

Cu-O vibrations of $\text{Ba}_2\text{YCu}_3\text{O}_x$

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We present Raman and infrared absorption data for $\text{Ba}_2\text{YCu}_3\text{O}_x$ with $7 > x > 6$ for several samples with well-characterized oxygen content. Over this range the material has an oxygen-deficient tripled perovskite structure whose superconductivity properties depend critically on x . An orthorhombic-to-tetragonal transition occurs for $x \approx 6.5$. We have examined both phases for the frequency range $\omega > 400 \text{ cm}^{-1}$ which contains the Cu-O bond-stretching vibrations. A force-constant model has been developed which allows us to assign the features in the spectra. Our results are consistent with the linear Cu-O-Cu-O chains in $\text{Ba}_2\text{YCu}_3\text{O}_7$ being absent in the nonsuperconducting $\text{Ba}_2\text{YCu}_3\text{O}_6$.

In recent months several groups have reported a superconductivity transition temperature, T_c , above 90 K for several oxides¹⁻⁶ of which the prime example is $\text{Ba}_2\text{YCu}_3\text{O}_7$. The properties of these materials depend critically on their oxygen content.^{2,7,8}

The structure of $\text{Ba}_2\text{YCu}_3\text{O}_7$, a previously unknown oxygen-deficient perovskite, is orthorhombic with a tripled c axis.⁹⁻¹² A unit cell is shown in Fig. 1. There are two square planar Cu(2)-O(2,3) layers that give rise to two-dimensional networks. In the center there is a linear chain of Cu(1)-O(4)-Cu(1)-O(4) along the x axis and O(1) atoms along the z axis that bridge the Cu(1) and Cu(2) layers. The tripled perovskite structure has been studied⁷ for $\text{Ba}_2\text{YCu}_3\text{O}_x$ as a function of x and has been found to be stable for $7 > x > 6$. An orthorhombic-to-tetragonal transition occurs for $x \approx 6.5$ where both phases coexist at room temperature.⁷ The tetragonal phase is semiconducting.^{7,8}

Here we present the results of Raman and infrared (ir) studies of $\text{Ba}_2\text{YCu}_3\text{O}_x$ for several samples with well-characterized oxygen content. We discuss the range $\omega > 400 \text{ cm}^{-1}$ where the vibrational features are due to Cu-O bond stretching. Assignments are proposed for the spectra in this frequency range. A physically reasonable force-constant model is developed to support the assignments and predict the phonon density of states.

For our experiments, pellets of $\text{Ba}_2\text{YCu}_3\text{O}_x$ were made by conventional ceramic methods.² Samples with $x \approx 7$ were prepared by annealing for 16 h at 700°C in oxygen and cooling slowly to room temperature in oxygen. Several samples with $x < 7$ were prepared by annealing further in argon. The oxygen content was determined by heating a portion of a sample in hydrogen to $\sim 1000^\circ\text{C}$ and measuring the weight loss on reduction to Cu metal and Ba-Y oxides, i.e., by a conventional thermogravimetric analysis. The unit-cell parameters were determined from x-ray powder diffraction data. In agreement with previous work,⁷ our samples with $x = 6.47$ clearly contained both orthorhombic and tetragonal phases as determined from the x-ray powder pattern at room temperature. Our samples with $x > 6.47$ were orthorhombic and samples with $x < 6.47$ were tetragonal.

Raman spectra were recorded at room temperature with a resolution of 5 cm^{-1} and with the laser power incident on the sample always less than 100 mW. Laser wavelengths of 5145 and 4880 Å gave similar Raman spectra. For infrared absorption measurements the pellets were reground, mixed with ethanol, and dried on the surface of a polished Si substrate. A film of the powdered $\text{Ba}_2\text{YCu}_3\text{O}_x$ remained. Transmission spectra were measured with a Fourier-transform infrared spectrometer at a resolution of 4 cm^{-1} . Spectra were divided by spectra from a clean Si wafer to eliminate substrate features.

Special care was taken to ensure the reproducibility of results. Spectra were measured for samples shortly after they were prepared and after a few days to investigate possible changes. Raman spectra were recorded on both the outside surface of annealed pellets and on freshly broken surfaces. In the later case especially, scattered laser light gave rise to the strong background observed for our

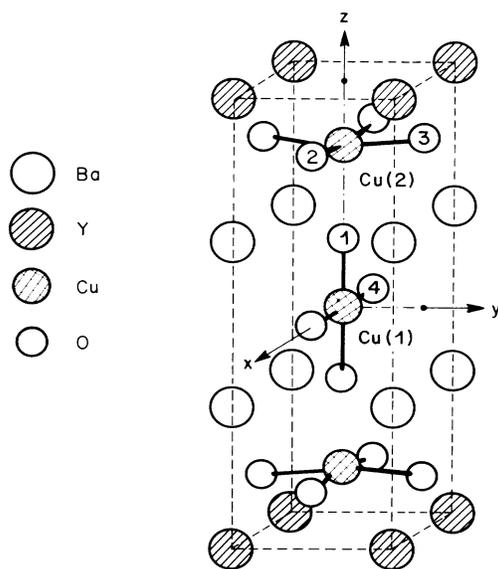


FIG. 1. A unit cell of $\text{Ba}_2\text{YCu}_3\text{O}_7$ that is convenient for the discussion of the Cu-O vibrational modes.

data. A few spectra were recorded for samples from different sources.

Raman spectra are shown in Fig. 2. The top two spectra of orthorhombic samples show a strong feature at 495 cm^{-1} and a weak feature at 435 cm^{-1} . The bottom two spectra of tetragonal samples show features at 470 , 590 , and 625 cm^{-1} . The sample with $x=6.47$ showed a mixture of orthorhombic and tetragonal phases in its powder diffraction pattern and also showed a Raman spectrum that appears to be a mixture of both phases. This is clearest for the band near 480 cm^{-1} that is broadest for the $x=6.47$ sample because it is a superposition of the 470 - and 495-cm^{-1} bands.

Phonon-related infrared absorption features were not observed in the orthorhombic samples in our measurements, presumably because these samples were too metallic. Phonon absorption features were observed at 636 , 592 , and 529 cm^{-1} in tetragonal samples as is shown in

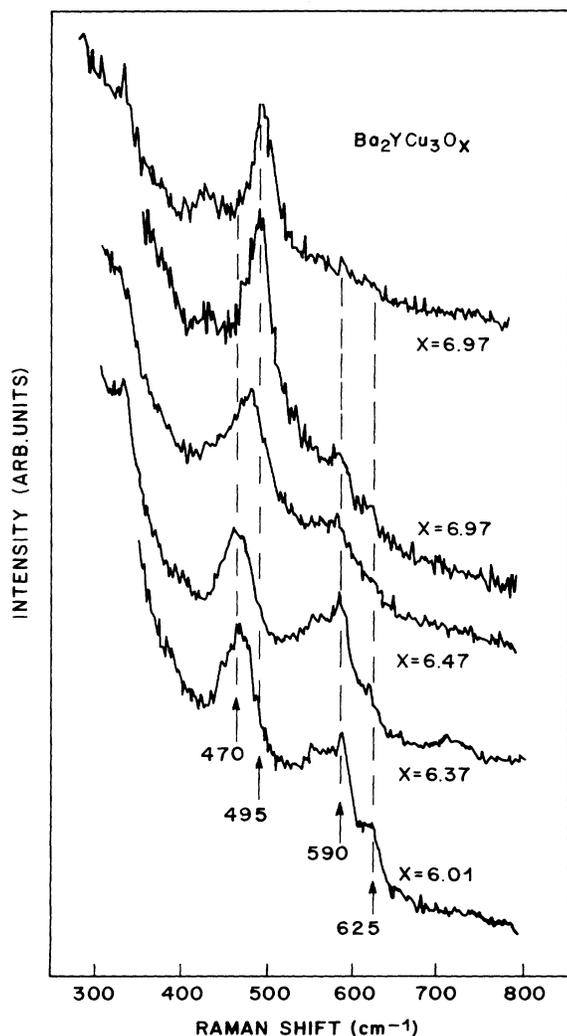


FIG. 2. Raman spectra for $\text{Ba}_2\text{YCu}_3\text{O}_x$. From top to bottom, the spectra are for samples that received the following final anneal in Ar: no anneal, 1 h at 350°C , 1 h at 450°C , 1 h at 550°C , and 2 h at 650°C .

Fig. 3. Bonn *et al.*,¹³ who have measured the reflectivity, obtain features at 548 and 609 cm^{-1} in the ir conductivity of $\text{Ba}_2\text{YCu}_3\text{O}_7$ in reasonable agreement with our ir observations for the tetragonal phase.

Several aspects of our Raman data show that laser heating did not give rise to spurious results. Annealing samples in Ar at 350° for 1 h did not cause oxygen removal. Thus our samples would be resistant to laser-induced damage even if locally heated to 350°C . Further, the sample with $x=6.47$ that consisted of mixed orthorhombic and tetragonal phases showed evidence of both phases in the Raman spectrum. Laser heating was not severe enough to cause sufficient oxygen evolution to make the sample fully tetragonal in the probed volume. We did find that after allowing samples to remain in laboratory air for a day, the Raman and ir features at $\sim 630\text{ cm}^{-1}$ increased in intensity with respect to other features. We do not assign the 630-cm^{-1} band separately but simply group it with the $\sim 590\text{-cm}^{-1}$ features with which it appears, because it is difficult to know whether or not any portion of it is intrinsic to the $\text{Ba}_2\text{YCu}_3\text{O}_x$.

The following considerations are independent of a specific force-constant model and allow the high-frequency features of $\text{Ba}_2\text{YCu}_3\text{O}_x$ to be assigned. The Cu-O vibrations are well known to exhibit the highest frequencies, in the range of 500 cm^{-1} and above, and should be well separated from all other modes which should lie at frequencies near 300 cm^{-1} and below. Of the 36 optic modes at the Γ point for orthorhombic (D_{2h}) $\text{Ba}_2\text{YCu}_3\text{O}_7$, there are just 7 Cu-O bond-stretching motions. Of these 7 modes there are 4 infrared-active modes (B_{1u} , B_{2u} , and two B_{3u}) and 3 Raman-active modes (A_g , B_{2g} , and B_{3g}). The B_{2g} , B_{3g} , B_{2u} , and B_{3u} modes all involve oxygen dis-

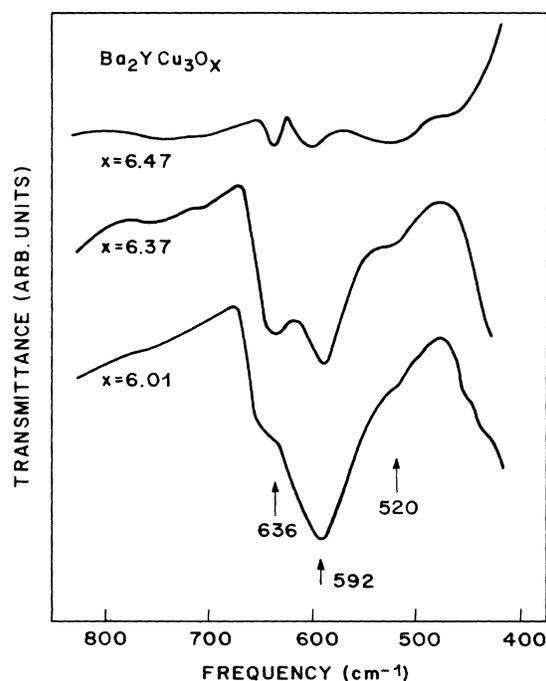


FIG. 3. Infrared absorption spectra for $\text{Ba}_2\text{YCu}_3\text{O}_x$. The bottom spectrum has been multiplied by 0.2.

placements in the x - y plane. For example, there are B_{3u} and B_{2g} modes that involve antisymmetric stretching of the Cu(2)—O(2) bonds in the upper and lower Cu planes along x . For the ir-active B_{3u} mode, the motions in the upper and lower copper planes are in phase, while for the Raman-active B_{2g} mode they have opposite phases. The B_{2u} and B_{3g} modes involve similar motions of the Cu(2)—O(3) atoms along y . The remaining ir-active in-plane B_{3u} mode involves antisymmetric stretching of the Cu(1)—O(4) bonds. All of these Cu-O stretching modes are expected to be nearly degenerate in any simple force-constant model because there is little coupling between Cu planes and chains. The A_g and B_{1u} modes involve symmetric and antisymmetric stretching, respectively, of the O(1) atoms that bridge the Cu planes.

Two tetragonal structures have been proposed⁷ for $Ba_2YCu_3O_6$. For the first, the bridging O(1) sites are empty and there are three complete Cu-O₄ layers perpendicular to the c axis. With this structure the A_g and B_{1u} modes that involve O(1) motions along the z axis are absent. For the second structure, the O(1) sites remain occupied and the O(4) sites are empty. In this case the z -axis A_g and B_{1u} modes are present and the B_{3u} mode, due to Cu(1)-O(4) stretching, is absent. A recent neutron-diffraction study¹¹ shows that additional oxygen vacancies introduced into the $Ba_2YCu_3O_7$ structure shown in Fig. 1 occur at the O(4) sites. This observation supports the second tetragonal structure where the O(4) atoms are all absent. Only this structure is consistent with the assignment of the Cu-O vibrations that we will propose. We note that certain modes of the orthorhombic phase become degenerate in the tetragonal phase; for example, the B_{2g} and B_{3g} modes becomes E_g modes. We will retain the notation for the orthorhombic phase throughout for simplicity.

We now attempt an assignment of the spectra. For tetragonal compositions of $Ba_2YCu_3O_x$, features appear in both the ir and Raman spectra at ~ 590 cm^{-1} leading us to assign these bands to the planar B_{2g} , B_{3g} , B_{2u} , and B_{3u} motions that involve Cu(2)-O(2,3) stretching because we expect these modes to appear at nearly the same energies as was discussed above and to have the highest frequencies. We associate the 470- cm^{-1} Raman band with the A_g symmetric stretching motion of the bridging O(1) atoms. No ir band appears at this frequency. The ir band at 520 cm^{-1} is assigned to the B_{1u} antisymmetric stretching motion of the bridging O(1) atoms. Consistent with general experience, the antisymmetric stretching frequency lies above the symmetric stretching frequency. It is the assignments of the 470- cm^{-1} Raman band and 520- cm^{-1} ir band to O(1) motions along z that assume the second tetragonal structure described above.

For the orthorhombic composition $Ba_2YCu_3O_7$ we assign the Raman band at 495 cm^{-1} to the A_g symmetric stretching of the bridging O(1). The c axis of the orthorhombic phase is shorter than for the tetragonal phase⁷ and is consistent with the increase in frequency for the A_g mode. The band observed¹³ in ir reflectivity at 548 cm^{-1} is assigned to the B_{1u} mode that also involves the bridging O(1) atoms and the 609- cm^{-1} band is assigned to the B_{2u} and B_{3u} modes. The B_{2g} and B_{3g} modes should

TABLE I. Frequencies in cm^{-1} of Raman and ir active vibrational modes from our force-constant model for $Ba_2YCu_3O_7$. The Bethe notation for the representations is included in parentheses.

Raman							
A_g (Γ_{1+})	496	352	346	193	125		
B_{2g} (Γ_{3+})	599	339	314	159	88		
B_{3g} (Γ_{4+})	600	339	260	160	86		
ir							
B_{1u} (Γ_{2-})	539	326	284	269	222	185	158
B_{2u} (Γ_{3-})	600	345	261	209	196	144	101
B_{3u} (Γ_{4-})	600	593	344	308	197	167	103

also be observed in the Raman spectrum near 600 cm^{-1} , but are very weak if present. For the sample annealed for 1 h in Ar at 350° C, weak features appear near 600 cm^{-1} , but we cannot rule out the presence of a small amount of the tetragonal phase. We suggest therefore that it may be difficult to observe phonons in the two dimensional metallic Cu(2)-O(2,3) planes which makes the B_{3g} and B_{2g} modes appear much weaker for the metallic orthorhombic phase than in the semiconducting tetragonal phase. The weak 435- cm^{-1} Raman band may be a two-phonon feature arising from lower-lying modes because it falls in the range where theory predicts the absence of single-phonon modes.

Our assignments are supported by the results of a model calculation of the lattice dynamics of $Ba_2YCu_3O_7$. We have used values for force constants similar to an earlier model¹⁴ for $La_{2-x}(Sr,B)_xCuO_4$ and have incorporated information from inelastic neutron-scattering data¹⁵ for La_2CuO_4 . The Cu-O force constants were adjusted to be consistent with the data and assignments presented here. These force constants are 120.0 kdyn/cm for the Cu(1)—O(1) bond, 40 kdyn/cm for the weak Cu(2)—O(1) bond, and 110.0 kdyn/cm for the planar Cu(2)—O(2), Cu(2)—O(3), and Cu(1)—O(4) bonds. We note that the highest-frequency in-plane stretching modes have moved lower by 80 cm^{-1} (10 meV) compared to La_2CuO_4 (Ref. 15). This decrease reflects a weakening of the Cu-O in-plane bonds in $Ba_2YCu_3O_7$ and leads to Cu-O force constants that are $\sim 20\%$ smaller than for La_2CuO_4 . All other force constants are much smaller and

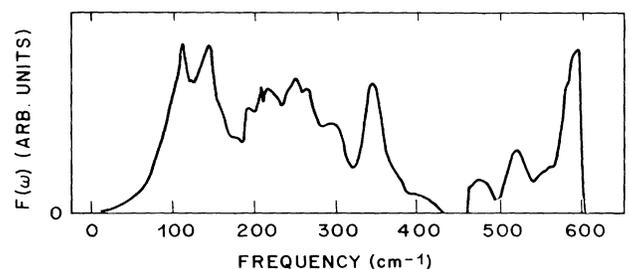


FIG. 4. The phonon density $F(\omega)$ calculated from our force-constant model.

range from 8.0 to 30.0 kdyn/cm. The calculated vibrational frequencies and their symmetries are given in Table I. The phonon density of states, $F(\omega)$, predicted by the model is shown in Fig. 4.

Our assignment of the Raman and ir data for $\text{Ba}_2\text{YCu}_3\text{O}_x$ requires that the Cu(1)-O(1) stretching vibrations along the z axis be present for the entire range $7 > x > 6$. This is only consistent with the tetragonal structure in which the O(1) sites are occupied and the O(4) sites are empty. Thus, in going from the superconducting orthorhombic to the nonsuperconducting tetragonal phase, our results indicate that the linear Cu(1)-O(4) chains are removed and therefore suggest that these chains are critical for superconductivity.

Note added in proof. Since the completion of this work, the structure of $\text{Ba}_2\text{YCu}_3\text{O}_6$ has been determined by neutron diffraction [A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Wasczak (unpublished)] and is consistent with the structure we have assumed here.

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