Article

Study of Low Frequency Phonon Modes in YBCO System

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Abstract: The phonon modes in $YBa_2Cu_3O_{7-\delta}$ and $YBa_{2-x}La_xCu_3O_{7-\delta}$ systems have been systematically studied by Raman spectroscopy. The new phonon modes of 104 cm^{-1}, 94 cm^{-1}, and 89 cm^{-1} were found in all these samples. A crude estimate about the wavenumber of the collective vibration of the stable CuO2 plane was given in this paper. The standard deviations of the new phonons in $YBa_2Cu_3O_{7-\delta}$ and $YBa_{2-x}La_xCu_3O_{7-\delta}$ systems were discussed. The results of the calculation indicated that the 104 cm^{-1} mode probably stands the c-direction collective vibration of the stable CuO2 plane, the 94 cm^{-1} mode stands the a-direction vibration, and the 89 cm^{-1} mode stands b-direction vibration. The relevance between these phonons and the superconductivity was discussed. It is found that, as the T_c decreased, the 104 cm^{-1} mode and the 94 cm^{-1} mode softened, and the 89 cm^{-1} mode hardened slightly.

Keywords: collective vibration; raman spectroscopy; superconductivity; CuO2 plane; YBCO system

**Yu and Li equally contributed to this paper.*

1. Introduction

High temperature superconductor (HTSC) has been found for many years, but its mechanism is still open. Conventional BCS theory [1], which core is electron-phonon interaction (EPI), once was abandoned by most researchers as some important properties of HTSC cannot been explained well by it. At the same time, many theories appeared to describe the HTSC, such as resonating valence bond (RVB) theory [2], exciton model [3], strong coupling theory [4], and so on. However, all these new theories were inadequate to account for the mechanism of HTSC. In 2001, Lanzara [5] et al studied different families of the cuprates with angle-resolved photoemission spectroscopy (ARPES), and they observed an abrupt change of the electron velocity at 50-80 meV. Meevasana [6] ascribed the "kink" to the coupling between electrons and special phonons of some collective behavior. Subsequently, many experiments focused on EPI occurred. Khasanov [7] observed evident oxygen-isotope (16O/18O) effect directly in the in-plane penetration depth of YBCO film, which demonstrated the significance of the EPI in the cuprates. Venturini et al [8] observed a pair-breaking peak in electron Raman spectra of Bi2212 when the samples were cooled below the critical temperature. Pallesy [9] et al reported that the frequencies of some phonons would change gradually with the content of Ca in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ system. And Jin et al [10] obtained similar results in $YBa_{2-x}La_xCu_3O_{7-\delta}$ system. In our previous work, these phenomenon was confirmed in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_{7-\delta}$ system [11]. All these experiments demonstrated the dominance of phonons in

HTSC. Some review articles emphasized the importance of the EPI in the cuprates also [12, 13]. Recently，some researchers [14] discovered pressurised hydrogen sulphide with T_c exceeding 200 K, which is a conventional superconductor. This result means that there is no limitation of Tc value for conventional superconductors, and EPI can result in very high Tc value superconductors.

Coincidently, some experiments proved that the stable CuO2 plane plays a great role in HTSC [10, 15-17]. Some researchers pointed out that there may exist a collective vibration of the stable CuO2 plane, which probably is the core of the EPI in HTSC. Guo et al [15] reported that they had calculated out the wavenumber of the collective vibration in c-direction of the stable CuO2 plane in $YBa_2Cu_3O_{7-\delta}$ system as about 105 cm^{-1}. However, phonons of the collective vibration have not been accurately observed yet and the relationship between the phonon and superconductivity is still open. A further study on the collective vibration of the stable CuO2 plane in cuprates is helpful to make clear whether the EPI is significant to superconductivity or not. In this paper, $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $Y_{1-x}Ba_{2-x}La_xCu_3O_{7-\delta}$ (YBLCO) systems were carefully studied by Raman spectroscopy. Fortunately, we found three new modes of phonons, which acted like the collective vibration of the stable CuO2 plane. By analyzation, the 104 cm^{-1} mode probably stands the c-direction collective vibration of the stable CuO2 plane, the 94 cm^{-1} mode stands the a-direction vibration, and the 89 cm^{-1} mode stands b-direction vibration. The relationship between the phonons and the superconductivity shows a positive evidence for EPI in HTSC.

2. Materials and Methods

The samples of $YBa_2Cu_3O_{7-\delta}$ (δ=0.08, 0.19, 0.23, 0.32, 0.51), $YBa_{2-x}La_xCu_3O_{7-\delta}$ (δ=0.08, x=0, 0.1, 0.2, 0.3, 0.4) were prepared by the standard solid-state reaction method. An X'pert MRD diffractometer with Cu$^{K\alpha}$ radiation was used to collect X-ray powder diffraction data. Rietveld refinement method with the X'pert Plus software was used to get the lattice parameters. The Tc was determined in a 20-Oe magnetic field by dc magnetic susceptibility measurements (Quantum Design MPMS). The samples of $YBa_2Cu_3O_{7-\delta}$(δ=0.19, 0.23, 0.32, 0.51) was obtained from $YBa_2Cu_3O_{7-\delta}$(δ=0.08) by releasing O atom in Ar atmosphere for different time. The oxygen contents were got by a method, estimating the oxygen content by the value of T_c [18, 19].

All the Raman spectra were collected from 50 cm^{-1} to 800 cm^{-1} at room temperature with a SP-2500 spectrometer equipped with a microscope and a CCD detector. The wavelength of laser is 532 nm. And the laser was focused to a spot of 2μm in diameter.

3. Results

In the YBCO system, the Roman spectra are shown in Figure 1. It is found that there were new peaks around 100 cm^{-1} in every sample never reported, which indicates new modes of phonons. For a further study, we picked the period nearby 100 cm^{-1} of the spectra and fitted these curves by Lorentz shapes, respectively. The adjusted R squares (Adj. R-Squares) of the fittings are all lager than 0.99, which demonstrates that the results were convincible. The peaks was consisted of 104 cm^{-1}, 94 cm^{-1}, and 89 cm^{-1} modes of phonons, which were shown in Figure 2.

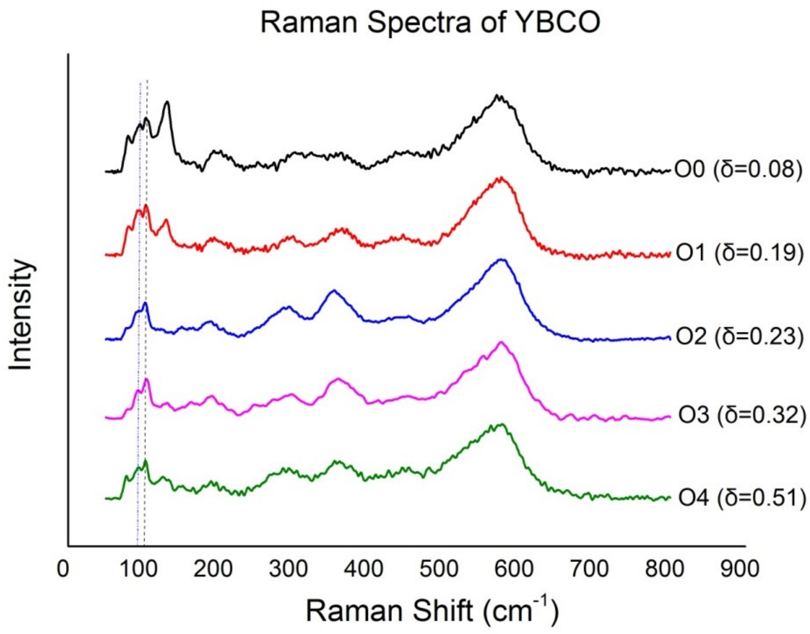

Fig. 1. Raman Spectra of theYBCO system. New peaks around 100 cm^{-1} were found.

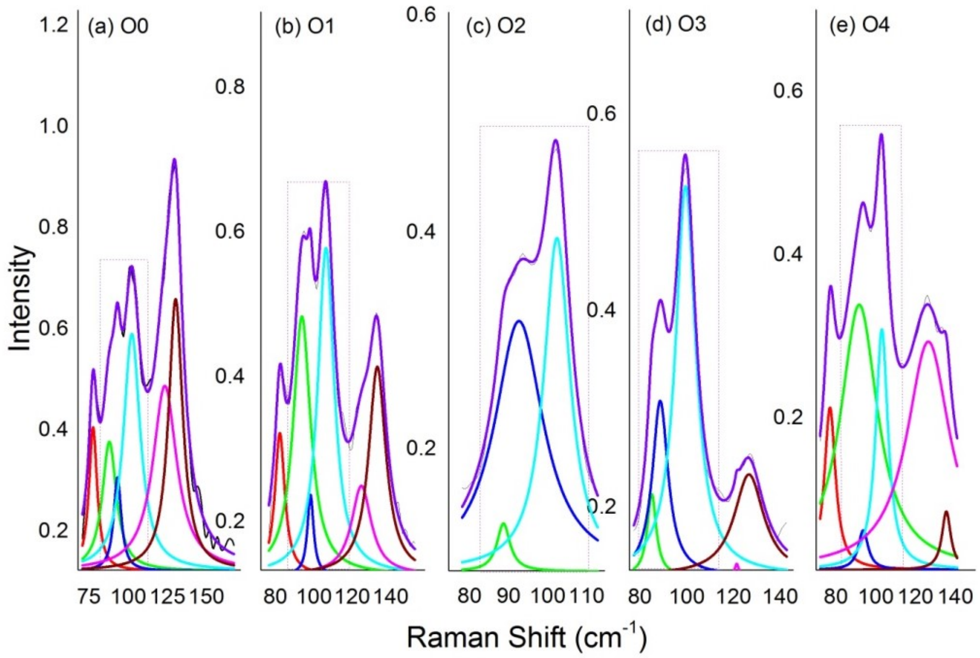

Fig. 2. Fitted Lorentz shape in YBCO system. The Adj. R-Square were all large than 0.99, indicating that the fitting results were reliable.

In the YBLCO system, the Raman spectra are shown in Figure 3. Also there existed new peaks around 100 cm^{-1} in each sample. Also the period nearby the 100 cm^{-1} mode were picked and fitted with Lorentz shape. The results were shown in Figure 4. The 104 cm^{-1}, 94 cm^{-1}, and 89 cm^{-1} modes existed in YBLCO system too.

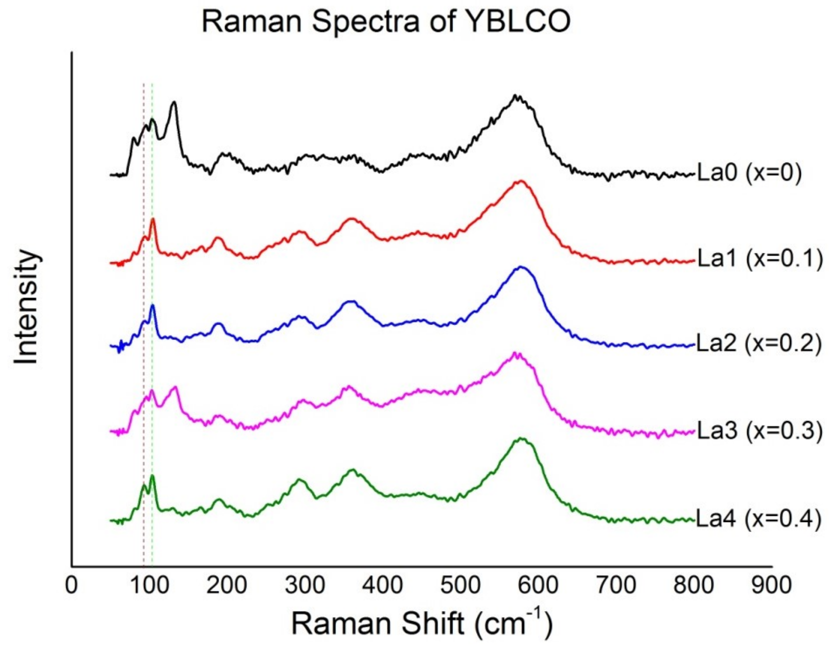

Fig. 3. Raman spectra of YBLCO system. New peaks around 100 cm^{-1} were found.

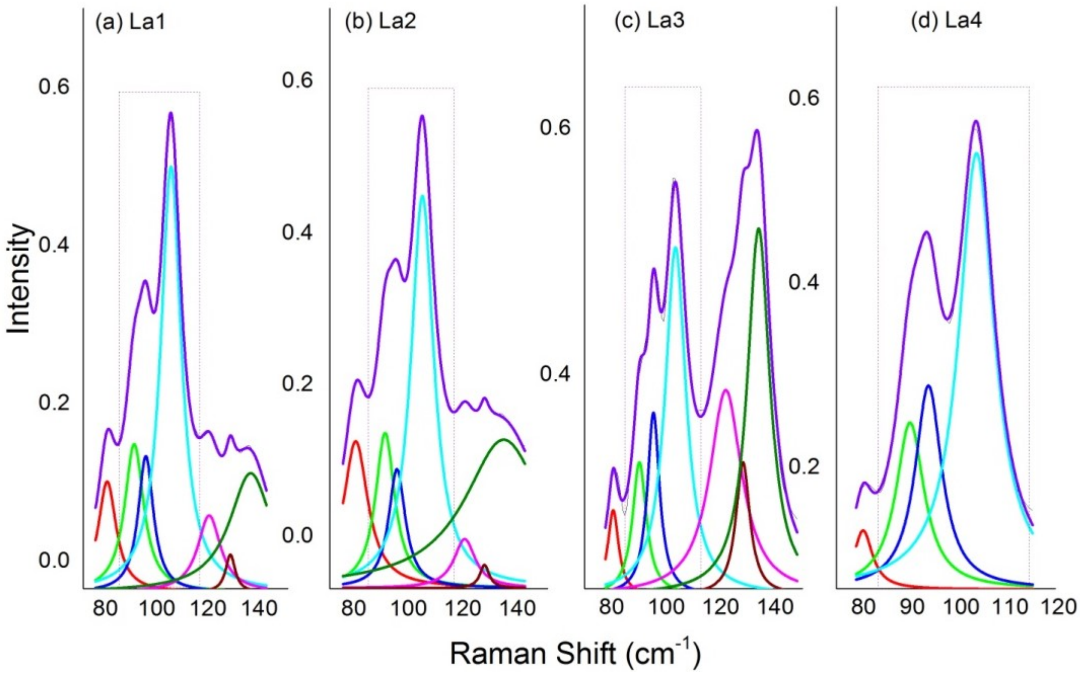

Fig. 4. Fitted Lorentz shape in YBLCO system. The Adj. R-Square were all large than 0.99, indicating that the fitting results were reliable.

4. Discussion

These three new phonons had never been reported. Maybe collective vibration of the stable CuO2 plane should be taken into consideration. Some authors [10, 15-17, 20, 21] have demonstrated by x-ray diffraction and Raman spectroscopy that CuO2 plane is very stable, and the bond length and bond angle in this plane is hardly changed by the variations of environments. The atoms in this plane may show some behaviors of collective movements, and they may play an important role in high Tc superconductivity. However, about these collective movements and their role in high Tc superconductivity is not clear. Here we try to understand it by analyzing of the Raman spectra got in this study. Guo et al [15] reported the calculation about the collective vibration in YBCO sample.

They assumed that the frequencies of phonons are inverse-square to its weight, the cluster of the stable CuO2 plane vibrates like a single atom, and the stable CuO2 plane is consisted of one Cu atom and four O atoms and they deduced the frequency of the phonon of the c-direction vibration of the stable CuO2 plane was about 106 cm^{-1}. In our model, the assumption that the frequencies of phonons are inverse-square to its weight and the cluster of the stable CuO2 plane vibrates like a single atom was accepted. However, what was taken into consideration is that the Cu and O atoms was not just belong to the given unit cell, but shared with the others. Figure 5 shows the unit cell of YBCO. The Cu(2) atom was shared by four cells, and the O(2) and O(3) atoms were shared by two cells. In our model, only a quarter of Cu(2) atom, half O(2) atom and half O(3) atom were taken into consideration as shown in Figure 6.

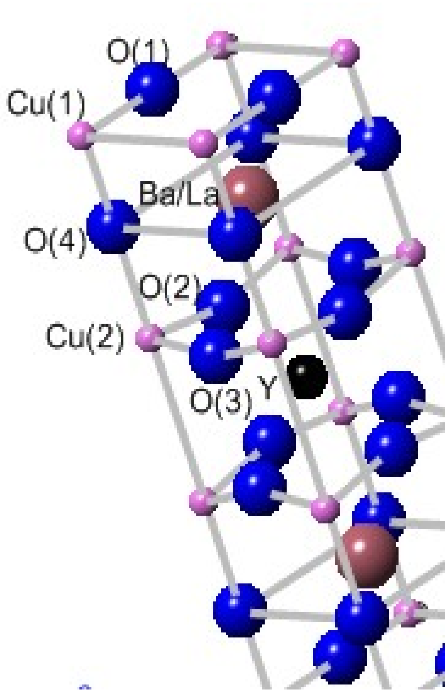

Fig. 5. Cell structure of YBCO.

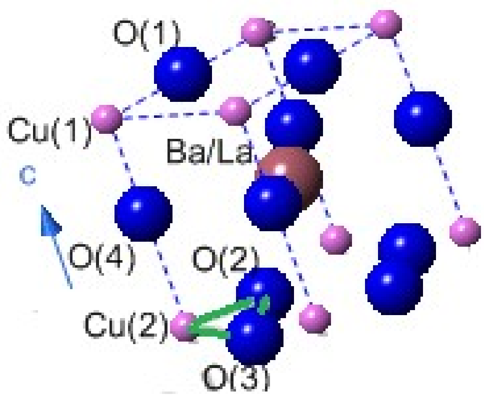

Fig. 6. The c-direction vibration of the stable CuO2 plane.

Thus, the ratio of the frequencies was deduced as

$$\frac{\omega_c}{\omega_{Cu}}=\sqrt{\frac{\frac{1}{4}m_{Cu}}{\frac{1}{2}m_o+\frac{1}{2}m_o+\frac{1}{4}m_{Cu}}}\approx 0.707 \quad (1)$$

The frequency of the c-direction vibration of Cu (2) was reported as about 145 cm^{-1} [22]. The c-direction vibration of the stable CuO2 plane could be obtained as $\omega_c \approx 145cm^{-1}\times 0.707 \approx 102.5cm^{-1}$. This result was coincident with the 104 cm^{-1} mode obtained above. However, no explanations have been given for 94 cm^{-1} and 89 cm^{-1} modes of phonons.

In our model, we took the a-direction and b-direction of the stable CuO2 plane into consideration also. We assumed that the nearest O atoms would vibrate together with the stable CuO2 plane as a single O atom. In c-direction, as shown in Fig. 5, the Cu(1) atom of heavy mass stand in the way of the c-direction vibration of O(4) atom. Thus the O(4) atom, the nearest atom to the stable CuO2 plane cannot vibrate together in c-direction. But in a-direction, as there is no roadblock, the O(4) atom, should vibrate together with the stable CuO2 plane. In this condition, as shown in Figure 7, a triangular pyramid was formed by Cu(2), O(2), O(3), and O(4) atoms, vibrating together.

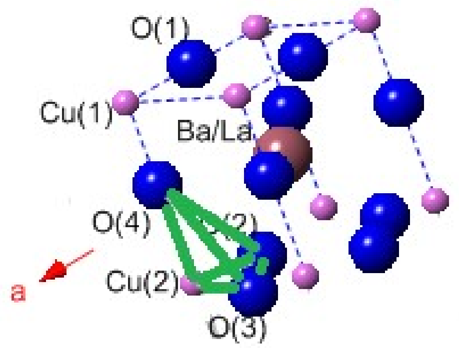

Fig. 7. The a-direction vibration of the stable CuO2 plane. The O(4) atom vibrates together with the stable CuO2 plane.

Noticed that the O(4) atom was shared by four cells, the ratio of the frequencies was deduced as

$$\frac{\omega_o}{\omega_{Cu}}=\sqrt{\frac{\frac{1}{4}m_{Cu}}{\frac{1}{2}m_o+\frac{1}{2}m_o+\frac{1}{4}m_o+\frac{1}{4}m_{Cu}}}\approx 0.667 \quad (2)$$

The frequency of the a-direction or b-direction of the Cu(2) was reported about 140 cm^{-1} [22]. We work out that phonon in the a-direction is $\omega_a \approx 140cm^{-1}\times 0.667 = 93.4cm^{-1}$, which matches very well with the new mode of 94 cm^{-1}.

In the b-direction, we assumed that the O(1) atom, as the nearest O atom to the triangular pyramid, contributes to the phonon also. In the a-direction, the O(1) atom cannot move together with the stable CuO2 plane, as the Cu(1) atom stand in the way of the a-direction vibration of the O(1) atom. But in b-direction, there was no roadblock in the b-direction vibration of the O(1) atom. Thus, we assumed that the Cu(2) atom and the O atoms vibrated together, as shown in Figure 8.

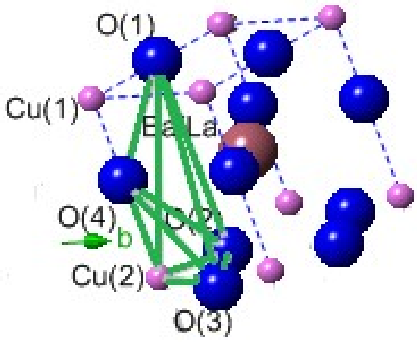

Fig. 8. The b-direction vibration of the stable CuO2 plane. The O(4) atom and the O(1) atom vibrate together with the stable CuO2 plane.

Considering that the O(1) atom was shared by four cells also, the ratio of the frequencies was deduced as

$$\frac{\omega_b}{\omega_{Cu}} = \sqrt{\frac{\frac{1}{4}m_{Cu}}{\frac{1}{2}m_o + \frac{1}{2}m_o + \frac{1}{4}m_o + \frac{1}{4}m_o + \frac{1}{4}m_{Cu}}} \approx 0.632 \qquad (3)$$

We work out the phonon in the b-direction is $\omega_b \approx 140cm^{-1} \times 0.632 = 88.5cm^{-1}$, which matches very well with the new mode of 89 cm^{-1}.

Another evidence to support our opinion is that the fluctuations of the frequencies of these three modes are not as drastic as others. In YBCO system, Figure 9(a) compared these modes with the 580 cm^{-1} mode, which represents the b-direction vibration of the O(2) atom [22] and was obtained by fitted Lorentz shape also. And Figure 9(b) shows their standard deviation (STDEV). It is found that the STDEV of 580 cm^{-1} mode is about two times as large as the 94 cm^{-1} mode or 89 cm^{-1} mode, and three times as large as the 104 cm^{-1} mode. As reported that the CuO2 plane in HTSCS is very stable [16], and the environment change hardly effects its structure. The standard deviations of the phonons related with the stable CuO2 plane should be very small. Coincidently, the similar phenomenon was observed in YBLCO system. The results are shown in Figure 10.

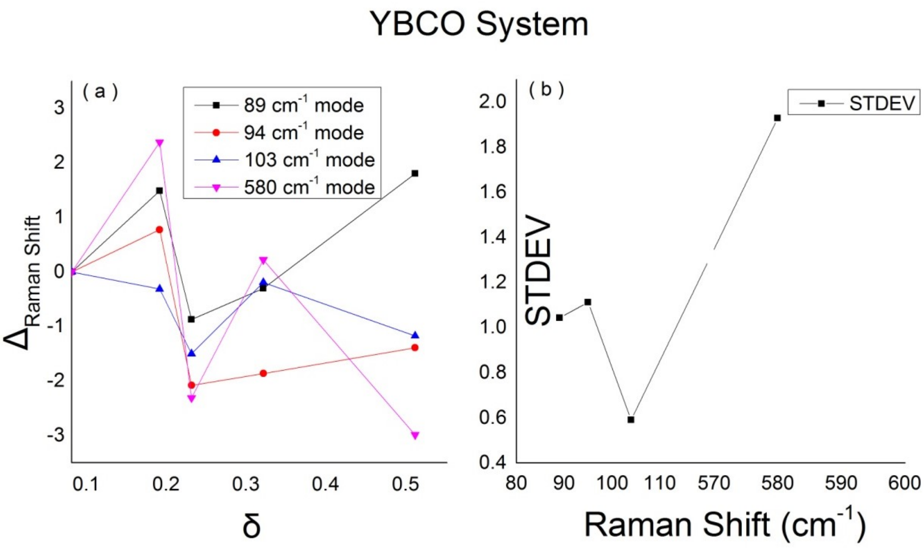

Fig. 9. (a) Fluctuations of the phonon modes in YBCO system; (b) STDEV of the phonons of in YBCO system.

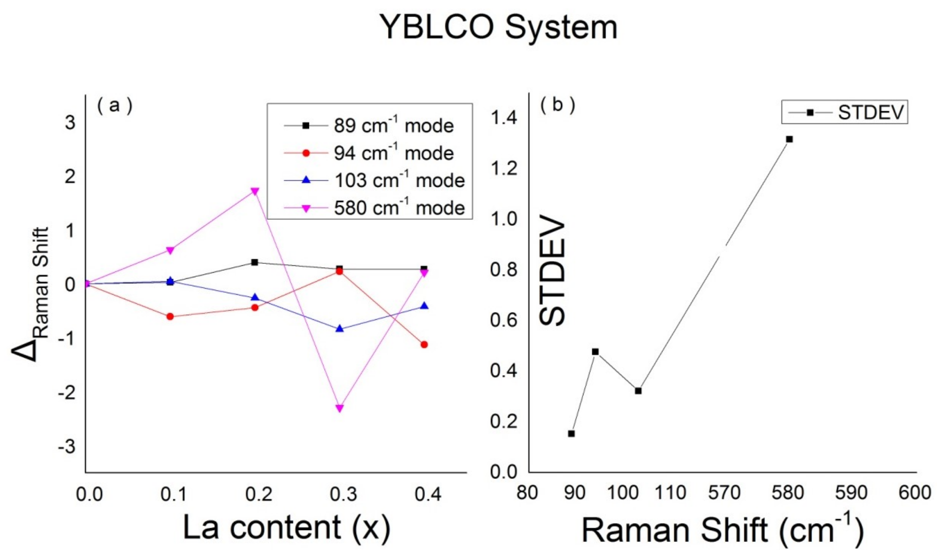

Fig. 10. (a) Fluctuations of the phonon modes in YBLCO system; (b) STDEV of the phonons of in YBLCO system.

Further searching about the relationship between the change of phonons and the superconductivity, we depicted the fluctuations of the phonon wavenumbers and the Tc in Figure 11. The wavenumbers were deposed by linear fitting. It is found that, in YBCO system, the 89 cm^{-1} mode phonon hardened slightly as the Tc decreased. On the contrary, the 94 cm^{-1} mode phonon and 104 cm^{-1} mode phonon softened obviously with the decreases of the Tc. The same trend was observed in YBLCO system. It indicated that the collective vibration of the stable CuO2 plane plays a great role in HTSC.

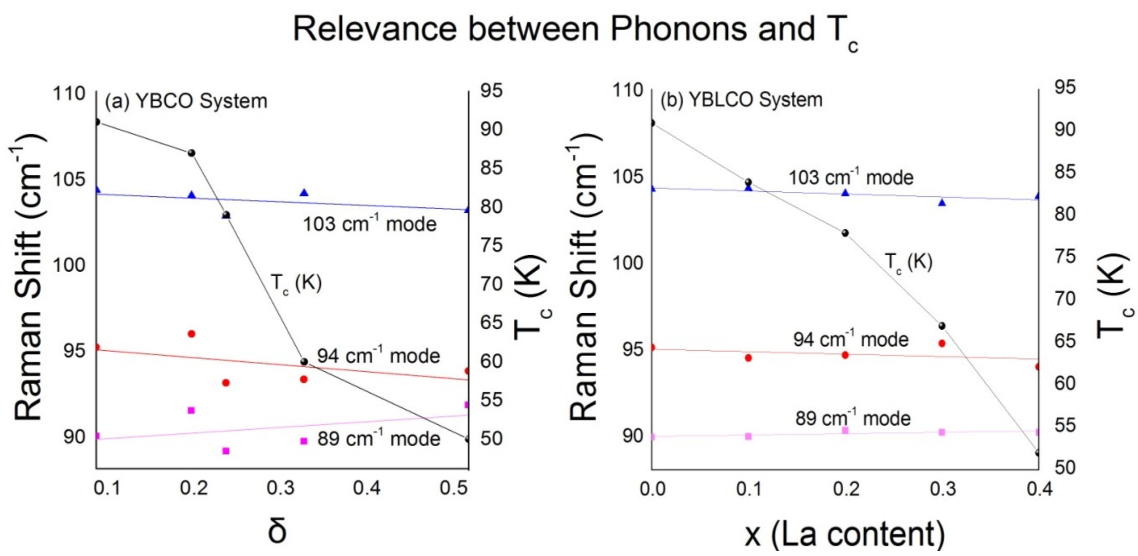

Fig.11. Relevance between the phonons and superconductivity. In both YBCO and YBLCO system, as the Tc decreased, the 89 cm^{-1} mode phonon hardened, but the 104 cm^{-1} mode and the 94 cm^{-1} mode phonons softened.

5. Conclusions

The low frequency phonon modes in YBCO and YBLCO system were studied by Raman spectroscopy. Three new modes of phonon around 100 cm^{-1} were found and a possible explanation relevant with collective behavior of the CuO2 plane was given. By computation, we found that the

104 cm^{-1} mode probably represents the c-direction collective vibration of the stable CuO2 plane, the 94 cm^{-1} mode represents the a-direction vibration, and the 89 cm^{-1} mode represents the b-direction vibration of the CuO2 plane. Besides, the relevance between the collective vibration and superconductivity is revealed. In both YBCO and YBLCO system, as the T_c decreased, the 104 cm^{-1} mode and 94 cm^{-1} mode phonons softened, and the 89 cm^{-1} mode phonon hardened. The results hint that the phonons of the collective vibration of the stable CuO2 plane obviously contribute to the high T_c superconductivity and need to be further studied.

Acknowledgments

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