Pressure effects on the structural phase transitions and superconductivity of $La_{2-x}Ba_xCuO_4$ ($x=0.125$)

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Neutron-diffraction experiments have been performed to study the effects of hydrostatic pressure on the structural phase transitions of $La_{2-x}Ba_xCuO_4$ with $x=0.125$. The phase transition to the low-temperature tetragonal (LTT) structure is greatly suppressed by the application of pressure. The LTT transition temperature, observed at around 80 K at ambient pressure, decreases at the rate of about -135 K/GPa, and this LTT phase disappears under a pressure of around 0.6 GPa. The superconducting properties of this compound under high pressure have also been investigated in detail by measurments of the ac magnetic susceptibility. The bulk superconducting transition temperature T_c remains constant at pressures of up to 0.5 GPa, and then increases with pressure at the rate of 10 K/GPa up to about 15 K at 1.5 GPa. From these results it is concluded that there is a clear correlation between the disappearance of the LTT phase and the enhancement of superconductivity. This conclusion supports earlier suggestions that there is a strong relationship between the crystal structure and superconductivity and that, in particular, the LTT phase is detrimental to the superconductivity in the $La_{2-x}Ba_xCuO_4$ system.

I. INTRODUCTION

The $La_{2-x}Ba_xCuO_4$ system has been extensively studied since the discovery of its high-T_c superconductivity.[1] In recent years careful investigations of this system revealed an anomalous x dependence of the superconducting transition temperature.[2,3] It has now been established that there exists a sharp dip in the T_c-x phase diagram, indicating that the bulk superconductivity is greatly suppressed in a narrow range of x around 0.125. Subsequent studies of the crystal structure clarified that this system undergoes complicated structural phase transitions. In the compound with $x=0.125$, a phase transition from a high-temperature tetragonal (HTT; space group $I4/mmm$) to a low-temperature orthorhombic phase (LTO; space group $Cmca$, or $Bmab$: the nonstandard setting of $Cmca$) takes place at about 200 K. A further transition to a low-temperature tetragonal phase (LTT; space group $P4_2/ncm$) occurs at around 80 K.[4] This study indicated that the LTT phase coexists with the LTO phase at least down to 10 K. Since the structural transition to the LTT phase appears near the Ba concentration where the dip in the T_c-x phase diagram occurs, it has been suggested that there is a correlation between the appearance of the LTT phase and the suppression of the superconductivity.[4]

Various efforts have been made to elucidate the relationship between the suppression of T_c and the onset of the structural transition to LTT. The substitution of Th^{4+} for La^{3+} in $La_{2-x}Ba_xCuO_4$ indicated that the anomalous behavior in the T_c of this system is characterized by the hole density of $\frac{1}{8}$ per Cu atom which is coupled with the LTT phase.[5] Another study showed that the Nd^{3+} substitution for La^{3+} in $La_{2-x}Sr_xCuO_4$ induces a different orthorhombic phase (LTO2; space group $Pccn$), and that the superconductivity is modified by this new structural transition.[6] These previous studies have indicated that a *small* dip in T_c can be observed even when structural transitions are not involved, and that the reduction of T_c is related to the instability of the CuO_6 octahedra. In the case of $La_{2-x}Ba_xCuO_4$ near $x=\frac{1}{8}$ this instability of the CuO_6 octahedra would be strong enough to drive the transition to the LTT phase and to significantly reduce T_c.

Recent high-pressure studies on $La_{2-x}Ba_xCuO_4$ have suggested that T_c of the system is restored when the LTT phase is suppressed under high pressure.[7] In this study, however, the suppression of the LTT phase was suggested from the observation of anomalies in the resistivity, and this suppression has not been observed directly. The direct observation of the structural phase transitions can be achieved using diffraction techniques.

In order to clarify the effects of pressure on the structural transitions and superconductivity of $La_{2-x}Ba_xCuO_4$ and, in particular, to explore the suggestion that the superconductivity in this system is recovered by the suppression of the LTT phase,[7] we have performed neutron-diffraction experiments and ac-susceptibility measurements on powder specimens with $x=0.125$. The neutron-diffraction measurements have been made at ambient pressure, and at 0.35 and 0.7 GPa. The magnetic susceptibility has been measured in detail under pressures up to 2.5 GPa. These measurements have directly shown that when the LTT phase is suppressed under high pressure, the transition temperature to the bulk superconductivity increases up to about 15 K. In this paper our measurements are described and the results are discussed.

II. EXPERIMENTAL

Specimens of $La_{2-x}Ba_xCuO_4$ with $x=0.125$ were prepared by the solid-state reaction of a mixture of predried La_2O_3, $BaCO_3$, and CuO. The powders were pressed into pellets, calcined at 900 °C for 24 h and then sintered at 1050 °C in air for several days with frequent grindings. The samples were finally annealed at 500 °C for 24 h in flowing O_2 gas.

The neutron-diffraction experiments were performed using the high-resolution powder diffractometer installed at the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory. The (115) reflection of Ge was used as the monochromator, and the neutron wavelength was 1.4000 Å. This instrument has Soller-slit collimators of 12′ and 20′ located before and after the monochromator crystal, and a collimator of 6′ at the detector position. For the high-pressure experiments a clamp-type cell assembly, specially designed for neutron-scattering experiments,[8] was used with a sapphire piston-cylinder. The pressure in the experiments was determined by the calibration curve shown in Ref. 8. As the pressure transmitting medium, 3M Fluorinert liquid was used. The diffraction experiments under pressures were performed at 0.35 and 0.7 GPa. These measurements were carried out at temperatures down to 15 K using a standard closed-cycle refrigerator. The amount of the powder specimen was limited by the size of the pressure cell, and thus the effective volume of the sample in the measurements was about 0.35 cm^3. This limitation compounded with the high background scattering from the pressure cell made the diffraction measurements at high pressures very difficult. For this reason the measurements at ambient pressure was performed with a larger amount of sample (~ 3 cm^3) using a vanadium holder.

The superconducting transition temperature T_c for this compound was examined under pressures of up to 2.5 GPa by the ac induction method. The sample used for these measurements was not the same one used in the neutron-diffraction experiments but was taken from the same batch. The ac measuring frequency was 353 Hz and driving field was 0.83 Oe. The pressure was generated by a clamp-type piston cylinder apparatus with a Teflon cell. 3M Flourinert liquid was also used as the pressure transmitting medium. In these measurements the sample was cooled down to 2 K by pumping liquid ^{4}He. The temperature was measured using a C.G.R. (Carbon glass resistance) thermometer.

III. RESULTS AND DISCUSSION

In Fig. 1, neutron-diffraction data of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) at ambient pressure are shown for the (220) reflection of the high-temperature tetragonal phase (HTT; $I4/mmm$). As the temperature is lowered from room temperature, this single peak starts to split below about 202 K, indicating the transition to the low-temperature orthorhombic structure (LTO; $Cmca$). These diffraction peaks are indexed as (004) and (400) of the LTO structure. This splitting becomes larger when the temperature is decreased. Below around 78 K, a central component appears, which indicates the transition to another low-temperature phase. The transition temperatures observed are in good agreement with those reported in the literature for this system.[4] At 70 K this peak becomes fairly sharp, and at 15 K it can be regarded almost as a single peak (within the instrumental resolution of 0.2°). Thus the sample in the present experiment shows an almost complete transition to a low-temperature phase, which is tetragonal (LTT; $P4_2/ncm$) within the experimental accuracy. This diffraction peak can be indexed as (400) of the LTT structure. (This low-temperature phase could also be, at least partially, ortho-

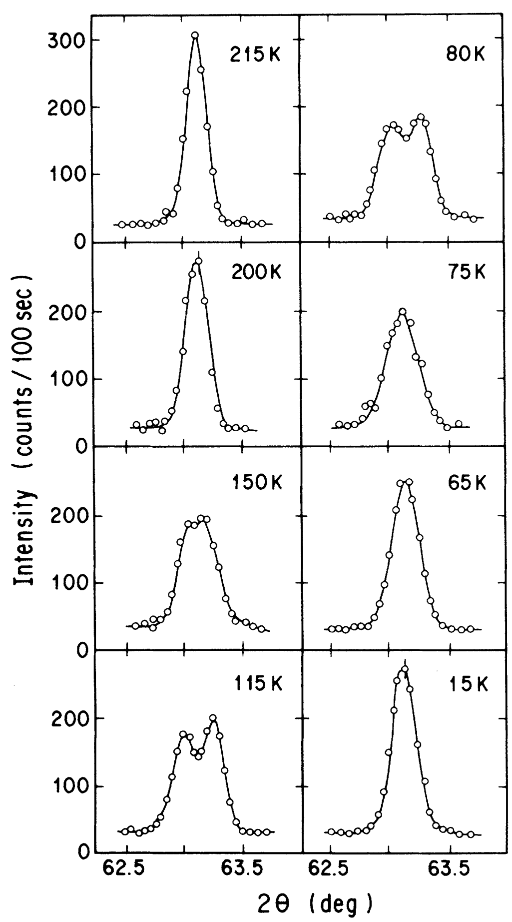

FIG. 1. Temperature dependence of the $(220)_{HTT}$ reflection of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) at ambient pressure. The system undergoes a HTT-LTO phase transition at about 202 K, and then a LTO-LTT phase transition at around 78 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2°.

rhombic *Pccn*. However, if this is the case, the orthorhombicity is at least an order of magnitude smaller than that of the LTO structure.[9])

Figure 2 displays the temperature dependence of the same reflection under 0.35 GPa. The broadening of this peak, which shows the transition from the HTT to the LTO phase, starts at around 190 K and it continues down to around 30 K. Below this temperature a central component appears but, unlike the ambient pressure case, this peak remains broad even at 15 K. This result indicates that although the transition to the LTT phase takes place at around 30 K, the phase transition may not be complete even at 15 K, and the system under pressure perhaps contains a small fraction of an orthorhombic phase.

Diffraction data of the same reflection under 0.7 GPa are shown in Fig. 3. In this case the transition temperature to the LTO phase, as estimated by the broadening of the HTT (200) reflection, is about 183 K. When the temperature is lowered, the split of the peak becomes clearer. Under this pressure, however, the appearance of a central component is not evident down to 15 K. The transition to the LTT phase, thus, seems to have disappeared under the pressure of 0.7 GPa.

These results show that the effect of pressure on the LTO-LTT transition is quite observable and that the orthorhombic phase is stabilized under high pressure. Furthermore, the results indicate that the temperature where the resistivity anomaly or other transport anomalies take place ($\sim$60 K at ambient pressure and dependent on pressure rather moderately)[7,10] may not be the same temperature where the structural phase transition occurs. The anomalies in the transport phenomena might be caused by some other electronic instability. A similar decoupling of the resistivity anomaly and the structure change has been reported in the experiments on the $(La_{1-x}Ba_{x-y}Sr_y)_2CuO_4$ system.[11] In order to clarify this suggestion, however, more detailed and systematic studies will be required.

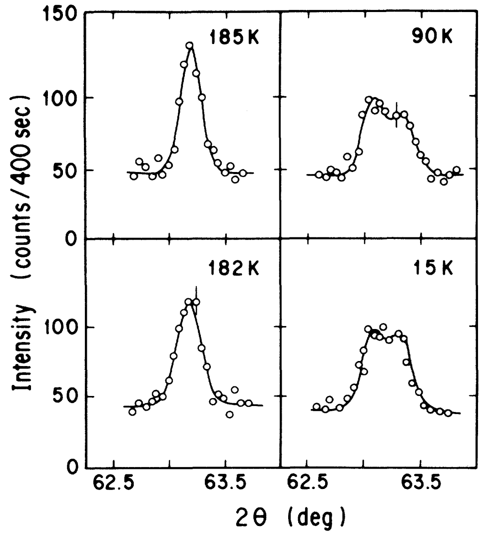

FIG. 3. Temperature dependence of the $(220)_{HTT}$ reflection of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) under 0.7 GPa. The system undergoes a HTT-LTO phase transition at about 183 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2°.

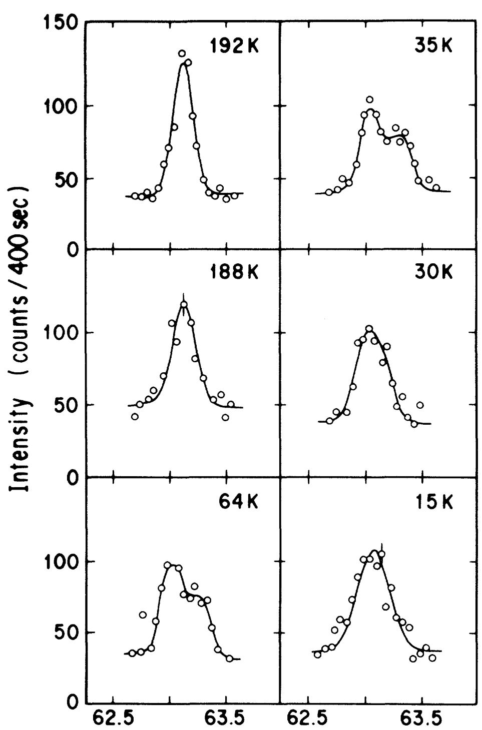

FIG. 2. Temperature dependence of the $(220)_{HTT}$ reflection of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) under 0.35 GPa. The system undergoes a HTT-LTO phase transition at about 190 K, and then a LTO-LTT phase transition at around 30 K. The data are fitted with one or two Gaussians. The bars show typical errors in the measurements. The instrumental resolution is 0.2°.

Although neutron-diffraction measurements have been performed at only three pressures (0, 0.35, and 0.7 GPa), the temperature-pressure phase diagram on the crystal structure of the present system can be sketched as shown in Fig. 4. The pressure coefficient of the transition temperature for the HTT-LTO phase transition dT_1/dP is -28 K (± 6 K)/GPa, and that of the LTO-LTT transition dT_2/dP is -135 K (± 10 K)/GPa. The value dT_1/dP is rather small, and is just about $\frac{1}{4}$ of that of the $(La,Sr)_2CuO_4$ system obtained from x-ray-diffraction experiments.[12] The value of dT_2/dP, on the other hand, is rather large. From this figure the pressure that causes the LTT phase to disappear can be extrapolated to about 0.6 GPa.

Figure 5 shows the magnetic susceptibility of the sample for several pressures as a function of temperature. As reported in previous investigations,[2] the diamagnetic susceptibility shows a two-step superconducting transition. The first component is quite small at ambient pressure, but it can be observed at about 30 K. (In the resistivity measurements, on the other hand, two anomalies which

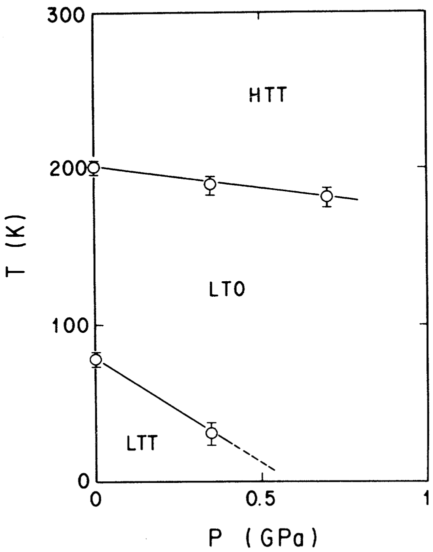

FIG. 4. Temperature-pressure phase diagram on the cyrstal structure for $La_{2-x}Ba_xCuO_4$ ($x=0.125$). HTT, LTO, and LTT denote high-temperature tetragonal, low-temperature orthorhombic, and low-temperature tetragonal, respectively.

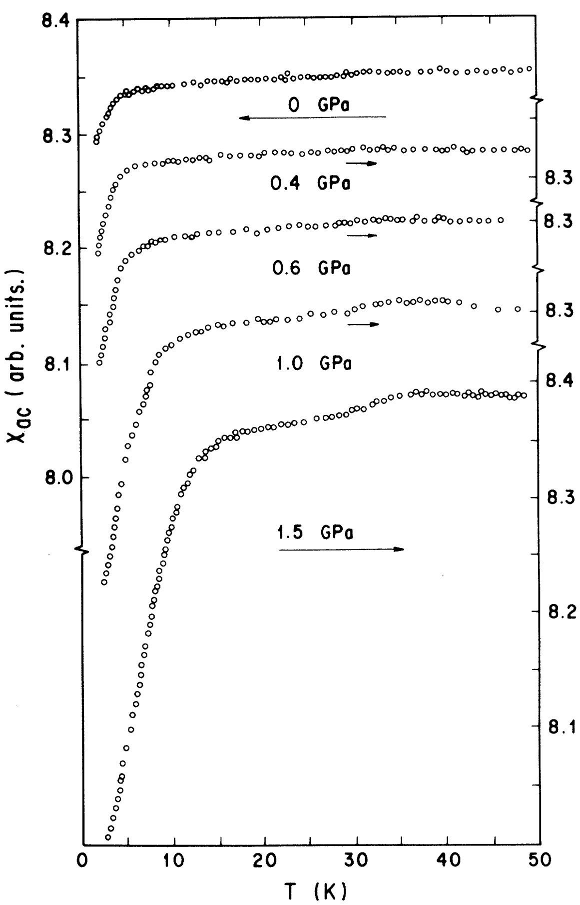

FIG. 5. Temperature dependence of the magnetic susceptibility of $La_{2-x}Ba_xCuO_4$ ($x=0.125$) under high pressures.

correspond with the two-step transition are clear.[2,7]) This component may be a trace of superconductivity which is due to the presence of a very small fraction of the LTO phase. The volume of this phase at ambient pressure would be too small to be observed in the diffraction data at low-temperatures (Fig. 1). With increasing pressure, this transition temperature increases and the volume fraction of this superconductivity also increases slightly. The second component is a bulk transition observed at about 4 K. As the magnetic susceptibility shows, however, the volume fraction of this bulk superconductivity is also small—a few percent—at ambient pressure. Under pressures up to 0.5 GPa, the behavior of this susceptibility does not significantly change: the superconducting transition temperature remains almost constant. However, above 0.6 GPa the bulk superconductivity is greatly enhanced. Both T_c and the volume fraction of the superconductivity increase significantly with pressure up to about 1.5 GPa, the pressure at which these characteristic values seem to saturate.

The pressure dependence of these superconducting transition temperatures is shown in Fig. 6. Here, the higher transition temperature is defined as the temperature where the signal deviates from the normal-state value, and the bulk T_c at lower temperatures is defined by the temperature at which the susceptibility deviates from the signal of the superconducting state at the higher temperatures. The transition temperature for the trace of the superconductivity at higher temperatures increases at the rate of 7($\pm$2) K/GPa, and saturates at around 2 GPa.

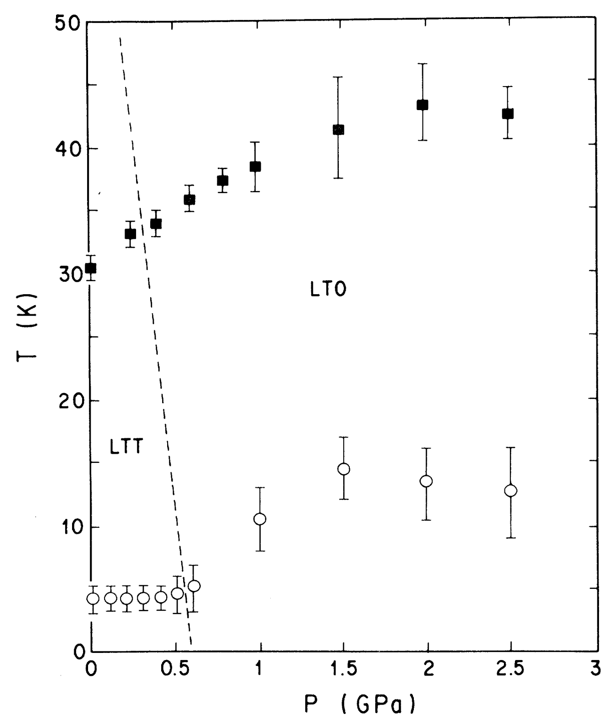

FIG. 6. Pressure dependence of the superconducting transitions for $La_{2-x}Ba_xCuO_4$ ($x=0.125$). The solid squares show the transition temperature of the trace of superconductivity at higher temperatures. The open circles show the transition temperature of the bulk superconductivity at lower temperatures.

On the other hand, the transition to the bulk superconductivity does not change up to 0.5 GPa; above this pressure T_c increases significantly. The pressure coefficient dT_c/dP is 10($\pm$2) K/GPa. At around 1.5 GPa the transition temperature seems to saturate, and then decrease somewhat. In the figure the LTO-LTT transition temperature is shown as a broken line. From this figure, it is apparent that the bulk T_c is greatly enhanced when the LTT phase disappears under high pressure. These results clearly show a correlation between the suppression of the bulk superconductivity and the structural phase transition to the LTT phase. The pressure derivatives of T_c mentioned above are two or three times larger than those for the Sr-substituted system.[13] Since the Sr substitution does not induce the transition to the LTT phase, there should be no suppression of T_c. Thus, the large pressure derivatives in the present system may arise from the restoration of the superconductivity due to the depression of the LTT phase under pressure. The value of 10 K/GPa is somewhat larger than that in other experiments on this system.[14] This difference would be due to the fact that the pressure effects on T_c appear only above 0.5 GPa as clarified in our detailed study.

As mentioned above, the superconducting transition at higher temperatures saturates at pressures above around 1.5 GPa. Similar behavior in T_c under high pressure has been observed also in some other oxide superconductors at certain pressures.[15,16] The saturation in T_c observed here, thus, suggests that the system attains an overdoped state with the increase in the hole density under high pressure.[17] The bulk superconductivity, moreover, remains around 15 K even at the highest pressure applied in this experiment (2.5 GPa). That is, the bulk T_c under pressure does not reach 30 K (T_c in the LTO phase of the 30-K class superconductors). This observation suggests that the electronic structure of the orthorhombic phase stabilized under high pressure is still complicated in this particular compound with the hole density of $\frac{1}{8}$. Possibly the density of states at the Fermi level (i.e., the density of holes which are responsible for the superconductivity) may be lower than that of the LTO phase in the 30-K class superconductors. The saturation of T_c in this system under pressure has also been reported.[7] Recently the same group suggested that impurity scattering may be the origin of the relatively low T_c under high pressure in this system.[18]

Another possibility for the saturation of the bulk T_c under pressure is as follows. In the experiments for the $La_{1.88-x}Nd_xSr_{0.12}CuO_4$ system,[6] the Nd substitution induces the structural change from the LTO to another orthorhombic *Pccn*, and then to the LTT phase. Furthermore, in this structure sequence T_c decreases systematically. The transition temperature of around 15 K, observed in the orthorhombic *Pccn* phase of that system, is close to the T_c obtained in the present high pressure experiment. Hence, if the same relation between the structure and T_c exists in the present system, it is possible that the structure induced under high pressure may be *Pccn*. Although within experimental uncertainty we cannot determine that this pressure-induced phase is orthorhombic *Pccn*, it is likely that this phase has some intermediate orthorhombic structure different from LTO (*Cmca*). In order to determine the exact structure of this phase, more detailed experiments under high pressures will be necessary.

The pressure effects on the crystal structure would be related to the contraction of the lattice. As was observed in the experiments on $(La,Ba)_2CuO_4$, the substitution of La with larger Ba expands the LaO/BaO polyhedra and contracts the CuO_6 octahedra. With these changes, the compressive stress exerted on the CuO_6 octahedra is reduced, and hence the crystal structure changes from LTO toward HTT.[19] Between these phases LTT appears sharply at around $x=0.125$. Under high pressure the whole crystal is contracted; accordingly, the correspondence with the case of the Ba substitution is not straightforward. However, if the effects of the contraction of the CuO_6 octahedra is dominant in the LTO phase, the stress on these octahedra is reduced, and the HTT phase may be stabilized. That is, the temperature for the HTT-LTO transition T_1 decreases under high pressure. The effect of pressure on the LTT phase might be explained similarly. If the CuO_6 octahedra is contracted effectively and the stress on them is decreased in the LTT phase also, the LTT structure may be unstabilized and consequently the orthorhombic structure would be stabilized. A similar effect of the lattice contraction on the LTT structure was observed in the Sr-substituted $(La,Ba)_2CuO_4$ system.[11] By the substitution of smaller Sr ions for Ba, the lattice is contracted, and the structural change to the LTO phase is induced. Furthermore, T_c increases also in this system.

In summary, the effects of pressure on the structural phase transition and on the superconductivity of $La_{2-x}Ba_xCuO_4$ with $x=0.125$ have been investigated. Neutron-diffraction experiments directly show that the structural transition temperatures, both HTT-LTO and LTO-LTT, decrease with pressure. The suppression of the LTT phase under a pressure of about 0.6 GPa is particularly noted. The pressure effects on the superconductivity are rather complicated, and a two-step transition to the superconducting states exists even under high pressures. The bulk superconductivity is greatly enhanced when the LTT phase disappears under high pressure. These results support earlier suggestions that there is a strong correlation between T_c and the crystal structure in this system.

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