Structural modifications and phonon softening in $Bi_2Sr_2Ca_{1-x}R_xCu_2O_{8+\delta}$ (R = Pr and Gd) single crystals

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Abstract

The phonon Raman spectra of $Bi_2Sr_2Ca_{1-x}R_xCu_2O_{8+\delta}$ (R = Pr and Gd) single crystals are systematically investigated. The experimental results show that the $O(2)_{Sr}\, A_{1g}$ mode softens with Pr and Gd doping, while the $O(1)_{Cu}\, B_{1g}$ mode softens with Pr doping but hardens with Gd doping. The changes of average ionic radius on the Ca site in Bi-based cuprates can account well for the Raman frequency shifts of the $O(1)_{Cu}$ mode, but have little influence on the $O(2)_{Sr}$ mode. The frequency softening of the $O(2)_{Sr}$ mode in Pr- and Gd-doped Bi2212 crystals mainly results from contraction of the BiO bilayers with doping content. The correlation between the $O(2)_{Sr}$ mode frequency and the c-axis parameter as well as the incommensurate modulation wavelength is discussed.

Introduction

Raman scattering has been extensively used to investigate phonons and other low-energy excitations in solids [1] and many studies have been done in high-T_c superconductors [2]. In contrast to the case of $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_4$ systems, the assignment of phonon eigenmodes in Raman spectra of the Bi-based high-T_c cuprates is more difficult for the following reasons. First, the complicated local structure of the BiO bilayers, characterized by incommensurate superstructure as well as local atomic displacements, gives rise to a number of disorder-activated phonons, which complicate interpretation of the spectra. Second, the mica-like nature of the Bi-based single crystals makes c-axis polarized measurements experimentally demanding, even though this scattering configuration has provided important information in other high-T_c cuprates. Hence, debate on the assignments of experimentally observed phonon

modes to vibrational eigenmodes of the lattice for Bi-based cuprates has lasted for a long time after discovery of the materials [3–7].

Raman spectroscopy has proved to be a useful tool due to its nature as a probe of the local atomic configurations through the phonon frequency shifts [8]. Cation substitution can alter the local lattice structure and lead to frequency shifts of some Raman modes, which would be helpful for assigning the Raman modes. Recently, Kakihana and colleagues [9, 10] gave reasonable assignments of the phonon eigenmodes in Raman spectra of the Bi-based cuprates by measuring the c-axis polarized configuration in single crystals as well as aliovalence cation substituted materials. However, cation substitution alters the effective cation valence, the effective cation size, the oxygen content, the carrier concentration and lattice parameters as well as the phonon spectrum in the cuprates, which makes the interpretation of the frequency shifts of some phonon modes in Raman spectrum more difficult. Some further studies on Bi-based materials confirmed the assignments of Raman phonons in [9], but no consistent conclusion was reached on the frequency changes of some phonon modes [11, 12] and this problem should be further addressed. Compared with the polycrystalline Bi-based cuprates, the single crystals show relatively weak Raman spectra for some modes in *ab* planar polarized measurement [9]. However, the single crystals can use different polarized measurements as well as exclude some impurity Raman modes in the polycrystalline materials, such as the mode at 540 cm^{-1} in Pb-doped Bi-based cuprates [12, 13]. In order to elucidate the reasons for the frequency shifts of certain phonon modes in cation substituted Bi-based cuprates, phonon Raman scattering in single crystals of $Bi_2Sr_2Ca_{1-x}R_xCu_2O_{8+\delta}$ (R = Pr and Gd) and $Bi_{1.8}Pb_{0.3}Sr_2CaCu_2O_{8+\delta}$ is investigated in this paper.

Experimental details

$Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ (Pr-doped Bi2212), $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+\delta}$ (Gd-doped Bi2212), and $Bi_{1.8}Pb_{0.3}Sr_2CaCu_2O_{8+\delta}$ single crystals were grown by a self-flux method with excess Bi_2O_3 to act as a flux. Details of the crystal growth have been described elsewhere [14, 15]. X-ray diffraction (XRD) data were collected using a rotating-anode diffractometer (Rigaku, D/Max-γ A) with graphite monochromatized Cu Kα radiation. No extra peak from the secondary phase was found in the crystals besides Bi2212 reflection peaks. The c-axis parameters decrease monotonically with increasing Pr and Gd content x and show an abrupt change at $x \approx 0.4$ and 0.7 for Pr- and Gd-doped Bi2212 crystals [14, 15] respectively. Note that the aliovalence cation substitution would result in structural distortions in the materials; the observed discontinuity of the c-axis parameter may be due to structural distortions. The cation stoichiometry of the single crystals was analysed by energy dispersive x-ray (EDX) analysis using a scanning electron microscope (Stereoscan 440, Leica). In the following discussion, the Pr and Gd content x is the actual content of the crystals determined by EDX. Raman spectra were measured on a LABRAM-HR Raman spectrophotometer using a backscattering technique. The 5145 Å laser was used as an excitation light source. The incident light is vertically polarized while the scattered light is observed without polarizers and the a- and b-axes of the crystal are not distinguished in the Raman measurement, which may influence the intensity of the modes in the Raman spectra [9]; thus the relative spectral intensity for different crystals gives little information in our data.

Results and discussion

Figures 1(a) and (b) show the Raman spectra of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ ($x = 0.11, 0.28$ and 0.45) and $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+\delta}$ ($x = 0, 0.19, 0.47, 0.69$ and 0.91) single crystals in the 50–800 cm^{-1} frequency range at room temperature. Five Raman modes around 60, 117, 290,

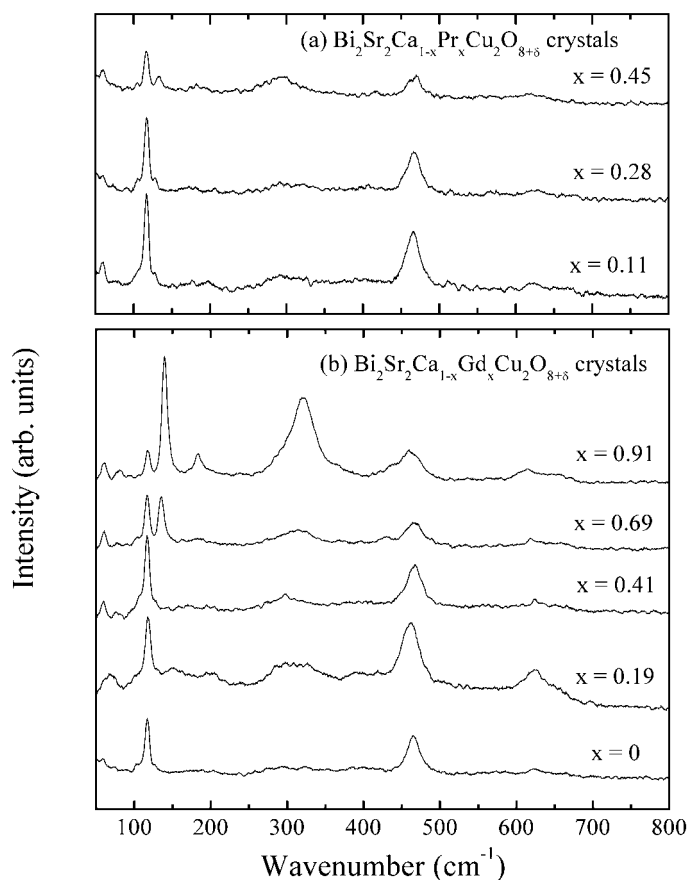**Figure 1.** Phonon Raman spectra of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ (a) and $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+\delta}$ (b) single crystals for different Pr and Gd contents at room temperature.

460 and 630 cm^{-1} are observed for Pr- and Gd-doped Bi2212 crystals, which correspond to the modes of Bi A_{1g}, Sr A_{1g}, $O(1)_{Cu}$ B_{1g}, $O(3)_{Bi}$ A_{1g} and $O(2)_{Sr}$ A_{1g} respectively in the Bi2212 system, according to the assignment of Kakihana *et al* [9]. It is found that the modes at 60, 117 and 460 cm^{-1} are essentially unchanged while the modes at 290 and 630 cm^{-1} show frequency shifts with increasing Pr and Gd content. When the Pr content increases from $x = 0$ to 0.45, the $O(2)_{Sr}$ A_{1g} and $O(1)_{Cu}$ B_{1g} phonons both soften by about 6 cm^{-1}, which is consistent with the results in polycrystalline Pr-doped Bi2212 samples [11]. As compared with Pr-doped crystals, the $O(2)_{Sr}$ A_{1g} phonon in Gd-doped crystals softens by about 13 cm^{-1} while the $O(1)_{Cu}$ B_{1g} peak shifts about 30 cm^{-1} to high frequency when the Gd content increases from $x = 0$ to 0.91. The Raman spectrum of a $Bi_{1.8}Pb_{0.3}Sr_2CaCu_2O_{8+\delta}$ single crystal is shown in figure 2. No mode at 540 cm^{-1} was found in the spectrum, which supports the idea that the mode at 540 cm^{-1} is due to an impurity phase rather than a Cu–O–Pb phonon mode [12].

It is noted that in figure 1 a mode at about 135 cm^{-1} appears when $x = 0.45$ for Pr-doped and 0.69 for Gd-doped Bi2212 crystals, which corresponds to the doping content where the c-axis parameter shows anomalous changes [14, 15]. This mode is not the eigenmode of the tetragonal space group $I4/mmm$ [9]. It is suggested that the mode at 135 cm^{-1} is related to a phonon mode induced by structural distortion.
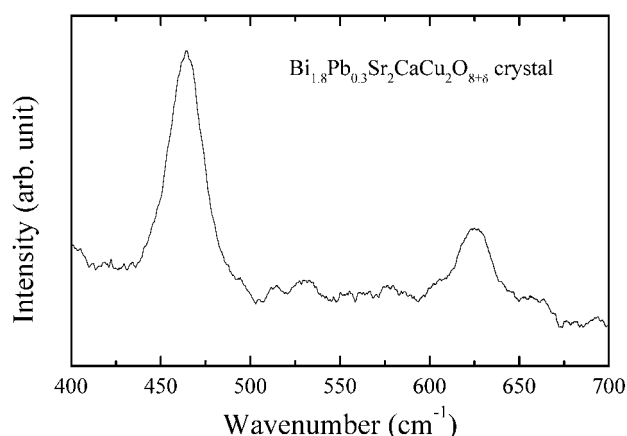
Figure 2. Room-temperature phonon Raman spectrum for a $Bi_{1.8}Pb_{0.3}Sr_2CaCu_2O_{8+\delta}$ single crystal.

As discussed in [9], the $O(1)_{Cu}$ B_{1g} phonon denotes the out-of-phase motion of the oxygen atoms in the CuO_2 plane; its frequency is primarily determined by the changes in the average Ca/Y radius, and the Cu valence has little effect on the frequency shifts of the mode in Y-doped Bi2212 polycrystalline samples. This explanation can well account for the frequency shifts of the phonon mode at $290 \, cm^{-1}$ in Pr- and Gd-doped Bi2212 crystals. Note that $r_{Gd^{3+}} < r_{Ca^{2+}}$ and $r_{Pr^{3+}} > r_{Ca^{2+}}$ and Gd substitution for Ca can result in a decrease of the average Ca/Gd radius, so the $O(1)_{Cu}$ phonon hardens by about $30 \, cm^{-1}$, less than the $40 \, cm^{-1}$ hardening in Y-doped Bi2212 materials [9], because the radius of Gd^{3+} is larger than that of Y^{3+}. On the other hand, Pr substitution leads to a slight increase of the average radius on the Ca site, which can account for the observed $O(1)_{Cu}$ phonon softening in Pr-doped Bi2212 crystals.

As for the frequency shifts of the $O(2)_{Sr}$ A_{1g} phonon characterized by the bridging oxygen vibration along the c-axis, the situation becomes controversial. The following three reasons have been proposed to interpret the phonon frequency shifts in cation- or oxygen-doped Bi-based cuprates:

 (i) the changes of the average radius on the Ca site [9],
 (ii) the changes of valence of Bi and Cu ions [9], and
(iii) the extra oxygen in BiO layers [12].

First, it was proposed that the variation of the average ionic radius of the Ca site may alter the $O(2)_{Sr}$ A_{1g} phonon frequency; decrease of the Ca site radius results in a softening of the $O(2)_{Sr}$ mode [9]. However, Pr substitution leads to an increase in the average Ca/Pr radius, which should harden the $O(2)_{Sr}$ mode if it were mainly affected by the average ionic radius on the Ca site. Figure 3(a) shows the doping dependence of the $O(2)_{Sr}$ mode frequency in Pr-, Gd- and Y-doped Bi2212 cuprates. It can be found that the x dependence of the phonon frequency for Pr- and Gd-doped Bi2212 crystals is almost identical, although Pr and Gd substitution have a different influence on the ionic radius of the Ca site, which further confirms that the average radius on the Ca site has little influence on the frequency changes of the $O(2)_{Sr}$ mode. Second, detailed work on different oxygen-doped Bi-based cuprates has ruled out the charge redistribution effect on the $O(2)_{Sr}$ phonon frequency shifts [11, 12]. This conclusion was also confirmed by the observed doping independence of the $O(3)_{Bi}$ A_{1g} phonon frequency, because the charge redistribution should lead to the weakening of the $Sr–O(3)_{Bi}–Bi$ bond in Pr- and
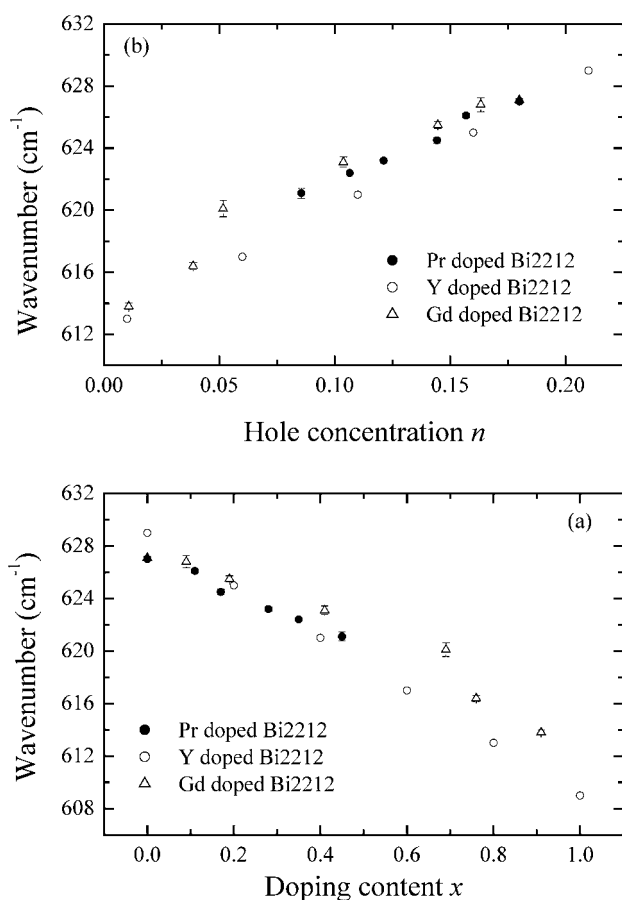
Figure 3. Variations of the $O(2)_{Sr}$ A_{1g} mode in $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$, $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+\delta}$ and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ cuprates with doping content x (a) and hole concentration n (b). For the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system, the Raman data are obtained from [9], and T_c values are obtained from [16].

Gd-doped Bi2212 crystals and give a mode softening result. Third, Pr- and Gd-doped Bi2212 crystals would result in an increase in the oxygen content in crystals with increasing Pr and Gd content. The extra oxygen in the crystals may account for the softening of the $O(2)_{Sr}$ A_{1g} mode [12].

The apical oxygen $O(2)_{Sr}$ A_{1g} phonon frequency should depend mostly on changes in the two nearest-neighbour distances in the vibrational direction [10]. In the Bi2212 case, the two relevant distances would be the $O(2)_{Sr}$–Bi and the $O(2)_{Sr}$–Cu bond lengths. The softening of the $O(2)_{Sr}$ mode in Pr- and Gd-doped Bi2212 crystals suggests that Cu–O–Bi distance expands a little as more cations are introduced in the materials. The excess oxygen could affect the $O(2)_{Sr}$ mode by causing a contraction of the weakly coupled BiO layers and an expansion of the Cu–O–Bi bond [12]. After removing the effect of the changes in radius on the Ca site, the $O(2)_{Sr}$ phonon frequency in Y-doped Bi2212 cuprates shows a similar dependence on excess oxygen to that of oxygen-doped Bi2212 [12]. However, our results indicate that the radius on the Ca site has little relation to the frequency changes of the mode. Thus, different $O(2)_{Sr}$ phonon softening rates with excess oxygen content δ could be obtained in different
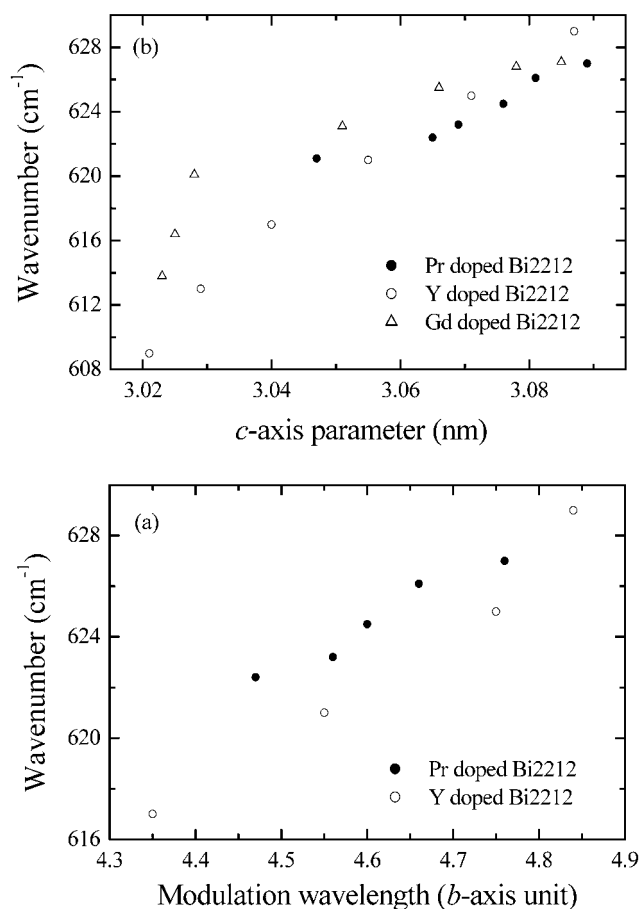
Figure 4. The variations of the $O(2)_{Sr}$ A_{1g} mode frequencies with modulation wavelength in $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (a) and with *c*-axis parameter in crystals of $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$, $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+\delta}$ and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (b). For the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system, the Raman data and *c*-axis parameter are obtained from [9] and the modulation wavelength data are deduced from [25].

ion-doped Bi2212 systems. The rate is about 30 cm^{-1} per oxygen atom in oxygen-doped Bi2212 [12], but it becomes about 70 cm^{-1} in Y-doped Bi2212 [9, 16, 17]. Figure 3(b) shows the dependence on hole concentration of the $O(2)_{Sr}$ phonon frequency in Pr-, Gd- and Y-doped Bi2212 cuprates. The hole concentration *n* was determined from the T_c values using the empirical relation $T_c/T_{c\,max} = 1 - 82.6(n - 0.16)^2$. It is found that the phonon frequency hardens with increase in hole concentration in the systems, in contrast to the softening results in Pb- and O-doped Bi2212 systems [12], which indicates that the hole concentration in the materials cannot dominate the frequency changes of the $O(2)_{Sr}$ mode.

It is well established that cation substitution could change the incommensurate modulation structure [14, 18–21]. In BiO bilayers, the site of Bi ions undulates in the *c*-axis as well as distributing sparsely and densely along the *b*-axis forming the incommensurate modulation structure, which has been observed by high-resolution STM images [22–24]. It is suggested that an increase of Pr and Gd doping in Bi2212 systems would lead to a decrease of the magnitude of the undulation of the Bi ion site in the *c*-axis accompanied by a decrease in the

incommensurate modulation wavelength q_b. Contraction of the BiO bilayers would result in a slight expansion of the Cu–O–Bi bond, which gives the $O(2)_{Sr}$ A_{1g} phonon softening.

There seem to be no reliable reports on interatomic bond lengths in Pr- and Gd-doped Bi2212 systems that can substantiate this hypothesis; however, some experimental results in the systems would give indirect support to the hypothesis. The contraction of BiO bilayers causes decrease of the modulation wavelength q_b in the Bi2212 system as well as softening of the $O(2)_{Sr}$ phonon; thus the $O(2)_{Sr}$ phonon frequency should decrease with decreasing q_b. Note that the modulation wavelength shows an abrupt increase at $x \approx 0.4$ and 0.8 for Pr- and Y-doped Bi2212 systems [14, 17] respectively, but no anomalous frequency change of the $O(2)_{Sr}$ mode is observed in our experiments. In the low substitution range, the modulation wavelength decreases linearly with $dq_b/dx = 1$ as the Y content increases in Y-doped Bi2212 cuprates [17, 25], in contrast to $dq_b/dx = 0.78$ with increasing Pr content in Pr-doped crystals [14]. Figure 4(a) shows the q_b dependence of the $O(2)_{Sr}$ mode frequency in Pr- and Y-doped Bi2212 systems. It is found that the $O(2)_{Sr}$ phonon frequency decreases with decreasing q_b in Pr- and Y-doped Bi2212 systems. In the high substitution range, q_b decreases with $dq_b/dx = 1.85$ as the Pr content increases [14]. Only one datapoint in this range is obtained in our Pr-doped crystals; however, based on the results in Pr-doped polycrystalline Bi2212 samples [11], a similar relationship between the phonon frequency and q_b can also be found in this range.

The observed decrease of c-axis parameter with increasing cation doping content in Bi2212 systems [14, 15, 26] mainly results from the contraction of weakly coupled BiO bilayers [27], while substituted cation radius and the expansion of other parts play some role too. Figure 4(b) shows the c-axis parameter dependence of the $O(2)_{Sr}$ mode frequency in Pr-, Y- and Gd-doped Bi2212 materials. The decrease of the $O(2)_{Sr}$ mode frequency with decreasing c-axis parameter also supports the hypothesis of the contraction of BiO bilayers. The observed c-axis parameter decreases more rapidly with Gd content than with Pr content in Pr- and Gd-doped Bi2212 crystals [14, 15] because $r_{Pr^{3+}} > r_{Gd^{3+}}$.

In summary, the phonon Raman scattering of Pr- and Gd-doped Bi2212 single crystals is investigated in this paper. The softening of the $O(2)_{Sr} A_{1g}$ phonon is mainly attributed to the contraction of weakly coupled BiO bilayers, and the $O(2)_{Sr}$ mode frequency decreases with decreasing c-axis parameter and incommensurate modulation wavelength, which gives indirect support for the hypothesis of contraction of the BiO bilayers.

Acknowledgments

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