

$(RE_{1-x}Sr_x)_8Cu_8O_{20}$ ($RE = Pr, Nd$) Synthesized under a High Pressure of Oxygen, $P_{O_2} = 20$ MPa

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$(RE_{1-x}Sr_x)_8Cu_8O_{20}$ compounds were prepared for $RE = Pr$ ($x = 0.35$) and $RE = Nd$ ($x = 0.40$) under 100 MPa of 20% O_2 –80% Ar gas ($P_{O_2} = 20$ MPa) at 1273 K. Their crystal structures characterized by X-ray diffraction and electron diffraction are tetragonal, space group $P4/mbm$, with lattice constants of $a = 1.07920$ and $c = 0.38057$ nm for $RE = Pr$ and $a = 1.07961$ and $c = 0.37841$ nm for $RE = Nd$. They are isostructural with $(La_{1-x}Sr_x)_8Cu_8O_{20-\delta}$ ($0.16 \leq x \leq 0.24$). The resistivity at 300 K was 3.4 m Ω cm for $RE = Pr$ and 7.0 m Ω cm for $RE = Nd$ and decreased with decreasing temperature down to 13 K. The magnetic susceptibility shows Curie–Weiss behavior for both compounds. © 1996 Academic Press, Inc.

1. INTRODUCTION

Compounds in the rare earth (RE)–copper–oxygen and RE –alkaline earth–copper–oxygen systems were prepared and isolated to investigate their crystal structures and properties (1, 2). The latter systems have received great attention since the discovery of a high T_c superconductor, $La_{2-x}Ba_xCuO_4$ ($x \approx 0.15$), in 1986 (3). In the RE –Ba–Cu–O systems $REBa_2Cu_3O_{7-\delta}$ (4–6), $RE_2Ba_4Cu_7O_{15-\delta}$ (7–9), and $RE_2Ba_4Cu_8O_{16}$ (10, 11) were prepared and found to be superconductors.

In the La–Sr–Cu–O system several compounds had been studied (12–15) before the discovery of the high T_c superconductor. Since the report on T_c up to 40 K for $La_{2-x}Sr_xCuO_4$ (16), much greater effort has been put into searching for new materials in the La–Sr–Cu–O system. To date, six ternary compounds have been prepared in air ($P_{O_2} = 20$ kPa). They are (i) $La_{2-x}Sr_xCuO_{4-\delta}$ ($0 \leq x \leq 1.34$) (14), with K_2NiF_4 structure; (ii) $La_{2-x}Sr_{1+x}Cu_2O_6$ ($0.05 \leq x \leq 0.15$) (13), which crystallizes in the $Sr_3Ti_2O_7$

structure without oxygen at the O(3) (0, 0, 0) site, 2126 type structure; (iii) $La_{2-x}Sr_{1+x}Cu_2O_{5+\delta}$ ($0.85 \leq x \leq 0.95$) (17, 18), possessing 2126 type unit cell with a threefold superstructure along the b axis, caused by both cation (La/Sr) and oxygen ordering, 2126 ($a \times 3a \times c$) type structure; and (iv–vi) $(La_{1-x}Sr_x)_8Cu_8O_{20-\delta}$ ($0.16 \leq x \leq 0.24$) (19–22), $La_2Sr_6Cu_8O_{17.6}$ (23–25), and $La_2Sr_6Cu_8O_{16}$ (23, 25, 26), having perovskite-derived structures with oxygen vacancies ordered. Additionally, $(La_{0.86}Sr_{0.14})_4Cu_4O_{10}$ (27) was obtained at an oxygen pressure of $P_{O_2} = 100$ kPa.

In the RE –Sr–Cu–O systems with heavier rare earth elements than La, however, the number of the compounds obtained is smaller. In the Pr–Sr–Cu–O system, four compounds were obtained in air: (i) $Pr_{2-x}Sr_xCuO_{4-\delta}$ ($0.96 \leq x \leq 1.25$) (28, 29), with an oxygen deficient K_2NiF_4 type structure; (ii) $Pr_{1.6}Sr_{0.4}CuO_{4-\delta}$ (29), in which half unit cells of the K_2NiF_4 type and the Nd_2CuO_4 type are alternately stacked; (iii) $Pr_{2-x}Sr_{1+x}Cu_2O_{6-\delta}$ ($0.10 \leq x \leq 0.15$) (30), crystallizing with 2126 type structure; and (iv) $Pr_{2-x}Sr_{1+x}Cu_2O_{5+\delta}$ ($0.6 \leq x \leq 1.0$) (31), having 2126 ($a \times 3a \times c$) type structure. In the Nd–Sr–Cu–O system, three compounds have been reported: (i) $Nd_{2-x}Sr_xCuO_{4-\delta}$ ($1 \leq x < 1.5$) (32, 33) with K_2NiF_4 type structure; (ii) $Nd_{2-x}Sr_{1+x}Cu_2O_{6-\delta}$ ($0.10 \leq x \leq 0.20$) (33) with 2126 type structure, and (iii) $Nd_{2-x}Sr_{1+x}Cu_2O_{5+\delta}$ ($0.6 \leq x \leq 1.0$) (34–36) with 2126 ($a \times 3a \times c$) type structure. In the cases of samarium, europium, and gadolinium, $RE_{2-x}Sr_{1+x}Cu_2O_{5+\delta}$, having 2126 ($a \times 3a \times c$) type structure, were obtained (37). No compounds have been reported in the cases of $RE = Tb$ –Lu whose atomic numbers are bigger than that of gadolinium. The number of the compounds decreased with decreasing rare earth ionic radius.

We recently investigated the system of Pr–Sr–Cu–O at 1353 K and $P_{O_2} = 100$ kPa. Under these conditions, the K_2NiF_4 type oxide $Pr_{2-x}Sr_xCuO_{4-\delta}$ ($x = 1.0$) (29), that had been prepared at 1353 K in air, decomposed into three anisostructural compounds, $Pr_{1.85}Sr_{1.15}Cu_2O_{6-\delta}$ (2126 type), $Pr_{2-x}Sr_{1+x}Cu_2O_{5+\delta}$ (2126 ($a \times 3a \times c$) type), and $Pr_8Sr_7Cu_2O_y$ (a new compound) (38). The K_2NiF_4 type and 2126 type compounds prepared at $P_{O_2} = 100$ kPa are richer

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in strontium than those obtained in air. These results show that the compositions and structures of the compounds in this system are susceptible to oxygen pressure (P_{O_2}). Thus, we did a further study on the RE - Sr - Cu - O ($RE = Pr, Nd$) systems under higher oxygen pressures and obtained the new compounds $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ and $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$ at $P_{O_2} = 20$ MPa. In the present paper, we describe the synthesis, structural characterization by X-ray power diffraction and electron diffraction, and the electric and magnetic properties of these compounds.

2. EXPERIMENTAL

Samples were synthesized by solid state reaction of CuO (99.9%), Pr_6O_{11} (99.9%), Nd_2O_3 (99.9%), and $SrCO_3$ (99.9%) powders. The powders were weighed, mixed by grinding in an agate mortar, and pressed into pellets. The pellets placed in alumina crucibles were put into a furnace and heated at 1273 K under flowing oxygen gas for 40 h with intermittent grinding, and then were removed from the furnace for quenching to room temperature. The resulting pellets were heated under a 20% O_2 -80% Ar gas (99.99% purity) atmosphere of 100 MPa ($P_{O_2} = 20$ MPa) at 1273 K for 20 h with the use of a hot isostatic pressing apparatus (O_2 -Dr.HIP, Krobe Steel Co. Ltd.), and then cooled to 400 K (7 K/min) in the apparatus. After cooling, the pressure was released and the samples were taken out of the apparatus. For some samples, the high-pressure heating process was repeated.

The copper formal valence was determined by iodometric titration. X-ray powder diffraction (XRD) data ($10^\circ \leq 2\theta \leq 80^\circ$, step width 0.04°) were collected at room temperature. $CuK\alpha$ radiation was used on a diffractometer with a pyrolytic graphite monochromator (RAD-C; Rigaku). Rietveld analysis of the powder XRD data was done with the program RIETAN (39). The interatomic distances and bond angles were computed by the ORFFE program (40). Electron diffraction patterns were taken with a 200 kV microscope (JEM-200EX) for powders crushed and dispersed on holey carbon films.

Resistivity measurements were made between 13 and 300 K with use of a 20 mA dc source on sintered samples, typically $1 \times 4 \times 10$ mm³, on which four In probes were attached. The magnetic susceptibility of powder samples (50 mg) wrapped with parafilm was measured between 5 and 100 K at a magnetic field strength of 20 mT with a SQUID magnetometer (Quantum Design Co.).

3. RESULTS AND DISCUSSION

The samples $RE_{1-x}Sr_xCuO_y$ ($RE = Pr$ and Nd ; $x = 0.0, 0.2, 0.4, 0.6$, and 0.8) were prepared first. At $x = 0.2$ and 0.4 , new compounds X ($RE = Pr$) and Y ($RE = Nd$) were obtained as main phases. The products in $x = 0.6$ and 0.8

samples were mainly $Pr_{2-y}Sr_{1+y}Cu_2O_{6-\delta}$ ($0.85 \leq y \leq 1.0$) and $(Sr_{1-y}RE_y)_{14}Cu_{24}O_{41-\delta}$ ($RE = Pr$ and Nd), both of which can be prepared at $P_{O_2} = 100$ kPa. At $x = 0.0$, CuO and Nd_2CuO_4 were obtained with $RE = Nd$, and PrO_2 and CuO with $RE = Pr$. $RECuO_{3-\delta}$ ($RE = Pr, Nd$) were not produced, although in the $LaO_{1.5}$ - CuO system $LaCuO_3$ (41) was synthesized at 1173 K and 6.5 GPa and $LaCuO_{3-\delta}$ (42, 43) at 1173 K and $P_{O_2} = 20$ -100 MPa.

We attempted to isolate the compounds X and Y in a composition range $0.3 \leq x \leq 0.5$. The series of samples were all multi-phase, but the impurity level was lowest for $x = 0.35$ ($RE = Pr$) and $x = 0.40$ ($RE = Nd$). We reheated these samples at the same high oxygen pressure and temperature for 20 h. The purity of the products was improved and the XRD peak intensities of the impurity phases diminished to 1.5 and 3% of the maximum peak intensities of the compounds X and Y , respectively.

These results suggest that the single phase compositions of X and Y are near $x = 0.35$ ($Pr_{0.65}Sr_{0.35}CuO_y$) and $x = 0.40$ ($Nd_{0.60}Sr_{0.40}CuO_y$) under the present equilibrium conditions. The copper formal valence for $Nd_{0.60}Sr_{0.40}CuO_y$ was +2.36, leading to an oxygen content of $y \approx 2.5$. We have assumed the valence of the Pr ion in $Pr_{0.65}Sr_{0.35}CuO_y$ to be Pr^{3+} based on the result of the magnetic susceptibility measurement shown in a later section, and the copper valence determined by iodometric titration of +2.35 leads us again to $y \approx 2.5$. We surmise the compositions to be $Pr_{0.65}Sr_{0.35}CuO_{2.5}$ and $Nd_{0.60}Sr_{0.40}CuO_{2.5}$ in the following crystal structure analysis.

The electron diffraction patterns were indexed with a tetragonal lattice of $a \approx 1.08$, $c \approx 0.38$ nm for both $Pr_{0.65}Sr_{0.35}CuO_{2.5}$ and $Nd_{0.60}Sr_{0.40}CuO_{2.5}$. Systematic absence occurred for $h00$, $h = 2n + 1$ and for $0kl$, $k = 2n + 1$, which were consistent with space groups $P4/mbm$, $P4b2$, and $P4bm$. Some grains in the $Nd_{0.60}Sr_{0.40}CuO_{2.5}$ sample showed weak satellite spots, which corresponded to a superstructure doubled along the c axis.

Based on the electron diffraction results, the XRD peaks of $Pr_{0.65}Sr_{0.35}CuO_{2.5}$ and $Nd_{0.60}Sr_{0.40}CuO_{2.5}$ could be indexed with tetragonal unit cells of $a = 1.079$, $c = 0.3807$ nm, and $a = 1.080$, $c = 0.3784$ nm, respectively. No extra peaks corresponding to the superstructure shown by electron diffraction were observed in the XRD patterns.

We carried out Rietveld refinement for the powder X-ray diffraction data choosing the most symmetrical space group, $P4/mbm$. The secondary phases were excluded from the collected data. We used the atomic parameters of $(La_{0.8}Sr_{0.2})_8Cu_8O_{20-\delta}$ ($P4/mbm$, $a = 1.074$ nm, $c = 0.3861$ nm) (19) for initial parameters because its space group, powder XRD pattern, and oxygen contents are similar to those of the present compounds. Figure 1a shows the observed and fitted patterns and the difference between them for $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$, and Fig. 1b for $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$. The refined atomic parameters are

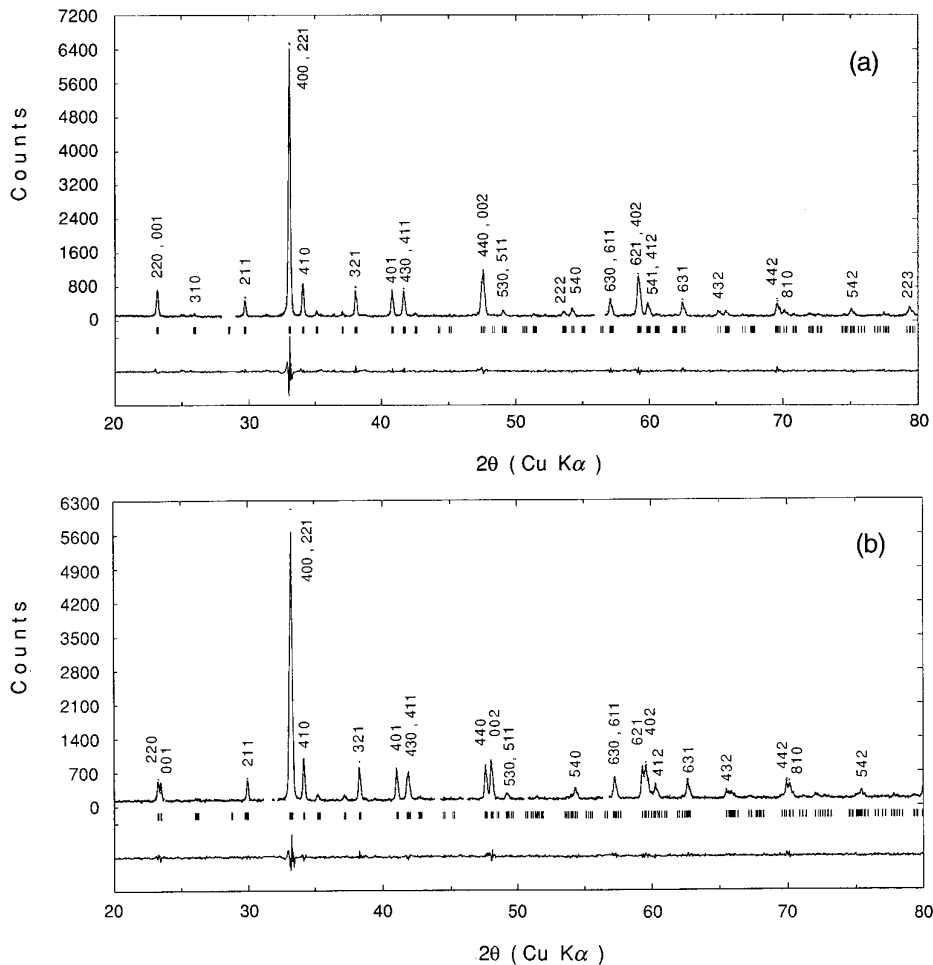


FIG. 1. Rietveld refinement profiles and X-ray powder diffraction data on $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ (a) and $(Nd_{0.40}Sr_{0.60})_8Cu_8O_{20}$ (b).

listed in Tables 1 and 2. The RE and Sr ions of a relative abundance coincident with the nominal compositions were assumed to occupy the $8j$ site randomly. The R factors were less than 10% for both compounds, showing that the calculated patterns fit those observed well. The lattice constants of the present compounds are similar to those of not only $(La_{1-x}Sr_x)_8Cu_8O_{20-δ}$ ($0.16 \leq x \leq 0.24$) (19) but also of $La_2Sr_6Cu_8O_{17.6}$ (24) and $La_2Sr_6Cu_8O_{16}$ (26), and all these compounds assume the same space group, $P4/mbm$. However, $La_2Sr_6Cu_8O_{17.6}$ lacks O(1) completely and $La_2Sr_6Cu_8O_{16}$ lacks both O(1) and O(2) in their crystal structures. When we performed the Rietveld refinement adopting the models of $La_2Sr_6Cu_8O_{17.6}$ and $La_2Sr_6Cu_8O_{16}$, R factors were about 3% larger.

Figure 2 shows a perspective of $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ ($RE = Pr, Nd$) projected along the c axis. The $Cu-O$ polyhedra and squares are shown with solid lines. The RE and Sr cations are omitted. The structure is derived from the perovskite structure, ABO_3 , the A site for large cations being occupied by the rare earth and strontium atoms

statistically, and the B site for small cations occupied by the copper atoms. One-sixth of the oxygen atoms are deficient, and the oxygen vacancies are ordered. The Cu(1), O(1), and O(5) atoms form CuO_6 octahedra, each sharing the corner oxygen atoms O(5) with four CuO_5 square pyramids built up from the Cu(3), O(3), O(4), and O(5) atoms. The CuO_5 pyramids share the apical oxygen atoms O(4) with the CuO_4 squares made up of the Cu(2), O(4), and O(2) atoms. All the polyhedra and the squares share their oxygen atoms along the c axis. Consequently, buckling CuO_2 sheets parallel to the (110) plane are formed from the CuO_6 octahedra and CuO_5 square pyramids.

Table 3 shows the selected interatomic distances and bond angles for the present compounds, together with those of $(La_{0.8}Sr_{0.2})_8Cu_8O_{19.84}$ (19). In all these compounds the CuO_6 octahedra are compressed along the c axis and the CuO_5 pyramids have a long Cu–O(4) distance. The average distances between the A site and oxygen atoms for $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ and $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$ are nearly equal to the La compound even though the smaller

RE^{3+} cations are contained. This is because the contents of large Sr^{2+} ions in the A site ($x = 0.35$ and 0.40) are greater than that for the La compound ($x = 0.2$). We believe that the average A site cation size is crucial to the formation of the $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ structure.

In general, a smaller cell volume is favorable for the formation of compounds under high-pressure. This tendency has already been shown for the high-pressure synthesis of RE_2CuO_4 and $RENiO_3$. RE_2CuO_4 , having Nd_2CuO_4 type structure, was prepared with $RE = Pr, Nd, Sm, Eu$, and Gd (1, 44, 45) and with combinations of La and other rare earths (Ce, Nd, Sm, Eu, and Gd) under atmospheric pressure (46, 47). Isostructural compounds were obtained with smaller RE^{3+} ions of $RE = Dy, Ho, Y, Er$, and Tm under a high pressure of 6 GPa (48). $RENiO_3$, possessing perovskite structure, was obtained with only $RE = La$ under atmospheric pressure (49). But when the oxygen pressure was raised up to $P_{O_2} = 15\text{--}20$ MPa, $RENiO_3$ was stabilized for $RE = La, Pr, Nd$, and Sm (50). Furthermore, under a higher pressure of 6 GPa, this structure is formed with $RE = La\text{--}Lu$ and Y (51). This volume effect was observed in the present compounds; the cell volumes of $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ ($RE = Pr, Nd$) synthesized under $P_{O_2} = 20$ MPa were 2–3% smaller than that of $(La_{0.8}Sr_{0.2})_8Cu_8O_{19.84}$ (19) prepared under atmospheric pressure. How-

TABLE 1
Final Atomic Parameters for $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$

Tetragonal, space group $P4/mbm$ (No. 127)
 $a = 1.07997(4)$ nm; $c = 0.38048(2)$ nm,
 $V = 0.44377$ nm³, $Z = 1$

Atom	Wyckoff symbol	x/a	y/b	z/c
Pr/Sr ^a	8j	0.2626(4)	0.4669(4)	0.5
Cu(1)	2a	0.0	0.0	0.0
Cu(2)	2d	0.5	0.0	0.0
Cu(3)	4g	0.2187(8)	0.7187(8)	0.0
O(1)	2b	0.0	0.0	0.5
O(2)	2c	0.5	0.0	0.5
O(3)	4h	0.209(4)	0.709(4)	0.5
O(4)	4g	0.380(4)	0.880(4)	0.0
O(5)	8i	0.157(3)	0.098(4)	0.0
$R_{WP} = 7.94\%$				
$R_P = 6.11\%$				
$R_c = 6.58\%$				
$R_I = 2.77\%$				
$R_F = 2.49\%$				
$S = 1.207$				

^a Site occupancy: Pr/Sr = 0.65/0.35.

Note. Overall isotropic temperature factor: 0.25(12).

TABLE 2
Final Atomic Parameters for $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$

Tetragonal, space group $P4/mbm$ (No. 127)
 $a = 1.07961(5)$ nm; $c = 0.37841(2)$ nm,
 $V = 0.44106$ nm³, $Z = 1$

Atom	Wyckoff symbol	x/a	y/b	z/c
Nd/Sr ^a	8j	0.2627(5)	0.4666(4)	0.5
Cu(1)	2a	0.0	0.0	0.0
Cu(2)	2d	0.5	0.0	0.0
Cu(3)	4g	0.220(1)	0.720(1)	0.0
O(1)	2b	0.0	0.0	0.5
O(2)	2c	0.5	0.0	0.5
O(3)	4h	0.212(4)	0.712(4)	0.5
O(4)	4g	0.378(4)	0.878(4)	0.0
O(5)	8i	0.160(4)	0.094(4)	0.0
$R_{WP} = 8.69\%$				
$R_P = 6.75\%$				
$R_c = 6.91\%$				
$R_I = 2.98\%$				
$R_F = 2.89\%$				
$S = 1.258$				

^a Site occupancy: Nd/Sr = 0.60/0.40.

Note. Overall isotropic temperature factor: 0.11(15).

ever, in the present case, the high oxygen pressure also plays a role in preventing the oxygen deficiency from the stoichiometric $(RE_{1-x}Sr_x)_8Cu_8O_{20}$.

The La compound $(La_{1-x}Sr_x)_8Cu_8O_{20-\delta}$ was prepared in the range of x from 0.16 to 0.24 in air. The oxygen deficiency

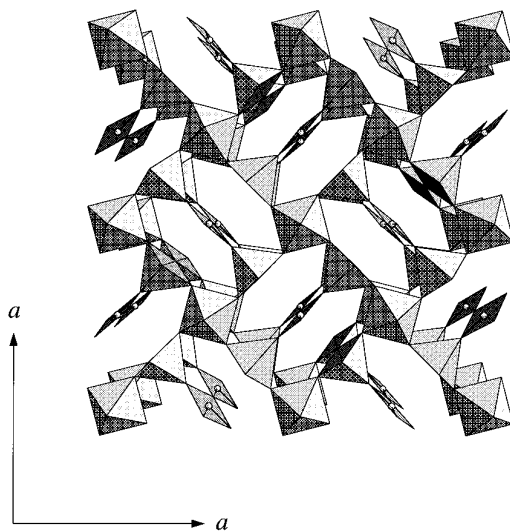


FIG. 2. Perspective of the Cu–O polyhedra and squares of $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ ($RE = Pr$ and Nd) structure.

TABLE 3
Selected Interatomic Distances (nm) and Bond Angles ($^\circ$)

	$(La_{0.8}Sr_{0.2})_8Cu_8O_{19.84}$ (19)	$(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$	$(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$	
$RE/Sr-O(1)$	0.2602	0.2589(4)	0.2587(6)	$\times 1$
$-O(2)$	0.2862	0.2858(4)	0.2854(5)	$\times 1$
$-O(3)$	0.2730	0.281(4)	0.271(3)	$\times 1$
	0.2747	0.267(3)	0.276(4)	$\times 1$
$-O(4)$	0.2645	0.2622(9)	0.261(1)	$\times 2$
$-O(5)$	0.2511	0.252(2)	0.248(2)	$\times 2$
	0.2848	0.277(3)	0.280(3)	$\times 2$
av. $RE/Sr-O$	0.2695	0.2675	0.2669	
$Cu(1)-O(1)$	0.1932	0.19024(1)	0.18920(1)	$\times 2$
$-O(5)$	0.2038	0.200(4)	0.200(5)	$\times 4$
$Cu(2)-O(2)$	0.1932	0.19024(1)	0.18921(1)	$\times 2$
$-O(4)$	0.1906	0.183(6)	0.186(6)	$\times 2$
$Cu(3)-O(3)$	0.1932	0.1909(5)	0.1896(3)	$\times 2$
$-O(4)$	0.2395	0.246(6)	0.242(6)	$\times 1$
$-O(5)$	0.1860	0.187(4)	0.188(5)	$\times 2$
$Cu(1)-O(5)-Cu(3)$	164.62	167.6(2.1)	164.3(2.2)	
$O(3)-Cu(3)-O(3)$	177.54	178.4(2.2)	177.6(2.3)	
$O(5)-Cu(3)-O(5)$	177.78	170.7(3.4)	173.1(3.5)	

δ increases from 0.08 to 0.32 with increasing x , keeping the copper valence around +2.15. When we use smaller RE^{3+} ions to prepare the $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ structure, Sr^{2+} substitution (x) should be carried out greater to keep the adequate average A site cation size. However, oxygen deficiency should also be larger with increase in x , so the structure could not be built. The reason for $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ formation in this study is probably that the defects were filled with oxygen atoms by a high oxygen pressure method. As a result, a high degree of Sr^{2+} substitution for RE^{3+} ($x = 0.35$ in $RE = Pr$ and $x = 0.40$ in $RE = Nd$) was achieved without oxygen deficiency; the Cu valence rose to +2.35–2.36. In the present study, $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ was not prepared for $RE = Sm, Eu,$ and Gd . It should be possible to synthesize $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ with these smaller RE cations at a larger x and under a higher oxygen pressure.

Figure 3 shows the resistivity of $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ and $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$ against temperature, together with that of $(La_{0.8}Sr_{0.2})_8Cu_8O_{19.84}$ (52). At room temperature (300 K) resistivity ($\rho_{R.T.}$) was 3.4 m Ω cm for $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$, while it decreased with decreasing temperature down to 13 K, but with a remarkable change in slope around 45 K. Resistivity above 45 K varied as $\rho = \rho_0(1 + \gamma T)$, while the parameters obtained by the least-squares method changed as $\gamma = 8.82 \times 10^{-3} K^{-1}$ and $\rho_0 = 0.93$ m Ω cm for 300–140 K and $\gamma = 6.23 \times 10^{-3} K^{-1}$ and $\rho_0 = 1.12$ m Ω cm for 140–45 K. The former γ values and $\rho_{R.T.}$ are similar to those ($\rho_{R.T.} \approx 3.0$ m Ω cm and $\gamma \approx$

$8.0 \times 10^{-3} K^{-1}$ for 300–5 K) of $LaCuO_{3-\delta}$ ($\delta = 0.33$, monoclinic) (43) possessing perovskite structure with oxygen vacancies ordered. $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ and $LaCuO_{3-\delta}$ ($\delta = 0.33$) have similar Cu formal valences of +2.34 and

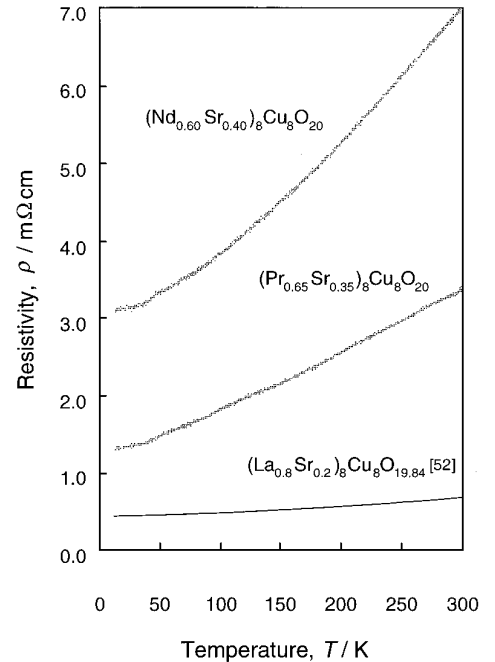


FIG. 3. Temperature dependence of electrical resistivity of $(RE_{1-x}Sr_x)_8Cu_8O_{20}$ ($RE = La$ (52), Pr , and Nd).

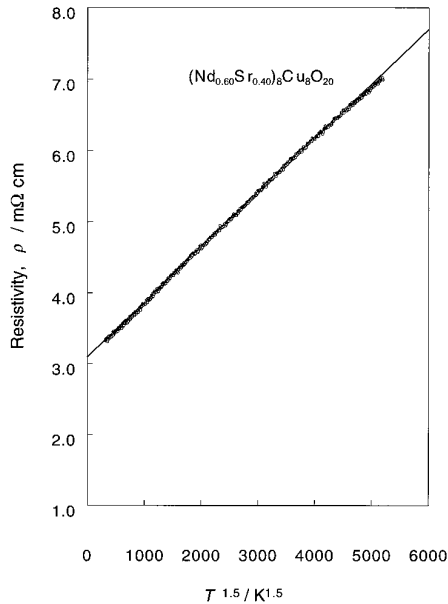


FIG. 4. Resistivity vs $T^{1.5}$ for $(\text{Nd}_{0.60}\text{Sr}_{0.40})_8\text{Cu}_8\text{O}_{20}$ from 47 to 300 K. The solid line is the best fit to $\rho = A + BT^{1.5}$; $A = 3.093 \text{ m}\Omega \text{ cm}$, $B = 7.669 \times 10^{-4} \text{ m}\Omega \text{ cm}/\text{K}^{1.5}$.

+2.36 but differ in the degree of oxygen deficiency and in the arrangement of oxygen vacancies. At temperatures lower than 45 K, the profile deviates from the linearity. This deviation may be due to the influence of defects and impurities on the electron transport properties.

Resistivity of $(\text{Nd}_{0.60}\text{Sr}_{0.40})_8\text{Cu}_8\text{O}_{20}$ was $7 \text{ m}\Omega \text{ cm}$ at room temperature (300 K) and decreased with decreasing temperature. We obtained the parameters $\gamma = 9.50 \times 10^{-3} \text{ K}^{-1}$ and $\rho_0 = 0.93 \text{ m}\Omega \text{ cm}$ for 300–180 K, below which a deviation from linear behavior occurred. Below 47 K, the ρ – T profile tends to be gentle, as observed in $(\text{Pr}_{0.65}\text{Sr}_{0.35})_8\text{Cu}_8\text{O}_{20}$.

It is interesting to notice that the resistivity of $\text{LaNiO}_{3.2}$ (53) varies as $\rho = A + BT^{1.5}$ from 300 to 100 K and as $\rho = A + BT^2$ below 80 K. Blasco *et al.* reported that $\text{La}_{1-x}\text{Nd}_x\text{NiO}_3$ ($x = 0.1$) (54) showed T -linear behavior above 120 K, but followed the $T^{1.5}$ law below 120 K. Xu *et al.* (53) and Blasco *et al.* (54) implied that the $T^{1.5}$ is intermediate between the T -linear dependence due to electron–phonon scattering and the T^2 dependence due to electron–electron interactions. The resistivity data of $(\text{Nd}_{0.60}\text{Sr}_{0.40})_8\text{Cu}_8\text{O}_{20}$ in this study can be fitted to $\rho = A + BT^{1.5}$ with the parameters $A = 3.092 \text{ m}\Omega \text{ cm}$ and $B = 7.669 \times 10^{-4} \text{ m}\Omega \text{ cm}/\text{K}^{1.5}$ ($R = 0.99972$; R is the coefficient of correlation) in a wide temperature range 300–47 K as shown in Fig. 4.

The magnetic susceptibility (χ) and the inverse susceptibility ($1/\chi$) of $(\text{Pr}_{0.65}\text{Sr}_{0.35})_8\text{Cu}_8\text{O}_{20}$ and $(\text{Nd}_{0.60}\text{Sr}_{0.40})_8\text{Cu}_8\text{O}_{20}$ are plotted as a function of temperature in Fig.

5. The data of $(\text{Pr}_{0.65}\text{Sr}_{0.35})_8\text{Cu}_8\text{O}_{20}$ were fitted with the Curie–Weiss equation, $\chi = C/(T + T_c) + \chi_0$, where C and T_c are the Weiss constant and Curie temperature, respectively. A least-squares fit yields $C = 4.85 \times 10^{-3} \text{ emu K/g}$, $T_c = 56 \text{ K}$, and $\chi_0 = 8.64 \times 10^{-5} \text{ emu/g}$ over the measured temperature range. The magnetic moment per Pr estimated from the Curie constant is $3.83 \mu_B$. This value is close to that ($3.80 \mu_B$) observed in PrNiO_3 below 130 K where the metal–insulator transition occurred (53). The theoretical magnetic moments expected for free ions Pr^{3+} and Pr^{4+} are 3.58 and $2.54 \mu_B$, respectively.

The magnetic susceptibility (χ) of $(\text{Nd}_{0.60}\text{Sr}_{0.40})_8\text{Cu}_8\text{O}_{20}$ can be fitted with the Curie–Weiss law, $\chi = C/(T + T_c) + \chi_0$, only for 100–70 K. Below 70 K the curve bends toward the temperature axis. Similar phenomena reported for NdNiO_3 (55) and Nd_2O_3 (56) were explained to be due to depopulation of the upper crystal field levels at lower temperatures. The Curie–Weiss behavior for 100–70 K gives us $C = 3.90 \times 10^{-3} \text{ emu K/g}$, $T_c = 34 \text{ K}$, and $\chi_0 = 1.15 \times 10^{-4} \text{ emu/g}$. The magnetic moment per Nd estimated from the above fit is $3.63 \mu_B$, which is comparable with that ($3.61 \mu_B$) of NdNiO_3 (55) and agrees well with the theoretical value of $3.62 \mu_B$ expected for a free Nd^{3+} ion.

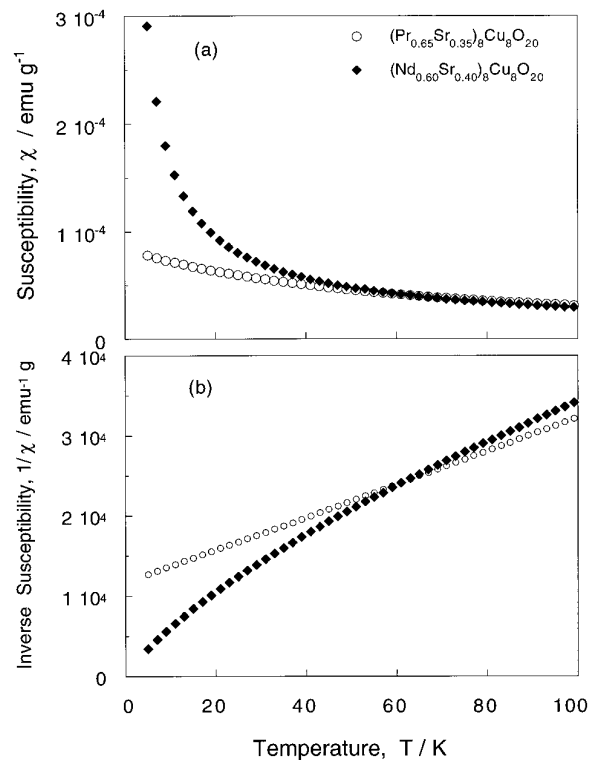


FIG. 5. Magnetic susceptibility vs temperature (a) and inverse magnetic susceptibility vs temperature (b).

4. SUMMARY

The new compounds $(Pr_{0.65}Sr_{0.35})_8Cu_8O_{20}$ and $(Nd_{0.60}Sr_{0.40})_8Cu_8O_{20}$ have been synthesized in the same structure as $(La_{1-x}Sr_x)_8Cu_8O_{20-\delta}$ with the use of high oxygen pressure ($P_{O_2} = 20$ MPa) at 1273 K. The copper formal valences of the compounds were estimated to be +2.35 and +2.36, which are larger than that (+2.16) of $(La_{0.8}Sr_{0.2})_8Cu_8O_{19.84}$. This may be due to the high oxygen pressure during the synthesis. The present compounds are metallic. The temperature dependence of susceptibility is paramagnetic for both compounds, mainly reflecting the free ionic behavior of Pr^{3+} and Nd^{3+} ions.

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