Single-Crystal Micro-Raman Spectroscopy of Phases in the Y-Ba-Cu-O Superconductor

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Single-crystal micro-Raman spectroscopy is used to characterize the structures and phonon properties of the $YBa_2Cu_3O_{6+x}$ and Y_2BaCuO_5 phases present in the original 93-K Y-Ba-Cu-O superconducting compound. The vibrational Raman spectrum of the opaque $YBa_2Cu_3O_{6+x}$ phase consists of prominent bands at 142, 338, 483, and 595 cm^{-1}. Polarized spectra of 10–30-μm single crystals of this phase are consistent with the tetragonal average structure determined by single-crystal x-ray diffraction measurements on the same samples.

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The search for high-temperature superconductivity has recently led to the attainment of a critical temperature T_c of 93 K in a mixed-phase Y-Ba-Cu-O compound system.[1] The mechanism of the unprecedented high-temperature superconductivity of this class of compounds is not yet known. Central to an understanding of the structure-property relationships of these new materials, and ultimately the basis of high-T_c superconductivity itself, are measurements of single-crystal properties. Single-crystal x-ray diffraction has been used to determine the crystal structures of the component phases.[2] Information on the phonon properties is necessary for constraining the vibrational density of states and electron-phonon coupling strengths in the superconducting component. This information is crucial for understanding superconductivity in this material, and in particular whether or not the mechanism is of the conventional phonon-mediated Bardeen-Cooper-Schrieffer type.[3] Because of the fine-grained nature of the material, microanalytical techniques are required for an accurate determination of single-crystal vibrational spectra of the component phases. In this Letter we present and describe room-temperature single-crystal micro-Raman spectra of the phases found in the superconducting compound originally reported by Chu and co-workers.[1] Together with the previously reported structural and compositional studies,[2] the Raman spectra are used both to identify individual components and to constrain structural and phonon properties of the phases.

Samples were obtained from Chu and co-workers and had been synthesized from a nominal starting composition of $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ as described in their original report.[1] Polished sections were prepared for both micro-Raman and scanning-electron-microprobe (SEM) analysis.[2] An example of one of the polished sections viewed through a light microscope is shown in Fig. 1. The sample was observed to be a polyphase assemblage containing at least one reflecting, nearly opaque phase together with a transparent green phase. The two phases were shown to have the compositions $YBa_2Cu_3O_{6+x}$ ($x \sim 0.5$) and Y_2BaCuO_5, respectively, by SEM, powder x-ray, and single-crystal x-ray methods.[2] The opaque material was shown under reflecting optics to contain elongated crystals of 10–30 μm in the longest dimension. Numerous opaque grains exhibit parallel extinction, whereas others did not. The transparent green phase appeared to be more finely crystallized, with crystals generally less than 5 μm.

Raman spectra were measured with a micro-optical spectrometer system described in detail elsewhere.[4] In the present experiments a backscattering geometry was used, along with reflecting microscope objectives. Excitation was provided by the 514.5-nm Ar^+ laser line. With this microscope system, the laser beam was focused to $\simeq 1$ μm on the sample. An optical scanning multichannel analyzer was used for detection. Both phases were found to decompose under the laser above a critical power level. The laser power at the sample was therefore kept below $\simeq 1$ mW and 10 mW for the Y_2BaCuO_5 and $YBa_2Cu_3O_{6+x}$ phases, respectively.

FIG. 1. Photomicrograph with reflecting optics of a polished section of the Y-Ba-Cu-O mixed-phase 93-K superconducting compound (Ref. 1). The white rectangular features are polished microcrystals of the opaque $YBa_2Cu_3O_{6+x}$ phase. The horizontal dimension of the image is 150 μm.

Micro-Raman spectra of random grains within the polished section are shown in Figs. 2 and 3. A large variation in the character of the spectra is observed, depending on the region that is excited by the laser. Excitation of a polished face of a randomly oriented crystal of $YBa_2Cu_3O_{6+x}$ is shown in Fig. 2. Because of the high degree of parasitic scattering at low frequencies due to the highly reflecting surface of the opaque crystals, we were unable to measure the spectrum below $\simeq 80$ cm^{-1}. Strong and comparatively broad bands at 483 and 338 cm^{-1} are observed, together with a narrow-lined peak at 142 cm^{-1}. A very weak band at $\simeq 450$ cm^{-1} was also observed in some of the crystals. No strong features were observed above 700 cm^{-1}.

The spectrum of the assemblage in the region of the transparent Y_2BaCuO_5 phase is shown in Fig. 3. This phase was the major component in the original sample described by Chu and co-workers.[1] Small (1–5 μm) inclusions in the opaque phase were also observed in the polished sections of the original material. Microprobe analysis of the inclusions indicated that they had element ratios that were similar to that of Y_2BaCuO_5. It was not known, however, if the inclusions constitute a third phase in the assemblage. The Raman spectra of these inclusions clearly indicate that they are due to the orthorhombic Y_2BaCuO_5 phase and do not constitute a third phase. In regard to the suggestion of possible interfacial superconductivity,[1] no unique properties of the interface between the two phases are observed by Raman scattering (at room temperature).

Microprobe analysis and both single-crystal and powder x-ray diffraction measurements of these samples indicate that the average structure of $YBa_2Cu_3O_{6+x}$ is tetragonal with $a = 3.859$ Å and $c = 11.71$ Å (probable space group $P\bar{4}m2$, $Z = 1$) and that of Y_2BaCuO_5 is orthorhombic ($Pbnm$, $Z = 4$).[2] The larger number of bands observed in the spectrum of the latter is therefore consistent with its larger unit cell and lower symmetry. From the x-ray results, we must conclude that a large number of phonons predicted to be Raman active are not yet observed for $YBa_2Cu_3O_{6+x}$. On the basis of the tetragonal average structure, one may proceed to obtain polarized spectra of microcrystals with prescribed orientations in the polished section. Those crystals that displayed a strong parallel extinction were assumed to be oriented such that the plane containing the a and c axes is perpendicular to the incident (and scattered) light.[5] Numerous crystals with this property appeared to be elongated. The opaque crystals that did not exhibit parallel extinction were assumed to be oriented with the c axis parallel to the incident light. This determination of the crystal orientations was supported by the observed Raman spectra, as discussed below.

Representative Raman spectra of the oriented single crystals identified optically are shown in Fig. 4. The corresponding elements of the Raman scattering tensor are indicated for each spectrum.[6] A total of four bands are observed in these polarized single-crystal spectra. In addition, a distinct separation of the phonons observed in Fig. 2 is achieved as a function of orientation and polarization, which indicates that the observed bands arise from first-order Raman scattering. The high degree of anisotropy in the spectra is consistent with the layered, oxygen-deficient perovskitelike structure determined by x-ray diffraction.[2] Moreover, the observed separation and orientation dependence of peaks are consistent with the tetragonal structure determined for these crystals. The broad diffraction peaks observed in the x-ray study, however, were also consistent with an orthorhombic structure that is heavily twinned to give a tetragonal average.[2] The effect of microtwinning in the present crystals would be to give a structure that appears uniaxial by optical microscopy and micro-Raman spectroscopy. The observed broadening of the higher-wave-number

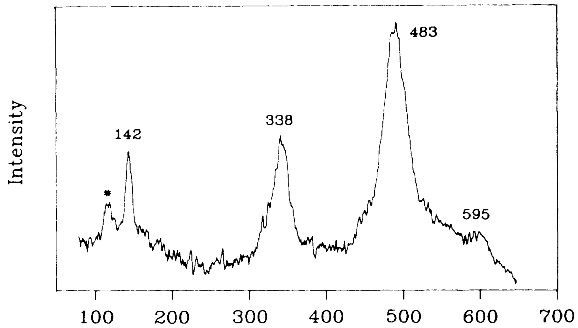

FIG. 2. Micro-Raman spectrum of a random crystal of $YBa_2Cu_3O_{6+x}$ identified optically in the polished section. The peak marked with an asterisk is an Ar^+ plasma line. The resolution is 5 cm^{-1}.

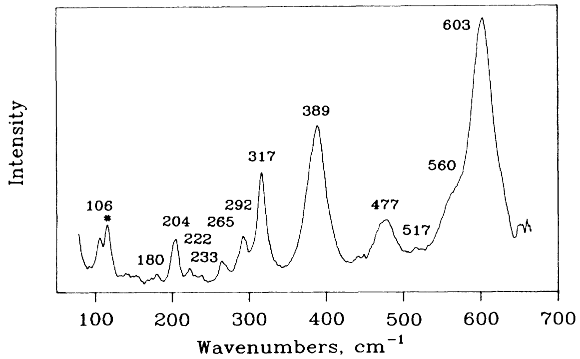

FIG. 3. Micro-Raman spectrum (mixed polarization) of a polycrystalline aggregate of the green Y_2BaCuO_5 phase. The laser was defocused to a beam waist of ~ 25 μm to minimize orientation effects. The uncertainty in frequencies is ± 1 cm^{-1}, except for the broad peaks or shoulders that are not fully resolved (uncertainty of ± 5 cm^{-1}).

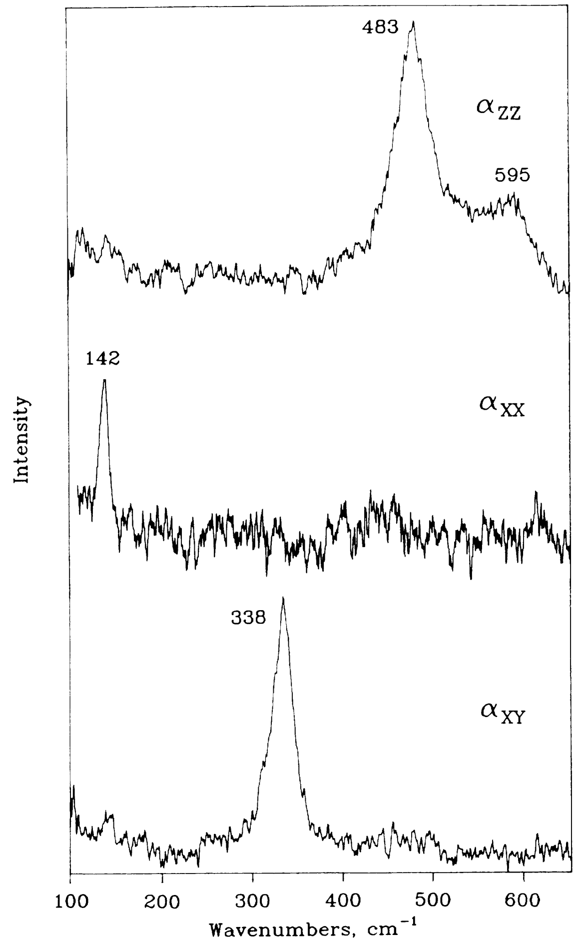

FIG. 4. Orientation and polarization dependence of Raman spectra of single crystals of $YBa_2Cu_3O_{6+x}$ in the polished section. Top: Polarization of incident radiation ($\mathbf{e}_i$) parallel to the polarization of the scattered radiation ($\mathbf{e}_s$) and both parallel to the c axis, giving the α_{zz} tensor component. Middle: $\mathbf{e}_i$ parallel to $\mathbf{e}_s$, and both perpendicular to the c axis; α_{xx}. Bottom: $\mathbf{e}_i$ perpendicular to $\mathbf{e}_s$, radiation propagation along the c axis; α_{xy}.

peaks in the Raman spectra may also be due microtwinning, which could cause a breakdown of $(\mathbf{k}=0)$ selection rules as well as introduce local strains. The possibility of small orthorhombic domains of order 100 Å in the present crystals[2] is consistent with the results of other diffraction studies[7] which have found an orthorhombic cell for $YBa_2Cu_3O_{6+x}$. Differences in quenching rates from high temperature as well as oxygen annealing conditions are likely to be responsible for the observed structural differences between samples.

Specific normal-mode assignments must await a more complete determination of the spectra and further structure refinements. At this point, however, it may be useful to point out that the 483-cm^{-1} phonon observed in $YBa_2Cu_3O_{6+x}$ is close to that of the A_{1g} breathing mode observed in Cu_2O (515 cm^{-1}),[8] a structure in which there are two short Cu-O distances (1.85 Å)[9] similar to the two short Cu(1)—O bonds (1.78 Å) in the superconductor.[2] It is therefore possible that the modes in the two crystals involve similar Cu-O displacements. A Cu-O breathing mode has been proposed as contributing to the high T_c of 36 K observed in $(La_{2-x}Sr_x)CuO_4$,[10] on the basis of the mechanism proposed for superconductivity in $Ba(Pb_{1-x}Bi_x)O_3$ and band-structure calculations.[11] A more complete determination of the spectra, including temperature dependence and possible soft-mode behavior, should be facilitated by the synthesis of larger and higher-optical-quality crystals with well-characterized structures and compositions.

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