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Effects of doping on phonon Raman scattering in the Bi-based 2212 system

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The polycrystalline samples of $Bi_2Sr_2CaCu_2O_y$ (Bi2212) with different oxygen content, $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ and $Bi_2Sr_{2-x}La_xCaCu_2O_y$, have been characterized by x-ray-diffraction and Raman-scattering measurements. It is found that the c-axis parameter decreases with increasing doping concentration (Pr or La) or oxygen content. The softening of the $O(2)_{\mathrm{Sr}}\,A_g$ mode corresponds to the decrease of the c-axis parameter. The effect of Pr substitution for Ca on this mode is smaller than that of La substitution for Sr. The shift of the $O(1)_{\mathrm{Cu}}\ B_{1g}$ mode is related to the ionic size of the doping element. The $O(3)_{\mathrm{Bi}}\,A_g$ mode does not exhibit remarkable frequency shift since the Bi-$O(3)$-Bi force constant nearly remains unchanged upon doping. The effect of oxygen content on the $O(2)_{\mathrm{Sr}}\,A_g$ mode in the Bi2212 system is in contrast to that on the corresponding $O(4)_{\mathrm{Ba}}\,A_g$ mode in the Y123 system. Change in valence is the dominating effect causing the frequency shift of the $O(2)_{\mathrm{Sr}}\ A_g$ mode. [S0163-1829(98)02433-3]

I. INTRODUCTION

Cation substitution in cuprate oxides has provided valuable information for understanding the mechanism of high-T_c superconductivity. Most important is the possibility of substantially altering the effective copper valence and the carrier concentration, which have been shown to be intimately linked with T_c. However, cation substitution leads to a change of local structure. Determination of the location of doped holes is important for the mechanism of the superconductivity. X-ray absorption measures the polarization direction of the hole orbital,[1] but cannot determine the location directly, while Raman-scattering experiments can determine the location from the shift of the energy and the scattering intensity of the vibrational mode of oxygen atoms on each site, and the frequencies of some phonon modes are sensitive to the relevant bond lengths,[2] which are changed by the cation substitution.

Up to now, it had been controversial to assign the experimentally observed phonon modes of 460 and 630 cm^{-1} to vibrational eigenmodes of the lattice for $Bi_2Sr_2CaCu_2O_8$. There exist the following assignments. One group[3] assigned the intense 460 and 630 cm^{-1} phonons to the in-phase $O_{\mathrm{Cu}}\,A_g$ mode and the $O_{\mathrm{Sr}}\,A_g$ mode, respectively; the other group[4–6] assigned the low-frequency phonon to the $O_{\mathrm{Sr}}\,A_g$ mode and the high-frequency phonon to the $O_{\mathrm{Bi}}\,A_g$ mode; and the reversed assignment was also reported for the two modes.[7–9] Raman scattering was widely studied[3,4,8] for the sample $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$; the observed changes in phonon frequencies with increasing Y content were mainly explained in terms of a combination of an internal-pressure effect induced by the change in the average Ca/Y radius and a charge-transfer effect induced by the aliovalent substitution of Y^{+3} for Ca^{+2}.[8] However, aliovalent cation substitution is more complicated in a Bi-based system than isovalent cation substitution in Y-based superconductors because aliovalent cation substitution leads to an increase of oxygen content incorporated into the double Bi-O layers, resulting in a remarkable decrease of the c-axis parameter.[10] Therefore, the effect of oxygen-content change induced by aliovalent cation substitution on the Raman scattering should be considered. In order to discuss the effect of cation substitution and oxygen content on the Raman scattering and the assignment of 460 and 630 cm^{-1} phonons, here we investigate the Raman spectra of Bi2212 samples of La-doped $Bi_2Sr_{2-x}La_xCaCu_2O_8$, Pr-doped $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_8$, and pure Bi2212 with different oxygen content.

II. EXPERIMENT

The samples of $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_{2-x}La_xCaCu_2O_y$, and $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ were prepared by the conventional solid-state reaction method. High-purity powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Pr_6O_{11}, La_2O_3, and CuO were ground and sintered in air at 850 °C for 12 h, then reground and sintered at the same condition for two more

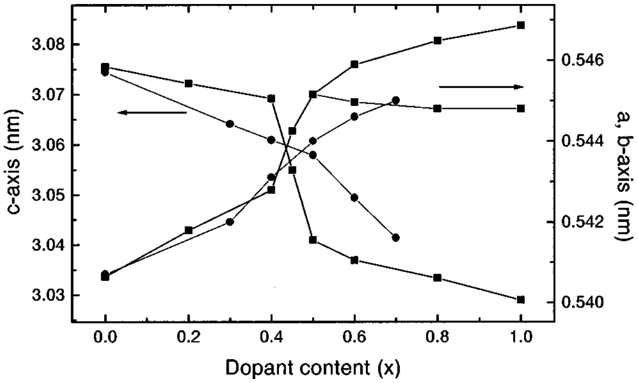

FIG. 1. Lattice parameters for $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ (squares) and $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ (circles) vs the dopant (Pr and La) content.

times. Finally, they were ground again and pressed into pellets and calcined at a temperature between 850 and 930 °C for 72 h, and cooled to room temperature by an air furnace. In order to obtain the samples with different oxygen content, the as-prepared samples of $Bi_2Sr_2CaCu_2O_8$ were annealed at 500 °C in the nitrogen and oxygen flow, respectively. The obtained samples were characterized by x-ray powder diffraction with Cu $K\alpha$ radiation. Lattice parameters for single-phase materials were refined using the Bragg peaks over the θ range. Raman spectra were measured on a Spex-1403 Raman spectrophotometer using a backscattering technique. The 5145-Å line from the argon ion laser was used as an excitation light source. All measurements were made at room temperature, and each spectrum shown was taken with refocusing on at least two different spots to assure reproducibility. The resolution of Raman spectra was 3 cm^{-1} and the laser spot size on the samples was about 1 mm.

III. RESULTS AND DISCUSSION

X-ray-diffraction patterns can be indexed with a tetragonal lattice for the samples of $Bi_2Sr_2CaCu_2O_8$, $Bi_2Sr_{2-x}La_xCaCu_2O_8$, and $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ ($x \leqslant 0.5$) systems, while the samples of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ ($x > 0.5$) were indexed with an orthorhombic lattice due to a splitting of the (200) peak observed in x-ray diffraction. A similar phenomenon has been observed in the Y-doped Bi2212 system. It suggests that the samples are a single Bi-2212 phase. The dopant content dependence of lattice parameters is plotted in Fig. 1. It shows a monotonous decrease in the c axis with substituting both Pr^{3+} for Ca^{2+} and La^{3+} for Sr^{2+}, but the a-axis parameter shows an opposite trend. The length of the a axis is considered to be controlled by the in-plane Cu-O bond distance, which is closely related to the carrier concentration. The increase in the a-axis parameter arises from the decrease of hole concentration that weakens the Cu-O bonding when dopant content is increased. It should be expected that the c-axis lattice parameter slightly increases when Ca is replaced by Pr^{3+} ($r_{eff} = 1.126$ Å), since Ca^{2+} has only an ionic radius of $r_{eff} = 1.12$ Å. But the c-axis parameter decreases by 0.047 nm on going from $Bi_2Sr_2CaCu_2O_{8+\delta}$ to the $Bi_2Sr_2PrCu_2O_{8+\delta}$. It could arise from the increase of excess oxygen incorporated between the Bi_2O_2 double layers induced by aliovalent substitution. One possible explanation[11] for the relation between the c-axis length and oxygen content is that extra oxygen incorporated into the BiO layers leads to a change of the orientation of the Bi^{3+} lone pair, which causes a decrease of the distance of the two adjacent BiO layers. Another explanation[12] is that the net positive charge and hence the repulsion between the Bi_2O_2 layers decrease, causing the slab sequence, SrO-BiO-BiO-SrO, to shrink. The c-axis parameters are 3.0694 and 3.0817 nm for the pure Bi2212 samples annealed at 500 °C in O_2 and N_2, respectively. It directly indicates that reduction of the pure Bi2212 sample leads to an increase of the c-axis lattice parameter, which is consistent with the previous reports.[13,14]

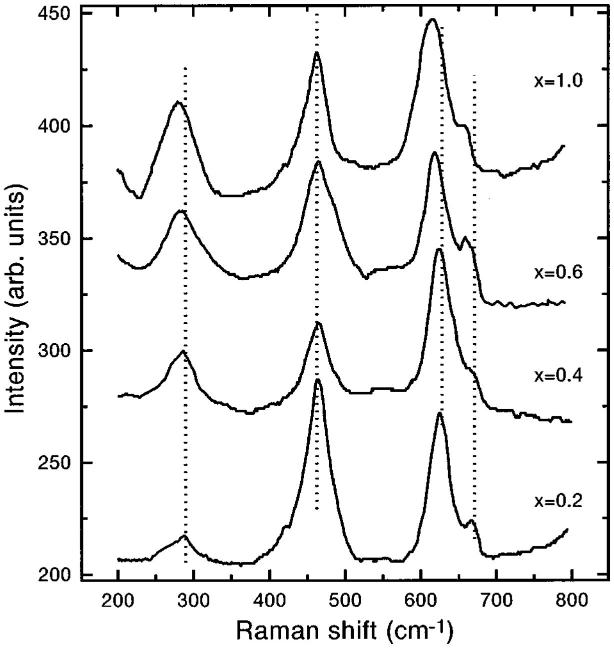

FIG. 2. Room-temperature Raman spectra for the samples of the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ system.

Figure 2 shows the Raman spectra of the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ ($x = 0.2$, 0.4, 0.6, and 1.0) in the frequency range of 200–800 cm^{-1} at room temperature. In Fig. 2, four Raman modes at 290, 464, 630, and 660 cm^{-1} were clearly observed within this frequency range. The 290- and 660-cm^{-1} modes have been identically assigned to the B_{1g} mode of vibration of $O(1)_{Cu}$ atoms along the c axis and to the vibration of extra oxygen within the Bi_2O_2 layers, respectively. The mode at 464 cm^{-1} remains essentially constant with increasing Pr content, while the 630-cm^{-1} mode changes significantly as a function of Pr concentration, and softens at about 12 cm^{-1} in going from $Bi_2Sr_2CaCu_2O_{8+\delta}$ to $Bi_2Sr_2PrCu_2O_{8+\delta}$.

The B_{1g} $O(1)_{Cu}$ phonon is directly related to the atoms in the conducting CuO_2 planes. Its intensity increases with decreasing metallicity (increasing x) as seen in Fig. 2. The similar behavior has also been observed for the corresponding vibrations related to the CuO_2 planes in $YBa_2Cu_3O_{6+\delta}$ (Ref. 15) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$.[8] These effects are direct manifestations of the decrease in the number of charge carriers induced by doping. The decrease of holes induced by doping leads to a reduced metallic screening both within and between adjacent CuO_2 planes, leading to larger CuO_2 bond

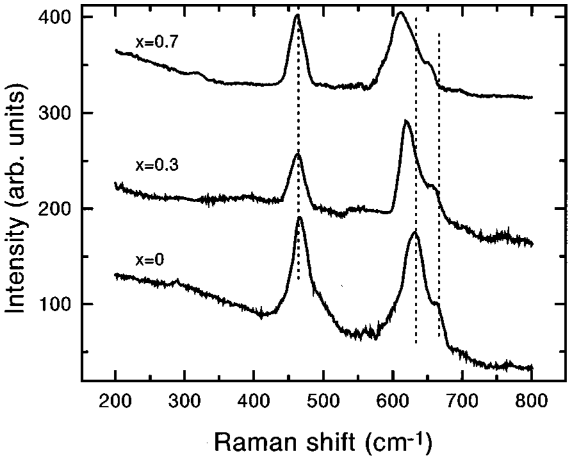

FIG. 3. Room-temperature Raman spectra for the samples of the $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ system.

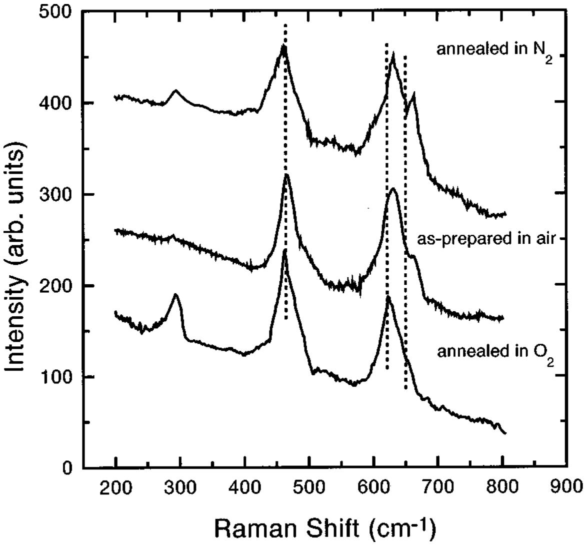

FIG. 4. Room-temperature Raman spectra of the as-prepared sample in air and the annealed samples at 500 °C in flowing O_2 and N_2, respectively, for the $Bi_2Sr_2CaCu_2O_{8+\delta}$ system.

polarizabilities and phonon intensities, and to a weaker electronic Raman background. The $O(1)_{\rm Cu}$ B_{1g} phonon softens by about 10 cm^{-1} when the Pr content increases from $x=0$ to 1. The shift of this phonon frequency has been believed to originate mainly from variation of the average ionic radius of Y (Ca) sites induced by R doping in Y123, Y124, and Y-doped Bi2212 systems.[8,16–18] Larger R ions lead to an elongation of the $O(1)_{\rm Cu}$-R bonds, smaller force constant, and a lower phonon frequency. It is found that rate of the Raman shift induced by variation of ionic radius of the Ca (Pr) sites in the Pr-doped Bi2212 system is nearly the same as that in Y123, Y124, and Y-doped Bi2212 phases.[8,16–18]

Raman spectra of the samples $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ $(x=0,0.3,$ and $0.7)$ are shown in Fig. 3. When compared with Raman spectra of the Pr-doped Bi2212 system, the B_{1g} $O(1)_{\rm Cu}$ phonon is not observed in Fig. 3. As discussed above, the intensity of the $O(1)_{\rm Cu}$ B_g mode increases with decreasing carrier concentration. La^{3+} substitution on Sr^{2+} also should result in a decrease of hole carrier, which is confirmed by resistivity measurement. The metal-insulator transition takes place at $x=0.6$ in the $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ system. It suggests that the effect on the $O(1)_{\rm Cu}$ B_g mode also could be related to the doping site. The phonon mode of 630 cm^{-1} apparently shifts to low frequency with increasing La.

Figure 4 shows the Raman spectra of an as-prepared sample and the annealed samples at 500 °C in O_2 and N_2 for the pure Bi2212, respectively. Three main peaks are observed in the spectra. In the three spectra, the two modes of low frequency nearly remain constant, while the intensity of the $O(1)_{\rm Cu}$ B_{1g} mode apparently decreases for the sample annealed in N_2 relative to the sample annealed in O_2. It indicates that the effect of oxygen content on the Raman shift of the $O(1)_{\rm Cu}$ B_{1g} mode is small in the Bi2212 system, which is consistent with that in the Y123 system, in which the frequency of the B_{1g} $O_{\rm Cu}$ mode increases only about 5 cm^{-1} on going from the superconducting $YBa_2Cu_3O_7$ to the nonsuperconducting $YBa_2Cu_3O_6$.[19] The frequency of the mode at about 630 cm^{-1} is 9 cm^{-1} lower for the sample annealed in O_2 rather than in N_2. It suggests that the increase of the excess oxygen incorporated into the Bi_2O_2 layers leads to a down-shift of the mode at about 630 cm^{-1}, which may be the main reason why Pr^{+3} substitution for the smaller Ca^{+2} leads to softening of this mode.

The Raman shifts and peak widths of the vibration modes were determined by fitting the peaks in the experimental spectra with distributions of Gaussian form since the 630- and 660-cm^{-1} phonons are not resolved by the Rayleigh criterion. The results in Table I were deduced by fitting the Raman data as shown in Figs. 2, 3, and 4. Figure 5 shows that the Raman frequency of the mode at about 630 cm^{-1} changes as a function of dopant (Pr and La) content and the c-axis parameter, respectively. Figure 5 indicates that the frequency of this mode decreases monotonously with increasing the dopant concentration and oxygen content. It is found that the effect of La substitution on this mode is larger than that of Pr substitution. Both Pr and La substitutions lead to a decrease in frequency of this mode although Pr^{3+} was substituted for a smaller Ca^{2+} and La^{3+} substituted for a larger Sr^{2+}. Therefore, the effect of La and Pr doping on 630 cm^{-1} cannot be explained only by average ionic radius. In Y123 system, the effect of rare-earth metal substitution for Y on the Raman shift of phonon modes has been well explained by average ionic radius.[2,16] In the case of Bi-based superconductors, the doping is generally carried out with an aliovalent element, then the aliovalent substitution leads to a change of oxygen content. Therefore, the oxygen content is an important factor causing the frequency shift.

As mentioned above, it is controversial to assign the 464- and 630-cm^{-1} mode. Kakihana *et al.* have pointed out that[8] the assignment of the 464-cm^{-1} phonon to a CuO_2-plane vibration is not correct. We agree with the assignment proposed by Kakihana *et al.*,[8] that is, the assignment of the 630-cm^{-1} phonon to symmetric A_{1g} vibrations of $O(2)_{\rm Sr}$ along the c axis, together with the assignment of the 464-cm^{-1} mode to $O(3)_{\rm Bi}$ A_g along the a-axis vibration. The reasons why this assignment is more likely an alternative rather than a reversed assignment made in several previous reports[4–6] are the following. (1) The effect of Pr substitution for Ca on the 630 cm^{-1} mode is smaller than that of La substitution for Sr, whereas the mode at 464 cm^{-1} re-

TABLE I. Phonon frequencies and widths of the phonon Raman modes for the samples of $Bi_2Sr_2CaCu_2O_y$ (Bi2212) with different oxygen content, namely, the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ and $Bi_2Sr_{2-x}La_xCaCu_2O_y$ systems.

samples	$O(1)_{\mathrm{Cu}}$	Half width	$O(3)_{\mathrm{Bi}}$	Half width	$O(2)_{\mathrm{Sr}}/O_{extra}$	Half width
As-prepared in air	290	26	464	34	628/660	42/20
Annealed in O_2	291	22	464	33	622.5/653	34/16
Annealed in N_2	293	18	464	43	632/662	31/15
Y-doped, $x=0.2$	287	32	463	31	626/659	28/18
Y-doped, $x=0.4$	285	34	464	28	623/657	28/18
Y-doped, $x=0.6$	282	33	464	37	618/654	28/21
Y-doped, $x=1.0$	279	39	462	26	615/649	41/28
La-doped, $x=0.3$			463	20	620/656	28/23
La-doped, $x=0.7$			462	22	610/649	35/20

mains unchanged with the substitution. In addition, the 464-cm^{-1} mode, which is forbidden for a single BiO layer, is not observed in $BiSr_2CaCu_2O_y$ (Bi1212), while a very strong peak at 627 cm^{-1} appears in the Raman spectra of Bi1212 sample.[20,21] (2) The mode at 464 cm^{-1} is only observed when the incident and scattered polarization vectors lie within the *ab* plane.[8] In addition, this mode nearly remains constant upon the substitution and the change of oxygen content. This is because the length of the Bi-O(3) bond depends mainly on the in-plane Cu-O bond. There exists a mismatch between the perovskite block containing a CuO_2 plane and the rocksalt block BiO-SrO. The CuO_2 plane is under compression, so that the length of in-plane Cu-O bond nearly remains constant upon the doping. Therefore, the Bi-$O(3)$-Bi force constant is hardly affected by the doping and the change of oxygen content, leading to little shift of the 464-cm^{-1} mode. Recently, Choy *et al.*[22] reported that the 630-cm^{-1} phonon line is more strongly influenced than the 464-cm^{-1} phonon line upon the intercalation of $HgBr_2$ into the Bi2212 system. It supports the present assignment of 464- and 630-cm^{-1} modes since the intercalant layer is stabilized in between Bi_2O_2 layers but far from the SrO one.

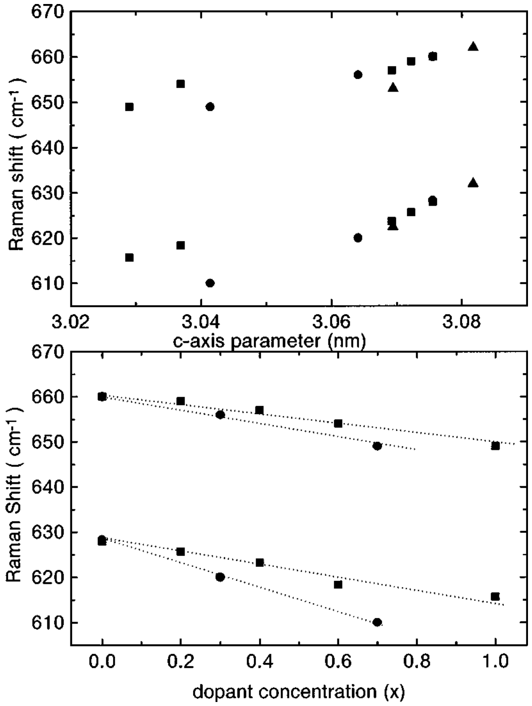

FIG. 5. Raman frequency for $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ (squares) and $Bi_2Sr_{2-x}La_xCaCu_2O_{8+\delta}$ (circles) for the 630- and 660-cm^{-1} lines vs the dopant content and the *c*-axis parameters. The *c*-axis parameter dependence of the Raman frequency is also plotted for the pure Bi2212 samples annealed in flowing O_2 and N_2 (triangles), respectively.

For the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_8$ system, Kakihana *et al.*[8] ascribed softening ($20\ cm^{-1}$) of the $O(2)_{\mathrm{Sr}}$ A_g mode to the charge redistribution induced by replacing Ca^{+2} with the different valence Y^{+3} besides variation of average ionic radius of Ca sites. As shown in Fig. 2, the frequency of the $O(2)_{\mathrm{Sr}}$ A_g mode downshifts by about 12 cm^{-1} when Ca is completely replaced by Pr. Based on the explanation of the Raman shift of the $O(2)_{\mathrm{Sr}}$ A_g mode discussed by Kakihana *et al.*, an upshift of the $O(2)_{\mathrm{Sr}}$ A_g mode is expected for a larger ion substitution of Pr^{+3} for Ca^{+2}. In fact, the trivalent rare elements substituting for the divalent Ca also leads to an increase of the oxygen content as discussed above. Figure 4 indicates that the $O(2)_{\mathrm{Sr}}$ A_g mode softens with increasing oxygen content. It suggests that the softening of the $O(2)_{\mathrm{Sr}}$ A_g mode induced by the increase of oxygen content offsets the hardening of this mode induced by ''internal pressure'' effect in the Pr-doped Bi2212 system. The mode expected to be most strongly affected by the removal of the extra oxygen is, due to its proximity, the Bi-$O(2)_{\mathrm{Sr}}$ vertical vibration at 630 cm^{-1}. This has been observed in Fig. 4. The lattice parameter *c* increases upon removal of oxygen; consequently, the Bi-$O(2)_{\mathrm{Sr}}$ distance becomes larger. So one might expect the frequency of this mode to decrease correspondingly. However, an upshift of this mode is observed experimentally in Fig. 4. The dependence of the Bi-$O(2)_{\mathrm{Sr}}$ frequency on oxygen content is therefore anomalous. The observed result suggests that the change in valence may be the dominating effect causing the frequency shift. In Fig. 5, the frequency of the $O(2)_{\mathrm{Sr}}$ A_g mode decreases with a decreasing *c*-axis parameter for the $Bi_2Sr_2CaCu_2O_y$ annealed in a different atmosphere, $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$, and $Bi_2Sr_{2-x}La_xCaCu_2O_y$ systems. It suggests that the *c*-axis parameter may be related to covalent $(Bi\text{-}O)^+$ complexes sharing the oxygen deficiency. It is well known[23,24] that Y123 and Y124 can be recategorized as Cu1212 and Cu2212 or 1212- and 2212-type two-CuO_2-layer systems, respectively, in analogy with Bi1212 and Bi2212 compounds. Compared with the structure of the Y123 system, the structure of $Bi_2Sr_2CaCu_2O_8$ is the same as that of Y123 except that the double Bi-O layers are replaced by one Cu-O chain in the Y123 system. Therefore, the Bi-$O(2)_{Sr}$ vertical vibration at $630\,cm^{-1}$ should correspond to the Cu(1)-$O(4)_{Ba}$ vertical vibration at $500\,cm^{-1}$ in the Y123 system. The effect of oxygen content on the $O(2)_{Sr}$ A_g mode is in contrast to that on the corresponding $O(4)_{Ba}\,A_g$ mode in $YBa_2Cu_3O_7$ (Y123), in which the frequency of the $O(4)_{Ba}\,A_g$ mode decreases upon removal of oxygen.[19,25] But the Cu(1)-$O(4)_{Ba}$ distance actually decreases with increasing the oxygen deficiency while the frequency is lowered. The effect of oxygen content on the $O(4)_{Ba}\,A_g$ mode is also dominated by the change in valence, while the behavior of Raman shift caused by the change in valence is contrast to that in Bi2212 system. In Fig. 5, it is easily found that the downshift of the $O(2)_{Sr}$ A_g mode in the $Bi_2Sr_{2-x}La_xCaCu_2O_y$ system is larger than that in the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ system. This is because La^{3+} substitution for Sr^{2+} leads to a larger change of the charge around the $O(2)_{Sr}$ sites and the length of the Sr-O(2) bond. This supports the assignment of 464- and 630-cm^{-1} phonon modes. It should be pointed out that the frequency shift of the mode at $660\,cm^{-1}$ as a result of the extra oxygen is always consistent with that of the $O(2)_{Sr}\,A_g$ mode upon doping as shown in Fig. 5, which is well understood since the frequency shift of the $O(2)_{Sr}\,A_g$ mode arises mainly from the extra oxygen, leading to a change of the charge distribution around the $O(2)_{Sr}$ sites.

IV. CONCLUSIONS

The following effects can be seen with use of Raman spectroscopy for $Bi_2Sr_2CaCu_2O_y$ (Bi2212), $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$, and $Bi_2Sr_{2-x}La_xCaCu_2O_y$ systems. The c-axis parameter of the samples decreases with increasing dopant concentration or oxygen content. The frequency of the $O(2)_{Sr}\,A_g$ mode decreases with a decreasing c-axis parameter. It is anomalous since the softening of the $O(2)_{Sr}\,A_g$ mode corresponds to decrease of the Bi-$O(2)_{Sr}$ bond. The change in valence around $O(2)_{Sr}$ sites is the dominating effect causing the frequency shift, which is why the effect of La^{+3} substitution for Sr^{+2} on the $O(2)_{Sr}\,A_g$ mode in the $Bi_2Sr_{2-x}La_xCaCu_2O_y$ system is stronger than that of Pr^{+3} substitution for Ca^{+2} on this mode in the $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_y$ system. The effect of oxygen content on the $O(2)_{Sr}\,A_g$ mode in the Bi2212 system is in contrast to that on the corresponding $O(4)_{Ba}\,A_g$ mode in the Y123 system. The $O(3)_{Bi}\,A_g$ phonon mode does not remarkably change upon the doping and change of oxygen content. This is because both substitutions in Ca and Sr sites and the change of oxygen content cannot apparently change the Bi-$O(3)$-Bi force constant.

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