

Systematic Raman study of effects of rare-earth substitution on the lattice modes of high- T_c superconductors

H. J. Rosen, R. M. Macfarlane, E. M. Engler, V. Y. Lee, and R. D. Jacowitz

IBM Almaden Research Center, San Jose, California 95120

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We report on the effect of rare-earth substitution on the Raman spectra of $R\text{Ba}_2\text{Cu}_3\text{O}_7$ perovskites where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$. These spectra show both the presence of Raman modes that are intrinsic to the superconducting material and also those due to impurity phases. The intrinsic Raman modes near 340 cm^{-1} and 500 cm^{-1} which have been attributed, respectively, to $\text{Cu}(2)\text{-O}(2,3)$ bending and $\text{Cu}(1)\text{-O}(4)$ stretching vibrations, show substantial and systematic variations in vibrational frequency as a function of the ionic radius of the rare earth. These variations are in good agreement with neutron-scattering determinations of bond lengths, which supports the vibrational assignment of these modes. $\text{PrBa}_2\text{Cu}_3\text{O}_7$ shows no anomalous behavior in its vibrational spectrum even though it was the only sample studied that was not superconducting. This suggests that the valency of Pr is similar to the other rare earths studied and cannot account for the absence of superconductivity in this material. Assignment of other Raman modes in the rare-earth spectra requires identification of impurity phases, which even in small concentrations, can significantly contribute to the Raman spectra. Impurity phases can be preferentially at the surface of samples and can be substantially modified by heat treatment in an argon atmosphere. These impurity phases have previously been confused with disorder-induced Raman modes.

INTRODUCTION

During the last two years, since the discovery of a new class of high-temperature superconductors by Bednorz and Müller,¹ there has been an explosion of experimental and theoretical studies on these new materials.² These studies include a substantial number of Raman³⁻¹⁷ and infrared^{7,8,16,18,19} spectroscopic investigations that could, in principle, lead to an improved understanding of the structure of these materials, impurity phases, and the superconducting mechanism itself. Several of these investigations show very interesting soft-mode behavior for some of the phonon features.^{6,7} Such studies could prove to be very informative since vibrational spectroscopy is a sensitive probe of microstructure, which plays an important role in these materials as illustrated by the strong dependence of superconductivity on oxygen stoichiometry and ordering.²⁰ Such investigations, however, can only be useful if one can isolate the intrinsic modes of the superconductor from that of impurities^{4,17} and identify these modes with the normal-mode displacement of atoms in the unit cell. There are many conflicting reports in the literature on the Raman spectra of $R\text{Ba}_2\text{Cu}_3\text{O}_7$ perovskites. These reports differ substantially in the identification of the intrinsic modes of the superconductor as well as their assignments.^{11,15,17}

In this paper, we present a systematic study of the effects of rare-earth substitution on the Raman spectra of $R\text{Ba}_2\text{Cu}_3\text{O}_7$ materials where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$. These studies take into account the important and sometimes subtle role of impurities in interpreting these spectra. After completion of this work, a similar study of these dependencies was reported by Cardona *et al.*^{20(b)}

EXPERIMENTAL DETAILS

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 \AA with a power of approximately 100 mW at the sample surface. The laser beam was incident at 60° and focused on the sample by a 7-cm focal-length cylindrical lens to give a line image on the sample with a maximum power density of 50 W/cm^2 . The temperature of the laser-excited volume was estimated by measuring the anti-Stokes-to-Stokes ratio for the 503 and 339 cm^{-1} lines of $\text{YBa}_2\text{Cu}_3\text{O}_7$. This was consistent with laser heating being less than 10 K at room temperature. Similar conclusions were reached by consideration of the heat-flow problem.²¹ The polarization of the incident beam was in the p direction and 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 in an optical cell in an atmosphere of flowing He in order to eliminate the rotational Raman spectra of air. The spectrometer slit widths were $500\text{ }\mu\text{m}$ which corresponds to a resolution of 4 cm^{-1} over the spectral range of interest. The reported spectra were obtained by summing 100 individual scans over the spectral region between 25 and 800 cm^{-1} with an integration time of approximately 12 h.

The superconducting samples were prepared by the technique described by Engler *et al.*²² Ultrapure R_2O_3 , BaO, and CuO powders were mixed in atomic ratios of $R:\text{Ba}:\text{Cu}$ of 1:2:3 where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$. This mixture was then heated in flowing oxygen for 12 h. The resulting black powder was

formed into a pellet, sintered at 950°C in oxygen for 12 h, and slow cooled to room temperature. Several of these samples contained substantial amounts of impurity phases which were predominantly BaCuO₂ after this preparation procedure. These samples were reground and sintered at 950°C. This procedure was repeated until the impurity concentrations reached a low enough level to give satisfactory Raman spectra. Some rare-earth samples (e.g., La, Pr, Nd, and Sm) were particularly difficult to purify which may be related to the phase diagram of these materials with BaCuO₂. All the samples, except for PrBa₂Cu₃O₇, were superconducting and had orthorhombic unit cells. The critical temperatures were above 90 K. Samples of BaCuO₂ and Y₂BaCuO₅ were produced by mixing the starting materials in appropriate atomic ratios and reacting them in flowing oxygen for 12 h.

RESULTS AND DISCUSSION

Intrinsic Raman spectrum and impurity phases

The RBa₂Cu₃O₇ superconducting materials crystallize into an orthorhombic structure with the centrosymmetry space group *Pmmm*(*O*_{2h})(*D*2h1) as shown in Fig. 1. The oxygen atoms occupy four different sites: two sites O(2) and O(3) within buckled Cu(2)-O planes, one site in Cu(1)-O(1) linear chains, and one O(4) site bridged between the linear chains and planes (Fig. 1). The copper atoms occupy two different sites Cu(1) and Cu(2) which are, respectively, in the linear chains and planes. The *R*

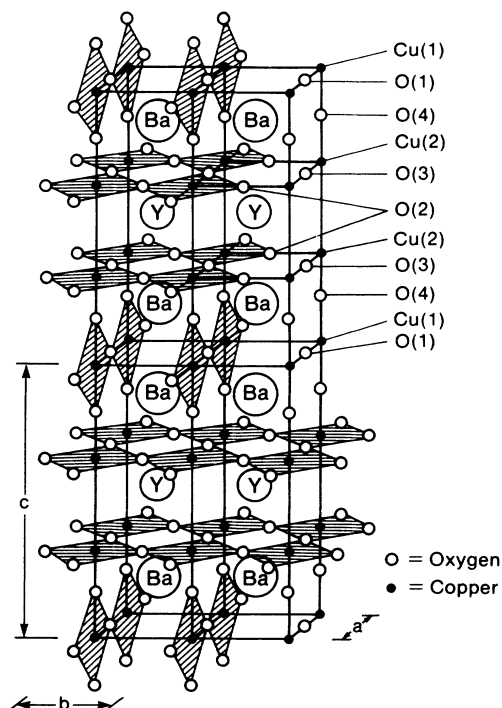


FIG. 1. Four unit cells of YBa₂Cu₃O₇ showing the copper-oxygen conducting planes and linear chains together with the positions of the atoms. The orthorhombic unit cell has dimensions $a = 3.8863$ Å, $b = 3.8231$ Å, and $c = 11.6809$ Å (Ref. 30).

and Ba atoms occupy only one site. The 13 atoms in the unit cell yield 36 vibrational modes of which 15 are Raman active. These 15 modes involve five vibrations of *A*_{1g}, *B*_{2g}, and *B*_{3g} symmetry. These normal modes do not involve displacements of the Cu(1) and O(1) atoms in the linear chains or the *R* atoms which all have *D*_{2h} site symmetry.

Figures 2(a) and 2(b) display the Raman spectra of YBa₂Cu₃O₇ and EuBa₂Cu₃O₇ in the spectral region between 25 and 800 cm⁻¹. These samples, as we shall discuss later, contain only minimal amounts of impurity phases. These spectra have four relatively strong features at 151, 339, 437, and 503 cm⁻¹ in the yttrium compound with corresponding features at 151, 311, 439, and 508 cm⁻¹ in the europium compound. Both spectra also show a weak feature near 220 cm⁻¹. Single-crystal studies of Krol *et al.*¹⁴ and Yamanaka *et al.*⁹ indicate that all these features have *A*_{1g} symmetry and involve normal-mode displacements only along the *z* crystallographic axis as illustrated by the normal coordinate calculations of Bates and Eldridge.²³ Krol *et al.*¹⁴ assign the spectral lines near 503, 437, 339, and 151 cm⁻¹, respectively, to stretching of the O(4) bridging oxygen, O(2,3) in-phase bond bending, O(2,3) out-of-phase bond bending, and Ba symmetric stretching. In agreement with these authors, we also identify these features as intrinsic to the superconducting material.

In general, Raman spectra obtained by other investigators contain these features. However, with a few exceptions these spectra also contain other Raman modes which can dominate the relatively weak modes due to the superconductor. In many cases, we suggest that these extra modes are due to impurity phases of BaCuO₂ and R₂BaCuO₅. Raman spectra of these materials are compared to that of the superconducting materials in Figs. 2(c) and (2d), respectively. The relative amounts of these

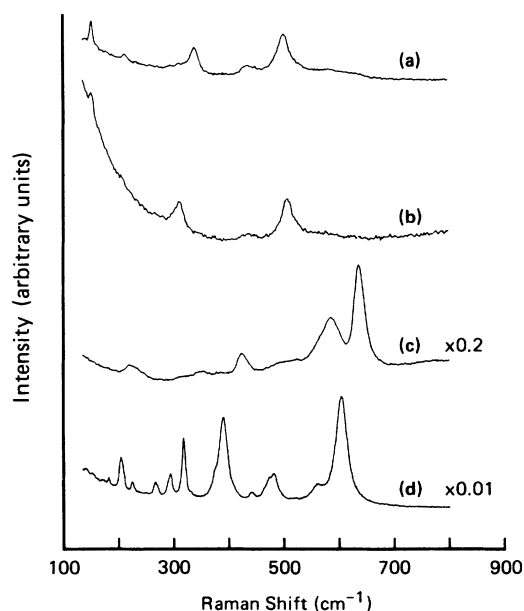


FIG. 2. Raman spectra of the following materials: (a) YBa₂Cu₃O₇, (b) EuBa₂Cu₃O₇, (c) BaCuO₂, and (d) Y₂BaCuO₅.

impurity phases depend in detail on the sample preparation conditions but often the major impurity appears to be BaCuO_2 with its characteristic strong Raman features near 641 and 587 cm^{-1} . These features are in the spectral region where disorder-induced modes are expected¹¹⁻¹³ and must be distinguished from them. Even small concentrations of this impurity phase can strongly influence the Raman spectrum. This is illustrated in Figs. 3(a) and 3(b) where the spectrum of a pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample is compared to that of the same sample prepared by mixing a 10% BaCuO_2 impurity with the superconducting material. At this impurity level, the intensity of the 641 cm^{-1} mode is about a factor of 3 larger than that of the strongest feature of the superconducting sample at 503 cm^{-1} . It also should be noted that there is considerable overlap between the BaCuO_2 modes at 430 and 221 cm^{-1} and those in the superconducting phase at 437 and 220 cm^{-1} . It is clear from these results that a BaCuO_2 impurity even at a 1% level will make a significant contribution to the Raman spectrum. Even smaller concentrations of $R_2\text{BaCuO}_5$ will affect these spectra since the stronger features of these spectra³ are about an order of magnitude more intense than that of the 641 cm^{-1} mode of BaCuO_2 (Fig. 2).

So far in our discussion, we have assumed homogeneous samples. In some cases, however, it appears that BaCuO_2 impurity is found preferentially either at the surface of the pellet or the surface of the small particulates in the sample. This is illustrated in Fig. 4 where we show the spectra of the following samples: (a) BaCuO_2 , (b) $\text{HoBa}_2\text{Cu}_3\text{O}_7$,

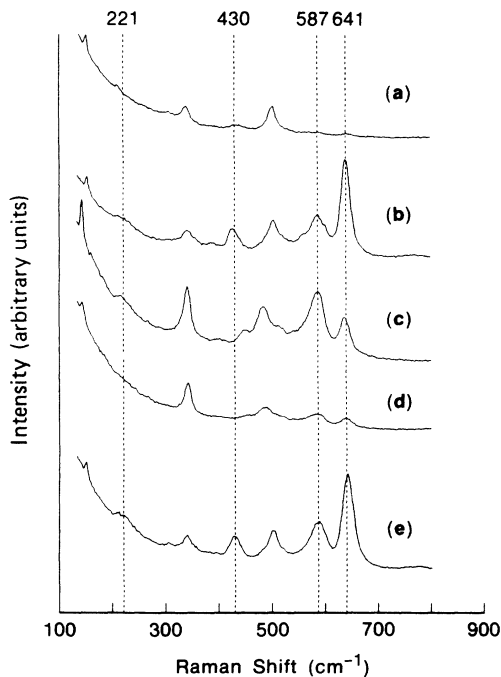


FIG. 3. Raman spectra of the following samples: (a) $\text{YBa}_2\text{Cu}_3\text{O}_7$, (b) $\text{YBa}_2\text{Cu}_3\text{O}_7 + 10\%$ BaCuO_2 , (c) $\text{YBa}_2\text{Cu}_3\text{O}_7 + 10\%$ BaCuO_2 heated 24 h at 500°C in an argon atmosphere, (d) $\text{YBa}_2\text{Cu}_3\text{O}_7 + 10\%$ BaCuO_2 heated 24 h at 800°C in an argon atmosphere, and (e) sample c annealed for 24 h in an oxygen atmosphere.

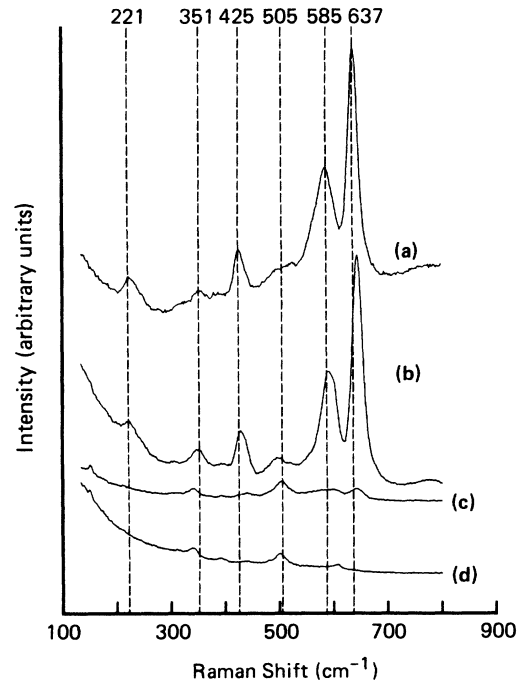


FIG. 4. Raman spectra of the following samples: (a) BaCuO_2 , (b) $\text{HoBa}_2\text{Cu}_3\text{O}_7$, (c) sample b after regrinding, and (d) sample c after annealing for 24 h at 800°C in an oxygen atmosphere.

(c) sample b reground and pressed into a pellet, and (d) sample c annealed at 900°C in an oxygen atmosphere. The spectra of the nominally $\text{HoBa}_2\text{Cu}_3\text{O}_7$ sample in Fig. 4(b) appears to be almost identical to that of the BaCuO_2 . The absolute intensities, relative intensities, and the line positions are very similar. The only significant difference in the spectra is a small systematic shift of all the modes to higher frequencies. This shift could be due to small variabilities in the structure of BaCuO_2 or oxygen stoichiometry as discussed later in this paper or possibly strain effects.²⁴ One might conclude from these data that the $\text{HoBa}_2\text{Cu}_3\text{O}_7$ sample is predominantly BaCuO_2 . However, as shown in Fig. 4(c), this sample after grinding has a spectrum characteristic of the superconducting material with only a small BaCuO_2 impurity. We suggest that these data indicate that our sample was inhomogeneous with large concentrations of BaCuO_2 either at the surface of the pellet or on the surface of the particulates in the compressed pellet. Annealing of the sample at 900°C in oxygen reduces this impurity level even further.

Impurities can also play an important role in studies of the effects of oxygen stoichiometry on the vibrational spectra of these materials. In these studies, the oxygen stoichiometry is usually varied by heating the superconducting material to various temperatures in an argon atmosphere or in vacuum. This heat-treatment procedure causes significant changes in the Raman modes^{6,17,25} but also in those due to impurity phases. This is illustrated in Figs. 3(c), 3(d), and 3(e) which shows the Raman spectra of the following samples: (c) 90% $\text{YBa}_2\text{Cu}_3\text{O}_7 + 10\%$ BaCuO_2 heated for 24 h at 500°C in an argon atmosphere,

(d) 90% $\text{YBa}_2\text{Cu}_3\text{O}_7$ +10% BaCuO_2 heated 24 h at 800°C in an argon atmosphere, and (e) sample c reoxygenated by annealing it in an oxygen atmosphere at 800°C. These spectra show large changes in both the absolute and relative intensities of the 641 and 587 cm^{-1} BaCuO_2 impurity modes. The absolute intensity of the 641 cm^{-1} mode decreases after the 500°C annealing and both modes reduce substantially in intensity after the 800°C annealing. The 641 cm^{-1} mode also appears to show an appreciable frequency shift after annealing at 500°C. These changes are reversible as illustrated in Fig. 3(e) and suggest that the argon heat-treatment procedures may modify the oxygen stoichiometry of BaCuO_2 in a similar fashion to that of the superconducting materials. It is obvious from these observations that it is essential to have very pure samples in these studies especially in interpreting modes which are related to oxygen disorder. Indeed, several studies have attributed the modes near 641 and 587 cm^{-1} to disorder-induced modes.¹¹⁻¹³

Effects of rare-earth substitution on intrinsic Raman spectrum

In Fig. 5, the Raman spectra of $\text{RBa}_2\text{Cu}_3\text{O}_7$ are presented where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$. These spectra show the intrinsic Raman modes of the 1:2:3 structure as well as spectral features which we identify as due to either BaCuO_2 or R_2BaCuO_5 impurities. The spectra of Y, Gd, and Eu materials are relatively clean with no obvious impurity phases. Spectra of Tm, Sm, Nd, Pr, and La show the clear signature of BaCuO_2 impurities which their characteristic Raman features at 641 and 587 cm^{-1} . The spectra of

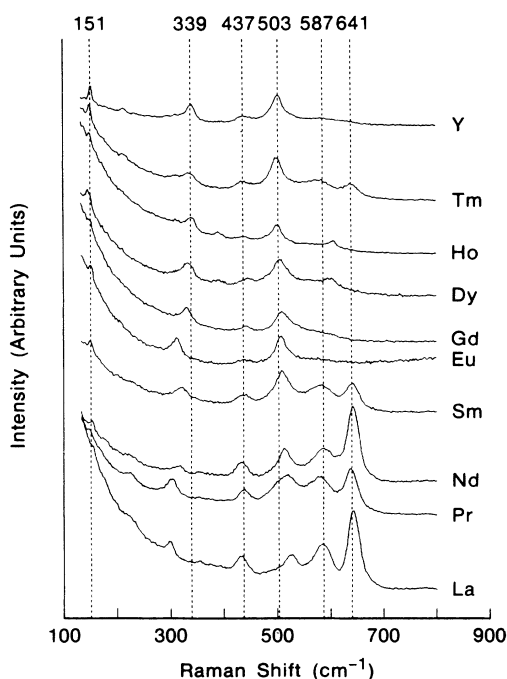


FIG. 5. Raman spectra of $\text{RBa}_2\text{Cu}_3\text{O}_7$ where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$.

$\text{HoBa}_2\text{Cu}_3\text{O}_7$ and $\text{DyBa}_2\text{Cu}_3\text{O}_7$ show extra weak modes near 600 and 400 cm^{-1} which we attribute to the 2:1:1 impurity phase. The small frequency shifts between the modes in these two different samples is presumably due to the different rare earths involved. In these samples, it is relatively easy to separate the intrinsic Raman spectra from that due to impurities and these results are presented in Table I. It should be noted that there is significant overlap between the 437 cm^{-1} intrinsic mode and the 430 cm^{-1} BaCuO_2 mode. For spectra in which there is a significant BaCuO_2 impurity, we do not tabulate the position of this mode. It is clear from these results that there is a large and systematic variation in the frequency of the 503 and 339 cm^{-1} lines. On the other hand, the frequency shifts of the 151 and 437 cm^{-1} modes are small and do not seem to have any obvious systematic variation. In Figs. 6(a) and 6(b) the frequency of the 503 and 339 cm^{-1} modes are plotted, respectively, versus the ionic radius of the rare earth as determined by Shannon and Prewitt.²⁶ The 503 cm^{-1} mode increases linearly in frequency with increasing ionic radius in a highly correlated fashion ($r^2 = 0.977$). The frequency changes by approximately 6% from Lu which has the smallest ionic radius to La which has the largest. This result would at first not seem consistent with the assignment of this mode to the O(4) bridging stretch vibration since the dimension of the unit cell in the z direction increases with increasing ionic radii.²⁰ This would be expected to lead to increasing bond lengths and decreasing force constants and vibrational frequencies. However, this is not the case since neutron-diffraction data show that although the c dimension increases the Cu(1)-O(4) bond length, which presumably controls the O(4) stretch frequency (Bates and Eldridge),²³ decreases. This is illustrated in Fig. 6(a) where the Cu(1)-O(4) bond length is plotted versus the ionic radius of the rare earth. Although there is only limited neutron-diffraction data available,^{27,28} there is good agreement between the trends in the Raman data and neutron data. These studies indicate the sensitivity of vibrational spectroscopy to small bond-length changes. As illustrated in Fig. 6(a) a change the vibrational frequency of 1 cm^{-1} , which is easily detectable, corresponds to a change in bond length of approximately 0.002 Å. In Fig. 6(b) the frequency of the 339 cm^{-1} Raman mode is plotted versus the ionic radius of the rare earth. Again, a high correlation is observed but in this case the vibrational fre-

TABLE I. Frequencies of intrinsic Raman modes of $\text{RBa}_2\text{Cu}_3\text{O}_7$.

Y	503	437	339	151
Lu	496	437	437	347
Tm	499	435	335	149
Ho	499	437	339	149
Dy	503	445	333	146
Gd	509	441	331	151
Eu	508	439	311	151
Sm	509	437	319	151
Nd	513	...	315	153
Pr	517	...	301	147
La	525	...	297	153

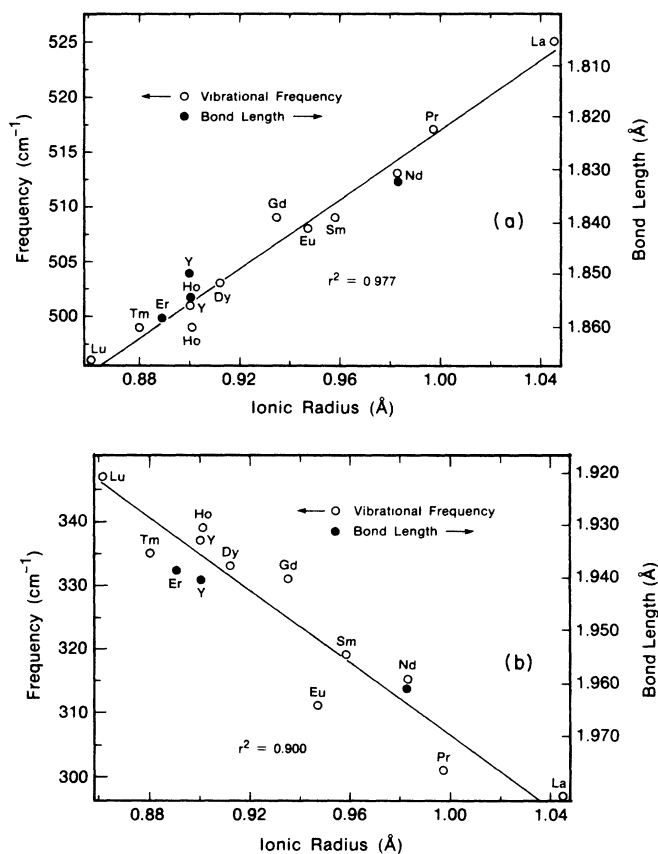


FIG. 6. (a) Plot of variation of the vibrational frequency of the 503 cm^{-1} mode vs the ionic radius of the rare earth. These results are compared to bond-length variations as determined from neutron-diffraction studies (Refs. 27 and 28). (b) Plot of variation of the vibrational frequency of the 339 cm^{-1} mode vs the ionic radius of the rare earth. These results are compared to bond-length variations as determined from neutron-diffraction studies (Ref. 27).

quency decreases with increasing ionic radius. This change is substantial and corresponds to approximately a 15% shift in the vibrational frequency. This shift is consistent with the identification of the 339 cm^{-1} mode as an in-plane $\text{Cu}(2)\text{-O}(2)$, $\text{O}(3)$ bending vibration since neutron-diffraction studies^{27,28} indicate that the in-plane Cu-O bond lengths increase with the ionic radius of the rare earth as shown in Fig. 5(b). The intrinsic modes near 151 and 437 cm^{-1} do not show any substantial variation as a function of R . This may be reasonable for the 151 cm^{-1} mode which has been attributed to a Ba vibration but is somewhat surprising for the 437 cm^{-1} mode which is attributed to an in-plane bending vibration in close

proximity to the rare earth. All the rare-earth samples reported here, except for $\text{PrBa}_2\text{Cu}_3\text{O}_7$, were superconducting with T_c greater than 90 K . It is interesting to note, however, that there appears to be no anomalous behavior in the vibrational spectrum of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ compared to that of the other rare-earth samples. This is illustrated in Figs. 6(a) and 6(b) where the vibrational frequencies of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ fit in quite well with the systematic behavior of the vibrational frequencies of the other rare earths as a function of their ionic radius. The fact that $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is not superconducting even when it is in the orthorhombic phase with ordered $\text{O}(1)$ is puzzling. It has been proposed by others²⁹ that this behavior is due to the $4+$ rather than $3+$ valency of the Pr ion in the $1:2:3$ structure. Our data suggest that this is not a likely explanation since such a change of valency would be expected to perturb the $\text{Cu}(1)\text{-O}(1)$ and $\text{Cu}(2)\text{-O}(2,3)$ vibrational frequencies significantly, which is not observed.

In conclusion, we have determined the dependence of the intrinsic Raman spectrum of $\text{RBa}_2\text{Cu}_3\text{O}_7$ as a function of R where $R = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, and Lu}$. Raman modes near 503 and 339 cm^{-1} , which are attributed, respectively, to $\text{Cu}(1)\text{-O}(4)$ and $\text{Cu}(2)\text{-O}(2,3)$ vibrations, show large and systematic variations in vibrational frequency as a function of the ionic radius of the rare earth. These findings are consistent with the limited neutron-diffraction studies available and give further support to the identification of these modes as $\text{Cu}(1)\text{-O}(4)$ symmetric stretch and $\text{Cu}(2)\text{-O}(2,3)$ in plane bending vibrations. $\text{PrBa}_2\text{Cu}_3\text{O}_7$ shows no anomalous behavior in its vibrational spectrum even though it was the only sample studied which was not superconducting. This result suggests that the valency of the Pr ion is similar to that of the other rare earths and cannot account for the absence of superconductivity in this material. It has also been shown that the interpretation of Raman spectra at high- T_c materials requires recognition of the important role of impurities. Even small concentration of impurity phases can strongly influence the Raman spectra since these insulating materials are less absorbing than the superconducting phases and have large Raman cross sections. Impurity phases can also be present preferentially at the surface of samples leading to a highly distorted Raman spectra. Furthermore, impurity spectra are substantially modified by heat treatment in an argon atmosphere. These effects are especially important in studies of oxygen stoichiometry and ordering where the identification of disorder-induced Raman modes is of great interest.

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