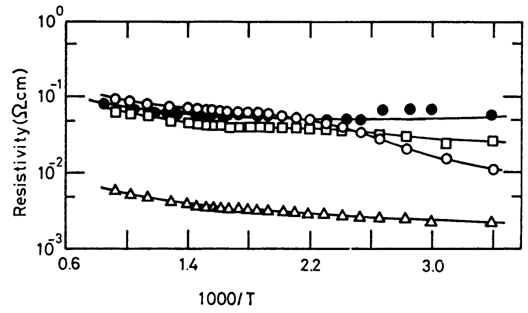

Fig. 4. Temperature dependence of resistivities of BaO-doped La_2CuO_4 compounds.
●: La_2CuO_4, ○: 2.5 mol% BaO-doped, □: 5 mol% BaO-doped, △: 10 mol% BaO-doped.

As described previously, the La atom, which has the lowest electronegativity of the Ln atoms, causes the π-bond formation of the $(Cu–O)_a$ bond to which the metallic conductivity of La_2CuO_4 is ascribable. One can expect that for metals less electronegative than La, the effective charge of the O^{2-} ions on the c axis are enhanced to a value greater than that for La_2CuO_4 so that the $(Cu–O)_c$ bond is longer and the $(Cu–O)_a$ bond is shorter than in the case of the La atom. Since the shortening of the $(Cu–O)_a$ bond enhances the degree of π-electron overlap and this results in an enhancement of the conducting electron mobility, the replacement of the La^{3+} sites with less electronegative atoms will enhance the conductivity of La_2CuO_4. Calcium and barium are less electronegative than La and it is known that they can replace parts of the Gd^{3+} ions in Gd_2CuO_4.[4)] Therefore, Ca^{2+} and Ba^{2+} ions can be expected to replace La^{3+} ions and to enhance the conductivity of La_2CuO_4. Figures 3 and 4 show the log ρ *vs.* $1000/T$ plots for CaO-doped and BaO-doped La_2CuO_4 compounds, respectively. These are seen to be metallic, with the resistivities of the former decreasing with increasing CaO content and, at 20 mol% doping, the ρ value decreases to one-tenth of that of undoped La_2CuO_4. Similarly, the BaO dopant lowers the resistivity; at 10 mol% doping the ρ value becomes one-tenth of that for undoped La_2CuO_4.

Table 1 gives the lattice parameters of undoped and 20 mol% CaO-doped and 10 mol% BaO-doped La_2CuO_4 compounds. Although the Ba^{2+} ion is larger than the La^{3+} ion, the a axis or the $(Cu–O)_a$ bond shortens due to the BaO-doping. This is evidence for

Table 1. LATTICE PARAMETERS FOR UNDOPED AND CaO- AND BaO-DOPED La_2CuO_4

	a(Å)	*c*(Å)	*c*/*a*
La_2CuO_4	3.808	13.200	3.466
$La_{1.6}Ca_{0.4}CuO_4$	3.790	13.189	3.480
$La_{1.8}Ba_{0.2}CuO_4$	3.796	13.274	3.497

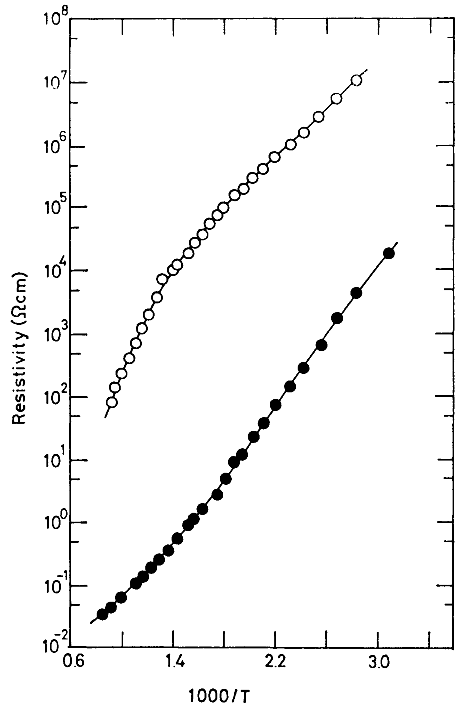

Fig. 5. Temperature dependence of resistivities of $Gd_{0.96}Tb_{1.04}Cu_2O_5$ (○) and $Gd_{0.84}Tb_{1.16}CuO_4$ (●).

an enhancement in the degree of π-electron overlap, which was expected. The CaO dopant shortens the a axis but enhances the *c*/*a* ratio. This suggests that the shortening of the a axis due to the CaO dopant is not only due to the smaller size of the Ca^{2+} ion, but is due partly to an enhancement of the π-electron overlap. Thus, the lowering of the resistivity due to doping with alkaline-earth oxides can be attributed to an increase in the degree of π-electron overlap in the conduction band.

The positive-charge deficiency in the La^{3+} site due to doping with divalent alkaline-earth ions may be balanced partly by the oxygen vacancies and partly by the formation of Cu^{3+} ions, as for alkaline-earth doped Gd_2CuO_4. This contributes to a decrease in the number of electron carriers, but the decrease in conductivity due to this effect is negligibly small in comparison with the increase in conductivity due to π-electron overlapping, since La_2CuO_4 is metallic.

The composition of the CuO–Ln_2O_3 system changes discontinuously between Gd and Tb; $CuO/Ln_2O_3=1$ for Ln=La—Gd and $CuO/Ln_2O_3=2$ for Ln=Tb—Lu. Since the $\bar{r}$ value can be varied continuously by varying the Gd/Tb ratio, the ternary system, Gd_2O_3–Tb_2O_3–CuO, will reveal how the CuO/Ln_2O_3 ratio depends upon the $\bar{r}$ value between Gd and Tb. Powder X-ray diffraction data reveal that the limit composition for a compound with $CuO/Ln_2O_3=1$ is $Gd_{0.84}Tb_{1.16}CuO_4$ and that for $CuO/Ln_2O_3=2$ is $Tb_{1.04}Gd_{0.96}Cu_2O_5$. This indicates that overlap occurs in both types of compounds for Gd/Tb ratios ranging from 0.72 to 1.08, that is, there is no critical ionic radius of the Ln^{3+} ions at which the Ln_2CuO_4 type compound transforms into the $Ln_2Cu_2O_5$ type compound.

$Tb_2Cu_2O_5$ is an insulator and Gd_2CuO_4 is a semiconductor.[1,2] It is not known whether this difference in the resistivities is ascribable to the difference in the crystal structures or to the difference in the ionic radii of the Gd^{3+} and Tb^{3+} ions. Figure 5 indicates that the resistivity of the $Tb_{1.04}Gd_{0.96}Cu_2O_5$ compound is still greater than that of the $Gd_{0.84}Tb_{1.16}CuO_4$ compound by three orders of magnitude, although the $\bar{r}$ value of the former is greater than that of the latter. Therefore, the difference in the resistivities of Gd_2CuO_4 and $Tb_2Cu_2O_5$ is not due to the difference in size of the Ln^{3+} ion but due to the difference in the crystal structures.

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