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# Systematic Raman study of $Tl_2Ca_{n-1}Ba_2Cu_nO_{4+2n}$ ($n=1,2,3$) high-temperature superconductors

M. Krantz, H. J. Rosen, R. M. Macfarlane, and V. Y. Lee

*IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*

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We report the results of Raman measurements performed on polycrystalline samples of superconducting $Tl_2Ca_{n-1}Ba_2Cu_nO_{4+2n}$ ($n=1,2,3$) with well-characterized transport, magnetic, and structural properties. The room-temperature first-order Raman spectra of polycrystalline samples of predominantly $Tl_2Ba_2CuO_6$, $Tl_2CaBa_2Cu_2O_8$, and $Tl_2Ca_2Ba_2Cu_3O_{10}$ phases, with respective superconducting transition temperatures of 10, 110, and 125 K display a systematic variation with the number of $CuO_2$ layers and great similarities with the Raman spectrum of $YBa_2Cu_3O_7$. Comparison with Raman spectra of the impurity phase candidates $BaCO_3$, $BaO_2$, $BaCuO_2$, $CaCuO_2$, $Tl_2O_3$, and $TlCa_5Cu_6O_x$ allows identification of intrinsic Raman modes of the superconducting phases. Factor group analysis of the three body-centered tetragonal structures, space group *I4/mmm*, yields the mode classifications and the atoms involved in the modes of $A_{1g}$ and $B_{1g}$ symmetry corresponding to *c*-axis motion that produce the strongest modulation of the polarizability. The systematic variation between the spectra of the three phases and comparison with the well-characterized $YBa_2Cu_3O_x$ Raman spectrum suggests mode assignments for the high-frequency modes of $A_{1g}$ and $B_{1g}$ symmetry involving oxygen motion.

## INTRODUCTION

Bulk superconductivity recently discovered in the Tl-based bi- and tri-$CuO_2$ layer perovskites at[1-7] 110 and 125 K has opened up a whole new class of materials to experimental investigations and added great opportunities to reach some understanding of the mechanism responsible for high-$T_c$ superconductivity. Raman scattering has advanced our understanding of the $YBa_2Cu_3O_x$ class of high-temperature superconductors[8-24] by identifying impurity phases, probing the microstructure and excitations possibly involved in the superconducting mechanism itself. Similar benefits can be expected from Raman studies of the Tl-based high-$T_c$ superconductors. The crystal structures of $Tl_2Ca_{n-1}Ba_2Cu_nO_{4+2n}$ ($n=1,2,3$) have been investigated with x-ray and transmission electron microscopy (TEM) techniques[2-7,25] and were found to be body centered with a tetragonal unit cell. The $n=2$ phase has essentially the same structure as $Bi_2CaSr_2Cu_2O_8$ and is built of Cu-O sheets alternating with double Tl-O layers.[26,27] The $n=1,3$ phases have single and triple Cu-O layers separating the Tl-O sheets. In all structures, Ca and Ba ions separate Cu-O layers from Cu-O and Tl-O layers, respectively. There are indications of a weak superstructure[5] in these materials but it is less pronounced than the one observed in the Bi superconductors.[28] The compounds are not as sensitive to oxygen stoichiometry as $YBa_2Cu_3O_7$. The exact site occupancies, oxygen stoichiometries, and Tl and Cu valencies are largely unknown at this stage but indications for Tl-Ca disorder, additional or deficient $CuO_2$-layers, and distortion within the Tl-O layers have been given for both phases.[4,6] As a powerful tool for studying the microstructure Raman spectroscopy in principle is capable of resolving many of these questions. In the following we present Raman spectra of polycrystalline materials of predominant compositions $Tl_2Ba_2CuO_6$ (denoted the 2:2:1 compound), $Tl_2Ca_1Ba_2Cu_2O_8$ (2:1:2:2 compound), and $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2:2:2:3 compound) with respective $T_c$'s of 10, 110, and 125 K using samples with well-characterized transport and magnetic properties. Since the samples were prepared under identical conditions we believe that the structural properties are the same as described by Parkin and co-workers.[3,5] Comparison with Raman spectra of impurity phase candidates allows identification of the intrinsic Raman spectrum of the respective superconducting 2:2:1, 2:1:2:2, and 2:2:2:3 phases. Systematic variations between spectra of the three superconducting phases and great similarities with the better understood $YBa_2Cu_3O_7$ spectrum suggests tentative assignments of the peaks to the Raman active modes derived from factor group analysis.

## EXPERIMENTAL DETAILS

The preparation of the superconducting samples has been described elsewhere.[3,5] All samples showed narrow superconducting transitions (< 10 K) in conductivity and susceptibility measurements and had 5-K Meissner volume fractions exceeding 15%. Identical preparation conditions and x-ray data suggest that the structural properties of these samples are the same as the ones more extensively analyzed with electron microprobe analysis and transmission electron microscopy by Parkin and co-workers.[3,5] Thus the observed stoichiometries indicate possible intergrowth of single Tl-O layers or thallium deficiency in the samples. In the 2:2:1 and 2:1:2:2 samples, the respective phases predominate but the 2:2:2:3 samples contained significant amounts of the 2:1:2:2 phase and a quaternary oxide containing the cations Tl, Ca, and Cu in approximate proportion Tl:Ca:Cu = 0.40:0.41 :0.55.[3,5] A sample with similar stoichiometry was prepared using a starting composition for Tl:Ca:Cu of 1:5:6, respectively, and will be referred to as the 1:5:6 phase in the following. $BaCuO_2$ and $CaCuO_2$ impurity compounds were produced by heating appropriate starting materials in $O_2$ to 900°C for several hours. The other impurity phase samples were pressed pellets of the chemical compounds. All samples were stored in dry air and no pronounced aging effects could be observed in the intrinsic Raman spectra and transport properties over a period of two months. The details of the Raman spectrometer have been described previously.[10]

## RESULTS AND DISCUSSION

Figure 1 shows the room-temperature Raman spectrum of fully oxygenated $YBa_2Cu_3O_7$, the three Tl high-temperature superconductors $Tl_2Ca_{n-1}Ba_2Cu_nO_{4+2n}$ ($n=1,2,3$), and one prominent impurity phase found in the $n=3$ sample. Intensive study has led to a partial understanding of the $YBa_2Cu_3O_7$ Raman spectrum with prominent peaks at 151, 337, 437, and 501 $cm^{-1}$ assigned in the following way as a result of single-crystal polarization data[12,14,16] and normal-mode calculations.[24] The 501-$cm^{-1}$ mode having *zz* polarization originates from the bridging O(4) atoms between the Cu(1) and Cu(2) planes. The 437- and 337-$cm^{-1}$ modes with respective *zz* and *xx* polarizations correspond to bond-bending modes of the oxygen atoms in the Cu(2) planes with respective in-phase and out-of-phase *c*-axis motion of the O(2) and O(3) atoms. The 337-$cm^{-1}$ mode shows substantial softening and broadening below 92 K indicating a significant interaction with the superconducting state.[10,22,23] The 151-$cm^{-1}$ mode with *zz* polarization has been assigned to *c*-axis motion of the Cu(2) atoms.[16] All modes discussed above have $A_g$ symmetry in the orthorhombic structure. Apparently, *c*-axis motion produces larger modulations of the polarizability than the *a*- and *b*-axis displacements associated with the $B_{2g}$ and $B_{3g}$ modes.

Utilizing our knowledge of the $YBa_2Cu_3O_7$ modes, what Raman spectrum does one expect for the single $CuO_2$-layer $Tl_2Ba_2CuO_6$ compound? The Cu(1) and O(1) atoms located in the Cu-O plane centered between O(2) and Ba atoms and Tl-O double layers have site inversion symmetry, and modes they participate in are thus Raman forbidden for one-phonon $k=0$ scattering processes. Thus, there are no Raman-active $CuO_2$ bond bending vibrations equivalent to the 337- and 433-$cm^{-1}$ modes in $YBa_2Cu_3O_7$ in this material. The bridging O(2) atoms similar to the O(4) atoms between the Cu(1) and Cu(2) planes in $YBa_2Cu_3O_7$ are expected to be strongly Raman active with slightly lower frequency than the 500-$cm^{-1}$ $YBa_2Cu_3O_7$ mode due to longer bond lengths to the adjacent Tl and Cu atoms. In addition one would expect a high-frequency mode associated with oxygen motion in the Tl-O planes and low-frequency modes originating from Tl and Ba motion along the *c* axis. The spectrum of $Tl_2Ba_2CuO_6$ (2:2:1) shown in Fig. 1 with four pronounced peaks at 125, 165, 485, and 603 $cm^{-1}$ is consistent with these predictions. In particular we identify the 603-$cm^{-1}$ mode with O vibrations in the Tl planes, the 485-$cm^{-1}$ mode with vibrations of the bridging O(2) atoms, and the 125 and 165 $cm^{-1}$ with either motion of the Tl or Ba atoms. Note the absence of modes in the frequency region between 200 and 450 $cm^{-1}$ that could be associated with $CuO_2$ bond-bending modes which are forbidden by symmetry.

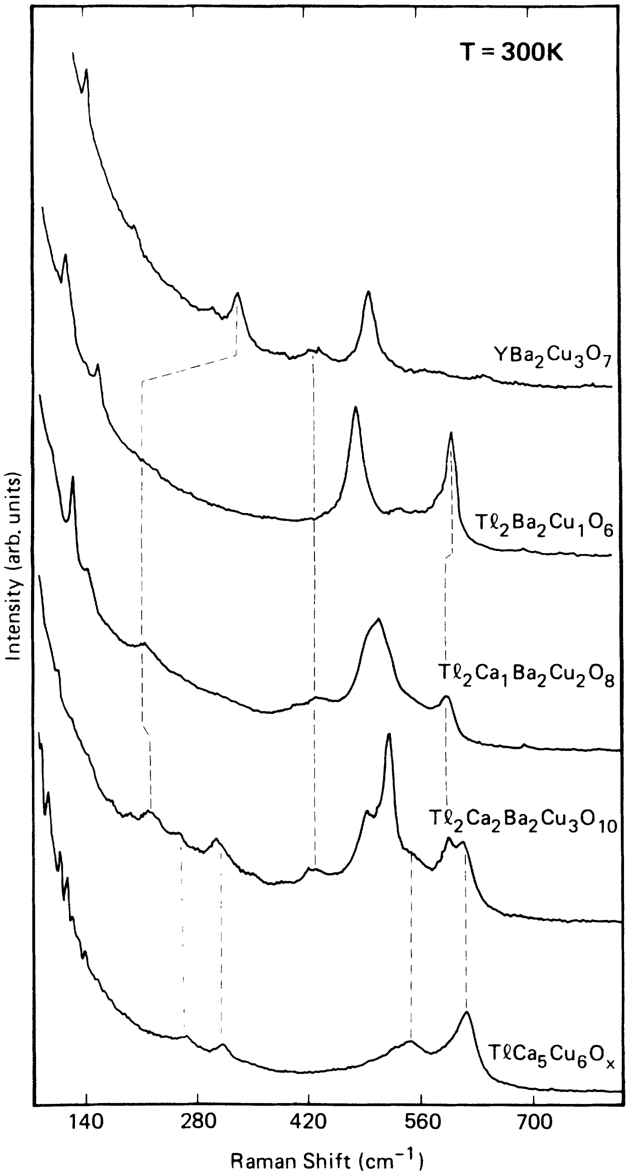

FIG. 1. Room-temperature Raman spectra of superconducting samples of $Tl_2Ca_{n-1}Ba_2Cu_nO_{4+2n}$ ($n=1,2,3$) with respective transition temperatures of 10, 110, and 125 K. The Raman spectrum of $YBa_2Cu_3O_7$ is included to emphasize similarities and aid in the mode assignments for the Tl compounds. Also shown is the spectrum of a quaternary oxide produced with starting stoichiometry Tl:Ca:Cu = 1:5:6 suggesting a presence of this impurity phase in the superconducting 2:2:2:3 sample.

The situation for the $Tl_2Ca_1Ba_2Cu_2O_8$ (2:1:2:2) and $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2:2:2:3) compounds with two and three $CuO_2$ phases and additional Ca atoms is more complex as will be discussed in the following. Both spectra show a large number of peaks. Thus, we first address the question of impurity modes and identify the intrinsic Raman spectra of the two compounds.

Comparison with the Raman spectrum of the 1:5:6 impurity phase (Fig. 1) shows characteristic peaks at 265, 311, 545, and 617 $\mathrm{cm}^{-1}$ appearing in the 2:2:2:3 spectrum with the same strength ratios and linewidths. This indicates non-negligible amounts of the 1:5:6 phase present in the 2:2:2:3 sample as predicted by TEM observations.[3] Comparison with the Raman spectrum of the 2:1:2:2 superconducting phase indicates no noticeable amounts of the 1:5:6 impurity in this sample in agreement with TEM observations.[5] The 2:1:2:2 spectrum, however, shows a set of peaks at 133, 151, 691, and 1060 $\mathrm{cm}^{-1}$ (not shown) with substantial strength variations in different superconducting samples. A set of peaks at identical positions observed from a pressed $BaCO_3$ pellet indicates $BaCO_3$ surface contamination of this sample. Other weak peaks at 355 $\mathrm{cm}^{-1}$ in the 2:2:2:3 and 643 $\mathrm{cm}^{-1}$ in the 2:1:2:2 phase coincide with impurity peaks, but the coincidences are insufficient to identify the respective phases.

The consistency in position and strength ratio of the remaining peaks observed in various samples of the same materials suggests that they are intrinsic to the superconducting phases. Thus, prominent peaks remain for the 2:1:2:2 sample with room-temperature positions at 595, 509, 495, 433, and 221 $\mathrm{cm}^{-1}$ and, possibly, weak ones at 521, 176, and 105 $\mathrm{cm}^{-1}$. Similarly for the 2:2:2:3 sample we have strong peaks at 597, 523, 494, 430, and 230 $\mathrm{cm}^{-1}$ and possibly weak ones at 511 and 179 $\mathrm{cm}^{-1}$. Comparison of the intrinsic spectra of $Tl_2Ba_2CuO_6$, $Tl_2Ca_1Ba_2Cu_2O_8$, and $Tl_2Ca_2Ba_2Cu_3O_{10}$ shows great similarities and systematic variations as expected from the crystal structures. A factor group analysis was performed for the respective materials assuming the fully occupied stoichiometry and tetragonal symmetry with the results shown in Table I. The orthorhombic symmetry imposed by the weak superstructure is neglected. The $A_{1g}$ and $B_{1g}$ modes which correspond to $c$-axis motion of the respective atoms are expected to dominate the Raman spectra as is the case in $YBa_2Cu_3O_x$. We will, thus, limit ourselves to the discussion of these modes. The four strong Raman peaks observed for the 2:2:1 sample agree well with the prediction from symmetry of four $A_{1g}$ modes for this structure. In the 2:1:2:2 and 2:2:2:3 structures the respective O(1) and O(2) atoms are not at sites of inversion symmetry and two bond-bending modes with $A_{1g}$ and $B_{1g}$ symmetry are predicted.

Comparing the three spectra we see modes at 430 and 230 $\mathrm{cm}^{-1}$ appearing in the 2:1:2:2 and 2:2:2:3 samples which were not present in the 2:2:1 material. The similar frequencies of the respective Cu-O bond-bending modes in $YBa_2Cu_3O_7$ (437 and 337 $\mathrm{cm}^{-1}$) thus suggests assignment of the 430-$\mathrm{cm}^{-1}$ modes to in-phase bond-bending motion of the O(1) and O(2) atoms in the 2:1:2:2 and 2:2:2:3 structures and the 230-$\mathrm{cm}^{-1}$ mode to the respective out-of-phase motions. Polarization results on a similar mode at 282 $\mathrm{cm}^{-1}$ observed in single crystals of the $Bi_2Ca_1Sr_2Cu_2O_8$ 2:1:2:2 superconductor[29] confirmed the $B_{1g}$ symmetry of this mode. The lower $B_{1g}$ frequency in the Tl compounds could be the result of the much smaller puckering of the Cu-O planes in these materials. Group theory predicts an $A_{1g}$ mode involving the oxygen atoms in the Tl-O planes in all three materials. Since $c$-axis motion of the oxygen atoms involves stretching of the Tl-O bonds this mode is expected at high frequency. An excellent candidate for this mode is the peak observed near 600 $\mathrm{cm}^{-1}$ in all three samples. The difference in intensity could be related to different Tl stoichiometries in the samples. The small shifts between the different structures are in agreement with the similar bond lengths. A corresponding assignment has been made for the respective mode in the $Bi_2Ca_1Sr_2Cu_2O_8$ 2:1:2:2 superconductor.[29,30]

In the 1:2:3 spectrum the strongest mode at 500 $\mathrm{cm}^{-1}$ has been assigned to the motion of the bridging oxygen atoms between Cu planes. In the Tl-based 2:2:1, 2:1:2:2, and 2:2:2:3 materials the respective strongest peaks appear at 485, 509, and 523 $\mathrm{cm}^{-1}$ with additional weaker ones at 495 and 494 $\mathrm{cm}^{-1}$ in the latter two compounds. For the 2:2:1 material, we identify the 485-$\mathrm{cm}^{-1}$ mode with the bridging O atoms. For the 2:1:2:2 and 2:2:2:3

TABLE I. Classification of the Raman-active modes in body-centered tetragonal $Tl_2Ca_{n-1}$-$Ba_2Ca_nO_{4+2n}$ ($n=1,2,3$) for the full stoichiometries. The atomic sites are specified according to the Wyckoff notation and the O and Cu atoms labeled along the $c$ axis starting from the site of inversion symmetry at the center of the conventional unit cell. The ellipses indicate Raman inactive atoms.

| Site | Atom | $Tl_2Ba_2CuO_6$ | Site | Atom | $Tl_2CaBa_2Cu_2O_8$ | Site | Atom | $Tl_2Ca_2Ba_2Cu_8O_{10}$ |
|---|---|---|---|---|---|---|---|---|
| $4e$ | Tl | $A_{1g}+E_g$ | $4e$ | Tl | $A_{1g}+E_g$ | $4e$ | Tl | $A_{1g}+E_g$ |
| | | | | | $\cdots$ | $4e$ | Ca | $A_{1g}+E_g$ |
| | | | $2a$ | Ca | | | | |
| $4e$ | Ba | $A_{1g}+E_g$ | $4e$ | Ba | $A_{1g}+E_g$ | $4e$ | Ba | $A_{1g}+E_g$ |
| $2a$ | Cu(1) | $\cdots$ | | | | $2a$ | Cu(1) | $\cdots$ |
| | | | $4e$ | Cu(1) | $A_{1g}+E_g$ | $4e$ | Cu(2) | $A_{1g}+E_g$ |
| $4c$ | O(1) | $\cdots$ | | | | $4c$ | O(1) | $\cdots$ |
| | | | $8g$ | O(1) | $A_{1g}+B_{1g}+2E_g$ | $8g$ | O(2) | $A_{1g}+B_{1g}+2E_g$ |
| $4e$ | O(2) | $A_{1g}+E_g$ | $4e$ | O(2) | $A_{1g}+E_g$ | $4e$ | O(3) | $A_{1g}+E_g$ |
| $4c$ | O(3) | $A_{1g}+E_g$ | $4c$ | O(3) | $A_{1g}+E_g$ | $4e$ | O(4) | $A_{1g}+E_g$ |
| Total | | $4A_{1g},4E_g$ | | | $6A_{1g},1B_{1g},7E_g$ | | | $7A_{1g},1B_{1g},8E_g$ |

compounds, this assignment is not as straightforward since there are two strong modes present near 500 $cm^{-1}$. One of these modes presumably is due to the bridging O atoms. Assignment of the additional peaks observed at 509 and 523 $cm^{-1}$ or 495 and 494 $cm^{-1}$ in the 2:1:2:2 and 2:2:2:3 structure, respectively, is difficult since all $A_{1g}$ and $B_{1g}$ modes predicted by group theory to involve oxygen motion are already accounted for. Heavier ions are unlikely to be oscillating at such high frequencies and Ca motion must be ruled out because it is not Raman active in the 2:1:2:2 structure. Possible explanations allowing other modes include intergrowth of single Tl-O layers, $E_g$ modes, and Tl-Ca disorder suggested to affect up to 15% of the lattice sites.[4,6]

Group theory predicts Ba and Tl atoms to be involved in modes of $A_{1g}$ symmetry in all three materials and we expect that they should have similar frequencies in the different compounds. For the 2:2:1 structure the Tl and Ba modes are the only remaining modes of $A_{1g}$ symmetry and we assign the two strong low-frequency peaks at 125 and 165 $cm^{-1}$ with either Ba or Tl motion. The weak low-frequency modes in the 2:1:2:2 and 2:2:2:3 samples are very difficult to assign because of the strong scattering background and impurity modes. Thus, assignments are open questions at this time.

In conclusion we have identified a number of modes which we believe to be intrinsic to the phonon spectrum of the $Tl_2Ba_2CuO_6$, $Tl_2Ca_1Ba_2Cu_2O_8$, and $Tl_2Ca_2Ba_2Cu_3O_{10}$ superconductors. The spectra show great similarities and systematic variations that are linked to the similarities between the three structures and constraints imposed by the different site symmetries. These findings together with similarities to the better understood Raman spectrum of $YBa_2Cu_3O_7$ suggest tentative mode assignments for the high-frequency peaks above 200 $cm^{-1}$ to certain $A_{1g}$ and $B_{1g}$ modes of different oxygen atoms.

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