Effects of Heating on the Raman Spectra of YBa$_2$Cu$_3$O$_{7-\delta}$

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Abstract. We report effects of heating to the intensities of Raman modes in the spectra of single-crystals embedded in ceramic YBa$_2$Cu$_3$O$_{7-\delta}$ pellets, and compare the results with those from YBa$_2$Cu$_3$O$_{7-\delta}$ thin-films. Heating was done by either increasing the laser-beam power or resistively heating in a heating cell. From the measurements on a single-crystal in $z(xx)$ polarization, we find that the relative intensity of the $B_{1g}$ mode of the plane oxygens to that of the $A_{1g}$ mode of apical oxygens decreases strongly as the samples are heated. For a crystal in near $x(zz)$ polarization, the relative intensity of the two modes increases up to a certain value. In thin-films, however, no such change was observed even when heated to higher temperatures than the crystals were. Therefore, we interpret that the change in the relative intensity of the two modes is not due to electronic or structural changes nor thermal decomposition in the heated samples. We propose that a single-crystal, when heated, is fractured into many “micro-crystals” and these micro-crystals thermally fluctuate in orientations. For thin-films, such fluctuation in orientations might be hindered because there are only a few layers of micro-crystals on top of the substrate. Scanning electron micrographs (SEM) of the heated part of the samples seem to provide the evidence of the micro-crystals.

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YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors (hereafter Y123) are well known to be sensitive to oxygen content in their structures and transition temperatures. The oxygen content of Y123 depends on the thermal history of the samples. Thus many works are concentrated on the effects of heating to the physical properties of Y123. There are at least two conflicting reports about the heating effect to the Raman spectra of Y123 crystals. Burns et al. [1] studied the effect of heating to the apical oxygen mode of Y123 single-crystals and compared it to that of laser heating. They found that a sharp new Raman mode (598 cm$^{-1}$) appeared at relatively low temperatures (near 50 °C) for oxygen-deficient Y123 samples. However, for fully-oxygenated samples, the new mode was much more hard to obtain by heating the samples. From measurements on single-crystals of variable oxygen content, [2] they assigned the new mode to oxygen atom vibration in the two-coordinated Cu “sticks”. However, Heyen et al. [3] could not confirm such a new peak near 600 cm$^{-1}$ for YBa$_2$Cu$_3$O$_6$ crystals. The new mode could be due to different local environments of Cu–O bond or due to leakage of $E_g$ modes induced either by Fröhlich electron-phonon interaction [3] or by disorderliness of defects [4].

In this report, we are interested not in the existence of the “new” mode. Rather, attention is focused on the relative intensity of the $B_{1g}$ mode of plane oxygens near 340 cm$^{-1}$ to the $A_{1g}$ mode near 502 cm$^{-1}$, denoted by $R_I(340/502)$ hereafter. It is known that the intensities of these modes do depend on the changes in electronic structure of Y123. [5, 6, 7, 8] However, these modes are sensitive to polarization, and thus would give us information regarding orientations of “micro-crystals” in the investigated part of the samples. From polarized micro-Raman measurements on single-crystals embedded in ceramic Y123, we find that $R_I(340/502)$ for a crystal whose c-axis is in the laser-beam direction and one of the square edges is in the polarization direction, i.e. in $z(xx)$ polarization, decreases strongly as the samples are heated. For a crystal whose c-axis is tilted approximately 90° from the laser-beam direction, i.e. in $x(zz)$ polarization, $R_I(340/502)$ increases at the initial increase of the sample temperature. Throughout this work, $x, y$ axes are not distinguished. In Y123 thin-films, however, no such change was observed even when heated to higher temperature than single-crystals were. Therefore, we interpret that the change in $R_I(340/502)$ of Y123 single-crystals as heated is not due to electronic or structural changes nor thermal decomposition in the heated samples. We propose that a single-crystal, when heated, is fractured into many “micro-crystals” and these micro-crystals thermally fluctuate in orientations, leading to change in $R_I(340/502)$ for single-crystals. For Y123 thin-films, such thermal motions are not favorable since there are only a few layers of micro-crystals on top of the substrate.
1 Experimental

Ceramic Y123 samples were prepared by the usual solid state reaction method. The superconducting critical temperature of the ceramic samples were near 92 K, and the 90%-10% transition width was less than 2 K. The X-ray diffraction pattern did not show any noticeable amount of impurities. Rietveld refinements to the X-ray diffraction data show that the structure of the ceramic Y123 samples is orthorhombic $Pmmm$ and the unit cell parameters are $a = 3.82 \text{ Å}, b = 3.89 \text{ Å}, c = 11.68$ in close agreement with the known values [9]. From iodometric titration technique, the oxygen content of the ceramic samples are determined to be $6.90 \pm 0.03$. Thin film Y123 samples were prepared in situ on (100) surfaces of SrTiO$_3$ substrates by dc magnetron-sputtering method in a mixture of 50 mTorr oxygen and 200 mTorr argon gases. The substrate temperature was kept at 720 °C during deposition. After deposition, the films were held at 450 °C for 1 h in 600 mTorr oxygen. Films were found to be grown in c-direction by X-ray diffraction and thickness of the films is about 2000 Å. This is well beyond the skin depth of the probing laser light used in the Raman measurements. Superconducting transition temperatures of the films were between 85–88 K and the critical current densities at zero field were measured to be $\approx 2 \times 10^6 \text{ A/cm}^2$ at 77 K. The oxygen content of the film is estimated to be $\approx 6.86$ from the Raman frequency of the apical oxygen mode.

The Raman spectra were excited with the 5145 Å line of an Ar-ion laser, dispersed with Jobin Yvon U1000 double monochromator, and recorded with a Hamamatsu PM tube R94302. The incident laser beam is polarized and all the measurements are done in the same polarization in back scattering geometry. The spectrometer slit widths were 500 μm which corresponds to a resolution of 4.6 cm$^{-1}$ over the spectral range of interest. The ceramic samples were mounted on an Olympus microscope, and each measurement was done on a surface of one crystal embedded in a freshly fractured surface of the ceramic samples. Measurements were repeated on many crystals to obtain representative results. The thin-film samples were measured in the same fashion as the ceramic ones. Heating was done either by increasing the power of the probing laser-beam or by directly heating in a Pyrex glass cell.

2 Results and Discussion

In Y123 crystals, five, $4A_{1g} + B_{1g}$ in tetragonal notation, Raman active modes are detectable in backscattering geometry [10]. All of the five allowed modes are due to displacements along the c axis. In our heating-effect experiment, all the allowed modes were observed in each measurement for quality evaluation of the spectra. However, we would concentrate on R1 (340/502), i.e. the relative intensity of the $B_{1g}$ mode near 340 cm$^{-1}$ (hereafter 340 mode) and the $A_{1g}$ mode near 502 cm$^{-1}$ (hereafter 502 mode), as explained in the introduction part. The 340 mode is a mode of plane oxygens involved in out-of-phase bending motion, and is forbidden in z(zz)$\bar{x}$ polarization. While the 502 mode is the apical oxygen mode and is allowed in both z(xx)$\bar{x}$ and z(zz)$\bar{x}$ polarizations.

Fig. 1. A typical Raman spectra of a YBa$_2$Cu$_3$O$_{6.9+}$ single crystal embedded in ceramic samples in z(xx)$\bar{x}$ polarization at different levels of laser power. All the spectra are from the same spot in the same crystal, and were recorded in the order that the laser power increases from 60 mW to 500 mW. The actual power at the sample surface is 1/75 of the laser power

Raman spectra of a crystal in ceramic samples whose c-axis is in the beam direction and one of the square edges is linear polarization, i.e. in z(xx)$\bar{x}$ polarization, are taken at different levels of laser power as shown in Fig. 1. In this polarization, the 340 mode is allowed and the intensity of it is strongest. All the spectra are from the same spot in the same crystal in ceramic samples, and were recorded in the order that the laser power increases from 60 mW to 500 mW. The beam power at the sample surface is approximately 1/75 of the laser power and the impinging area is about $0.3 \times 10^{-10} \text{ m}^2$. After the measurement at 500 mW, the center of the beam spot was found to be partially evaporated. The frequency of the 502 mode varies with the oxygen content [2, 11], and the frequency of 502 cm$^{-1}$ of the mode taken at 60 mW, which was found to be low enough not to produce any local-heating, indicates that the oxygen content of the crystal under investigation is near 6.91 in excellent agreement with the titration result. The peak positions of the 340 mode and the 502 mode, determined by fitting a Gaussian function to each spectrum, are shown in Table 1. In parentheses are the peak widths determined by full-width at the half-maximum (FWHM) of each peak. The peaks are broadened as the laser power increases, as expected. The peak position of the 502 mode changes from 502 cm$^{-1}$ at 60 mW to 496 cm$^{-1}$ at 500 mW of laser power. The ratios of the peak values, not the peak areas, as function of the laser power are graphed in the Fig. 2 (filled squares). As is seen in the