Synthesis and Crystal Structure of $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$

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A new compound, $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$, has been prepared and its crystal structure has been determined by the Rietveld method using a combination of neutron and X-ray powder diffraction data. The compound has hexagonal symmetry, $P\bar{6}2m$ (No. 189), with lattice parameters $a = 10.18494(5)$ Å and $c = 3.62891(3)$ Å. The coexistence of tetra- and trivalent rare-earth ions appears to be prerequisite for the formation of the compound. Three distinct crystallographic sites are occupied by the Ce, Nd, and Sr atoms. The Ce atoms prefer the octahedral sites, whereas the Sr atoms are located at sites with seven and nine oxygen neighbors. The Nd atoms occupy all three sites. The formal oxidation state of Cu atoms is found to be $+1.47$, resulting in a statistical coordination with either two or four oxygen atoms according to the valence state of copper ions, namely Cu^{1+} and Cu^{2+}. In either coordination, highly distorted environments around the Cu atoms are found. In contrast to the related compound, $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$, the proposed structure of the title compound shows no evidence of a one-dimensional Cu−O chain along the *c*-axis.

Introduction

Extensive studies have been carried out to explore the crystal chemistry and electronic/magnetic properties of compounds in the rare-earth (RE), alkali-earth (AE), copper, and oxygen, i.e., RE−AE−Cu−O systems.[1−3] Amamoto et al.[4] reported the phase compatibilities of the Pr−Sr−Cu−O system at 1080 °C under 1 atm of O_2 and discovered a new phase, $Pr_8Sr_7Cu_2O_z$. Amamoto et al.[5] subsequently examined this compound in detail and established the formation of a solid solution with the formula $Pr_{4+x}Sr_{4-x}CuO_z$ ($-0.10 \leq x \leq 0.80$). The X-ray powder diffraction pattern of the phase was indexed to a hexagonal structure of $a \sim 10.16$ Å and $c \sim 3.62$ Å, but the detailed crystal structure was not determined. The mixed state of the tetra- and trivalent rare-earth ion is believed to be necessary for the formation of the phase, since no relevant phase has been reported for the other RE^{3+}−Sr−Cu−O systems.[2,3] Such a mixed valence of cations often causes carrier doping into the Cu/O networks and might realize new electric and magnetic phenomena. It is thus necessary to investigate which valence states the cations have and which networks the Cu and O atoms construct. It appears, however, difficult to distinguish the precise valence states of Pr ions and their site occupancies in the compound. We have attempted to prepare the corresponding Nd and Ce compounds, with the two lanthanide ions being recognizable by neutron diffraction, instead of tri- and tetravalent Pr ions. The title compound in the Nd−Ce−Sr−Cu−O system, $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$, has thus been obtained. In this paper, we report the results of the structure determination of the phase using combined Rietveld refinement of both time-of-flight neutron and X-ray powder diffraction data. The structure is closely related to that of previously reported compounds $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$,[6,7] but the arrangements of Cu and O atoms are different.

Experimental Section

Powders of Nd_2O_3, CeO_2, $SrCO_3$, and CuO with purity higher than 99.9% were used as starting materials. Nd_2O_3 and CeO_2 powders were heated at 1000 °C for 12 h in an oxygen stream before weighing. These powders were intimately mixed and pelletized and subsequently heated at 1000 °C for 8 h under flowing oxygen. The pellet was then heated at 1100 °C for 96 h under flowing oxygen with intermediate grindings. The sample was furnace cooled to room temperature. X-ray powder diffraction (XRD) data were collected using a Siemens D5000 diffractometer in transmission mode. The oxygen content of the samples was measured from the mass reduction using

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(7) Babu, T. G. N.; Greaves, C. *J. Solid State Chem.* **1991**, *95*, 417.

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thermogravimetric analysis (TGA) in a flowing $N_2-10\%\ H_2$ atmosphere.

Neutron powder diffraction data ($0.39 \le d \le 3.1$ Å) were collected at room temperature on a time-of-flight (TOF) diffractometer, POLARIS, installed at the ISIS facility, Rutherford Appleton Laboratory. XRD data were collected at room temperature in the angular range 20−90° with a 2θ step of 0.020°. The absorption correction of the observed intensities was made using the equation of Alexander.[8] Rietveld analysis was carried out for the neutron and X-ray diffraction data simultaneously using the GSAS program.[9] Neutron scattering lengths used for the refinement were $b_{Nd} = 0.769$ pm, $b_{Ce} = 0.484$ pm, $b_{Sr} = 0.702$ pm, $b_{Cu} = 0.772$ pm, and $b_O = 0.581$ pm, respectively. Interatomic distances and angles were computed using the program ORFFE.[10] Parts of crystal structure were drawn using the program ORTEP.[11]

Results and Discussion

Several compositions having the formula $(Nd_{1-y}Ce_y)_{4+x}Sr_{4-x}CuO_z$ ($-1.00 \le x \le 1.00$ and $0.30 \le y \le 0.80$, with a step of 0.10 but of 0.01 in the vicinity of the single-phase composition) were examined, and the single-phase sample was prepared only at $x = 0.13$ and $y = 0.62$. The color of the single-phase sample was ocher. The phases obtained after TGA measurement were confirmed to be Sr_2CeO_4, $(Nd, Ce)_2O_3$, and metallic Cu by XRD. The oxygen content of the sample, z, determined from the weight change of three TGA runs was 12.08(3), where the number in parentheses represents the standard deviation in the last digit. Thus, the composition of the single-phase sample is represented as $(Nd_{0.38}Ce_{0.62})_{4.13}Sr_{3.87}CuO_{12.08(3)}$ and the formula gives the formal oxidation state of Cu as +1.47(6). The XRD pattern of the phase was indexed with a hexagonal structure, $a \sim 10.16$ Å and $c \sim 3.63$ Å, and no systematic absences were observed.

A search of the ICSD inorganic crystal structure database[12] using the cell parameters yielded the compound $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$. The crystal structure of the solid solution was determined first by Kim et al.[6] using single crystal XRD and then independently by Babu and Greaves[7] for samples with different stoichiometry using neutron powder diffraction. Although this phase does not contain any rare-earth elements, Pb could be present in either the tetra- or divalent state. The compound $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$ crystallizes as a hexagonal structure with space group $P\bar{6}2m$ (No. 189), $a \sim 10.1$ Å and $c \sim 3.5$ Å,[6,7] which has a structural similarity to Ca_2IrO_4.[13] In the $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$ structure, tetravalent Pb ions favor the octahedral Ir sites in the Ca_2IrO_4 structure. Sr atoms and the remaining Pb atom are reported to locate at two of the three possible Ca sites, except for the origin.

Structure refinement was carried out using the crystallographic data for the $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$ structure[6,7] as an initial model. A combined refinement using neutron and XRD data allows a clear distinction between Nd and Ce ions. In the first refinement, using no linear constraints, Ce atoms clearly preferred the octahedral site of 3f (x, 0, 0), and Sr atoms favored the other cation sites of 2d (1/3, 2/3, 1/2) and 3g (x, 0, 1/2). Occupation factors, g, of the Nd and Sr atoms were subsequently refined using linear constraints in accordance with their stoichiometry assuming that the Ce atom occupies only the 3f site: $g(Nd(1)) + g(Ce) = 1.0$, $g(Sr(1)) + g(Nd(2)) = 1.0$, $g(Sr(2)) + g(Nd(3)) = 1.0$, $3 \times g(Nd(1)) + 2 \times g(Nd(2)) + 3 \times g(Nd(3)) = 1.57$ and $2 \times g(Sr(1)) + 3 \times g(Sr(2)) = 3.87$.

The existence of a one-dimensional Cu−O chain was initially anticipated, as reported for $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$.[7] With the Cu atom placed at the 1b (0, 0, 1/2) site and its coordinated O atom, O(4), set at the origin, divergence occurred, and large isotropic thermal displacement parameters, U, were obtained for both atoms. The Cu atoms were then shifted to the 2e (0, 0, z) site with half-occupancy, and a statistical arrangement of O(1) and O(4) atoms around Cu atoms was assumed by taking into account the valence state of Cu ions; Cu^{1+} and Cu^{2+} ions should coordinate to two and four (or more) oxygen atoms, respectively. Since the placement of O(4) atom at either 2e (0, 0, z) or 6i (x, 0, z) site still gave high R factors as well as a high U parameter for O(4), the O(4) atom was finally placed at the 6j (x, y, 0) site. In the final refinement, anisotropic thermal parameters were introduced. Owing to high correlation between the g and U parameters, the g parameters of partially occupied atoms, O(1) and O(4), were then fixed at 2/3 and 1/6, respectively. For the O(4) atom, with low g parameter, an isotropic thermal parameter, B_{iso}, was adopted. Finally, the refinement converged with a low χ^2 (~2.9), and all parameters refined to reasonable values. The refined atomic parameters are summarized in Table 1. Observed, calculated, and difference powder diffraction patterns of neutron and X-ray data are shown in Figure 1 and 2, respectively. Final R factors were $R_{WP} = 1.84\%$ and $R_P = 4.22\%$ for neutron diffraction data, and $R_{WP} = 7.81\%$ and $R_P = 4.77\%$ for XRD data. The goodness-of-fit indicator, S, for the overall patterns was 1.69. The refined lattice parameters were $a = 10.18494(5)$ Å and $c = 3.62891$ (3) Å ($Z = 1$).

In Figure 3 a and b we present an ORTEP drawing and an overall network of polyhedra of $(Nd_{0.38}Ce_{0.62})_{4.13}Sr_{3.87}CuO_{12.08}$, as projected along the c-axis. The refined positions of Cu and O(4) atoms are neglected in Figure 3a for clarity but are shown in Figure 3b. The linking of each polyhedron is illustrated in Figure 4 a−c. No significant deviation is observed for the positional parameters of metallic atoms from those reported earlier for $Pb_{3+x}Sr_{5-x}Cu_yO_{12}$.[6,7] However, the site occupancy, anisotropic thermal displacement of each atom, and the arrangements of Cu and O atoms are different.

Ce and Nd(1) atoms are located at the 3f site with the occupancies of 0.86:0.14. These atoms coordinate to six oxygen neighbors, as shown in Figure 4a, to form edge-shared octahedra linking along c-axis. In Table 2 we present selected interatomic distances and angles. The bond distances of Ce/Nd(1) and three O atoms are 2.21−2.38 Å, which are in good agreement with that

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Table 1. Refined Atomic and Thermal Displacement (Å^2) Parameters for $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$[a]

atom	site	occupancy	x	y	z	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	B_{eq}
Ce	3f	0.857[b,c]	0.3325(1)	0	0	1.56(4)	0.53(5)	0.41(3)	0.27(2)	0.66(4)[d]
Nd(1)	3f	0.143[b,c]	0.3325	0	0	1.56	0.53	0.41	0.27	0.66
Sr(1)	2d	0.942(16)[c]	1/3	2/3	1/2	1.19(4)	U_{11}	0.93(6)	0.59(2)	0.87(5)
Nd(2)	2d	0.058[c]	1/3	2/3	1/2	1.19	U_{11}	0.93	0.59	0.87
Sr(2)	3g	0.660[c]	0.6913(1)	0	1/2	0.74(3)	0.62(3)	0.75(3)	0.31(2)	0.55(3)
Nd(3)	3g	0.340[c]	0.6913	0	1/2	0.74	0.62	0.75	0.31	0.55
Cu	2e	1/2	0	0	0.4048(7)	0.60(5)	U_{11}	3.86(17)	0.30(2)	1.33(9)
O(1)	3g	2/3[b]	0.1809(1)	0	1/2	0.97(4)	3.01(10)	0.94(8)	1.51(5)	1.29(7)
O(2)	3g	1	0.4597(1)	0	1/2	1.21(4)	2.96(6)	0.99(5)	1.48(3)	1.36(5)
O(3)	6j	1	0.2497(1)	0.4449(1)	0	1.34(3)	2.01(5)	1.28(3)	0.89(3)	1.22(3)
O(4)	6j	1/6[b]	0.1396(8)	0.1108(8)	0					2.8(4)[e]

[a] R_{WP} = 1.84%, R_P = 4.22% (neutron diffraction data) and R_{WP} = 7.81%, R_P = 4.77% (X-ray diffraction data). S = 1.69 (for overall diffraction data). Space group: $P\bar{6}2m$ (No. 189). a = 10.18494(5) Å and c = 3.62891(3) Å. Z = 1. [b] Fixed at these values. [c] Site occupancies are determined from the following constraints assuming that Ce atom occupies only the 3f site: $g(Nd(1)) + g(Ce) = 1.0$, $g(Sr(1)) + g(Nd(2)) = 1.0$, $g(Sr(2)) + g(Nd(3)) = 1.0$, $3 \times g(Nd(1)) + 2 \times g(Nd(2)) + 3 \times g(Nd(3)) = 1.57$ and $2 \times g(Sr(1)) + 3 \times g(Sr(2)) = 3.87$. [d] Anisotropic thermal factors are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12})]$. B_{eq} is defined by $8\pi^2/3\Sigma U_{ii}$. [e] Isotropic thermal displacement parameters, B_{iso}, are refined due to the low occupancy of the O(4) atom.

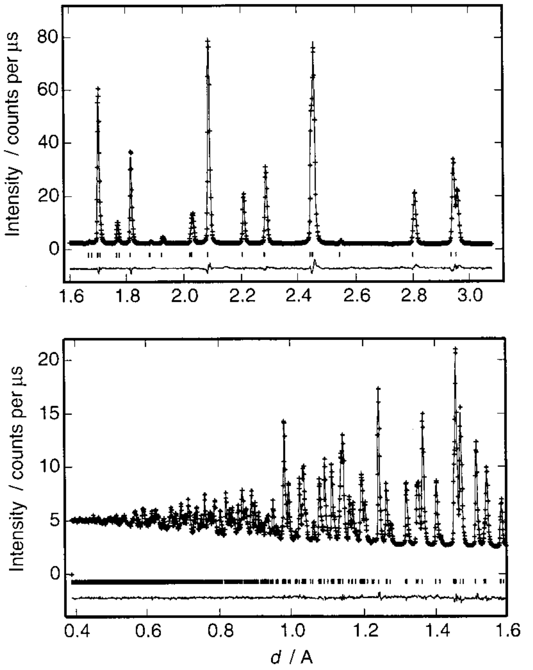

Figure 1. Observed (+), calculated, and difference time-of-flight neutron diffraction profiles for $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$; the reflection positions are marked by vertical lines.

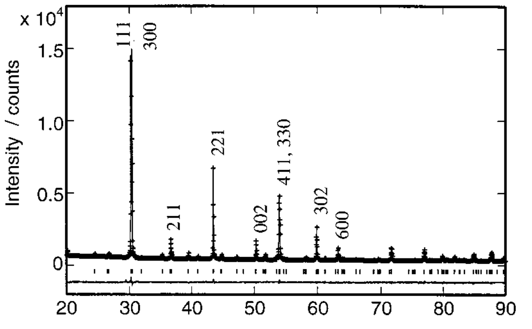

Figure 2. Observed (+), calculated, and difference XRD profiles for $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$.

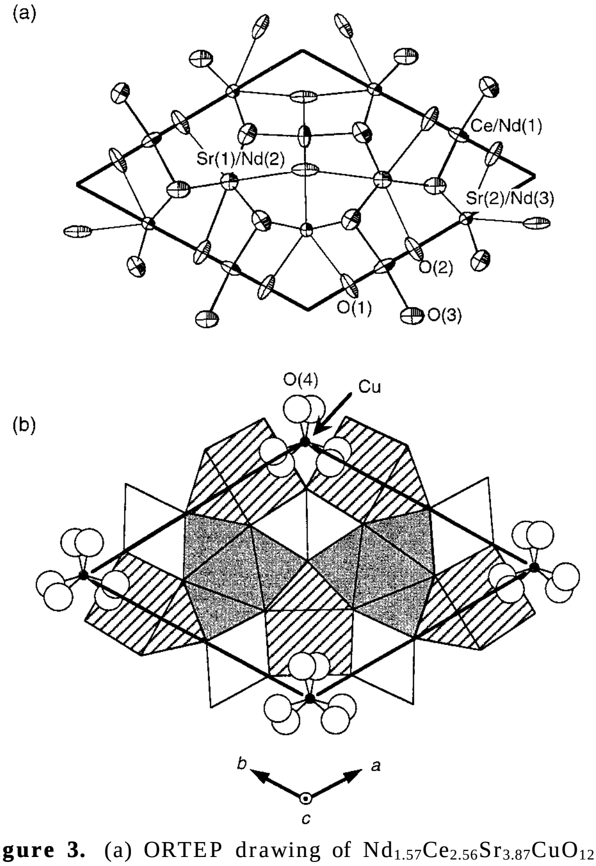

Figure 3. (a) ORTEP drawing of $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$ projected along the c-axis, except for the Cu and O(4) atoms. (b) Representation of polyhedra and refined positions of Cu and O(4) atoms.

calculated from the effective ionic radii[14] of Ce^{4+}, Nd^{3+}, and O^{2-}, 2.29 Å. Since one-third of O(1) atoms are statistically deficient, alternative bonding with Ce/Nd(1) and O(4) atoms should be considered. On this occasion, the Ce/Nd(1) atoms bond to O(4) atoms with a distance of 2.71 Å. The 2d site is occupied mainly by Sr(1) with a small amount of Nd(2) atoms (0.94:0.06). These atoms are coordinated to nine oxygen atoms, with distances of 2.99 Å to three O(2) atoms and 2.68 Å to six O(3) atoms; the former is rather longer than that estimated from the effective ionic radii, 2.73 Å. Since O(2) and O(3) atoms have full site occupancy, every polyhedron forms a perfect tricapped prism (shaded area in Figures 3b and 4b). The polyhedra link along the c-axis, sharing their triangular faces each other. The 3g site is occupied by Sr(2) and Nd(3) atoms with a ratio of 0.66:0.34. As shown in Figures 3b and 4c with hatched area, these atoms are surrounded by seven oxygen

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[14] Shannon, R. D. *Acta Cryst.* **1976**, *A32*, 751.

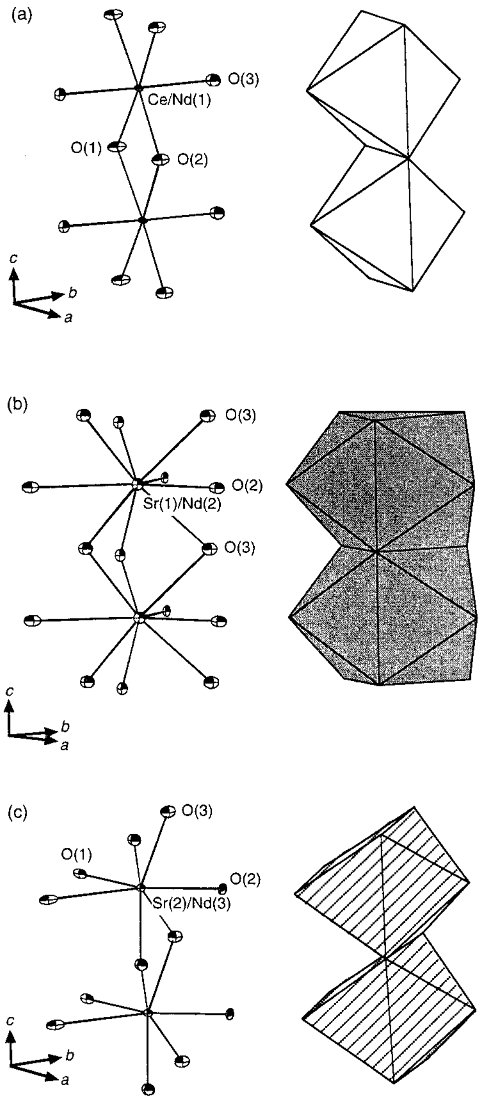

Figure 4. Linking of (a) $[Ce_{0.86}Nd_{0.14}]O_6$, (b) $[Sr_{0.94}Nd_{0.06}]O_9$, and (c) $[Sr_{0.66}Nd_{0.34}]O_7$ polyhedra of $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$; no deficiency of the O(1) atom is considered in each polyhedron.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$

Distance	
Nd(1)/Ce−O(1)	2 × 2.383(1)
Nd(1)/Ce−O(2)	2 × 2.230(1)
Nd(1)/Ce−O(3)	2 × 2.206(1)
Nd(1)/Ce−O(4)[a]	2.711(5)
Sr(1)/Nd(2)−O(2)	3 × 2.9686(2)
Sr(1)/Nd(2)−O(3)	6 × 2.683(1)
Sr(2)/Nd(3)−O(1)	2 × 2.7362(7)
Sr(2)/Nd(3)−O(2)	1 × 2.359(2)
Sr(2)/Nd(3)−O(3)	4 × 2.5317(8)
Sr(2)/Nd(3)−O(4)[a]	2.617(6)
Cu−O(1)	3 × 1.874(1)
Cu−O(4)	1.962(5), 2.521(5)
Angles	
O(1)−Cu−O(1)	3 × 116.7(1)
O(1)−Cu−O(4)	141.0(3), 85.9(2), 73.1(2)

[a] The bond should be taken into account when the O(1) atoms are deficient.

atoms to form a capped prism. Although the O(1) and O(3) atoms have reasonable bond lengths to Sr(2)/Nd(3) atoms, the "capped" O(2) atom has a considerably shorter distance of 2.36 Å. The thermal ellipsoid of the O(2) atom elongates perpendicularly to the bonding direction to release the contraction. These capped prisms link along the *c*-axis, sharing their edges with each other.

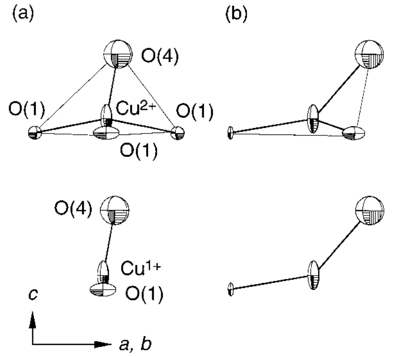

Figure 5. Proposed local arrangements of Cu^{2+}, Cu^{1+}, and O atoms for $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$ projected along (a) [100], and along (b) [120] on the basis of refined basic structure.

Figure 5 a and b show the proposed local arrangements of Cu^{2+}, Cu^{1+}, and O atoms projected along [100] and [120] on the basis of a refined basic structure. Since the amount of Cu^{1+} and Cu^{2+} ions is almost equal in the compound, an ordered arrangement of these ions along the *c*-axis might be expected. No superstructure is, however, observed in the XRD and neutron diffraction patterns; further studies, using HREM, are now underway. Therefore, these ions should be statistically distributed along the *c*-axis. Two oxygen atoms, O(1) and O(4), are bonded to monovalent Cu ions, while two additional O(1) atoms are bonded to divalent Cu ions. The bond distances of Cu−O(1) and Cu−O(4) are 1.87 and 1.96 Å, respectively, regardless to the valence state of Cu ions. The tetrahedron formed by Cu and O atoms is significantly distorted from an ideal one. The O−Cu−O angles are quite different from that observed in $CuCr_2O_4$[15] spinel, 103°. Highly anisotropic thermal ellipsoids of Cu and O(1) atom as well as a large B_{iso} parameter of the O(4) atom reflect structural inadequacies due to local coordination differences between Cu^{2+} and Cu^{1+}. Monovalent Cu ions should have a linear coordination in this compound, as seen in the $SrCu_2O_2$ structure.[16] Local deviations of Cu, O(1), and O(4) atoms should be considered in the actual structure according to the valence state of the Cu ions. Another Cu−O(4) distance is calculated to be 2.52 Å, which is an unacceptably long distance for either two- or four-coordination of O atoms to Cu atoms. Therefore, no long-range one-dimensional Cu−O chain exists in this compound. The compound was an electrical insulator with a resistivity of 10^7 Ω cm at room temperature. A magnetic susceptibility measurement using a SQUID magnetometer showed paramagnetic behavior, and no magnetic order was observed down to 4 K. These facts seem to support the proposed arrangements of Cu and O atoms.

Since Nd atoms are distributed over the three cation sites, the formula should be represented as $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$ rather than $(Nd_{0.38}Ce_{0.62})_{4.13}Sr_{3.87}CuO_{12.08}$. The following expression helps to understand the valence state of each cation site: $(M_1)_3^{3.86+}(M_2)_2^{2.07+}(M_3)_3^{2.34+}CuO_{12.08}$, where M_1, M_2, and M_3 are the virtual

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(15) Prince, E. *Acta Cryst.* **1957**, *10*, 554.

(16) Hoppe, R.; Röhrborn, H. J. *Z. Anorg. Allg. Chem.* **1964**, *329*, 110.

atoms which occupy the 3f, 2d, and 3g site, respectively. Attempts to synthesize the corresponding phase in the Ce−Sr−Cu−O system gave no phase formation. In this respect, the coexistence of tetra- and trivalent ions appears to be a prerequisite for the formation of this compound. This may be the reason the compound was first discovered in the Pr−Sr−Cu−O system.[4] With respect to the relevant phase, $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$, which does not contain any rare-earth elements, no trivalent ion is included. An essential difference between $Nd_{1.57}Ce_{2.56}Sr_{3.87}CuO_{12.08}$ and $Pb_{3+x}Sr_{5-x}Cu_yO_{12-d}$ can be expressed by the formal valence state of Cu ions. The latter consists mainly of divalent Cu ions and forms a one-dimensional Cu−O network along the *c*-axis.[7] In both compounds, the Ca atoms were able to substitute the Sr atoms up to ∼25%. Such substitution effects on the stereochemistry of Cu atoms, as well as on the electric and magnetic properties, are currently underway.

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