Raman study of lattice modes in the high-critical-temperature superconductor Y-Ba-Cu-O

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Raman spectra of high-temperature superconducting materials composed of Y-Ba-Cu-O compounds are reported for the first time. These spectra show numerous lattice modes which are attributed both to the superconducting phase $YBa_2Cu_3O_x$ and also to the impurity phases of $BaCuO_2$ and Y_2BaCuO_5. Raman spectroscopy is shown to be a sensitive probe of both the phonon structure of the superconductor and of the impurity phases in the material.

In recent months a new class of superconductors has been discovered with critical temperatures above the boiling point of liquid nitrogen. This important development was catalyzed by Bednorz and Müller's discovery[1] of a 30 K transition temperature in La-Ba-Cu-O compounds. Subsequently these results were extended to temperatures above 90 K by Wu *et al.*,[2] Chu *et al.*,[3] Tarascon *et al.*,[4] and Zhongxian *et al.*[5] in various mixtures of Y-Ba-Cu-O compounds.

In this paper we report on a study of the Raman-active lattice phonons of the material $YBa_2Cu_3O_x$, which has a transition above 90 K as described by Grant *et al.*[6] There are several motivating factors behind this work. First, lattice modes are a sensitive probe of the structure of materials and can lead to a better understanding of the superconducting phase, and second, these lattice modes may be of critical importance to understanding the superconducting mechanism.[7] Furthermore, Raman spectroscopy is seen to be a sensitive probe of impurity phases in superconducting samples.

The experiments were conducted using a Jobin Yvon U1000 spectrometer equipped with holographic gratings and photon-counting electronics. The excitation source was an argon laser operating at 5145 Å with a power of approximately 100 mW at the sample surface. The laser beam was focused on the sample by a 7-cm-focal-length cylindrical lens. The axis of the beam was inclined at an angle of 70° to the sample normal. The polarization of the incident beam was in the p direction. The scattered light was collected at right angles to the incident laser radiation with no polarization analysis of the outgoing radiation. The samples, which were in pellet form, were mounted on a motor rotating at 60 Hz to reduce heating effects. The laser radiation was incident on the sample approximately 5 mm from the axis of rotation producing an annulus of irradiance with an area of 60 mm^2. This produced a rather low power density of 1.7 W/cm^2 while still retaining a high throughput for the spectrometer. The spectrometer slit widths were 500 μm, which corresponds to a resolution of about 5 cm^{-1} over the spectral range of interest.

The superconducting samples were produced by mixing ultrapure Y_2O_3, BaO, and CuO powders in atomic ratios of [Y]:[Ba]:[Cu] of 1:2:3. This mixture was then heated in flowing oxygen for 12 h. The resulting black powder was formed into a pellet and sintered at 950 °C in oxygen for 12 h. The superconducting properties of these samples, which were primarily single-phase material of $YBa_2Cu_3O_x$, are described by Grant *et al.*[6] Prior to these experiments, Y_2BaCuO_5 was assumed to be the most likely impurity phase in the superconductor. Samples of this material as well as the other possible impurity phases, $Y_2Cu_2O_5$ and $BaCuO_2$, were prepared by mixing the starting materials in the appropriate atomic ratios and heating them at 950 °C in flowing oxygen for 12 h. The resulting powders were formed into pellets and sintered at 950 °C for 4 h. These materials were studied along with the superconductor.

Two batches of superconducting samples with transition temperatures greater than 90 K and slightly varying barium composition were investigated. The Raman spectrum

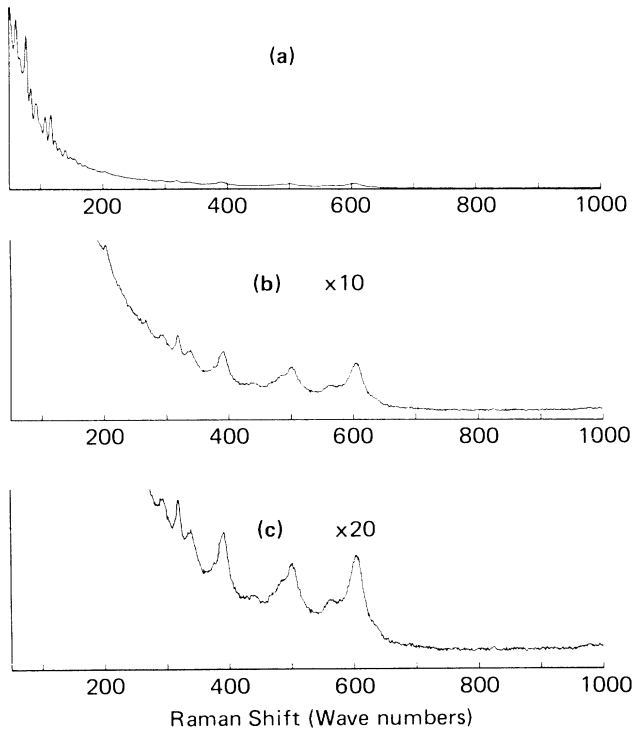

FIG. 1. Raman spectrum of the Y-Ba-Cu-O superconductor (batch 1) from 50 to 1000 cm^{-1} with various scale expansions.

of a sample from the first batch of superconducting material is shown with various expansion factors in Fig. 1. The spectra were obtained with 20 h of integration and a separation between each spectral point of 1 cm^{-1}. In the spectral region between 180 and 700 cm^{-1} 12 Raman lines occurring at frequencies of 187, 204, 267, 293, 319, 337, 391, 438, 480, 502, 563, and 605 cm^{-1} are evident. The line widths range from about 10 to almost 40 cm^{-1}. These broad features may be characteristic of the mixed valency of the Cu^{3+}-Cu^{2+} expected in the superconducting phase. The sharp lines below 180 cm^{-1} are due to laser plasma lines and the Raman spectrum of air.

In order to exclude the possibility that some of these spectral features might be due to some of the initial materials which were not reacted to completion, we have compared the background-subtracted Raman spectra of this superconducting material to that of the various starting materials (i.e., CuO, Y_2O_3, BaO) as shown in Fig. 2. It is clear from a comparison between these spectra that the Raman modes observed in the superconductor are not due to the starting materials.

In Fig. 3 the spectra of a sample from the first batch of superconducting material are compared to possible final reaction products, which by themselves do not show superconducting properties, but could occur in small concentrations in the superconductor. The phase diagram of this system with possible final products of $YBa_2Cu_3O_x$, Y_2BaCuO_5, $BaCuO_2$, and $Y_2Cu_2O_5$ is described by Hwu *et al.*[8] Of the 12 lines previously identified, 8 are coincident, within the experimental error (± 2 cm^{-1}), with the spectral features of Y_2BaCuO_5, which is the green phase found in the original Chu superconductor.[3] However, x-ray analysis indicates that the concentration of this phase is small. We speculate that these features show up distinctly in the spectra because the Y_2BaCuO_5 has large Raman cross sections and is relatively transparent at the 5145-Å excitation wavelength of the laser. $BaCuO_5$ and $Y_2Cu_2O_5$ spectra show no similarity to that of the superconducting material. Of the four remaining Raman modes we attribute the distinct lines at 337 and 502 cm^{-1} to lattice vibrations of the $YBa_2Cu_3O_x$ superconductor. The analysis of the weak mode at 187 cm^{-1} and that at 563 cm^{-1} is more uncertain due to marginal signal-to-noise ratio and possible interference of air Raman lines for

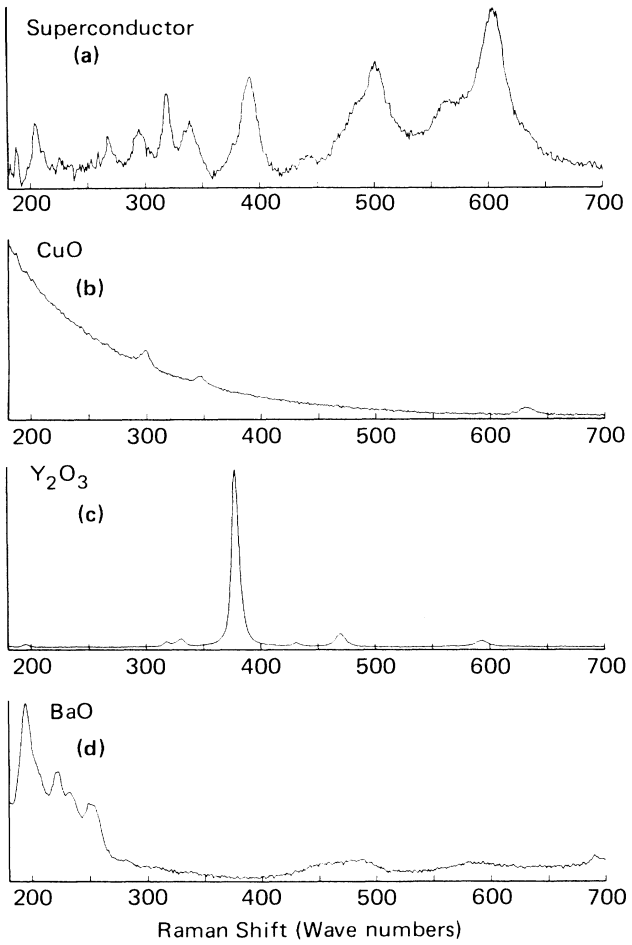

FIG. 2. Comparison of the background subtracted Raman spectrum of the superconductor (batch 1) to that of the various starting materials.

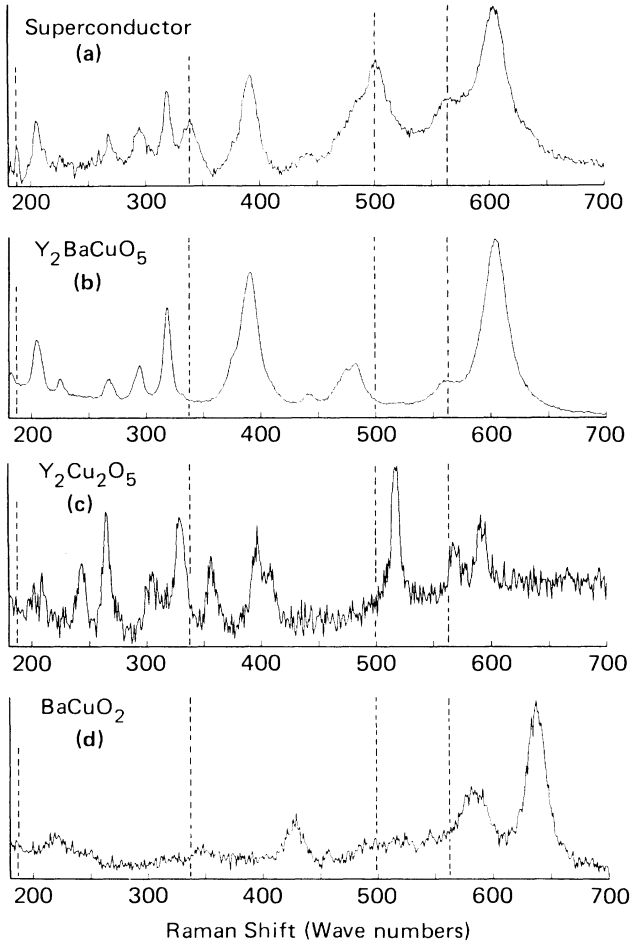

FIG. 3. Comparison of the background subtracted Raman spectrum of the superconductor (batch 1) to that of the various possible final products.

the low-frequency mode and overlap of the 563-cm^{-1} mode with spectral features of Y_2BaCuO_5.

To further substantiate the above findings, a second batch of superconducting materials with a slightly higher barium stoichiometry were investigated. The spectra of these samples again show the characteristic lines at 327 and 502 cm^{-1}, which we have identified as modes of the superconducting phase. A spectrum from this batch is shown in Fig. 4(a). These spectra still leave open the possibility of superconducting modes at the 187 and 563 cm^{-1}. The spectrum of Fig. 4(a) does not show the presence of the impurity mode Y_2BaCuO_5 as seen in the first batch. However, the presence of the impurity $BaCuO_2$ is clearly indicated by comparison with the $BaCuO_2$ reference spectrum shown in Fig. 4(b) as expected from the phase diagram.[8]

In summary, we report here for the first time the Raman spectra of high-temperature superconducting Y-Ba-Cu-O compounds. These spectra contain numerous low-frequency modes which cannot be attributed to any of the starting materials. At least two and possibly four of these lattice vibrations are attributed to the $YBa_2Cu_3O_x$ superconducting phase. These features were consistent in two separate batches of material. The other spectral features are attributed to the impurity phases Y_2BaCuO_5 in the first batch and to $BaCuO_2$ in the second batch. These phases can be identified with more specificity and sensitivity by Raman spectroscopy than by x-ray diffraction analysis. Future studies will investigate the temperature dependence of these modes and the feasibility of measuring the superconducting gap with Raman spectroscopy.

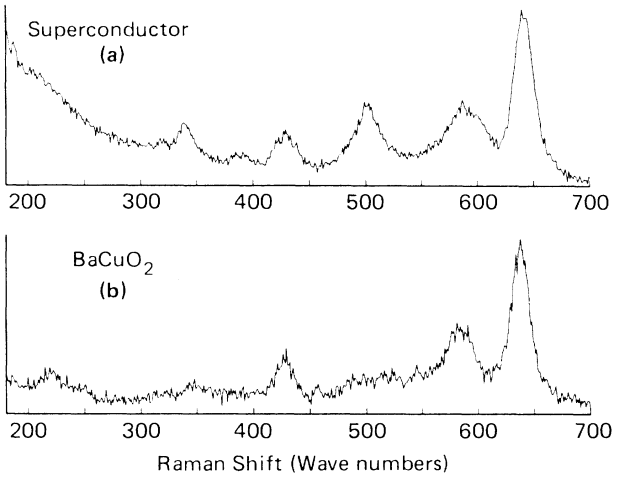

FIG. 4. Comparison of the Raman spectrum of the superconductor (batch 2) to that of the final product $BaCuO_2$.

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