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Preparation and Raman analysis of single-phase $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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A series $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ materials with $0 \leq x \leq 1$ have been prepared that do not show phase separation and have sharp superconducting transitions for $x \leq 0.45$. These samples have been characterized by x-ray-diffraction, resistivity, field-cooled magnetization, and thermogravimetric analysis. Raman spectra have been obtained for the entire series, including the nonsuperconducting regions. The O(4) stretching mode at ~ 500 cm^{-1} is seen to harden by 15 cm^{-1}, while the Cu(2)-O(2,3) out-of-phase bending mode at ~ 340 cm^{-1} is seen to soften by 40 cm^{-1} on going from $YBa_2Cu_3O_7$ to $PrBa_2Cu_3O_7$. These changes fall on a universal curve for the Raman shifts of all the compounds $RBa_2Cu_3O_7$ (R=rare earth) as a function of the radii of the rare-earth ions. No abrupt changes in the Raman shifts are observed at $x=0.5$, where the superconductivity is destroyed.

INTRODUCTION

The $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is particularly interesting since superconductivity is destroyed for $x > 0.5$,[1-3] in contrast with the other rare-earth substitutions that remain superconducting with T_c at ~ 90 K.[4-7] Despite intensive investigation, the reason that Pr substitution quenches superconductivity is not understood. One problem in this system is its tendency to phase separate into $YBa_2Cu_3O_7$ with $T_c=90$ K and $Y_{1-x}Pr_xBa_2Cu_3O_7$ of varying x value with reduced T_c. This type of phase separation can be clearly seen in field-cooled Meissner measurements,[8] while not showing up at all in the powder x-ray-diffraction patterns. In this paper, we report the preparation and Raman analysis of a series of high-quality samples that include both the superconducting and nonsuperconducting regions. The samples, for which the phase-separation problems have been overcome, have well-determined oxygen contents and sharp superconducting transitions. These results allow us to study in detail the dependence of the phonon frequencies with Pr content, and to conclude that no abrupt changes occur at $x=0.5$, where the superconductivity is destroyed.

EXPERIMENTAL DETAILS

$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples were prepared for $x=0.0$ to 0.7 in $\Delta x=0.1$ increments, 0.9 and 1.0. High-purity Y_2O_3, BaO, CuO, and Pr_6O_{11} powders were mixed and fired in air for 50 h at 975 °C. The powders were reground and fired at 1000–1010 °C for 48 h, with several intermediate regrindings. The loose powder was then pressed into a pellet and annealed in flowing oxygen for several hours at 1000 °C, followed by a furnace cool to 400 °C. The pellet remained at 400 °C for 24 h, followed by a furnace cool to room temperature. Firing above 1000 °C and frequent regrinding appear crucial for achieving single-phase samples. Techniques that are sufficient to produce good-quality samples of the standard $YBa_2Cu_3O_{7-\delta}$ material tend in this mixed Y-Pr system to produce phase-separated materials with as much as 30% of the 90-K phase.

The synthesis procedure described above resulted in single-phase material with oxygen contents between 6.9 and 7.0, as determined by thermogravimetric analysis (TGA). The oxygen contents listed in Table I were determined as previously described[9] using a Dupont 951 TGA system. A typical scan involved flowing forming gas (6% H_2, 94% N_2) through the sample chamber and ramping the temperature to 1000 °C at 5–10 °C/min. The reaction products Y_2O_3, Pr_2O_3, BaO, and Cu have been identified using x-ray diffraction. A small amount of $BaCuO_2$ ($\sim 1\%$) was observed in some of the samples from the Raman spectra. This was not included in the TGA analysis, and introduces an error of ≈ 0.02 in the oxygen contents for these samples.

Figure 1 shows the x-ray diffraction, resistivity, and field-cooled Meissner signal for one of the ten samples, $x=0.3$. This x-ray pattern is representative of all the samples with orthorhombic symmetry. Across the series, x-ray-diffraction analysis showed all samples to have orthorhombic structures, with the exception of $x=0.9$ and 1.0, which were tetragonal. No second phases were present at the detectable level of a few percent. The resistivity and Meissner measurements show a single, sharp transition. The data of Fig. 1 are typical of all ten samples. The transition temperatures are plotted in Fig. 1(d), establishing that superconductivity disappears before the concentration $x=0.5$

TABLE I. Transition temperature, Raman shifts, and measured oxygen content are listed for all ten samples in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ series. Values for $x=0.40$ are given for two different samples. Error bars on the oxygen content results are estimated to be ± 0.05. All samples were orthorhombic except $x=0.9$ and 1.0, which were tetragonal.

x	Raman shifts (cm^{-1})					O content
0.0	503	~440	340	151	119	6.96
0.1	503	~440	335	150	118	6.91
0.2	509	~440	337	151	119	6.91
0.3	509	~440	330	151	123	6.88
0.4	507	~435	322	147	120	6.90
	511	~440	322	153	123	
0.5	510	~435	323	150	119	7.01
0.6	513	~440	315	150	122	7.03
0.7	514	~445	312	153	122	7.03
0.9	514	~435	298	149	128	7.03
1.0	516	~430	298	149	128	6.96

In samples that have phase-separation problems, the onset of the diamagnetic signal [see Fig. 1(b)] would be seen starting at 90 K. This feature is a clear indication of the presence of the $YBa_2Cu_3O_7$ phase. X-ray diffraction results on less rigorously prepared phase-separated materials and phase-pure materials were very similar and do not provide a reliable test for phase separation in this series. Further details of the preparation procedure, oxygen-content determination, and characterization data for all ten samples, along with the magnetization and critical-field results will be published separately.[10]

The Raman data were taken at room temperature in a backscattering geometry using 15 mW of 488-nm light from an Ar-ion laser. The scattered light was dispersed using a Spex Triplemate spectrometer equipped with a two-dimensional photon-counting detector. The samples were continually flushed with a flow of argon gas in order to remove the background at low frequencies resulting from atmospheric gases.

RESULTS AND DISCUSSION

Figure 2 shows the Raman data for all ten samples. Five main peaks are visible that are intrinsic to $Y_{1-x}Pr_xBa_2Cu_3O_7$, i.e., not resulting from impurities. For the $x=0$ samples these peaks are at 503, ~440, 340, and 151, and 119 cm^{-1}. These have been assigned,[11,12] respectively, to the O(4) stretching mode, the in-phase Cu(2)-O(2,3) bending mode, out-of-phase Cu(2)-O(2,3) bending mode, the Cu(2) stretching mode, and the Ba stretching mode. The assignment of the ~440-cm^{-1} mode, however, has been recently challenged.[13] Peaks at ~635 and ~580 cm^{-1} resulting from $BaCuO_2$ impurities are present in some of the spectra. These features show up prominently at even small impurity concentrations ($<1\%$) due to the large Raman cross section of $BaCuO_2$, as well as its tendency to migrate to grain boundary surfaces.[14] Several spectra were taken for each sample, moving to different spots and cleaving the samples to expose fresh surfaces. While the intensity of the impurity peaks varied considerably relative to the intrinsic peaks of

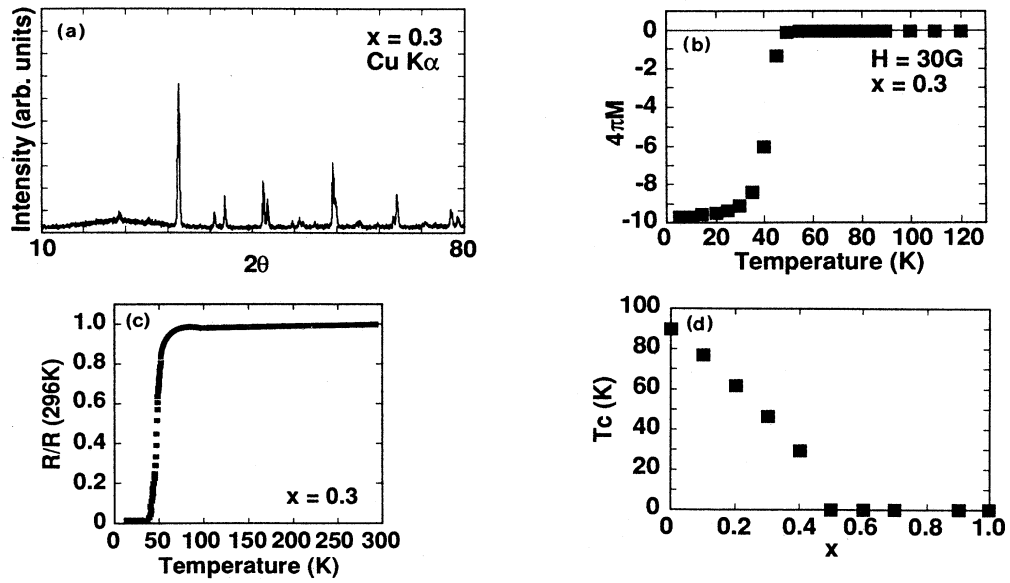

FIG. 1. (a) x-ray-diffraction; (b) field-cooled magnetization; (c) resistivity for the $x=0.3$ $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ sample; (d) superconducting transition temperature T_c vs x. Transition temperatures are taken from the onset of diamagnetism in the field-cooled magnetization data.

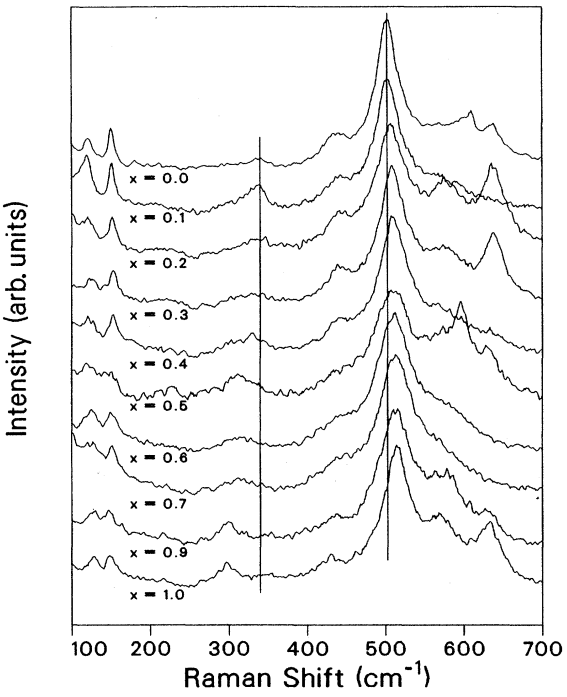

FIG. 2. Raman spectra for the series $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, $0 \leq x \leq 1$.

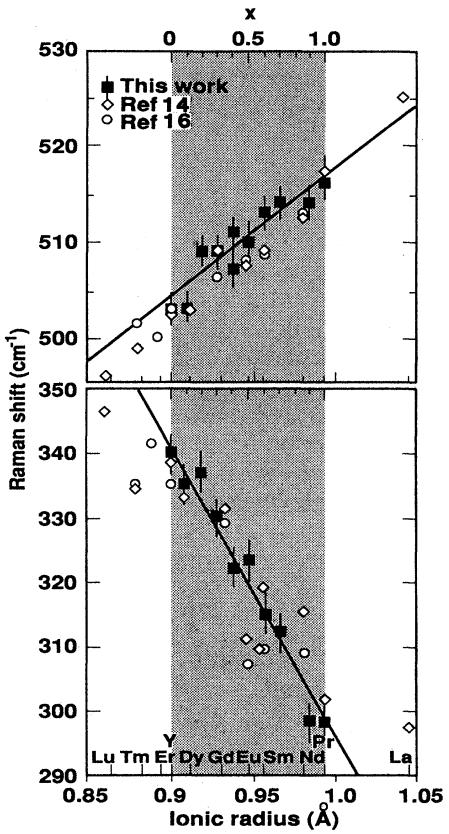

FIG. 3. Raman frequency for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for the $\sim$500- and $\sim$340-cm^{-1} lines vs Pr content and average ionic radii of Y^{3+} and Pr^{3+}. Also plotted are the Raman shifts for different rare-earth materials $RBa_2Cu_3O_7$ plotted vs radii of the rare-earth ions, taken from the tabulated data in Refs. 14 and 16.

$Y_{1-x}Pr_xBa_2Cu_3O_7$, the intrinsic peak positions were essentially constant for all the different spectra of each sample. The values given in Table I represent an average of three spectra taken at three different spots on each sample. In addition, two different $x=0.4$ samples were characterized, with both results given in Table I.

Figure 3 shows that two of the Raman-active modes change significantly as a function of Pr concentration. The $\sim$500-cm^{-1} mode is seen to harden some 15 wave numbers, while the $\sim$340-cm^{-1} mode is seen to soften nearly 40 wave numbers in going from $YBa_2Cu_3O_7$ to $PrBa_2Cu_3O_7$. The mode at $\sim$150 cm^{-1} remained essentially constant, while the mode at 120 cm^{-1} increased by $\sim$10 cm^{-1} in going from $YBa_2Cu_3O_7$ to $PrBa_2Cu_3O_7$. These results are in reasonable agreement with previous results for ceramic samples on the superconducting members of this series,[15] and on the Pr end member.[14,16] Thomsen *et al.*[17] report very different values for the $\sim$500- and 340-cm^{-1} modes. Our studies of the shifts of the peak positions with oxygen content in $PrBa_2Cu_3O_{7-\delta}$ confirm that the O(4) stretch for fully oxygenated $PrBa_2Cu_3O_7$ occurs near $\sim$516 cm^{-1}.[18] For the mixed $Y_{1-x}Pr_xBa_2Cu_3O_7$ system, the shifts of the $\sim$500- and $\sim$340-cm^{-1} lines are plotted in Fig. 3 against the average ionic radius Y^{3+} and Pr^{3+} defined as $r(\text{Å}) = 0.900 \times (1-x) + 0.997x$. Also plotted in Fig. 3 are the tabulated results[14,16] for the other rare-earth phases versus radii of the rare-earth ions.[19] In general, the results for the mixed Y-Pr system fit well with the results for the changes in these modes in going across the rare-earth series.[14,16] This indicates that the dominant effect on the $\sim$500- and $\sim$340-cm^{-1} modes is caused by the increased ionic size of the Pr ion relative to the Y ion. In contrast, a Raman study of these modes at high pressure shows for the $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ systems that the $\sim$500- and $\sim$340-cm^{-1} modes both harden with increasing pressure.[20] The high-pressure data serves to illustrate the unusual shortening of the Cu(1)–O(4) bond length upon the addition of large rare-earth ions. The shortening of this bond, which causes the increase in the Raman frequency of the $\sim$500 cm^{-1} mode,[14] is in contrast with the overall increase in the c-axis dimension with the substitution of a larger ion for Y. In the high-pressure case, the material is uniformly compressed, resulting in both the $\sim$500 and $\sim$340-cm^{-1} modes increasing in frequency.

The observation that the lattice vibrations as a function of Pr concentration are well behaved still leaves to be resolved the question of why T_c decreases for Pr doping, but remains constant for doping with the other rare earths. Several groups find that the valence of the Pr ion is +3 across the entire series[21–23] indicating that the presence of Pr^{4+} is not responsible for the quenching of T_c, as was initially thought. One possible explanation for the depression of T_c is that Pr causes a true magnetic pair-breaking effect. This point of view is supported by the magnetization results which show that the Pauli sus-

ceptibility increases with Pr content in this system.[10,24] This increase in the susceptibility correlates with the decrease in T_c. This is in contrast with oxygen-content experiments[8] on $YBa_2Cu_3O_{7-\delta}$ where the decrease in T_c correlates with a decreasing value of the Pauli susceptibility. The presence of magnetic pair-pair breaking is also supported by the behavior of the critical-field curves which begin to show a "bell"-shaped behavior for $x > 0.30$.[10]

Recent work has shown that the bending mode at ~ 340 cm^{-1} softens below T_c if the sample is fully oxygenated.[25] It has also been shown that this mode reflects the critical-field H_{c2} relation,[26] indicating once more its close connection with the superconducting properties. The ~ 340-cm^{-1} mode has been shown to be coupled to the electronic continuum, and that the softening below T_c is connected with the opening of an anisotropic energy gap.[27] Given the importance of the softening of the ~ 340-cm^{-1} mode, coupled with the possibility that the destruction of superconductivity with Pr content is a magnetic pair-breaking effect,[10] further work on the temperature dependence of the ~ 340-cm^{-1} mode across the Pr series would be useful.

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