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Synthesis, Crystal Structure and Physical Properties of $Li_xMg_{0.857-x}Cu_{2.143}O_{3-y}$

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Solid solutions of Li-doped $Mg_{0.857}Cu_{2.143}O_3$ ($Li_xMg_{0.857-x}Cu_{2.143}O_{3-y}$) were prepared at 950°C for 12 h in air by the solid-state method using Li_2CO_3, MgO and CuO powders. The solid solutions were obtained as the single α phase with the güggenite structure in $0 \leqq x \leqq 0.06$ region. With the increasing of the Li content *x*, the lattice parameters *a*, *b* and unit cell volume *V* decreased, while *c* increased. On the basis of the charge neutrality, hole carrier estimated by the oxygen content increased with the Li substitution. The Seebeck coefficient at room temperature of $x = 0.03$ sample was $+400\,\mu V/K$. The electrical resistivity *ρ* at room temperature drastically decreased with the increasing *x*. Temperature dependences of *ρ* for $x = 0.01$, 0.03 and 0.06 samples were semi-conductive behavior from room temperature to about 12 K. Interaction between Cu^{2+} and Cu^{2+} through O^{2-} seems to be somewhat large antiferromagnetic one. Sperconducting transition was not detected in the temperature range. © 2002 Elsevier Science (USA)

Key Words: **magnesium copper oxide; crystal structure; hole doping; X-ray powder diffraction; oxygen content; superconductivity.**

INTRODUCTION

It is well known that physical properties of transition metal oxides can notably be changed by varying chemical valence of the transition metal ion in the oxides. The change of the chemical valence would correspond to a change of the band structure for the electrical conduction, to an introduction of hole or electron carrier into the band, and, otherwise, to a change of the magnetic behavior. A technique has been known to substitute a cation with different chemical valence for the host cation in the oxide in order to change the chemical valence of the transition metal ion. The technique has quite often been used in the researches for the superconducting oxides, e.g., $M_xLa_{2-x}CuO_{4-y}$ (M = Ba, Sr, Ca, Na) (1–3) and $Ce_xLn_{2-x}CuO_{4-y}$ (Ln = Pr, Nd, Sm, Eu) (4–6). In these cases, La_2CuO_4 and Ln_2CuO_4 (Ln = Pr, Nd, Sm, Eu) are called the Mott insulator (7).

On the other hand, another technique has been known to change the chemical valence of the transition metal ion without these substitutions. In the technique, oxygen content of the oxides should be varied by annealing condition. Case of the $SrTiO_{3-y}$ with the perovskite structure (8) has been well known. The $SrTiO_{3-y}$ with oxygen defect becomes highly conductive, and shows superconductivity when the $SrTiO_3$ is annealed in a reductive condition. It is considered that the superconductivity seems to depend upon the mixed valence ($+3 : +4$) of the titan ion in the perovskite structure.

Recently, we contributed an article to a paper investigating that the single α phase of the Mg–Cu–O series oxides with the güggenite structure is obtained as $Mg_{1-x}Cu_{2+x}O_3$ ($0.130 \leq x \leq 0.166$) (9).

This time, we select the $Mg_{0.857}Cu_{2.143}O_3$ (with $x = 0.143 = \frac{1}{7}$) as a transition metal oxide like the Mott insulator and try to substitute Li^+ for the Mg^{2+} in order to introduce hole carrier into the CuO_2 plane. The Mg^{2+} is coordinated by six oxygen ions. According to the ionic radii table by Shannon and Prewitt (10), the ionic radii (VI) of Li^+, Mg^{2+} and Cu^{2+} are 0.74, 0.72 and 0.73 Å, respectively. Thus, Li^+ could substitute for Mg^{2+}.

It is the purpose of this study to report preparation, variations of crystal structure and physical properties of the $Li_xMg_{0.857-x}Cu_{2.143}O_{3-y}$ oxide by the Li substitution.

EXPERIMENTAL

Samples of $Li_xMg_{0.857-x}$ $Cu_{2.143}O_{3-y}$ oxides were prepared from appropriate amounts of 99.99% pure MgO, CuO powders (Rare Metallic Co., Ltd) and reagent grade Li_2CO_3 powder (Wako Pure Chemical Industries, Ltd). Before weighing, the MgO and CuO powders were heated at 900°C for 1 h, and the thermogravimetry was performed

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on the Li_2CO_3 in order to examine whether water adsorbed or not on the powder. The powders were weighed and thoroughly mixed for 1 h, pressed into pellets, prefired at 950°C for 12 h and then furnace cooled in air. Prefired materials were ground, pressed into pellets, sintered at 950°C 12 h and the furnace cooled in air.

The samples were examined by the X-ray diffraction analysis using monochromatized Cu*Kα* radiation with the Rigaku goniometer (Rint 2100). Lattice parameters of the samples were refined by the least-squares method to better than 0.01 percent accuracy.

Oxygen content $3-y$ of the samples was measured by the thermogravimetry using the Shinku-Riko thermobalance (TDG9600). Details of the measurement have been described in our previous paper (11). Seebeck coefficient was measured at room temperature. Electrical resistivity of the samples was measured by the four-probe method from room temperature to 12 K. Magnetic susceptibility of the samples was measured by the SQUID susceptometer (Quantum Design MPMS) under field-cooled condition 500 Oe from room temperature to 4.2 K.

RESULTS AND DISCUSSION

The XRD patterns of the prepared samples were shown with x value in Fig. 1. All X-ray diffraction peaks in $x = 0.03$, 006 samples were identified as those of the α phase with the güggenite structure. It was noted that a remarkable preferred orientation appeared in the diffraction peaks by the Li substitution. Details of the orientation were described under Rietveld analysis part. Two diffraction peaks at 35.6 and 38.9 in 2θ from extra phases were found in $x = 0.09$, 0.214 samples. The intensities of the peaks were large in $x = 0.214$ sample. The phase was identified as the CuO phase. Phases containing the Li element were not detected in the samples. The result would depend upon disappearance of Li element due to the melting of the remnant Li_2CO_3 ($T_m = 618°C$) phase which did not react with MgO and CuO phases. From these results, it was found that the samples were obtained as single phase in $0 \leqq x \leqq 0.06$, and the substitution of the Li ion was very weak. Lattice parameters a, b, c and unit cell volume V were plotted with x in Figs. 2(a) and 2(b). Although the variations of the lattice parameters were weak, tendencies of monotonous decrease in a, b and V were found, while a tendency of monotonous increase in c was found with the increasing x in $0 \leqq x \leqq 0.06$ region. The weak variations were consistent with the weak substitution of the Li ion.

Rietveld analysis was performed on $x = 0.06$ sample in order to determine on which site the Li existed in the structure. The $x = 0.06$ sample was the single phase with the highest Li content. The multiphase samples ($x > 0.06$) disturb the Rietveld analysis although the multiphase samples contained more Li content. In the beginning of the analysis, we calculated the R indexes by varying the preferred orientation and FWHM factors, finally, obtained the most suitable R indexes when the preferred orientation was (011) direction. The structure of the $Mg_{0.857}Cu_{2.143}O_3$ with $x = 0$ was shown in Figs. 3(a) and 3(b). There are two metal sites, which are 4e (Cu1/Mg1) and 2b (Cu2/Mg2) sites, respectively. For the Rietveld analysis on the basis of the preferred orientation and FWHM of (011), we considered the next two points. (1) The Li could exist on the 4e site or the 2b site. (2) The X-ray scattering activity of the Li ion is very weak, and the content of the Li is also weak. Thus, we performed the analysis in two cases, that is, (1) the Li exits on the 4e site, and (2) the Li exits on the 2b

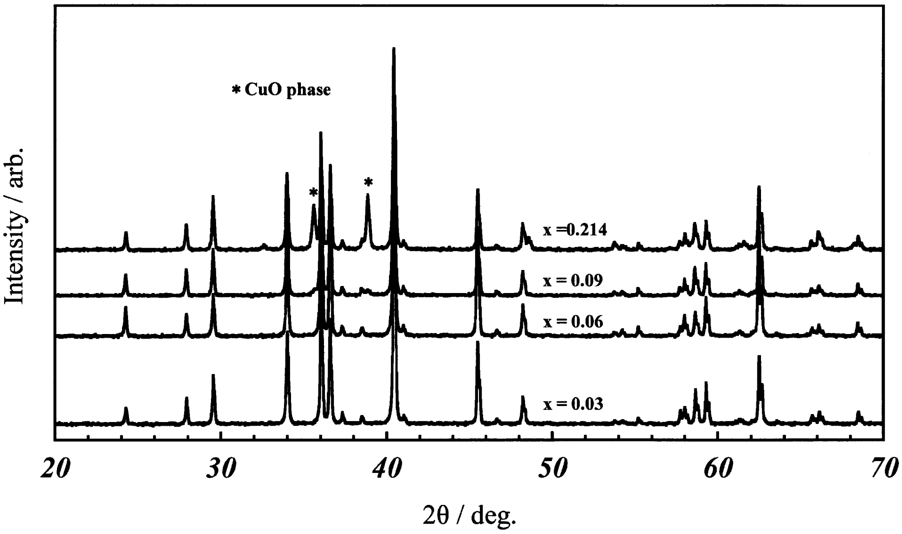

FIG. 1. The XRD patterns of the prepared samples with $x = 0.03$, 0.06, 0.09, and 0.214 in starting composition.

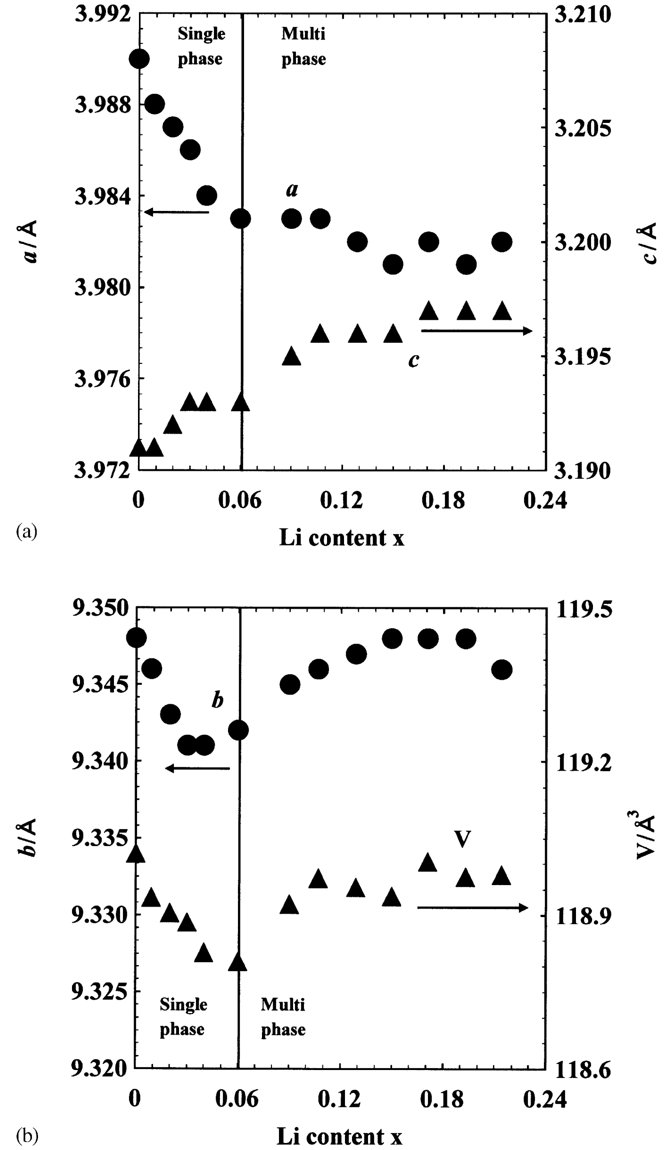

FIG. 2. (a) The variations of the lattice parameters *a* and *c* of the samples with *x*. (b) The variations of the lattice parameter *b* and unit cell volume *V* of the samples with *x*.

site. In the two cases, we fixed the occupancy factor as the starting composition for the Li ion. After the analyses, we compared the *R* indexes of the two cases and determined the Li site.

The good-fitness and *R* indexes in the case of the Li on the 4e site were $S = 1.4801$, $R_{WP} = 3.50\%$, $R_P = 2.62\%$, $R_I = 2.15\%$, and $R_F = 1.53\%$, while those in the case of the 2b site were $S = 1.5597$, $R_{WP} = 3.69\%$, $R_P = 2.71\%$, $R_I = 3.49\%$, and $R_F = 2.25\%$. Considering these results, the Li seems to substitute for Cu(1) on the 4e site and the pushed Cu(1) moves on the 2b Mg site, that is, $(Mg_{0.797}Cu_{0.06})_{2b}(Li_{0.06}Cu_{2.083})_{4e}O_3$. For the $x = 0.06$ sample, the profile fit and difference patterns of the Rietveld analysis in the case of the 4e site were shown in Fig. 4. The crystallographic data and results of the refinement were listed in Tables 1 and 2. Comparing the lattice parameters of $x = 0$ of Ref. (9) with them of the $x = 0.06$ sample, it was found that *a* and *b* decreased, while *c* increased by the Li substitution. These tendencies were consistent with the results of the lattice parameters in the Figs. 2(a) and 2(b).

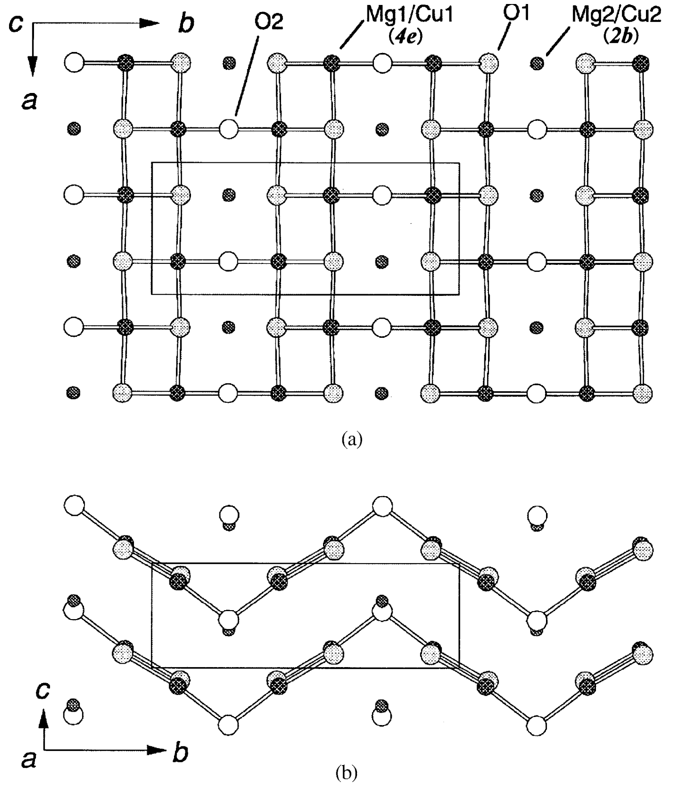

FIG. 3. (a) The crystal structure of the $Mg_{0.857}Cu_{2.143}O_3$ projected on the *a*–*b* plane, (b) projected on *b*–*c* plane.

Oxygen contents of the single phase samples of $x = 0.03$, 0.04 and 0.06 were plotted with *x* in Fig. 5. The oxygen contents were constant and did not depend on the Li content *x*. The result seems to be due to the weak solubility of the Li ion. By using the Li content *x* and measured oxygen content $3-y$ $(y \div 0)$ on the basis of the charge neutrality, we would estimate hole content introduced by the Li substitution with the formula $P = \frac{1}{2}x - y$. The result is also shown in the Fig. 5. It was found that the hole content increased with increasing *x*. The Seebeck coefficient at room temperature of $x = 0.03$ sample was measured as $+400\,\mu V/K$. This value suggests existence of the hole carrier, and consistent with the oxygen content measurement.

The monotonous increase of the lattice parameter *c* would depend upon the substitution of the larger L^+ ion, while the decreases of *a*, *b* and *V* cannot be explained well. Considering the coordination around Cu(4e) ion in

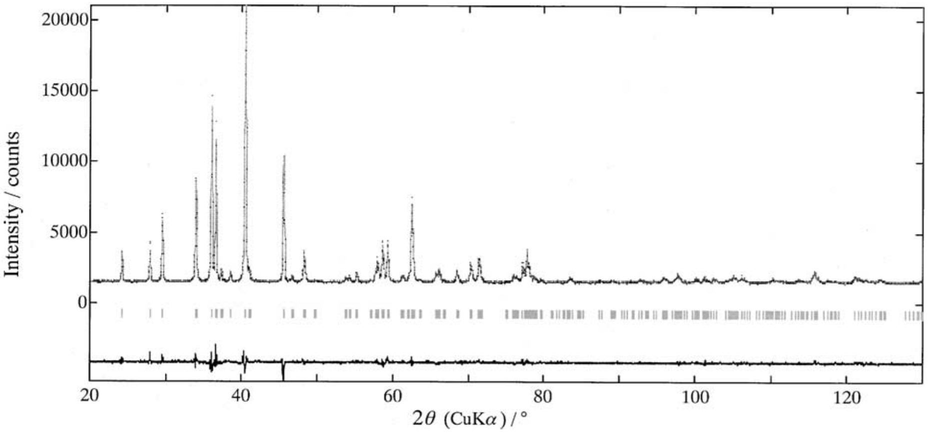

FIG. 4. The observed (dots) and calculated (solid) X-ray diffraction profiles for $Li_xMg_{0.797-x}Cu_{2.143}O_{3-y}$ ($x = 0.06$). Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

Fig. 3(a), the Cu(4e)–O bond would shorten by introduction of hole carrier by the Li^+ substitution like the case of the $Sr_xLa_{2-x}CuO4$-y, in which the Cu-O bond shortens by the introduction of hole carrier corresponding the Sr^{2+} substitution (3). These results mean that Li could well substitute in the structure in the $0 \leqq x \leqq 0.06$ region. Further, considering that the variations of the lattice parameters and unit cell volume were found in $x > 0.06$, it seems that Li could also substitute in $x > 0.06$ region (multiphase region).

The electrical resistivity ρ at room temperature was plotted with x in Fig. 6. The resistivity drastically decreased with x. Particularly, the decrease was notable in $0 \leqq x \leqq 0.06$ region which was the single phase region. The result is consistent with that of the estimated hole content by the oxygen content measurement. Temperature dependences of the resistivities $\rho(T)$ for $x = 0.01$, 0.03, 0.06 samples were shown in Fig. 7. The dependences were semiconductive behavior for all the samples. On a assumption of the introduction of the hole carrier by the Li substitution, logarithm of resistivity ρ could almost be in proportion to $E_a/2k_BT$ (E_a is energy gap between valence level and acceptor level). Logarithm of the resistivities for the samples was plotted versus $1/T$ in Fig. 8. Linearity was found between them. From these slopes, values of the E_a were estimated 0.38, 0.27, and 0.22 eV for $x = 0.01$, 0.03, and 0.06 samples. A tendency was found that these E_a values gradually decreased with the increasing x. The decrease would correspond to the width of the acceptor band. Superconducting transition was not found in the temperature range.

Temperature dependence of the magnetic susceptibility χ for $x = 0.06$ sample was shown in Fig. 9. The magnetic susceptibility had a behavior of non-zero asymptotic limit at 300 K and increased with the decreasing temperature, and a transition was found around 50 K marked with an arrow in the Fig. 9. According to the Curie Weiss law $1/\chi = 1/c(T - \Theta)$, $1/\chi$ was also plotted versus T in the Fig. 9. Curie behavior was found from 300 to 180 K in Fig 9. Curie constant C and Weiss temperature Θ were estimated 0.4 emu/(K mol) and −573 K from the slope and intercept to T-axis. The measured curie constant of 0.4 emu/(K mol) was almost consistent with calculated

TABLE 1
Crystallographic Data and Structure Refinement for $Li_xMg_{0.857-x}Cu_{2.143}O_3$ ($x = 0.06$)

Formula	$Li_{0.06}Mg_{0.797}Cu_{2.143}O_3$
Formula weight	203.98
Space group	*Pmmn* (No.59, setting 2)
Unit cell dimensions	$a = 3.9858(1)$ Å $b = 9.3462(2)$ Å $c = 3.1938(1)$ Å
Cell volume	$V = 118.98(2)$ Å
Z	2
Density (calculated)	5.69 Mg/m^3
Goodness-of-fit	$S = 1.480$
R indexes	$R_{wp} = 0.0350$ $R_p = 0.0262$ $R_I = 0.0215$ $R_F = 0.0153$

TABLE 2
Atomic Coordinates and Isotropic Displacement Parameters for $Li_xMg_{0.857-x}Cu_{2.143}O_3$ ($x = 0.06$)

	Site	Occupancy	x	y	z	B (Å^2)
Cu1/Li1	4*e*	0.97/0.03	$\frac{1}{4}$	0.0868	0.1799(3)	0.56(3)
Cu2/Mg2	2*b*	0.203/0.797	$\frac{1}{4}$	$\frac{3}{4}$	0.3650(7)	0.56^a
O1	4*e*	1.000	$\frac{1}{4}$	0.5961 (5)	0.866(1)	1.11(8)
O2	2*a*	1.000	$\frac{1}{4}$	$\frac{1}{4}$	0.566(1)	1.11^b

[a] Constrained with the value of Cu1/Mg1.

[b] Constrained with the value of O1.

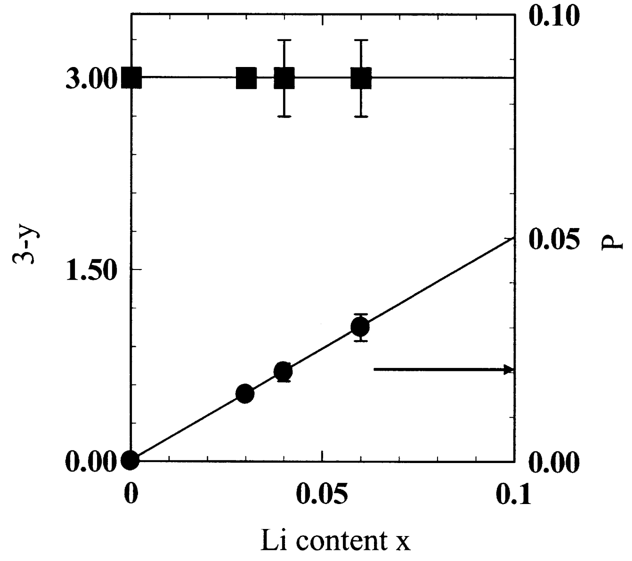

FIG. 5. The variation of the oxygen content $3-y$ and estimated hole content P of the single phase samples with x.

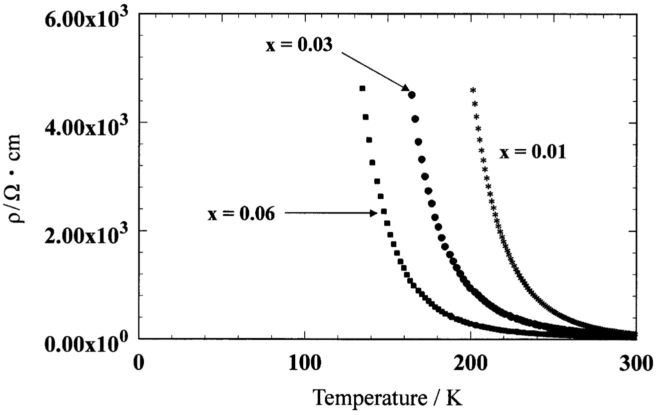

FIG. 7. The temperature dependences of the electrical resistivities of the $x = 0.06$ and 0.15 samples.

one of 0.375 emu/(K mol) for Cu^{2+}. The result would show that the magnetism depends upon the copper ion in the sample. The Weiss temperature of -573 K would mean that there is somewhat large antiferromagnetic interaction between the Cu^{2+} and Cu^{2+} through the O^{2-}. The transition around 50 K would be antiferromagnetic one. The non-zero asymptotic limit found at 300 K would depend upon the antiferromagnetic interaction at the temperature.

SUMMARY

In this work, we tried to prepare the Li-doped $Mg_{0.857}Cu_{2.143}O_3$ and studied the crystal structure, oxygen content and physical properties of the oxide by the XRD, Rietveld analysis, thermogravimetry, Seebeck coefficient, four-probe method, and SQUID measurements. The solid solutions were obtained as the single α phase with the

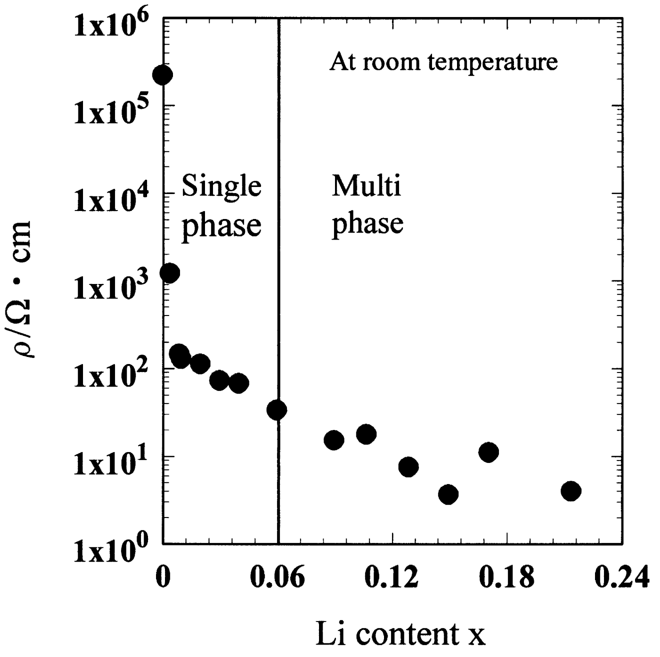

FIG. 6. The variation of the electrical resistivity ρ at room temperature of the samples with x.

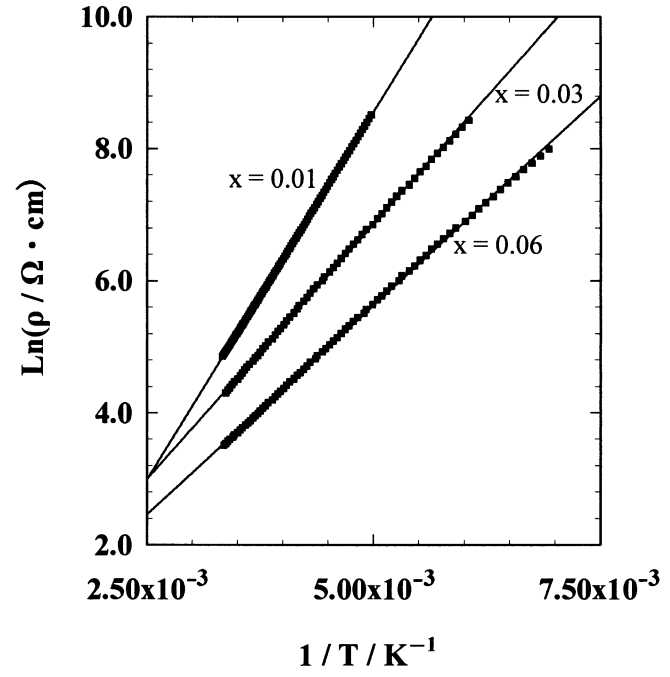

FIG. 8. The dependence of the Ln (ρ) of the $x = 0.01$, 0.06, and 0.15 samples on $1/T$.

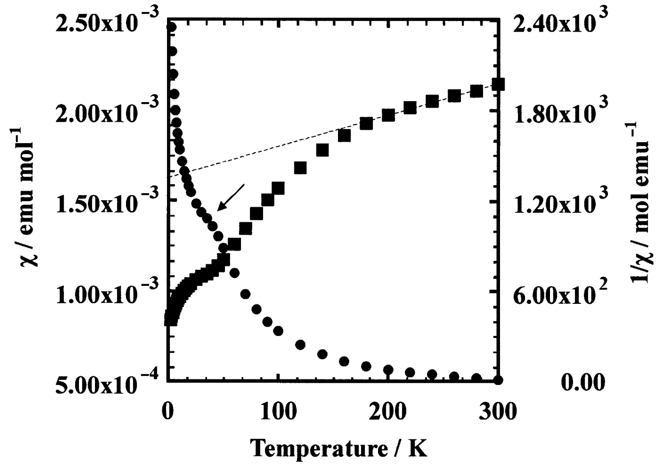

FIG. 9. The temperature dependences of the magnetic susceptibility $\chi(T)$ and $1/\chi(T)$ of $x = 0.15$ sample.

güggenite structure in $0 \leqq x \leqq 0.06$ region. The Li could exist on 4e site in the structure. The lattice parameters a, b and unit cell volume V decreased, while c increased with the increasing x in the region. The resistivity decreased with the Li substitution. The Seebeck coefficient at room temperature was $+400\,\mu$V/K. The conducting carrier should be hole carrier introduced by the Li substitution. The interaction between Cu^{2+} and Cu^{2+} through O^{2-} seems to be antiferromagnetic one in the oxide. Superconductivity was not detected in the oxide although electrical resistivity at room temperature of the samples drastically decreased by the Li substitution.

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