PHYSICAL REVIEW B VOLUME 54, NUMBER 1 1 JULY 1996-I

Evidence of apical oxygen in artificially superconducting $SrCuO_2$-$BaCuO_2$ thin films: A Raman characterization

Shen Zhu
Department of Physics and Astronomy, University of Missouri, Columbia, Missouri 65211

D. P. Norton
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 63831

J. E. Chamberlain, F. Shahedipour, and H. W. White
Department of Physics and Astronomy, University of Missouri, Columbia, Missouri 65211

(Received 18 December 1995)

The artificially layered superlattices, $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ ($n=0,1,2,3$) have been investigated by Raman spectroscopy. Raman frequency shifts were observed in the $n=2$ and $n=3$ films, while no vibrational modes were observed in the $n=0$ and $n=1$ films. The crystalline structures of the $n=0$ and $n=1$ films have an infinite-layered structure. The Raman peaks located at 604 cm^{-1} in the $n=2$ film and at 587 cm^{-1} in the $n=3$ film can be assigned to the apical oxygen vibration along the c axis. These observations indicate films with compositions $n=2$ and $n=3$ are superlattice structures with a Ba-O sublattice. [S0163-1829(96)07126-3]

The simple structures of the family of compounds (Sr, Ca, or Ba)CuO_2, without rare-earth atoms, continue to attract interests because these are the parent materials of high-temperature superconductors (HTSc).[1–5] Indeed, these elementary compounds and structures are the building blocks for all of the high-T_c cuperate superconductors. It is important to investigate the artificially layered structure of these HTSc parent materials, both for an improved understanding of the nature of how hole carriers are provided, and for improved techniques for synthesizing higher T_c superconductors.

An infinite-layer compound, such as (Sr,Ca)CuO_2, has a layer-type structure with fourfold coordinated CuO_2 planes separated by oxygen free alkaline-atom layers.[1,2] $(Sr_{1-x}Ca_x)_{1-y}CuO_2$ has been synthesized under high pressure process with a T_c onset at 110 K.[1] The defect layers arising from the alkaline-earth deficiencies create hole carriers that in turn introduce superconductivity into the infinite-layer structure. Recently, the first artificially layers HTSc films, consisting of three unit cells—one unit cell $BaCuO_2$-$CaCuO_2$ superlattice, were grown on $SrTiO_3$ substrates by laser-molecular-beam epitaxy. This superlattice, which was suggested to have an infinite-layer structure, has a T_c (resistance $R=0$) $\sim$40 K.[4]

Using a pulsed-laser deposition technique, Norton *et al.* have synthesized the artificially superconducting materials, $Ba_2Sr_{n-1}Cu_{n+1}O_{2(n+1)}$ and $Ba_4Sr_{n-1}Cu_{n+1}O_{2(n+1)}$ ($n=1$–3) with T_c ($R=0$)$\sim$50 K.[5] Based on the empirical observation that, in all of the hole-doped HTSc, the apical oxygen within the pyramidal structure provides holes in the CuO_2 layers is the basis for superconductivity in many HTSc, they proposed a crystallographic structure that, within the Ba layers, oxygens located at the apex positions are responsible for the superconductivity in the artificially layered superlattices.[5] Therefore, the question arises for these artificially layered $BaCuO_2$-(Sr,Ca)CuO_2 films as to whether there could be an ideally layered structure (infinite-layer), or whether within the Ba-O subunit layer there could be some apical oxygens which could exist because of the difference in size of Ba and Sr (Ca) atoms. To date, there has been no experimental evidence reported for the direct determination of the structure for these superlattices.

Raman spectroscopy has proven to be a useful technique for investigating the properties of cuprate superconductors. Studies include contributions from lattice vibrations, measurement of the superconducting gap, characterization of crystal structure, and determination of the oxygen stoichiometry and elemental substitution.[6–13]

Of particular interest to this study are the high-frequency Raman modes in the Raman spectra of the superconducting materials $YBa_2Cu_3O_{7-x}$ (YBCO),[6] Bi compounds,[9] and Hg systems[12] that have been assigned to oxygen vibrations. Three oxygen Raman-active phonon modes with frequency shifts at 335, 440, and 500 cm^{-1} in YBCO can be correlated with the Cu-O bond strength.[6] These three Raman modes were observed for both the superconducting and normal states, with slight changes in line shapes and phonon shifts noted. It was suggested that the 500 cm^{-1} Raman band should be associated with the stretching vibration of the pyramidal oxygen. A softening of the 500 cm^{-1} mode was also observed at different temperatures and laser powers, due to the distribution of oxygen in the base plane.[14–17] Two high-frequency bands occurring at 460 and 630 cm^{-1} in the Bi-2212 superconducting material have been assigned to the apical oxygen vibration along the c axis and to a planar Bi-O motion, respectively. In a micro-Raman spectroscopy study of mercury-based superconductors, Ren *et al.* observed apical oxygen A_{1g} modes located at $\sim$585 cm^{-1} for all of the one-Hg-layered systems.[12] This peak shifts to lower wave number with increased laser power due to a redistribution of oxygen in the Hg-O planes. This vibrational mode was observed to shift from 585 to 640 cm^{-1} with increase in bond strength due to an increase of external pressure on the sample.[18]

0163-1829/96/54(1)/97(4)/$10.00

In this paper we report a study of the Raman spectra of several $SrCuO_2$-$BaCuO_2$ artificially layered superconducting films. Several phonon modes were observed. Based on an analysis of the structural symmetry and the corresponding Raman spectra of superlattices with composition $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ $(n=0,1,2,3)$, we have proposed structures for the $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ films. The observed value for Raman tensor can be tentatively assigned to the apical oxygen vibration in the artificially layered superlattices.

The preparation details for the $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ superlattice samples have been described elsewhere.[5] The $SrCuO_2$ and $BaCuO_2$ compounds have a tetragonal structure with cell spacing of 3.55 and 4.28 Å, respectively. The in-plane (a-b plane) cell length is 3.9 Å, matching that of the $SrTiO_3$ substrate. The thickness of these films varies from 100 to 130 nm including a 9-nm-thick $SrCuO_2$ buffer layer that was grown before depositing the superlattices. The $n=0$ and $n=1$ compounds do not have a superconducting transition, while the other $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ films (with $n>1$) are superconductors with T_c $(R=0)$ as high as 50 K.

Room-temperature Raman spectra of these layered compounds were obtained using a 0.6 m Spex Triplemate spectrometer equipped with a CCD multichannel detector. The exciting source was an ion-argon laser operating at 514.5 nm. The operating power was ~40–100 mW with ~1 mm^2 spot size on the films. The p-polarized beam was incident 55° to the film normal. The scattered light, without polarization, was focused onto the entrance slit of the spectrometer by an off-axis paraboloidal reflector located in a backscattering geometry. Several spectra were measured for each sample at different areas. Spectra for each film showed the same features, indicting good uniformity over the surface of the films.

Figures 1(a) and 1(b) illustrate the Raman spectra obtained on the $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ films. Two broad peaks that were observed in the spectra of the $n=0$ and $n=1$ films are similar to those observed in the spectrum of the $SrTiO_3$ substrate. The first peak covers the region 220–400 cm^{-1}, while the second is located in the region 625–750 cm^{-1}. The fact that the $n=0$ and $n=1$ films as well as the substrate show the same spectral features suggest that there are no Raman-active modes in these two film systems.

For the $n=2$ superlattice, however, phonon modes in the Raman spectra are observed at 236, 288, 368, and 604 cm^{-1}. The lower frequency shifts, located at 236, 288, and 368 cm^{-1}, are very weak because of strong scattering contributions from the substrate. These three, very weak eigenmodes should be enhanced and more distinguished in measurements at lower temperatures. A very large shoulder in the region of 724 cm^{-1} was observed on the 604 cm^{-1} peak, and partially is due to contributions form the substrate.

Only two strong Raman lines, located at 587 and 642 cm^{-1}, are observed in the $(Sr_{0.8}Ca_{0.2})_2Ba_3Cu_5O_{10+x}$ $(n=3)$ film. It can be expected that the 20% substitution of Ca for Sr atoms in the film will generate a small distortion in the film structure. Any low-frequency Raman modes, and the underlying structural distortion, associated with this substitution would not be distinguished in these spectrum. This distortion, however, may be responsible for the broad full-width-at-half-maximum of both the 587 and 642 cm^{-1} peaks.

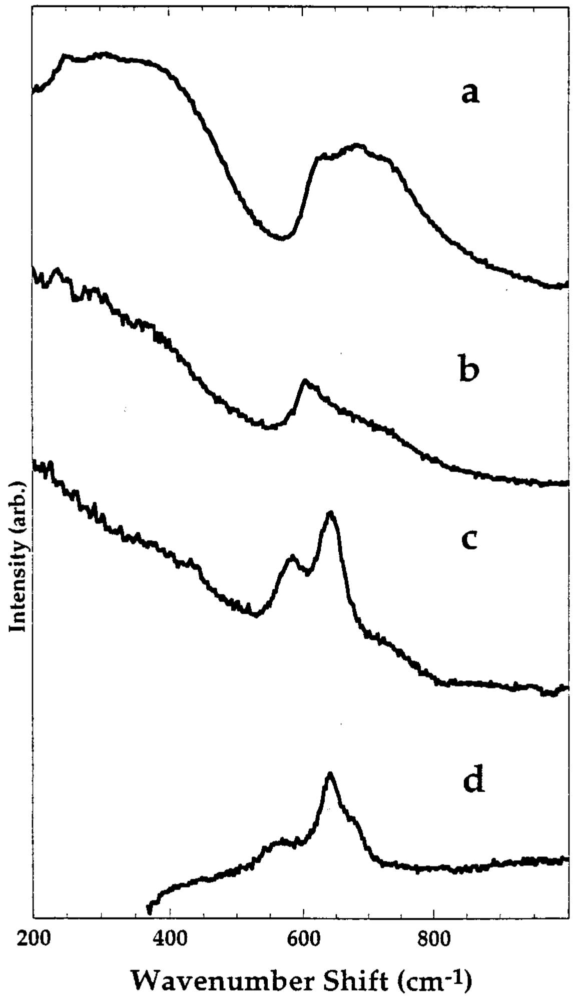

FIG. 1. Raman spectra of $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ films, $SrTiO_3$ substrate, and $BaCuO_2$: (a) $n=0$ and $n=1$ films, and substrate; (b) $n=2$ film; (c) $(Sr_{0.8}Ca_{0.2})_2Ba_3Cu_5O_{10+x}$ $(n=3)$ film; and (d) $BaCuO_2$ target.

The vibrational modes located at 604 cm^{-1} for $n=2$ and at 587 cm^{-1} for $n=3$ in the superlattice films do not originate from the cubic $BaCuO_2$ impurity, which is the starting material. The Raman spectrum for $BaCuO_2$ is shown in Fig. 1(d). The combination of a strong phonon mode at 640 cm^{-1} and a weak shoulder located near 580 cm^{-1} is similar to that observed by other groups.[19–23] The intensity of the 580 cm^{-1} mode in the Raman spectrum of $BaCuO_2$ is much weaker than the intensity for the 640 cm^{-1} mode. In contrast, for the $n=3$ film the intensity ratio for the 587 peak to the 642 cm^{-1} peak is quite large. If substrate effects are factored in, the intensity difference associated with these two peaks would be even smaller. These results suggest that the 604 and 587 cm^{-1} peaks are the Raman frequency shifts for the $n=2$ and $n=3$ films, respectively. As discussed later, the 642 cm^{-1} vibrational mode may also be the Raman mode in the $n=3$ film.

The proposed primitive cell structures for the $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ $(n=1,2,3)$ films are shown in Fig. 2.

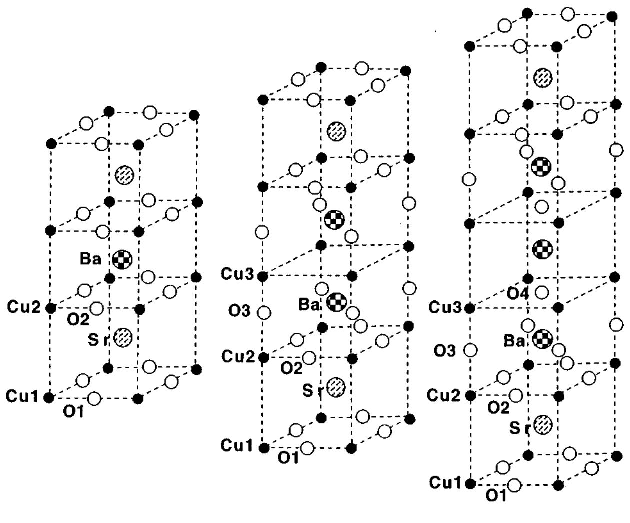

FIG. 2. Primitive cells of $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ ($n=1$, 2, and 3) films.

Each of the three cells belongs to the $P4/mmm$ (D_{4h}) space group. The $n=1$ cell has an infinite structure, the same as for the $n=0$ film.[1] Both $n=2$ and $n=3$ structures have Ba-O subunit layers. The O(3) in the Ba-O layer and the fourfold oxygens in the adjacent Cu(2)-O(2) layer form a pyramidal structure similar to other hole-doped HTSc. The position of the apical O(3) depends on the O(4) occupation in the Cu(3)-O(4) layers.

The vibrational eigenvectors of heavy mass atoms, i.e., Ba, Sr, Ca, and Cu, are at low wave-number Raman shifts, $\leqslant 230$ cm^{-1}, that are barely detectable in our measurements. Only the 236 cm^{-1} shift in the $n=2$ film may be associated with the Cu vibration. The oxygen vibrational modes are located at higher Raman shifts. No Raman-active modes exist, since the symmetry of the $n=0$ infinite structure is similar to that for perovskite materials. No phonon modes exist in the $n=1$ infinite structure, as well. For this film the O(1) atoms are the inversion centers. Therefore, for this film there is no evidence for active phonon modes that would originate from the Cu(2)-O(2) planes, which are common to most of high-T_c superconductors. The $n=1$ superlattice, therefore, can be treated as an infinite layer superlattice with the same oxygen structure as the $n=0$ film.

If the $n=2$ film has the infinite layer structure with no oxygen on the Ba plane, there would be no active Raman modes due to symmetry. However, in the $n=2$ film there is a strong peak at 604 cm^{-1} that can be assumed to arise from the high-frequency oxygen vibrations. Therefore, the most reasonable structure, such as exists for most of the HTSc, is one where there are two Ba-O layers in the $n=2$ film. This structure is shown in Fig. 2(b). Since the polarization is strong along the c axis, the mode at 604 cm^{-1} may be assigned to the stretching vibration of the oxygens located at apex positions. This frequency shift is somewhat larger than those observed in YBCO, Tl compounds, and Hg systems, for which the stretching phonon modes of the apical oxygen vibration are in the 480–590 cm^{-1} range. The Raman shifts directly relate to Cu(3)-O(3) bond strengths, which can be estimated from the corresponding distances between Cu(3) and O(3) sites. Typically, the apical Cu-O distances that involve the Cu atoms with pyramidal coordination are ~ 2.32 Å for YBCO, ~ 2.45 Å for Tl-2233, and ~ 2.75 Å for Hg-1223.[24] The strong bond between apical oxygens and Cu (YBCO), Tl (Tl compounds), and Hg (Hg compounds) atoms leads to the higher frequency shifts in the G zone. The location of the Raman mode of the apical oxygens in $HBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ varies from 580 to 590 cm^{-1}, depending on the oxygen concentration in the Hg-O layers.[12,13] The core structure of the central block with two Ba-O sublattices in the $n=2$ film is similar to that of the $HgBa_2CuO_4$ system, except the oxygen is located in the Hg-O plane for the latter structure. It is reasonable to consider the 604 cm^{-1} phonon mode to be due to the stretching vibration of the apical oxygens along the c axis. It is also reasonable to assume that the Cu(3) atoms located in the fourfold coordinated Cu plane have a stronger bond to an apical oxygen than would Hg in the Hg systems. This latter effect is even more obvious for the $n=3$ superlattice structure.

For the $n=3$ film, two Raman peaks were observed, located at 587 and 642 cm^{-1}. It should be noted that in this superlattice structure there are also two more Cu-O layers, with the oxygen in the diagonal center. These Cu(3)-O(4) layers are similar to the Hg-O layers that occur in Hg systems. Because the Cu(3) bonds both O(3) and O(4), it is obvious that the bond strength is reduced between Cu(3) and O(3), although the distance (~ 2.76 Å) is large between Cu(3) and O(4). Therefore, the apical oxygen eigenmode shifts to a low photon energy value. The 587 cm^{-1} mode in the $n=3$ film can be tentatively assigned also to the A_{1g} vibration of pyramidal oxygen. An argument may be made for the origin of the strong 642 cm^{-1} line if it is compared to the oxygen E_{1g} Raman tensor in the Bi-O layer in the Bi-2212 compound.[25] The 642 cm^{-1} peak may come from the O(4) vibration at the Cu(3)-O(4) layer. The 642 cm^{-1} peak also could be possibly due to the Raman mode of the impurity $BaCuO_2$ material. The 580 cm^{-1} shoulder is very weak in the Raman spectrum for $BaCuO_2$ and as a consequence may be overlapped by the broad 587 cm^{-1} peak. The exact origin of the 642 cm^{-1} phonon mode is still an open question, to be determined in future experiments.

Also observed in the $n=3$ film was a softening of the phonon mode at 587 cm^{-1} that corresponded with increased exciting laser power and measuring time. This phonon softening can be associated with change in the coupling strength between O(3) and Cu(3). The peak shifts from 587 to 583 cm^{-1} after the laser power and heating time are increased by a fact of 10. Similar results were obtained for Raman spectra of apical oxygen vibrations in YBCO single crystals and polycrystalline Hg-1212 samples. The Raman phonon line of oxygen at the apex position softens from 500 to 485 cm^{-1} in YBCO, from 585 to 581 cm^{-1} in the Hg-1212 compound, and from 590 to 587 cm^{-1} in Hg-1201. These softenings are attributed to the changes in bond lengths, arising from slight displacement of the oxygens. The resulting frequency shifts are small in the Hg compounds; however, displacement of oxygens in the Cu-O chain of YBCO results in a much larger shift of the vibrational line of the apical oxygen.[12–18]

In summary, we have measured the vibrational Raman modes in artificially layered $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ ($n=0,1,2,3$) superconducting films. Raman shifts of peaks observed at 604 and 587 cm^{-1} in the $n=2$ and $n=3$ films, respectively, were assigned to be due primarily to the stretching vibrations of the oxygen atoms located at apex positions. A phonon softening effect was observed in the $n=3$ film, arising from a change in the bonding force of the apical oxygen. The $n=0$ and $n=1$ superlattices have an infinite-layered structure. A model for the crystalline structure of the Ba-O subunit layers in the $Sr_2Ba_nCu_{2+n}O_{4+2n+x}$ ($n=2$ and 3) films were proposed based on the Raman spectra.

This work was supported in part by the University of Missouri Research Board under Grant No. RB95-061 and the U.S. Army Research Office (Research Triangle Park, N.C.) under Grant No. DAAH04-94-G-0305.

---

[1] M. Azuma, Z. Hiroi, M. Takano, Y. Bando, and Y. Takeda, Nature (London) **356**, 775 (1992).

[2] T. Siegrist, S. M. Zahurak, D. W. Murphy, and R. S. Roth, Nature (London) **334**, 231 (1988).

[3] Z. Hiroi, M. Takano, M. Azuma, and Y. Takeda, Nature (London) **364**, 315 (1993).

[4] X. Li, T. Kawai, and S. Kawai, Jpn. J. Appl. Phys. **33**, L18 (1994).

[5] D. P. Norton, B. C. Chakoumakos, J. D. Budai, D. H. Lowndes, B. C. Sales, J. R. Thompson, and D. K. Christen, Science **265**, 2074 (1994).

[6] R. Feile, Physica C **159**, 1 (1989), and references therein.

[7] B. Stadlober, G. Krig, T. Nemetschek, and R. Hackl, Phys. Rev. Lett. **74**, 4911 (1995).

[8] E. T. Heyen, S. N. Rashkeev, I. I. Mazin, O. K. Anderson, R. Liu, M. Cardona, and O. Jepsen, Phys. Rev. Lett. **65**, 3048 (1990).

[9] K. F. McCarty, J. Z. Liu, R. N. Shelton, and H. B. Radousky, Phys. Rev. B **42**, 9973 (1990).

[10] F. Slakey, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **42**, 2643 (1990); F. Slakey, M. V. Klein, E. D. Bukoski, and D. M. Ginsberg, *ibid.* **41**, 2109 (1990).

[11] C. Thomson, A. P. Litvinchuk, E. Schonger, and M. Cardona, Phys. Rev. B **45**, 8154 (1992).

[12] Y. T. Ren, H. Chang, Q. Xiong, Y. Q. Wang, Y. Y. Sun, R. L. Meng, Y. Y. Xue, and C. W. Chu, Physica C **217**, 273 (1993).

[13] Y. T. Ren, H. Chang, Q. Xiong, Y. Y. Xue, and C. W. Chu, Physica C **226**, 209 (1994).

[14] K. F. McCarty and J. C. Hamilton, Phys. Rev. B **38**, 2914 (1988).

[15] I. Poberaj, D. Mihailovic, and S. Bernik, Phys. Rev. B **42**, 393 (1990).

[16] G. Burns, F. H. Dacol, C. Feild, and F. Holtzberg, Solid State Commun. **75**, 893 (1990).

[17] E. Altendorf, X. K. Chen, J. C. Irwin, R. Liang, and W. N. Hardy, Phys. Rev. B **47**, 8140 (1993).

[18] I. Yang, H. Shin, H. Lee, S. Jeon, H. Ahn, J. Yu, S. Lee, S. Lee, and N. Hur, Phys. Rev. B **51**, 644 (1995).

[19] M. Kakihana, L. Borjesson, L. M. Torell, Z. Liu, and S. G. Eriksson, Physica C **156**, 420 (1988).

[20] H. Rosen, E. M. Engler, T. C. Strand, V. Y. Lee, and D. Bethune, Phys. Rev. B **36**, 726 (1987).

[21] A. Mascarenhas, S. Geller, L. C. Xu, H. Katayama-Yoshida, J. I. Pancove, and S. K. Deb, Appl. Phys. Lett. **52**, 240 (1988).

[22] E. Bahadra, T. O. Brun, M. A. Beno, B. Dabrowski, D. G. Hinks, J. Z. Liu, J. D. Jorgensen, L. J. Nowicki, A. P. Paulikas, I. K. Schuller, C. U. Segre, L. Soderholm, B. Veal, H. H. Wang, J. M. Williams, K. Zhang, and M. Grimsditch, Phys. Rev. B **37**, 5142 (1988).

[23] H. Chang, Y. T. Ren, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, and C. W. Chu, Physica C **228**, 383 (1994).

[24] O. Chmaissem, Q. Huang, E. V. Antipov, S. N. Putilin, M. Marezio, S. M. Loureiro, J. J. Capponi, J. L. Tholence, and A. Santoro, Physica C **217**, 265 (1993).

[25] M. Cardona, C. Thomsen, T. Liu, H. G. von Schnering, M. Hartweg, Y. F. Yan, and Z. X. Zhao, Solid State Commun. **66**, 1225 (1988).