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Structural properties of the superconductor $LaBa_2Cu_{3-y}O_{7-z}$ in the solid solution system $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$

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We present time-of-flight (TOF) neutron-powder-diffraction results of four samples in the solid-solution orthorhombic $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ system. The data for all of the samples were taken at room temperature. The average crystal structures of $LaBa_2Cu_{2.90}O_{6.82}$ ($T_c=45$ K), $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (nonsuperconductor), and the impurity-free $LaBa_2Cu_3O_{6.85}$ ($T_c=93$ K) were refined by the Rietveld analysis which includes the refinement of the occupancies of the La and/or Ba atoms. The remaining sample was imhomogeneous $LaBa_2Cu_{3-y}O_{7-z}$ ($T_c=85$ K). The obtained structures are essentially isomorphous with the oxygen-deficient triperovskite structure (space group *Pmmm*). The refined results show that the subunit around the La at the 1*h* site is well ordered as is shown in the 90-K superconductor $YBa_2Cu_3O_7$. The valence-sum calculation indicates that Cu(1) and Cu(2) atoms are dominantly divalent in both the 45-K and 93-K superconductors, $LaBa_2Cu_{2.90}O_{6.82}$ and $LaBa_2Cu_3O_{6.85}$, while there exists trivalent copper at the Cu(1) site in nonsuperconducting $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$. The difference and resemblance between the crystal structures of 45-K and 93-K superconducting samples were also clarified based on the obtained microscopic crystal parameters with respect to the structure of the two-dimensional CuO_2 network, where the parameter of the degree of coplanarity was introduced. In the structure of the solid solution, it is also remarked that the excess La ion occupies the site of a Ba ion and most of the La ions have a larger ionic radius with twelve coordination numbers to oxygen atoms in contrast to eight coordination numbers of the La ion at the 1*h* site. It is shown to be quite significant to analyze the TOF powder-diffraction data for both material characterization and the study of the physical properties of superconducting oxides in these solid-solution systems.

I. INTRODUCTION

In the last few years, superconductivity above liquid nitrogen temperature has been mainly surveyed in a series of compounds with the oxygen-deficient triperovskite structure[1–4] whose unit cell is fundamentally composed of one subunit including a lanthanidelike ion with eightfold coordination to oxide ions and two subunits including a Ba ion with a tenfold coordinations to oxide ions.[1–4] The crystal symmetry of these systems is orthorhombic with space group *Pmmm*, and their chemical formula is represented by $RBa_2Cu_3O_{7-z}$, where R is one of rare-earth metals. They have characteristic lattice parameters in which $c/3$ is almost equal to that of the a or b axis. Among them, an oxide containing La has been shown to be an end member of the solid-solution family $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$.[5–10] Similar types of solid solutions have also been found in R-Ba-Cu-O (R=Nd, Sm, and Eu) systems.[11–13] In the $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ system, this solid solubility poses a serious problem on the real composition of the obtained crystal. The crystal does not always have the nominal composition of $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ or $La_1Ba_2Cu_{3-y}O_{7-z}$, since the La-Ba-Cu-O system easily forms different coexisting phases of the solid solution owing to the similarity in the ionic radii of La^{3+} and Ba^{2+}.[6–10] In solid solutions, superconducting properties are degraded with increasing x, and the existence of the end member, orthorhombic $La_1Ba_2Cu_{3-y}O_{7-z}$ in which La and Ba are ordered, has been doubted.[7,9] Therefore it is important to clarify the crystal structure together with precise occupancies of lanthanide and barium ions for the advancement in the study of superconductivity in these solid-solution systems. In the case of materials including La, Song *et al.*[14] have studied the structure of two samples of the composition $La_1Ba_2Cu_3O_{9-\mu}$ with the transition temperatures (T_c) 26 and 43 K. It was shown that the structure closely resembles that of $Y_1Ba_2Cu_3O_{7-z}$ and the crystal symmetry has been assigned as tetragonal. Any determination of site occupancies of atoms by profile analysis such as the Rietveld method was not performed in their study. The crystal structures of the solid solution $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$, where $0.5 \geq x \geq 0.1$ (tetragonal,[7,15] space group *P4/mmm*) and $0.5 \geq x \geq 0.25$ (orthorhombic,[9] space group *Pmmm*) have been determined by the Rietveld analysis of neutron-powder-diffraction data. Especially, Torardi *et al.*[15] extensively studied the structure of nonsuperconducting tetragonal $La_{1.5}Ba_{1.5}Cu_3O_{7.3}$. Its structure is closely related to that of the superconductors of the type $YBa_2Cu_3O_7$, but it is tetragonal with excess oxygen atoms which are densely populated on the basal plane at $z=0$. The previously obtained results on the crystallographic study in the system $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ are summarized as follows.

(1) La^{3+} ions preferentially substitute for Ba^{2+} ions at $2t$ ($2h$) in the space group *Pmmm* (*P*4/*mmm*); these sites are occupied by only Ba^{2+} ions with a larger ionic radius in other kinds of orthorhombic (tetragonal) oxygen-deficient triperovskites such as $YBa_2Cu_3O_{7-z}$.

(2) Since the La^{3+} atoms in the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ site prefers eight-fold coordinations as in the lanthanide subunit,[10] both the $1e$ and $1b$ sites are occupied by oxide ions due to the substitution of La^{3+} for Ba^{2+} in the case of the orthorhombic phase. This breaks the formation of the so-called one-dimensional (1D) (Cu-O) chain on the basal plane, and the length of the c axis becomes short because the length of the subunit including the Ba^{2+} ion along the c axis becomes short due to the increase in negative charge on the basal plane. (Refs. 7 and 8). Concerning the role of excess oxygen in the basal plane, Tsurumi *et al.*[16] have shown that $Nd_{1.5}Ba_{1.5}Cu_3O_{7-z}$, isomorphous with $La_{1.5}Ba_{1.5}Cu_3O_{7-z}$, exhibits superconductivity at 5 K after the annealing under oxygen at 49 atm ($z \approx -0.22$). This finding eliminates the possibility that the ordering of the 1D (Cu-O) chain is essential for the appearance of the superconductivity in the oxygen-deficient triperovskite structure.

(3) Associated with both (1) and (2), the occupancies of the oxygen atoms at the O(3) site ($2q$) just above and below the Cu ion at (0,0,0) become slightly deficient.[8–10] In the orthorhombic samples of $YBa_2Cu_3O_{7-z}$, no such effect can be seen.[9]

These microscopic variations of the structure lead to the fact that the a/b ratio of the lengths of the lattice constants approaches 1 even if the symmetry is orthorhombic and that the $7-z$ value exceeds 7.0 (Refs. 6, 7, and 15). This provides us with some interesting problems which may lead us to solve a mechanism of high-T_c superconductivity because the deficiency at site O(3) and/or the degree of ordering of the 1D (Cu-O) chain can be controlled by substituting La^{3+} for Ba^{2+}. As described above, the site O(3) may be somewhat deficient in the La-rich compounds. Such deficiency at site O(3) is considered to play an important role in superconductivity because it is located between the 1D (Cu-O) chain and the 2D CuO_2 layer at $z \approx 0.35$. It is now understood that the carriers contributing to superconductivity are holes that occupy the $2p_{x,y}$ and/or $2p_z$ orbits which originate from the 2D CuO_2 layer and the O(3) oxygen atoms at the $2q$ site.[17] Takayama-Muromachi *et al.*[18] and subsequently Bianconi *et al.*[19] have proposed that the charge carriers are doped mainly in the oxygen $2p$ orbitals of the O(3) atom. In spite of the importance of excess La, no one has ever reported the determination of the occupancies of Ba and/or La by Rietveld refinement[20] on the neutron-diffraction data in the previous studies, where only the nominal compositions have been used. In this respect, neutron diffraction is the only powerful tool to refine accurately structural parameters such as the occupancies of La, Ba, and oxygen. The difference in coherent scattering length (CSL) between La (8.24 fm) and Ba (5.25 fm) is enough to obtain reliable information of the Ba and La ions on the same or different cation sites. In contrast, the analysis of the x-ray powder-diffraction data cannot be applied to the determination of the occupancies of La, Ba, and O atoms, since the atomic numbers of La and Ba are very close and that of oxygen is small. The remaining CSL's were 7.718 fm for Cu and 5.805 fm for O.

On the study of preparation and properties of the 90-K superconductor $LaBa_2Cu_3O_{7-z}$, Maeda *et al.*[21] have reported the existence of a 90-K superconductor, orthorhombic $LaBa_2Cu_3O_{7-z}$ in nominal composition for the first time. Subsequently, transport, magnetic, and x-ray studies have been performed on the material.[22,23] Later, Yoshizaki *et al.* reported similar results,[24] where $LaBa_2Cu_3O_{7-z}$ with a large a/b ratio was obtained with the nominal composition. Recently, Wada *et al.*[25] have synthesized samples of $LaBa_2Cu_3O_{7-z}$ in nominal composition which exhibited the superconducting transition with the onset temperatures at 93 K and zero resistance at 92 K. These temperatures are the highest among La oxides which have ever been reported and even higher than those of $YBa_2Cu_3O_{7-z}$. The magnetic susceptibility measurement has also shown that it has superconducting transition with onset in the vicinity of 93 K.[25,26] In a previous study, we have refined the crystal structure of the La compound by x-ray Rietveld analysis[27] on the basis of the orthorhombic cell under the assumption that the chemical formula is $La_1Ba_2Cu_{3.0}O_{6.7}$.[28] It was shown that the structure is isomorphous with oxygen-deficient triperovskite such as $YBa_2Cu_3O_{7-z}$ (space group *Pmmm*). The obtained lattice parameters were $a=3.8973(2)$, $b=3.9337(2)$, and $c=11.7911(8)$ Å, where a small fraction of $BaCuO_2$ was excluded from the Rietveld analysis. Subsequently, we have performed the Rietveld analysis of time-of-flight (TOF) neutron-powder-diffraction data and have briefly reported on the existence of the end-member $LaBa_2Cu_{3-y}O_{7-z}$ as an orthorhombic superconductor.[29]

In this paper the detailed results of the Rietveld analysis of TOF neutron-powder-diffraction data are given on four samples (Nos. 1–4) which have been synthesized from the mixture of powders as $La_1Ba_2Cu_3O_{7-z}$ in nominal composition. Three of the samples are bulk superconductors with the onset temperatures 45 (No. 1), 85 (No. 3), and 93 K (No. 4), and the remaining is a nonsuperconductor (No. 2). In contrast to the previous Rietveld analysis, the refinement of the occupancies of La and Ba ions was effectively carried out for the first time. We attempt to clarify not only the existence of the orthorhombic $La_1Ba_2Cu_{3-y}O_{7-z}$, i.e., the end member of the solid-solution system, but also the correlation between physical properties and microscopic crystal parameters in addition to the precise composition of the solid-solution system. Electrical and magnetic properties of each sample are also described. Interatomic distances, bond valence sums on the refined crystal parameters, are discussed to understand the fruitful physical properties of the present samples. In the discussion, a parameter of the degree of the coplanarity of the 2D CuO_2 plane is introduced to obtain a clue to explain the difference of T_c in the samples of 45- and 93-K superconductors. We also discuss the effect of an excess La ion on the atomic coordination in the solid-solution system.

II. EXPERIMENTS

The polycrystalline samples were prepared by heating a 4:1:6 mixture of $BaCO_3$, La_2O_3, and CuO, as has been reported by Maeda *et al.*[26] For the sample Nos. 1–3 the mixed powders were calcined in air at around 1000 °C, pressed into pellets, and sintered in O_2 gas at 1050 °C for 10 h. Sintered pellets were annealed in O_2 at 300 °C for 20 h. Sample No. 4 was prepared by sintering at 970 °C in N_2 gas[25] and post-annealed in an atmosphere of dried O_2. Preheat treatment of La_2O_3 was performed prior to the above procedures to remove water in the synthetic processes for sample Nos. 1 and 4.[26]

The reason to make pellets is to carry out the neutron diffraction and electrical transport on identical samples. In the pellet form, generally, the above-mentioned sintering and annealing processes are not as effective as for the powder form itself. In the preparation of sample No. 4, the process of the formation of the pressed pellet has not been done to encourage homogeneity and only a magnetization study was done. The oxygen content of each sample was determined by an iodometric titration technique.[30] The physical properties of the presently used samples are listed in Table I. The temperature dependence of the dc magnetic susceptibility for sample Nos. 1–3 can be found in Fig. 3 of Ref. 26 (sample Nos. 1, 2, and 3). The dc magnetic susceptibility as a function of temperature for sample No. 4 is shown in Fig. 1. All of the data were taken with decreasing temperature from the normal state for the magnetic field of 10 Oe. Sample No. 1 shows a relatively sharp bulk-superconducting transition with a T_c of 45 K.[26] On the other hand, sample Nos. 3 and 4 showed relatively high T_c's at 80 (Ref. 26) and 93 K, respectively. However, their transitions are broad and the volume fraction of the superconducting phase at the low-temperature limit is the smallest in sample No. 3. These results indicate that sample No. 1 is structurally more homogeneous than sample Nos. 3 and 4. As shown in Fig. 3 of Ref. 26 sample No. 2 does not show superconducting transition down to the lowest temperature.

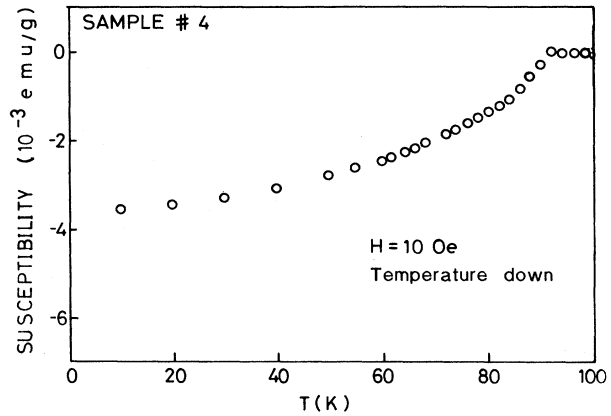

FIG. 1. Magnetic susceptibility as a function of temperature of $LaBa_2Cu_3O_{6.85}$.

TOF neutron-diffraction data were taken on a high-resolution neutron powder diffractometer (HRP) at the KENS pulsed spallation neutron source at the National Laboratory for High Energy Physics (KEK).[31] A high resolution of $\delta d/d = 3\times10^{-3}$ has been realized at inter-

TABLE I. Summary of the physical properties of sample Nos. 1–4 used in the present TOF neutron-powder-diffraction study. For these samples x-ray powder diffraction exhibited that sample No. 1 is orthorhombic, sample No. 2 is quasitetragonal, and both sample Nos. 3 and 4 are inhomogeneous. Nominal compositions for sample Nos. 1–4 were $LaBa_2Cu_3O_{7-z}$.

	$LaBa_2Cu_3O_{7-z}$ (nominal composition)			
Samples	No. 1	No. 2	No. 3	No. 4
x-ray	Orthorhombic	Quasitetragonal	Inhomogeneous	Orthorhombic
Lattice parameters by x-ray	$a=3.8982(2)$ $b=3.9355(3)$ $c=11.8222(9)$			
oxygen content[a] $(7-z)$	6.78	6.83	6.89	6.80
$R(T)$				
T_c(onset)	52 K		85 K	
T_c(zero)	20 K		70 K	
$M(T)$				
T_c(onset)	45 K		85 K	93 K
Meissner volume fraction	30%		20%	30%

[a] Determined by chemical analysis. The error was ±0.03.

planar spacings d of 1.5 Å.[31] The size of a cylindrical vanadium sample cell was 5 mm in radius, 42 mm in height, and 25 μm thick. Intensity data were collected at room temperature with a gate width of 4 μs.

III. RESULTS

The resulting neutron-diffraction patterns for four samples are shown in Figs. 2(a)–2(d) together with the results

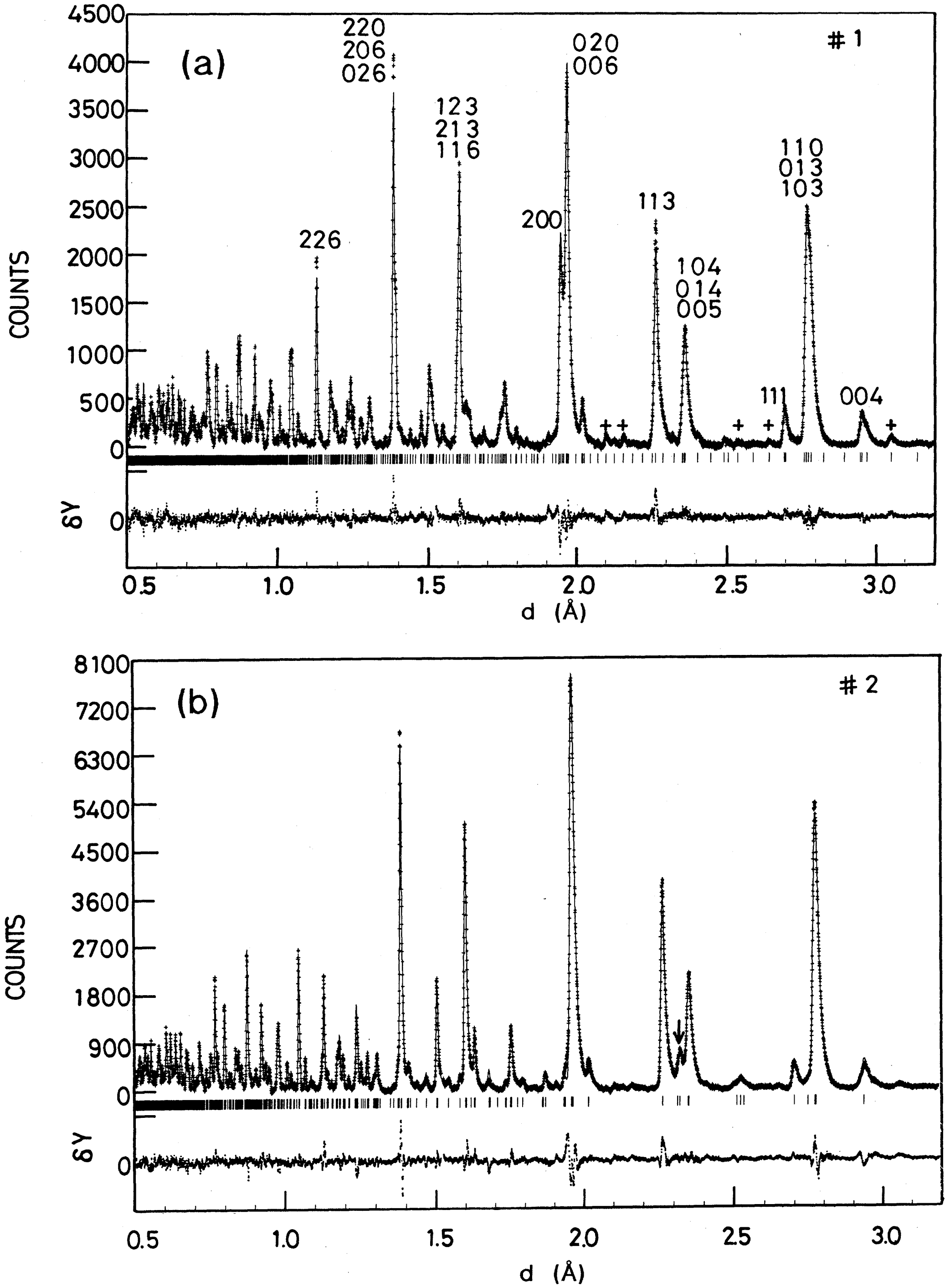

FIG. 2. (a) TOF neutron diffraction and Rietveld refinement patterns of orthorhombic $La_1Ba_2Cu_{2.90}O_{6.82}$ (sample No. 1). Plus marks in the refinement profiles indicate the positions of the prominent reflections of $BaCuO_2$. (b) TOF neutron powder diffraction and Rietveld refinement patterns of orthorhombic $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (sample No. 2). (c) TOF neutron-powder-diffraction pattern in sample No. 3. (d) $LaBa_2Cu_3O_{6.85}$ as sample No. 4. The background was subtracted.

of the profile analysis by the Rietveld method for the sample Nos. 1 [Fig. 2(a)], 2 [Fig. 2(b)], and 4 [Fig. 2(d)]. All of the data exhibit sharp diffraction peaks to which it is appropriate to apply the Rietveld analysis. X-ray and neutron-powder-diffraction data indicated the dominant formation of $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-x}$ as oxygen-deficient triperovskite and noticeable amounts of $BaCuO_2$ (Ref. 32) for sample No. 1 [Fig. 2(a)] and No. 2 [Fig. 2(b)] and CuO for sample No. 2 [Fig. 2(b)]. In the diffraction profiles of sample No. 4 [Fig. 2(d)], no impurity peaks could be seen. In the first three samples we understand that we cannot perfectly avoid the small amount of impurities in the sample preparation process in pellet form. It is quite difficult to obtain enough quantity of homogeneous samples for neutron diffraction study, as far as we make pellets for the measurements of both resistivity and neutron

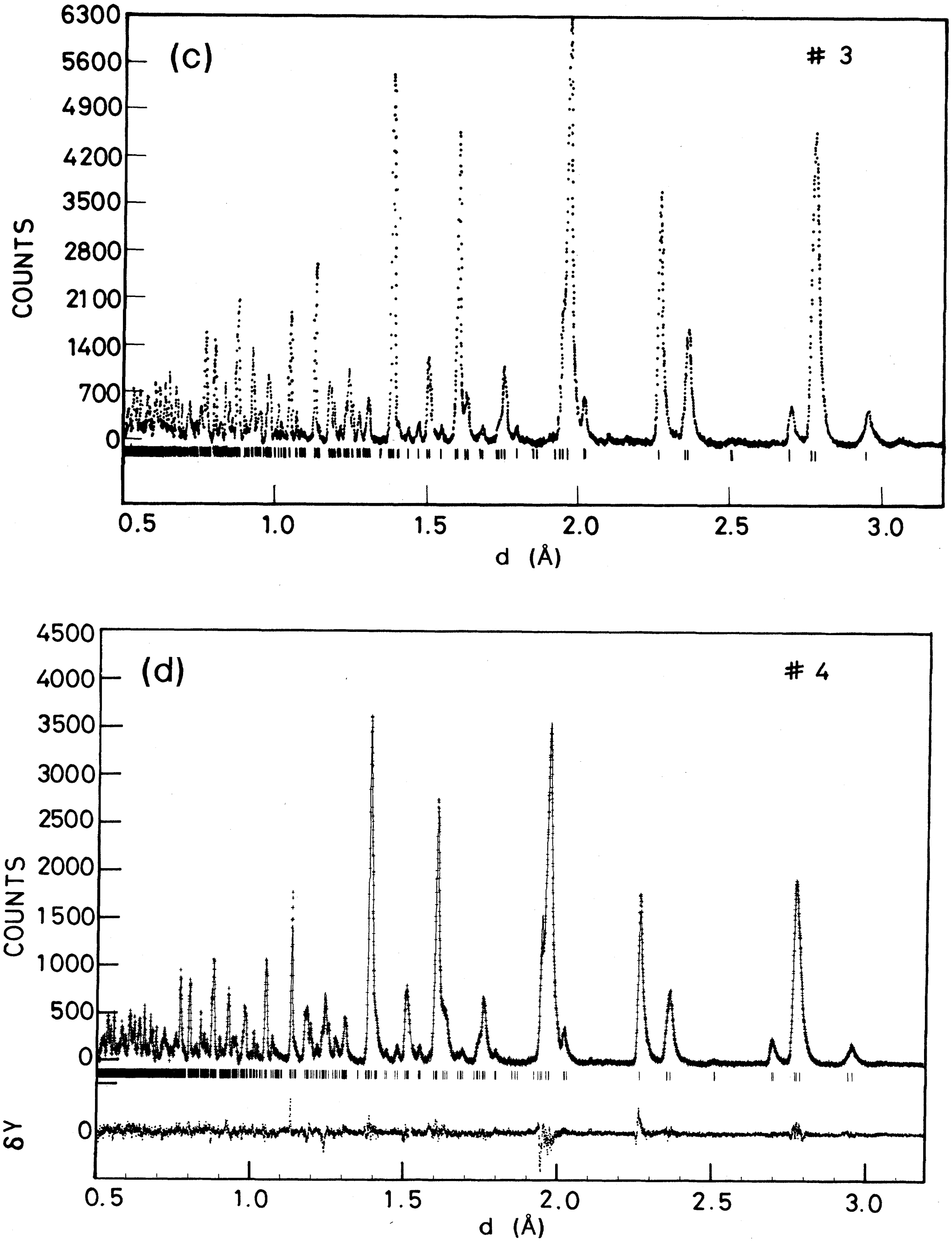

FIG. 2. (*Continued*).

diffraction on the same sample (the TOF neutron diffraction study of KEK-HRP requires the powdered sample of 3.22 cm^3 in volume). However, the Rietveld profile analysis of the neutron-powder-diffraction has recently become a useful tool for the quantitative analysis of a binary or ternary mixture. Hill and Howard[33] have shown that the content of each constituent can be determined from its scale factor when the effect of preferred orientation is negligible.

We refined the structure parameters (atomic positions, isotropic temperature factors and atomic occupancies) with a program[34] RIETAN for the Rietveld analysis of TOF neutron diffraction data, which is valid for the case of the existence of a binary or ternary mixture. The calculation was done by a HITAC-M680H/VOS3 at the Computer Center of The University of Tokyo. Intensity data for interplanar spacings between 0.5 and 3.2 Å were used except for a TOF region of 1.5164–1.5245 Å, where the (200) reflection of the sample holder made of vanadium noticeably appeared. The correction of the effect of the preferred orientation was not necessary, which keeps the essential condition in the quantitative analysis method after Hill and Howard.[33]

A. Sample of the 45-K superconductor (sample No. 1): orthorhombic $La_1Ba_2Cu_{2.90}O_{6.82}$

For sample No. 1, x-ray powder diffraction revealed separable peaks due to (200) and (020) reflections, which is characteristic of the existence of a orthorhombic triperovskite phase as in $YBa_2Cu_3O_{7-z}$. The Rietveld refinement showed that the unit cell is orthorhombic (*Pmmm*) with $a=3.8982(2)$, $b=3.9355(3)$, and $c=11.822(9)$ Å, ($R_{wp}=7.0\%$). Therefore, in the present Rietveld refinement of the neutron-powder-diffraction data we adopted the structure of $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ with the space group *Pmmm* (No. 47),[35] which is identical to that of orthorhombic $YBa_2Cu_3O_{7-z}$.[2,3]

In Fig. 2(a) the obtained neutron-diffraction profile of sample No. 1 is shown by crosses. It is also shown that the diffraction profiles of (200) and (020) lines separably exist. Prominent diffraction peaks are indicated by the indices of diffraction in Fig. 2(a).

Preliminary refinements were carried out under the assumption of the existence of single phase of orthorhombic $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$. Two asymmetric units of La at $1h$ and $2t$ sites and two units of Ba at $1h$ and $2t$ sites have been taken into account in the refinement. Thus the occupancies of La(1) and Ba(1) at the $1h$ site and both the occupancies and coordinates of La(2) and Ba(2) at the $2t$ sites were refined together with other structural, profile, and background parameters simultaneously. It was revealed that a $1h$ site and a $2t$ site are fully and preferentially (exclusively) occupied by La and Ba atoms, respectively ($R_{wp}=6.44$, $R_p=4.75$, $R_e=4.19$, $R_I=3.25$, and $R_F=3.17\%$). In the subsequent refinements including very small portion of impurity phases, the occupation factors g of La(1) and Ba(2) were also found to be 1. Thus these refinements showed that the majority of the constituent of the sample is almost a single phase of a 1:2:3 compound like $LaBa_2Cu_{3-y}O_{7-z}$. The final refinement has been done under a model that assumes the co-existence of three phases, i.e., (1) the orthorhombic $La_1Ba_2Cu_{3-y}O_{7-z}$, (2) the tetragonal $La_{1.5}Ba_{1.5}Cu_{2.98}O_{7.12}$,[8] and (3) $BaCuO_2$.[32] A fraction of the "tetragonal constituent" was effectively introduced for convenience to deal with very weak inhomogeneity of the sample pulverized from the pellet. We have used the crystal data of $La_{1.5}Ba_{1.5}Cu_{2.98}O_{7.12}$ (Ref. 8) to take into account the contribution of the tetragonal constituent, since the existence of tetragonal $La_1Ba_2Cu_3O_{7-z}$ has never been reported. Actually, the Rietveld refinement pattern near the (200) and (020) peaks revealed that the sample includes small amounts of tetragonal and/or quasitetragonal phases in which $a=b$ or $(b-a)/a$ is small in terms of the lengths of the lattice parameters a and b. The contribution of probable La_2CuO_4 (Ref. 36) and CuO (Ref. 37) was detected. However, the contents of both of them were negligible.

In the orthorhombic phase, the occupancies of O(1), O(2), O(3), and Cu(1) were refined without any constraints, whereas those of Cu(2), O(4), and O(5) were assumed to be 1. It was revealed that the O(3) position remained fully occupied when permitted to vary, which is quite consistent with the fact that the La atom does not substitute for Ba at the $2t$ site. Concerning the second and third phases, the profile parameters of their diffraction peaks were made equal to those of the first phase at any cycle of the refinement.

Finally refined parameters for orthorhombic $La_1Ba_2Cu_{3-y}O_{7-z}$ are listed in Table II. The resulting chemical composition was $La_1Ba_2Cu_{2.90}O_{6.82}$. Lattice constants were refined to be $a=3.8938(4)$, $b=3.9374(4)$, and $c=11.8155(11)$ Å, where $b<3.939=c/3$. R factors were $R_{wp}=5.87$, $R_p=4.49$, $R_e=4.19$, $R_I=3.46$, and $R_F=2.89\%$ for the orthorhombic phase, $R_I=3.19$ and $R_F=2.74\%$ for the tetragonal phase, and $R_I=10.6$ and $R_F=4.26\%$ for $BaCuO_2$. The goodness of the fit index is $\mu^2=(R_{wp}/R_e)^2=1.96$. The volume fractions of the orthorhombic phase, the tetragonal phase, and $BaCuO_2$ were determined to be 97.0, 0.6, and 2.4% from the refinement of the scale factors[33] (see Table III). The magnetic susceptibility measurement showed a fairly sharp bulk-superconducting transition in the vicinity of 45 K, which indicates that the fraction of the superconductor is very homogeneous (No. 1 in Fig. 3 of Ref. 26). On the other hand, temperature dependence of the electrical resistance showed rather semiconducting behavior down to around 60 K; it then exhibits gradual decrease. Therefore the increase of resistance with decreasing temperature above 60 K must originate from the existence of some kinds of grain due to extrinsic phases such as $BaCuO_2$, quasitetragonal, and tetragonal triperovskites. The refined oxygen content 6.82 ± 0.03 is in good agreement with the value determined by the chemical analysis, 6.78 ± 0.03. Table IV shows metal-oxygen interatomic distances and bond valence sums of Cu(1) and Cu(2).[38] In Fig. 2(a) the solid curve is the calculated intensity, the crosses overlying them are the observed intensities, and δy is the difference between the observed and calculated

TABLE II. Structural parameters of $LaBa_2Cu_{2.90}O_{6.82}$ (sample No. 1). Space group is *Pmmm* (No. 47). $a=3.8938(4)$ Å, $b=3.9374(4)$ Å, and $c=11.8155(11)$ Å, where $b<3.939=c/3$. B is the isotropic thermal factor and g is the occupation factor. Numbers in parentheses are estimated standard deviations of the last significant digit. R factors were $R_{wp}=5.87$, $R_p=4.49$, $R_e=4.19\%$, $R_I=3.46$, and $R_F=2.86\%$ for the orthorhombic phase, $R_I=3.19$ and $R_F=2.74\%$ for the tetragonal one, and $R_I=10.6$ and $R_F=4.26\%$ for $BaCuO_2$. The goodness of fit index is $\mu^2=(R_{wp}/R_e)^2=1.96$.

Atom	Site	x	y	z	B (Å^2)	g
La	1*h*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.28(3)	1
Ba	2*t*	$\frac{1}{2}$	$\frac{1}{2}$	0.1842(2)	0.76(4)	1
Cu(1)	1*a*	0	0	0	0.18(5)	0.90(1)
Cu(2)	2*q*	0	0	0.3461(1)	0.56(2)	1
O(1)	1*e*	0	$\frac{1}{2}$	0	1.89(16)	0.71(1)
O(2)	1*b*	$\frac{1}{2}$	0	0	1.89(16)	0.11(1)
O(3)	2*q*	0	0	0.1569(2)	0.94(4)	1
O(4)	2*s*	$\frac{1}{2}$	0	0.3659(3)	0.43(4)	1
O(5)	2*r*	0	$\frac{1}{2}$	0.3666(3)	0.39(4)	1

intensities. The short vertical lines represent the total possible Bragg reflections of three phases. In the δy spectrum [Fig. 2(a)] the remaining peak at 1.904 Å^{-1} can be identified as the (006) reflection of La_2CuO_4 (Ref. 36). Figure 3 shows the schematic view of the presently refined crystal structure.

B. Sample of solid solution (sample No. 2): $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$

We have performed the refinement of the neutron-diffraction data of sample No. 2, which is orthorhombic but not superconducting. The purpose of this section is to check the validity of the preceding La/Ba refinement on the 2*t* and 1*h* sites and to clarify the crystal structure of the solid solution. The neutron-diffraction data were obtained in the same experimental condition of the measurement of the first sample as reported in Sec. III A. The magnetization and resistivity showed no sign of the superconducting transition at low temperatures (see also No. 2 in Fig. 3 of Ref. 26). A significant intensity of a CuO phase [shown by arrows in Fig. 2(b)] was found in the diffraction data together with small peaks of impurities such as $BaCuO_2$ and probably La_2CuO_4. Finally a series of the refinement of La/Ba occupancy showed that the chemical composition is $La_{1.56(8)}Ba_{1.44(8)}Cu_{2.86(2)}O_{6.98(9)}$ and $a=3.9182(7)$, $b=3.9277(7)$, and $c=11.742(2)$ Å, where $b>3.914=c/3$, $R_{wp}=6.85$, $R_p=5.00$, $R_e=3.42$, $R_I=3.18$, and $R_F=2.52\%$ for the orthorhombic phase, and $R_I=4.10$ and $R_F=2.74\%$ for the CuO phase. The calculated goodness of fit was $\mu^2=(R_{wp}/R_e)^2=4.01$. The refined crystal parameters for $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ are shown in Table V. The composition of the present sample is close to that of tetragonal $La_{1.5}Ba_{1.5}Cu_{2.98}O_{7.12}$, which also shows no superconductivity.[6,7,10] The analysis of the averaged structure by x-ray and neutron powder diffractions is not very effective for the discrimination between the orthorhombic and the tetragonal phases when the a/b ratio is close to 1. In our case the orthorhombic

TABLE III. Summary of the phase analysis of sample No. 1.

Parameter	Phase 1	Phase 2	Phase 3
Formula	$La_1Ba_2Cu_{2.90}O_{6.82}$	$La_{1.5}Ba_{1.5}Cu_{2.98}O_{7.12}$ (Ref. 8)	$BaCuO_2$ (Ref. 32)
Space group	*Pmmm*	*P*4/*mmm*	*Im*3*m*
Z	1	1	90
M	706.9	713.6	232.8
V (Å^3)	181.1	180.8	6144.6
ZMV[a]	128 058	129 789	128 783 000
Scale factor[b]	4.434×10^{-3}	4.260×10^{-4}	3.913×10^{-7}
Composition (wt. %)	97.2	0.5	2.3
Composition (vol. %)	97.0	0.6	2.4

[a] Product of Z, the number of formula units in the unit cell, M, the mass of the formula unit, and V, the unit cell volume (in Å^3). Also see Eq. (11) of Ref. 33.

[b] Presently obtained scale factors by RIETAN include the multiplicity due to the inversion symmetry and/or the complex lattice such as *I*, *C* crystal symmetry, etc. Therefore we must use the scale factor divided by these multiplicities to apply the present results to the formula by Hill and Haward (Ref. 33).

TABLE IV. Interatomic distances and bond valence sums of Cu(1) and Cu(2) for $La_1Ba_2Cu_{2.90}O_{6.82}$ (sample No. 1).

r (Å)	r (Å)	Multiplicity	s
La—O(4) 2.527(2)	Cu(1)—O(1) 1.969	2	0.44
La—O(5) 2.505(2)	Cu(1)—O(2) 1.947	2	0.47
Ba—O(1) 2.920(2)	Cu(1)—O(3) 1.854(2)	2	0.64 $\sum s$ 2.00
Ba—O(2) 2.934(2)	Cu(2)—O(3) 2.236(3)	1	0.20
Ba—O(3) 2.787(1)	Cu(2)—O(4) 1.961(1)	1	0.45
Ba—O(4) 2.913(3)	Cu(2)—O(5) 1.984(1)	2	0.42 $\sum s$ 1.95
Ba—O(5) 2.904(3)			
La—O 2.516 (average)	Ba—O 2.896 (average)		

symmetry was adopted because of the obtained lower values of the R factors. Associated with the occupation of La at the $2t$ site, site O(3) was clearly deficient when permitted to vary. On the $2t$ site it is noticeable that the partially substituted La(2) atom is at $[\frac{1}{2},\frac{1}{2},0.172(3)]$ with $B=1.3(2)$ Å^2. On the other hand, the remaining Ba atom is located at $[\frac{1}{2},\frac{1}{2},0.189(2)]$ with $B=1.32(22)$ Å^2. In principle, both La^{3+} and Ba^{2+} ions can take eightfold or 12-fold coordinations. But the ionic radii are different from each other.[39] Therefore it is unlikely that La^{3+} has exactly the same coordinates or chemical environment in the case of Ba^{2+}, as has been suggested by Segre *et al.*[9] The above obtained results seem to be consistent with previously mentioned symmetry (1)–(3) in Sec. I . They may be valid for the structure of the orthorhombic solid solution $La_{1+x}Ba_{2-x}Cu_3O_{7-z}$.[9] Nakai and Izumi[40] have suggested that the phase in which the composition ratio La/Ba is equal to $\frac{1}{2}$ is more stable than the solid solution from the viewpoint of crystal chemistry. The calculated interatomic distances and bond valence sums of Cu(1) and Cu(2) are shown in Table VI. Figure 2(b) shows the output of the final profile refinement of sample No. 2 ($La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$).

C. Sample of the 80-K superconductor (sample No. 3): a $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ mixture

Figure 2(c) shows the TOF neutron-powder-diffraction pattern of sample No. 3 of nominal $La_1Ba_2Cu_3O_{7-z}$. Preliminary x-ray Rietveld analysis of the sample showed that this sample is predominantly orthorhombic. The Rietveld profile refinement of the neutron-diffraction data was, however, not successful. Even when the coexistence of both orthorhombic and tetragonal phases were assumed, the obtained R factors were not sufficiently low, i.e., $R_{\rm wp}=9.09$, $R_p=6.46$, and $R_3=3.73$ %. These R factors are extremely larger than those obtained in the case of sample Nos. 1 and 2. It was immediately understood that the present powder sample was quite inhomogeneous, i.e., a mixture of $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ with a distribution of z and x values. The δy spectra showed a relatively large difference between the calculated diffraction profile and the experimental one. Most likely the reason for unsuccessful refinement in sample No. 3 originates from the coexistence of different phases in the solid solution. In the sample there might exist many phases with a distribution of the a-b axis. This hy-

TABLE V. Structural parameters of $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (sample No. 2). Space group is $Pmmm$ (No. 47). $a=3.9182(7)$ Å, $b=3.9277(7)$ Å, and $c=11.742(2)$ Å, where $b>3.914=c/3$. B is the isotropic thermal factor and g is the occupation factor. Numbers in parentheses are estimated standard deviations of the last significant digit. R factors were $R_{\rm wp}=6.85$, $R_p=5.00$, and $R_e=3.42$ %; $R_I=3.18$ and $R_F=2.52$ % for the orthorhombic phase, $R_I=4.10$ and $R_F=2.74$ % for CuO.

Atom	Site	x	y	z	B (Å^2)	g
La(1)	$1h$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.22(8)	1
La(2)	$2t$	$\frac{1}{2}$	$\frac{1}{2}$	0.172(3)	1.3(2)	0.28(4)
Ba	$2t$	$\frac{1}{2}$	$\frac{1}{2}$	0.189(2)	1.32(22)	0.72(4)
Cu(1)	$1a$	0	0	0	0.7(1)	0.86(2)
Cu(2)	$2q$	0	0	0.3466(4)	0.39(6)	1
O(1)	$1e$	0	$\frac{1}{2}$	0	5.0(9)	0.75(9)
O(2)	$1b$	$\frac{1}{2}$	0	0	1.0(9)	0.28(8)
O(3)	$2q$	0	0	0.1570(7)	2.0(2)	0.95(2)
O(4)	$2s$	$\frac{1}{2}$	0	0.3701(9)	0.7(2)	1
O(5)	$2r$	0	$\frac{1}{2}$	0.3603(8)	0.1(1)	1

TABLE VI. Interatomic distances and bond valence sums of Cu(1) and Cu(2) for $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (sample No. 2).

	r (Å)		r (Å)	Multiplicity	s
La(1)—O(4)	2.486(7)	Cu(1)—O(1)	1.964	2	0.45
La(1)—O(5)	2.555(6)	Cu(1)—O(2)	1.959	2	0.46
La(2)—O(1)	2.818(26)	Cu(1)—O(3)	1.843 (8)	2	0.66 $\sum s$ 2.18
La(2)—O(2)	2.821(26)	Cu(2)—O(3)	2.227 (9)	1	0.21
La(2)—O(3)	2.780(3)	Cu(2)—O(4)	1.978 (2)	2	0.43
La(2)—O(4)	3.040(29)	Cu(2)—O(5)	1.971 (1)	2	0.44 $\sum s$ 1.95
La(2)—O(5)	2.950(29)				
Ba—O(1)	2.964(19)				
Ba—O(2)	2.961(18)				
Ba—O(3)	2.799(4)				
Ba—O(4)	2.894(20)				
Ba—O(5)	2.808(19)				
La(1)—O	2.521 (average)				

pothesis is strongly supported by the behavior of the diamagnetic susceptibility as shown in Ref. 26 (sample No. 3 in Fig. 3). The onset temperature was 85 K (with zero resistance around 70 K); however, the diamagnetic susceptibility exhibits a quite broad transition together with relatively small Meissner fraction (about 20%) and large hysteresis.[26]

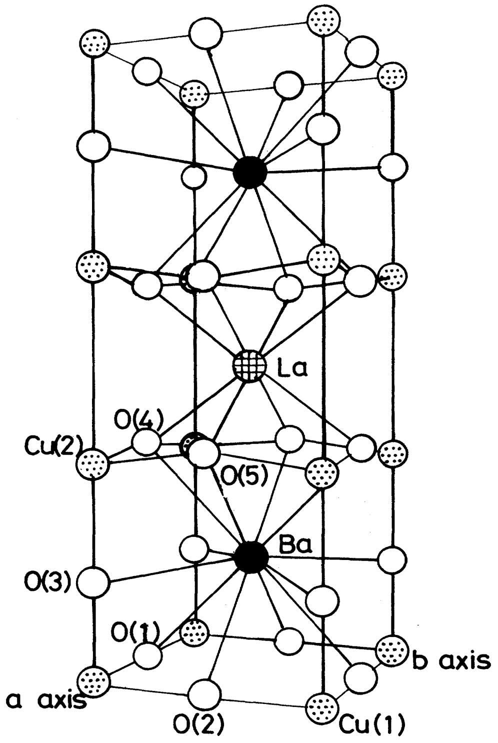

FIG. 3. Schematic view of the crystal structure of $La_1Ba_2Cu_{2.90}O_{6.82}$. ⊕, La; ●, Ba; ◌, Cu; ○, O. The deficiency of the copper and oxygen at 1*a*, 1*b*, and 1*e* sites are neglected in the present view.

D. Sample of the 93-K superconductor (sample No. 4): orthorhombic $LaBa_2Cu_3O_{6.85}$

Figure 2(d) exhibits the output from the Rietveld analysis of the diffraction pattern of sample No. 4. Previously referred impurity phases, such as $BaCuO_2$ and/or CuO, have not been found in this sample. This shows the striking importance of the sample preparation, that is, the sintering process in the flowing N_2 gas atmosphere[25] and the annealing process in powder form. The refinement of the data assuming a single phase of $LaBa_2Cu_3O_{7-z}$, however, yielded *R* factors that were too large ($R_{wp} > 7.0$). Therefore we were forced to take into account effectively the contribution of a second phase in the refinement for convenience. Concerning the possibility of a small amount of the second-phase contamination in the present sample, we performed a two-phase analysis under the assumption of the coexistence of orthorhombic $La_1Ba_2Cu_3O_{7-z}$ and tetragonal $La_{1.5}Ba_{1.5}Cu_{2.98}O_{7.12}$ (Ref. 8) as prescribed in Sec. III A. Table VII exhibits the obtained structural parameters in the final refinement where the refinements of the occupancies of La and Ba sites have not been done. The result of the two-phase analysis after Hill and Howard[33] indicated that 6.6 wt. %, that is, 5.6 vol % of total amounts of the sample is the "tetragonal phase," which represents the contribution of the inhomogeneity, again as in the preceding three samples. However we should note that the diffraction profile in Fig. 2(d) does not show any extrinsic impurity. The oxygen content was determined by the refinement to be 6.85 ± 0.03, i.e., $z = 0.15$, which is in good agreement with the oxygen content by chemical analysis, 6.80 ± 0.03. Table VIII shows the calculated interatomic distances and bond valence sums of Cu(1) and Cu(2).[38]

IV. DISCUSSION

A. Oxygen ordering on the basal plane

In orthorhombic $La_1Ba_2Cu_{2.90}O_{6.82}$ (sample No. 1, see Table II) the 1*b* and 1*e* sites in the basal plane are 11 and

TABLE VII. Structural parameters of impurity-free $LaBa_2Cu_3O_{6.85}$ (No. 4), where the refinements of the occupancies of La and Ba sites have not been done owing to the relatively insufficient conversion. The space group is *Pmmm* (No. 47). $a=3.8930(4)$ Å, $b=3.9380(4)$ Å, and $c=11.818(1)$ Å, where $b=3.939=c/3$. B is the isotropic thermal factor and g is the occupation factor. Numbers in parentheses are estimated standard deviations of the last significant digit. R factors were $R_{wp}=6.64$, $R_p=4.89$, $R_e=4.95\,\%$, $R_I=3.17$ and $R_F=2.14\,\%$ for the orthorhombic phase, $R_I=3.16$ and $R_F=2.11\,\%$ for the tetragonal one.

Atom	Site	x	y	z	B (Å^2)	g
La	1*h*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.28(6)	1
Ba	2*t*	$\frac{1}{2}$	$\frac{1}{2}$	0.1798(4)	0.61(8)	1
Cu(1)	1*a*	0	0	0	0.73(8)	1
Cu(2)	2*q*	0	0	0.3466(4)	0.39(6)	1
O(1)	1*e*	0	$\frac{1}{2}$	0	0.95(24)	0.79(3)
O(2)	1*b*	$\frac{1}{2}$	0	0	1.0(9)	0.06(2)
O(3)	2*q*	0	0	0.1584(3)	0.92(10)	1
O(4)	2*s*	$\frac{1}{2}$	0	0.3642(5)	0.64(9)	1
O(5)	2*r*	0	$\frac{1}{2}$	0.3669(6)	0.45(9)	1

71% occupied by oxygen ions, respectively. Segre *et al.*[9] proposed an order parameter q defined as the normalized difference between the occupancies of the O(1) 1*e* and the O(2) 1*b* sites, that is,

$$q=(g_{O(1)}-g_{O(2)})/(g_{O(1)}+g_{O(2)})\ .$$

We obtain $q=0.73$, which is the largest value among q values reported in orthorhombic $La_{1+x}Ba_{2-x}Cu_3O_{7-z}$ (Ref. 9) but less than 1, which corresponds to the complete ordering of the 1D (Cu-O) chain in the basal plane. On the other hand, for sample No. 4, which is a 93-K superconductor, the calculated q is 0.86. The precision of the obtained profile fits was sufficient to discuss the site occupancy. A value of 0.86 suggests a complete ordering of the 1D (Cu-O) chain in the basal plane compared with that shown in sample No. 1. Segre *et al.*[9] have studied the neutron powder diffraction and electrical resistance of several samples of $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ in which nominal values of x are 0.5, 0.375, 0.125, and 0.0. And they have determined the site occupancies of O(1) and O(2) ions and q values. In their discussion it has been concluded that the transition temperature varies merely by changing the degree of order of the 1D (Cu-O) chain, although their work lacks the detailed description and discussion of other microscopic crystal parameters in the 2D CuO_2 layer unit. In the present study the sample with higher ordering of the 1D chain achieves a higher superconducting transition temperature. Since it is commonly accepted that carriers on the 2D CuO_2 network composed of Cu(2), O(4), and O(5) atoms play a principal role in the occurrence of the superconductivity in the triperovskite, the change of the degree of order, i.e., the value of q, should contribute to the variation of the microscopic crystal parameters of the 2D CuO_2 layer through the Ba-O(3) layer. The electronic state in the 2D CuO_2 layer is affected by the oxygen ordering at sites O(1) and O(2) through the 2*p* orbit of the bridging O(3) oxygen at the 2*q* site. Attention should be paid to the degree of deficiency at the O(3) site. The detailed discussion will be given in Sec. IV D.

In sample No. 1 it is also noticeable that thermal factors of atoms around the site Cu(1), 1.89(16), 1.89(16), and 0.94(4) for O(1), O(2), and O(3), are fairly large if we compare them with those of the corresponding sites in orthorhombic $YBa_2Cu_3O_{7-z}$ and other $RBa_2Cu_3O_{7-z}$ (R=Y,Er,Ho, . . .); for example, 0.48 at O(1), O(2), and O(3) sites when R=Y (Ref. 3). On the other hand, the thermal factors in the 2D CuO_2 layers [0.56, 0.43, and 0.39 at Cu(2), O(4), and O(5) sites] are roughly equal to

TABLE VIII. Interatomic distances and bond valence sums on Cu(1) and Cu(2) for $LaBa_2Cu_3O_{6.85}$ (No. 4).

r (Å)	r (Å)	Multiplicity	s
La—O(4) 2.540(4)	Cu(1)—O(1) 1.969	2	0.44
La—O(5) 2.503(4)	Cu(1)—O(2) 1.946	2	0.47
Ba—O(1) 2.882(3)	Cu(1)—O(3) 1.872(4)	2	0.60 $\sum s$ 1.95
Ba—O(2) 2.897(3)	Cu(2)—O(3) 2.224(6)	1	0.21
Ba—O(3) 2.780(5)	Cu(2)—O(4) 1.958(1)	2	0.46
Ba—O(4) 2.937(6)	Cu(2)—O(5) 1.984(1)	2	0.42 $\sum s$ 1.97
Ba—O(5) 2.946(6)			
La—O 2.522(average)	Ba—O 2.887 (average)		

those previously reported in other $RBa_2Cu_3O_{7-z}$ [e.g., 0.42, 0.53, and 0.53 at Cu(2), O(4), and O(5) in R=Ho (Ref. 4)]. This fact shows that some kind of disorder exists in the Cu-O network on the basal plane, which may be strongly related to the deficiency of Cu(1) site ion, even if we take into consideration that the thermal factor is not so reliable because of its strong correlation to the site occupancy in the refinement. Any marked improvement in the fit was not obtained when anisotropic temperature factors were assigned to these O(1), O(2), and O(3) atoms. The smallness of the thermal factors of the 2D CuO_2 layer and La atom showed the existence of comparatively good ordering. It has been reported that the crystallographic geometry of the 2D CuO_2 layer is relatively unaffected by varying the quench temperature.[41] The change in electronic structure caused by the oxygen disorder in the basal plane affects the electronic property of the 2D CuO_2 layer in a way that is disadvantageous to superconductivity.

In other $RBa_2Cu_3O_{7-z}$, the bond lengths Cu(1)—O(3) and Cu(2)—O(3) show characteristic dependence on z as has been reported in the early stages by Asano *et al.* (Fig. 4 of Ref. 4), where the O(3) oxygen ion is pulled down toward the Cu(1) ion with increasing z in consequence of diminished repulsion between O(3) and O(1) ions. Figure 4 shows the bond lengths for Cu(1)—O(3) and Cu(2)—O(3) as a function of oxygen deficiency z. These have been calculated from the refined crystal parameters determined by either neutron powder diffraction or single-crystal x-ray diffraction (this work and previous works). This figure includes the results of our present sample Nos. 1 and 3. The bond length Cu(2)—O(3) increases linearly with increasing z (with decreasing oxygen content). It can be appreciated in this figure that the increase of the negative charge on the basal plane leads to the shortening of the interatomic distance between Cu(2) and O(3) atoms in the subunit including Ba.

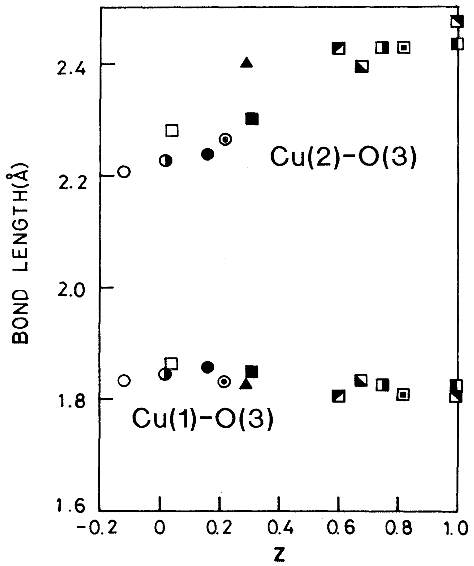

FIG. 4. Bond length for Cu(1)-O(3) and Cu(2)-O(3) as a function of oxygen deficiency z based on the crystal parameters determined by neutron diffraction and single-crystal x-ray diffraction in various triple perovskites. ○, tetragonal (T-)$La_{1.5}Ba_{1.5}Cu_{2.90}O_{7.12}$ (Ref. 8); ◑, T-$La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (present result); □, orthorhombic (O-)$HoBa_2Cu_3O_{6.96}$ (Ref. 4); ●, O-$La_1Ba_2Cu_{2.90}O_{6.82}$ (present result); ◉, T-$Nd_{1.8}Ba_{1.2}Cu_{2.95}O_{6.78}$ (Ref. 8); ▲, O-$Y_1Ba_2Cu_3O_{6.71}$ at 623 °C (Ref. 2); ■, O-$Y_1Ba_2Cu_3O_{6.69}$ (Ref. 3); ◩, T-$Y_1Ba_2Cu_{2.91}O_{6.4}$ (Ref. 55); ◪, T-$Y_1Ba_2Cu_3O_{6.32}$ (Ref. 3); ◨, T-$Dy_1Ba_2Cu_3O_{6.25}$ (Ref. 56); ▣ T-$Y_1Ba_2Cu_3O_{6.18}$ (Ref. 57); ◪, T-$Y_1Ba_2Cu_3O_6$ (Ref. 56); ◧, T-$Ho_1Ba_2Cu_3O_6$ (Ref. 56); ◐, O-$NdBa_2Cu_3O_{7.18}$ (Ref. 58); ⊙, O-$LaBa_2Cu_3O_{6.85}$ (present work).

In the present study it was revealed that the samples with $b > c/3$ and $a < b$ would have a nonzero value of x in the orthorhombic solid solution. In other orthorhombic 1:2:3 phases and solid solutions this criterion is valid; for example, $b = 3.8829 > a$ and $b < 3.897 = c/3$ in $YBa_2Cu_3O_{6.69}$ (Ref. 3), $b = 3.8851 > a$ and $b < 3.894 = c/3$ in $HoBa_2Cu_3O_{6.96}$ (Ref. 4), and $b > a$ and $b > c/3$ in the reported orthorhombic solid solution $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ with $x = 0.375$ with $z = -0.25$, $x = 0.25$ with $z = -0.18$, -0.11, and -0.25 (Ref. 9). In this respect the samples synthesized by Yoshizaki *et al.*,[24] with $b = 3.9342 > a$ and $b < 3.936 = c/3$, were probably samples of 1:2:3 phases. The onset temperature of the resistive transition is 89 K and a sharp transition has been observed in magnetization study. Samples of $LaBa_2Cu_3O_{7-z}$ (nominal) which exhibit superconducting transition above 90 K have been synthesized by Wada *et al.*[25] One of the samples showed the superconducting transition with the onset of 93 K and zero resistance at 92 K and also with the onset at around 93 K in magnetization. Lattice parameters of the typical sample were $a = 3.885$, $b = 3.938$, and $c = 11.817$ Å, where $b > a$ and $b < 3.939 = c/3$ are satisfied. Thus we can easily distinguish whether an orthorhombic sample is a solid solution or not by means of only the precise determination of the lattice constants. It is tempting to conclude that the samples with $b > c/3$ and $a < b$ would be a solid solution and those with $b < c/3$ and $a < b$ would be a 1:2:3 compound.

B. The effect of annealing on the transition temperature in $La_1Ba_2Cu_{2.90}O_{6.82}$ (sample No. 1)

The sample of the 1:2:3 compound $La_1Ba_2Cu_{2.90}O_{6.82}$ showed a fairly low transition temperature. The obtained oxygen content $7-z$ was 6.82 (6.78 in chemical analysis), which is less than 7.0. The order parameter q of the formation of the 1D (Cu-O) chain is 0.73, which is far less than 1.0 for the 90-K superconductor such as $YBa_2Cu_3O_7$. Therefore we think that a more appropriate thermal treatment would make $7-z$ and q become 7.0 and 1.0, which promises the highest transition temperature of the orthorhombic $LaBa_2Cu_3O_{7-z}$ system. This is supported by the following observations. After the TOF neutron-diffraction measurements we annealed parts of the sample in powder form for various periods at 300 °C and the temperature dependence of the magnetic susceptibility was measured as shown in Fig. 5. The onset temperatures were 46 K (no annealing after the neutron diffraction), 55 K (annealing time of 20 h), 67 K (50 h), 70

K (100 h), and 77 K (200 h).

Table IX shows the lattice parameters determined by Rietveld analysis of x-ray powder-diffraction data and superconducting onset transition temperatures on the samples annealed by various periods. They are also plotted in Fig. 6. It can be seen that the lattice constants *a* and *b* change linearly as a function of the onset temperature, T_{onset}. It is noticeable that the length of the *c* axis significantly decreases between $T_c = 46$ and 55 K. This result shows that the first cycle of the annealing process was the most effective to increase the oxygen content on the basal plane. These facts exhibit that the comparatively low T_c of the sample really comes from the insufficient oxygen content and probably insufficient 1D Cu-O ordering on the basal plane. The present result indicates that the longer annealing time is needed to take O into the orthorhombic $LaBa_2Cu_{3-y}O_{7-z}$ and it seems that the increase of T_c up to 90 K is not so easy from the results in Table IX. In the study of the synthesis of the samples of 90-K superconductors by Wada *et al.*[25,42] the sintering above 950 °C in a flowing N_2 gas atmosphere was revealed to be important for diminishing the amounts of the impurity phase in addition to the annealing at 300 °C in a dried O_2 gas atmosphere for well ordering of the Cu-O chain. In the sintering process on sample No. 1 we did not use N_2 gas flow; instead we used O_2 gas flow. And the drastic increase of T_c up to 90 K cannot be achieved only by the annealing as shown in Fig. 6. Therefore the depression of the increase of T_c is considered to be due to the existence of impurities such as $BaCuO_2$. From the present study it is also evidenced that even the 45–50 K superconductor as well as the 90-K one has an orthorhombic structure.

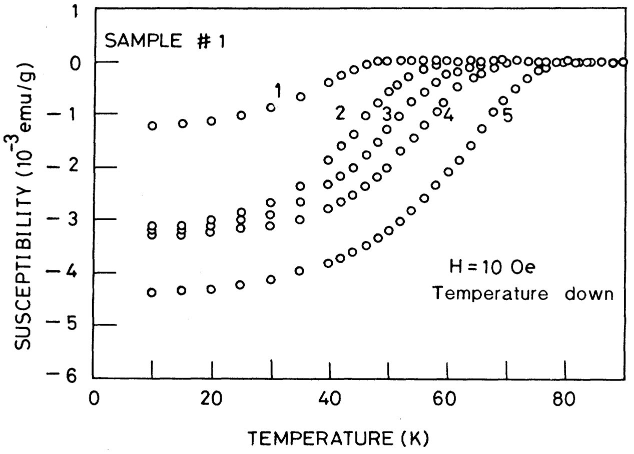

FIG. 5. Magnetization as a function of temperature on sample No. 1 (orthorhombic $La_1Ba_2Cu_{2.90}O_{6.82}$) with various periods of annealing at 300 °C. The onset temperature was 45 K (no annealing after the neutron diffraction), 1; 55 K (annealing time of 20 h), 2; 67 K (50 h), 3; 70 K (100 h), 4; and 77 K (200 h), 5.

C. Solid solution $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$ (sample No. 2)

From the Rietveld refinements it is clear that the excess La, *x*, is close to 0.5 in the solid-solution sample (No. 2). The occupation factors for La(2) and Ba were 0.28(4) atom/site and 0.72(4) atom/site, respectively, as shown in Table V. It is noted that the *z* coordinates and thermal factors for La(2) and Ba ions were refined independently in the present study because it is unlikely that La(2) occupies exactly the same position and surroundings as in the case of the Ba ion.[9] On the other hand, the smaller and more negatively charged La(2) ion will attract oxygen more strongly than the Ba ion, which leads to the displacement of the oxygen ions towards the La ions. Oxygen ions at O(1), O(2), and O(3) exhibited relatively large isotropic thermal factors, 5.0(9), 1.0(9), and 2.0(2) Å^2, respectively. These results should originate from the statistical disorder of the La(2) and Ba ions on the 2*t* site. The positions of the O(1) and O(2) oxygen atoms have been fixed at $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,0)$, as shown in Table V, and therefore it is not very meaningful to discuss the calculated interatomic distances between La(2), Ba and O(1), O(2), and O(3). An attempt to face this problem has been tried by Torardi *et al.*[15] Macroscopic parameters such as lattice constants are important in the sense of describing the averaged crystal structure. As has been presented in Sec. III, the substitution of La^{3+} for Ba^{2+} at the 2*t* site substantially affects the oxygen content and the crystal structure. The excess oxygen was put in the Cu-O basal plane at $z \cong 0$, resulting in a quasitetragonal structure and at the same time the length of the *c* axis became short due to the shrinkage of the subunit including La(2)/Ba ions. In some samples ordering of the La/Ba cations at the 2*t* site may result in a superstructure as has been observed in $LaCaBaCu_3O_{6.85}$.[43]

In the present study it was revealed that La^{3+} ions

TABLE IX. Lattice parameters determined by Rietveld analysis of x-ray powder diffraction data and superconducting onset transition temperatures (T_c^{onset}) on the samples annealed by various periods at 300 °C.

a (Å)	*b* (Å)	*c* (Å)	$\delta[(b-a)/a]$	R_{wp}	T_c^{onset}	Period (h)
3.8982(2)	3.9355(3)	11.822(1)	0.0096	7.00	45	0
3.9295(5)	3.8886(2)	11.797(1)	0.0105	7.80	55	20
3.9274(7)	3.8857(3)	11.787(2)	0.0107	8.71	67	50
3.9310(6)	3.8859(3)	11.783(3)	0.0116	7.87	70	100
3.9224(5)	3.8817(3)	11.785(2)	0.0105	8.17	77	200

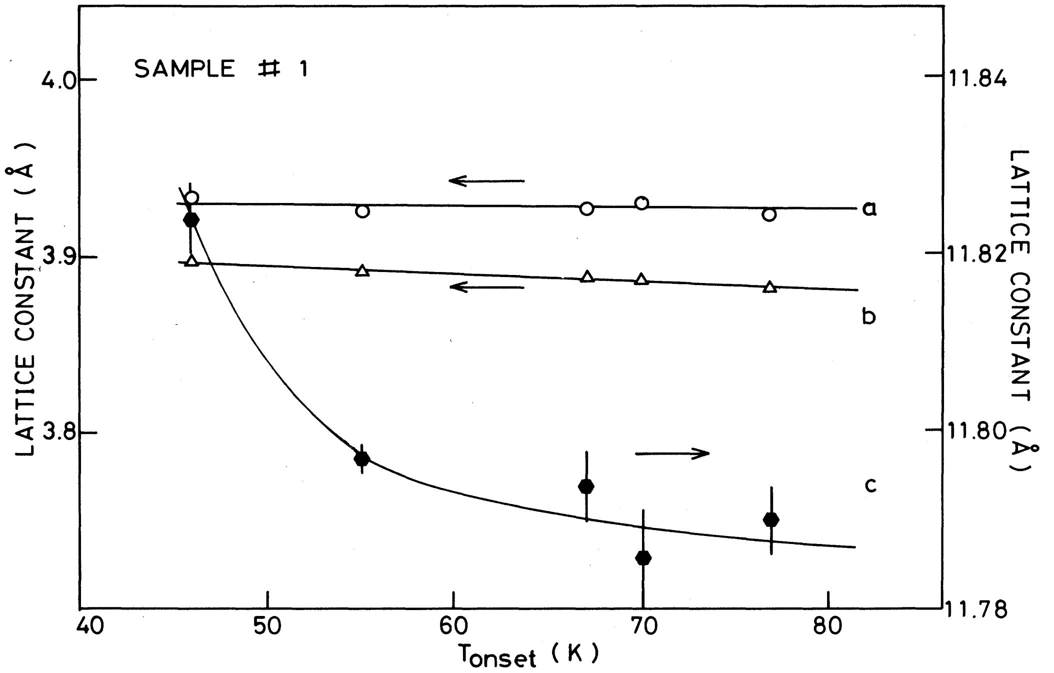

FIG. 6. Onset temperature of the superconductivity by magnetization vs lattice constants determined by Rietveld analysis of the x-ray powder diffraction data after Table IX. The solid lines and curve are only guides for the eye.

preferentially substitute for Ba^{2+} ions in these solid solutions. If the substitution of the larger Ba^{2+} ion for the smaller La^{3+} ion at the $1h$ site occurs, the structure of the subunit around the $1h$ site is no longer rigid and the 2D CuO_2 network would have some vacancies of oxygen as on the basal plane, which must lead to the drastic degradation of the superconductivity. Nakai *et al.*[44] have also indicated that the large Ba ion does not substitute for the smaller La ion in their discussion. Some kinds of stacking disorder in the sequential arrangement of (La/Ba)-La-(La/Ba) may occur and it is intrinsically out of the framework of the averaged crystal structure. This type of disorder may contribute to some kind of diffuse streak and/or superconductor. A high density of stacking faults with a fault vector of $\frac{1}{3}[001]$ and with a fault plane nearly parallel to $\{101\}$ have been observed in $La_{1.5}Ba_{1.5}Cu_3O_{7.11}$ by Suzuki *et al.*[45] They suggested that such stacking faults may be related to a variation in composition.

D. Valencies and bonds

On the discussion and consideration of the mechanism of the superconductivity, the determination and precise study of the bonds and valencies of Cu and O ions are important from the viewpoint of an ionic crystal. From crystallochemical considerations and various experiments such as photoelectron spectroscopy, many workers concluded that the Cu ions at the Cu(2) sites are divalent, and that the valency of the copper ion at the Cu(1) site changes from the mixture of 2+ and 3+ to 1+ and 2+ as oxygen contents at the O(1) sites decreases.[17] $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$ is a solid solution. Therefore it is not trivial to consider the bonds and valencies with respect to the charge neutrality and crystal instability.

Tables IV, VI, and VIII show not only the calculated interatomic distances but also bond valence sums of Cu(1) and Cu(2) for the 45-K superconductor $La_1Ba_2Cu_{2.90}O_{6.82}$, solid solution $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$, and the 93-K superconductor $LaBa_2Cu_3O_{6.85}$, respectively. The bond valence sums were calculated after the method established by Brown and Altermatt.[38] The calculation of the valence sum shows that Cu(2) is divalent in all of the three samples. On the other hand, Cu(1) is divalent in sample Nos. 1 and 4, and the valence of Cu(1) is much larger than 2 in sample No. 2, which is a nonsuperconducting solid solution. This fact shows that the appearance of partial trivalent state of Cu(1) strongly correlates to the quasitetragonal symmetry induced by the substitution of La(2) for the Ba site. Quasitetragonal symmetry corresponds to nearly equal occupations of O(1) and O(2) ions.

Concerning the valencies of Cu and O ions, from the experimental results showing only the Cu^{2+} contribution (for example, Refs. 46 and 47), it is clear that we can suppose there are O $2p$ holes, i,e., O^{1-} ions, in $YBa_2Cu_3O_7$. In the x-ray absorption spectra, the line at $E = 528.5$ eV is interpreted as the transition $1s$-$2p$.[48] Thus the spectroscopic studies support the hypothesis of cation Cu^{2+} and oxygen ions O^{1-}. The Cu $2p$ or O $1s$ spectra of several oxide superconductors have been found to indicate only a Cu^{2+} contribution and O $2p$ holes, i.e., O^{1-}. An attempt has been made to explain such results based on crystal structure and consideration of bonds by Oudet[49,50] and other workers.

On the valence of La(1) and Ba ions, we consider the respective sums of the ionic radii for La^{3+} with 8 coordination numbers (CN's), Ba^{2+} with 12 CN's, and O^{2-} with 6 CN's after Shannon.[39] Thus we simply obtain the respective sums of ionic radii for La-O and Ba-O to be 2.56 and 3.01 Å, respectively. These values are in good agreement with the calculated average interatomic distances of La-O and Ba-O as shown in Tables IV, VI, and VIII. It clearly indicates that the valence states of La (at the 1*h* site) and Ba are trivalent and divalent, respectively.

The next problem is why some of the 90-K class of superconductors have solid solutions. Mitzi *et al.*[51] have claimed that the origin of the formation of the solid solution La-Ba-Cu-O system comes from the similarity of the atomic ionic radii of La and Ba atoms. In the Y-Ba-Cu-O system, the yttrium ion has eight coordination polyhedra of Y^{3+} with an ionic radius of about 1.1 Å. On the other hand, La^{3+} has eight coordination numbers with 1.22 Å in its ionic radius of 12 coordination numbers with about 1.4 Å in its ionic radius.[39] The present Rietveld refinement of neutron-powder-diffraction data clearly shows that the coordination numbers of the 1*h* site ion is 8. Then we take as the ionic radius of the La ion (at the 1*h* site) the smaller one, that is, 1.22 Å, which is less than the value of the ionic radius 1.67 Å of Ba^{2+} with 12 coordination numbers. Fundamentally, it is not appropriate to conclude that the origin of the solid solution is due to the similarity of the ionic radii of La^{3+} and Ba^{2+} ions. In fact, the Pr-Ba-Cu-O system (around 1.21 Å in ionic radius of Pr^{3+}) does not have a solid solution, although the Nd-Ba-Cu-O system, where the ionic radius of Nd^{3+} is a little smaller than that of Pr^{3+} and La^{3+} (8 coordinations), has a solid solution. Nakai *et al.*[44] have emphasized that La^{3+} also has 12 coordination numbers. It seems that some of the Ba ions should be divalent with eight coordination numbers for matching the ionic radius between the Ba and substituted La ions, because the O(3) atom is deficient, as shown in Table V. Then it is possible for the La^{3+} ion to substitute for Ba^{2+} ions at 2*t* sites with 12 coordination numbers. Certainly, the ionic radius of La^{3+} with 12 coordination numbers has a relatively large ionic radius of around 1.4 Å, which is comparable to that of the Ba^{2+} ion with eight coordination numbers. In conclusion, the valence at the La(1), 1*h* site is trivalent with a smaller ionic radius, the La(2) atom is also trivalent with a larger ionic radius, and the Ba atom at the 2*t* site is divalent with a larger ionic radius with a very small fraction of the smaller ionic radius.

We estimate the excess charge per Cu—O bond, $[\text{Cu-O}]^{+p}$, under the assumption of charge neutrality after Torrance *et al.*[52] In $(La_{1-x}A_x)_2CuO_4$, where $A = \text{Sr,Ba}$, high transition temperature of the superconductivity has been achieved in the range $p = 0.15-0.22$ and also $p = 0.18-0.25$ in the so-called 1:2:3 oxides. The calculated values of p were 0.29 in the 45-K superconductor $La_1Ba_2Cu_{2.90}O_{6.82}$, 0.24 in $La_{1.56}Ba_{1.44}Cu_{2.86}O_{6.98}$, and 0.23 in the 93-K superconductor $LaBa_2Cu_3O_{6.85}$, respectively. It is a remarkable feature that the excess charge per Cu—O bond of the solid solution is close to that of the 93-K superconductor. This result shows that further consideration is needed for the validity of the explanation of T_c by the estimation of excess charge in the system of the solid solution.

E. Microscopic crystal view and the origin of the high-T_c superconductivity

In this section we discuss the structure of the 2D CuO_2 layer unit which is composed of Cu(2), O(4), and O(5). Figure 7 shows the detailed structures of the 2D CuO_2 layer unit above and below La in sample Nos. 1, 4, and 2. The former two samples are superconductors and the magnetic transition temperatures are different from each other as shown in Fig. 7 and Table I. Sample No. 2 is not superconducting. The calculated interatomic distance and bond angles should be paid attention to. First of all,

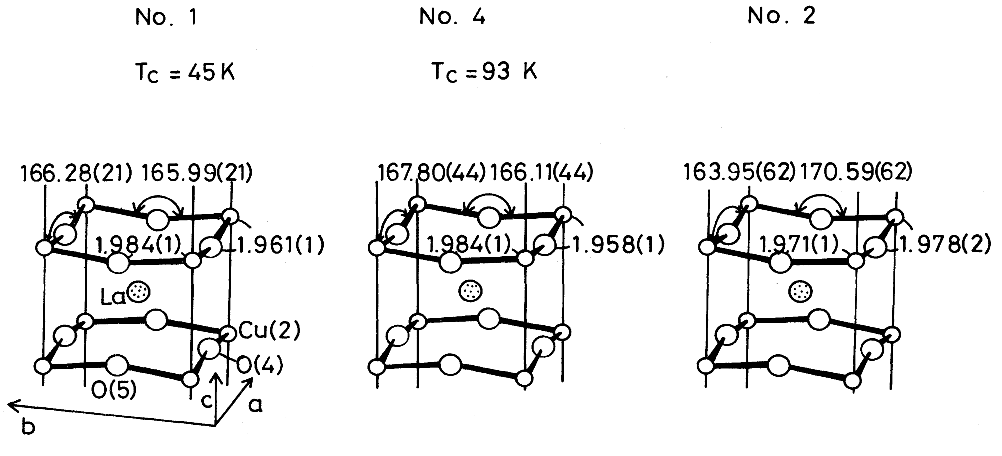

FIG. 7. Partial structural view of the 2D CuO_2 network unit above and below La in sample No. 1 (45-K superconductor), No. 4 (93-K superconductor), and No. 2 (nonsuperconducting solid solution).

it is noticed that the sum of the interatomic distances Cu(2)—O(4) and Cu(2)—O(5) are similar in three samples. Especially, the lengths of both Cu(2)—O(4) and Cu(2)—O(5) on sample No. 1 are almost equal to those of sample No. 4. Next we consider the comparison on the bond angles between the sample Nos. 1 and 4. As shown in Fig. 7 two bond angles α,β of Cu(2)—O(4)—Cu(2) and Cu(2)—O(5)—Cu(2), respectively, are calculated (together with their error), where we denote the bond angle to be atom 1-central atom-atom 2. In terms of the magnitudes of the two angles, both of them in sample No. 4 are larger than those of sample No. 1. We define the parameter of degree of coplanarity of the 2D CuO_2 network as follows:

$$D=(\alpha-\beta)/(\alpha+\beta)\ .$$

The obtained D parameters for samples Nos. 1 and 4 are 9×10^{-4} for No. 1 (45-K superconductor) and 5.1×10^{-3} for No. 4 (93-K superconductor). The degree of coplanarity of sample No. 1 is much higher than that of sample No. 4. The difference $\alpha-\beta$ in sample No. 4 is much larger than that of No. 1. Therefore the difference of the superconducting transition temperature may be due to both the largeness of the α and β in addition to the largeness of the difference of α and β (see Fig. 7).

In $YBa_2Cu_3O_{7-z}$, from the ^{89}Y NMR studies, Alloul *et al.*[53] showed that the Pauli susceptibility in the 2D Cu-O planes of the 60-K phase is approximately one-half of that of the 90-K phase. Imai *et al.*[54] have also studied for ^{63}Cu at the Cu(2) sites in $YBa_2Cu_3O_{6.52}$ ($T_c^{\text{onset}}=60$ K) and they found strong suppression of nuclear spin-lattice relaxation rate ($1/T_1$) compared with the case of $YBa_2Cu_3O_{6.91}$ ($T_c^{\text{onset}}=90$ K) in the normal state. They discussed that the result indicates less significant contributions of spin fluctuations to $1/T_1$ and low density of states at the Cu(2) sites. These phenomena may strongly correlate to the above described structure of the 2D CuO_2 layer unit.

V. CONCLUDING REMARKS AND SUMMARY

The averaged crystal structures were refined by Rietveld analysis of TOF neutron diffraction on powdered samples of oxygen-deficient triperovskite $La_{1+x}Ba_{2-x}Cu_{3-y}O_{7-z}$. Two of the samples are 45- and 93-K orthorhombic superconductors and the last one is nonsuperconducting quasitetragonal. The refined results support the fact that the subunit around the La ion at the 1*h* site is well ordered, as shown in other so-called 1:2:3 90-K superconductors. On the remaining subunits around Ba ions strong disorder was found in the O(1) and O(2) sites in the basal plane, and the Ba ion, with a relatively large ionic radius, has 12 coordinations to oxygen ions, in contrast to 10 coordinations to oxygen ions in $YBa_2Cu_3O_{7-z}$. However the study of appropriate heat treatment (long-time and low-temperature annealing) showed that the increase of the transition temperature is fully possible. It shows that the coordination numbers of the Ba ion may change from 12 to 10, as shown in orthorhombic $YBa_2Cu_3O_7$. The valence sum calculation indicates that Cu(1) and Cu(2) are almost divalent in both the 45- and 93-K superconductor $LaBa_2Cu_{3-y}O_{7-z}$, while the sums of Cu(1) in the solid solution is much larger than 2. It was therefore clarified that there exists trivalent copper at the Cu(1) site in the nonsuperconducting solid solution. The difference and resemblance between the two superconducting oxides were clarified based on the calculated microscopic crystal parameters with respect to the structure of the 2D CuO_2 network. In the structure of the solid solution, it was remarked that the excess La ion occupies the site of a Ba ion and most of the La ions (at 2*t* site) have a larger ionic radius with 12 coordination numbers to oxygen atoms. On the other hand, the La ion at the 1*h* site has eight coordination numbers. The precise determination of the correlation of the superconductivity and the crystal structure will require further studies, but the present results provide a basis for further progress of the study of these systems of the solid solution in superconducting ceramics.

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[1] F. Izumi, H. Asano, T. Ishigaki, A. Ono, and F. P. Okamura, Jpn. J. Appl. Phys. **26**, L611 (1987).

[2] J. D. Jorgensen, M. A. Beno, O. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[3] F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, and Y. Uchida, Jpn. J. Appl. Phys. **26**, L649 (1987).

[4] H. Asano, K. Takita, T. Ishigaki, H. Akinaga, H. Katoh, K. Masuda, F. Izmui, and N. Watanabe, Jpn. J. Appl. Phys. **26**, L1341 (1987).

[5] L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, J. Solid State Chem. **37**, 151 (1987).

[6] F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, Y. Matsui, and Y. Uchida, Jpn. J. Appl. Phys. **26**, L1153 (1987).

[7] E. Takayama-Muromachi, Y. Uchida, A. Fujimori, and K. Kato, Jpn. J. Appl. Phys. **26**, L1546 (1987).

[8] F. Izumi, E. Takayama-Muromachi, Y. Uchida, H. Asano, T. Ishigaki, and N. Watanabe (unpublished).

[9] C. U. Segre, B. Dabrowski, D. G. Hinks, K. Zhang, J. D. Jorgensen, N. A. Beno, and I. K. Schuller, Nature **329**, 227 (1987).

[10] F. Izumi, E. Takayama-Muromachi, M. Kobayashi, Y. Uchida, H. Asano, T. Ishigaki, and N. Watanabe, Jpn. J. Appl. Phys. **27**, L824 (1988).

[11] F. Izumi, S. Takekawa, Y. Matsui, N. Iyi, H. Asano, T. Ishigaki, and N. Watanabe, Jpn. J. Appl. Phys. **26**, L1616 (1987).

[12] S. Takekawa, N. Iyi, H. Nozaki, and Y. Ishikawa, Jpn. J. Appl. Phys. **26**, L2076 (1987).

[13] S. Tsurumi, T. Iwata, Y. Tajima, and M. Hikita, Jpn. J. Appl. Phys. **26**, L1865 (1987).

[14] Yi-Song, J. G. Golben, S. Chittipeddi, S. I. Lee, R. D. McMichael, X. D. Chen, J. R. Gaines, D. L. Cox, and A. J. Epstein, Phys. Rev. B **37**, 607 (1987).

[15] C. C. Torardi, E. M. McCarron, M. A. Subramanian, A. W. Sleight, and D. E. Cox, Mat. Res. Bull. **22**, 1563 (1987).

[16] S. Tsurumi, T. Iwata, Y. Tajima, and A. Hikita, Jpn. J. Appl. Phys. **27**, L80 (1988).

[17] See, for example, *Proceedings of the International Conference on High Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, 1988,* edited by J. Muller and J. L. Olsen (North-Holland, Amsterdam, 1988), Parts I and II.

[18] E. Takayama-Muromachi, Y. Uchida, A. Fujimori, and K. Kato, Jpn. J. Appl. Phys. **26**, L223 (1987).

[19] A. Bianconi, M. de Santis, A. M. Flank, A. Fontaine, P. Lagarde, A. Marcelli, H. Katayama-Yoshida, and A. Kotani, Physica C **153-155**, 1760 (1988).

[20] H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).

[21] A. Maeda, K. Uchinokura, T. Yabe, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1368 (1987).

[22] A. Maeda, K. Uchinokura, T. Yabe, M. Izumi, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1550 (1987).

[23] K. Uchinokura, A. Maeda, T. Yabe, M. Izumi, and S. Tanaka, Jpn. J. Appl. Phys. Suppl. **26-3**, 2109 (1987).

[24] R. Yoshizaki, H. Sawada, T. Iwazumi, Y. Saito, Y. Abe, H. Ikeda, K. Imai, and I. Nakai, Jpn. J. Appl. Phys. **26**, L1703 (1987).

[25] T. Wada, N. Suzuki, T. Maeda, A. Maeda, S. Uchida, K. Uchinokura, and S. Tanaka, Appl. Phys. Lett. **52**, 1989 (1988).

[26] A. Maeda, T. Noda, H. Matsumoto, T. Wada, M. Izumi, T. Yabe, I. Uchinokura, and S. Tanaka, J. Appl. Phys. **64**, 4095 (1988). Note that the value of the ratio La:Ba:Cu for sample No. 3 in Table II in this paper should be eliminated.

[27] F. Izumi, Nippon Kessho Gakkai Shi **27**, 23 (1985).

[28] M. Izumi, K. Uchinokura, A. Maeda, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L1555 (1987).

[29] M. Izumi, A. Maeda, K. Uchinokura, T. Yabe, H. Asano, F. Izumi, T. Wada, T. Hasegawa, and S. Tanaka, Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, 1988, edited by J. Muller and J. L. Olsen [Physica C**153-155**, 964 (1988)].

[30] K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L1228 (1987).

[31] N. Watanabe, H. Asano, H. Isawa, S. Sato, H. Murata, K. Kurahashi, S. Tomiyoshi, F. Izumi, and K. Inoue, Jpn. J. Appl. Phys. **26**, 1164 (1987).

[32] JCPDS Powder Diffraction File, No. 30-123, International Centre for Diffraction Data, Swarthmore, 1980 (unpublished); R. Kipka and H. Muller-Buschbaumm, Z. Naturforsch. **32b**, 121 (1977).

[33] R. J. Hill and C. J. Howard, J. Appl. Crystallogr. **20**, 467 (1987).

[34] F. Izumi, H. Asano, H. Murata, and N. Watanabe, Jpn. J. Appl. Phys. **20**, 411 (1987).

[35] *International Tables for Crystallography, Vol. A,* edited by T. Hahn (Reidel, Dordrecht, 1983).

[36] JCPDS Powder Diffraction File No. 30-487, International Centre for Diffraction Data, Swarthmore, 1980 (unpublished).

[37] JCPDS Powder Diffraction File No. 5-0661, International Centre for Diffraction Data, Swarthmore, 1985 (unpublished).

[38] I. D. Brown and D. Altermatt, Acta. Crystallogr. B **41**, 244 (1985).

[39] R. D. Shannon, Acta Crystallogr. A **32**, 751 (1976).

[40] I. Nakai and F. Izumi, Kotai Butsuri **22**, 989 (1987).

[41] J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, Phys. Rev. B **36**, 5731 (1987).

[42] T. Wada, N. Suzuki, A. Maeda, T. Yabe, S. Uchida, K. Uchinokura, and S. Tanaka, Phys. Rev. B **39**, 9126 (1989).

[43] H. W. Zandbergen, W. T. Fu, and L. J. de Jongh Physica C **156**, 307 (1988).

[44] I. Nakai, K. Imai, T. Kawashima, and R. Yoshizaki, Jpn. J. Appl. Phys. **26**, L1244 (1987).

[45] K. Suzuki, M. Ichihara, S. Takeuchi, H. Takeya, and H. Takei, Jpn. J. Appl. Phys. **27**, L814 (1988).

[46] T. Iwazumi, I. Nakai, M. Izumi, H. Oyanagi, H. Sawada, H. Ikeda, Y. Saito, Y. Abe, K. Takita, and R. Yoshizaki, Solid State Commun. **65**, 213 (1987).

[47] H. Kuroda, N. Kosugi, and H. Tajima, National Laboratory for High Energy Physics, Tsukuba, Photon Factory Activity Report No. 5, 1987 (unpublished).

[48] J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[49] X. Oudet, Ann. Chim. Fr. **8**, 483 (1983).

[50] X. Oudet, Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, 1988, edited by J. Muller and J. L. Olsen [Physica C **153-155**, 1189 (1988)].

[51] D. B. Mitzi, A. F. Marshall, J. Z. Sun, D. J. Webb, M. R. Beasley, T. H. Geballe, and A. Kapitulnik (unpublished).

[52] J. B. Torrance, Y. Tokura, A. I. Nazzal, and S. S. P. Parkin, Phys. Rev. Lett. **60**, 542 (1988).

[53] H. Alloul, P. Mendels, G. Collin, and P. Monod (unpublished).

[54] T. Imai, T. Shimizu, H. Yasuoka, Y. Ueda, and K. Kosuge, J. Phys. Soc, Jpn. **57**, 1771 (1988).

[55] I. Nakai, S. Sueno, F. P. Okamura, and A. Ono, Jpn. J. Appl. Phys. **26**, L788 (1987).

[56] M. Onoda, S. Shamoto, M. Sato, and S. Hosoya, Jpn. J. Appl. Phys. **26**, L876 (1987).

[57] F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, Y. Uchida, and N. Watanabe, Jpn. J. Appl. Phys. **26**, L1214 (1987).

[58] Y. Ren, H. B. Tang, Q. W. Yan, P. L. Zhang, Y. L. Liu, C. G. Cui, T. S. Ning, Z. Zhang, and S. W. Niu, Phys. Rev. B **38**, 11 861 (1988).