Research Article

Investigation of Phonon Vibrational Modes in Ga, Al, Fe, Co, Ni, and Zn Doped (110)-Oriented PBCO Thin Films

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We performed Raman scattering measurements and a comprehensive study of different types of Raman modes associated with phonon vibrations on pure and Ga, Al, Fe, Co, Ni, and Zn doped (110)-oriented PrBa2Cu3O7 (PBCO) thin films to identify the substitution of Cu (1) or Cu (2) ions in PBCO lattice. In Raman spectrum of (110)-oriented PBCO thin film, we observed four prominent Ag type Raman modes at $\sim 130$ cm$^{-1}$, $\sim 150$ cm$^{-1}$, $\sim 440$ cm$^{-1}$, and $\sim 520$ cm$^{-1}$ corresponding to Ba, Cu (2), O (2)–O (3) in-phase, and O (4) apical oxygen vibration along c-axis, respectively. The Raman mode of pure PBCO at $\sim 520$ cm$^{-1}$ softened on Ga, Al, Fe, and Co doped PBCO thin films while it remained unaffected on Zn and Ni doped PBCO thin films. We explain these results in the context of their correlation with Cu (1)–O (4) and Cu (2)–O (4) bond lengths. In addition, we observed a new Raman mode near 610 cm$^{-1}$ in the Raman spectra of Ga, Al, Fe, and Co doped PBCO thin films, an infrared (IR) active mode that became Raman active when the symmetry was broken at the Cu-O chain site after the partial substitution of Cu (1) ion. Moreover, the “O (2)–O (3) in-phase Raman mode” near 440 cm$^{-1}$ remained unaffected in Fe, Co, Ga, and Al doped PBCO thin films but softened in Zn and Ni doped PBCO thin films. Based on these results, we argue that Ga, Al, Fe, and Co ions replace Cu (1) ion at the Cu-O chain site, break the crystal symmetry, and produce disorder locally, whereas Zn and Ni ions replace Cu (2) ion at the CuO$_2$ plane of the PBCO lattice structure.

1. Introduction

Raman spectroscopy is an ideal analytical tool for site detection of Cu ion substitution in the family of cuprate oxide compound RBA$_2$Cu$_3$O$_7$ (R = Rare Earth element). Two of the most useful members of this family are high critical temperature ($T_c$) superconductors YBA$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and cuprate oxide insulator PrBa$_2$Cu$_3$O$_{7-\delta}$ (PBCO), which share similar lattice structure and oxygen chemistry [1] and are used in wide range of superconducting electronic and magnetic devices. The substitution of Pr for Y in Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ suppresses $T_c$ with superconductivity disappearing for $x \geq 0.50$ [2]. Substitutions of Cu ions in PBCO by trivalent metal ions such as Fe, Co, Ga, and Al and divalent metal ions such as Ni and Zn are of special interest in applied superconductivity and materials science as these elements have preferential role in the substitution of Cu ions, i.e., from the Cu-O chains or CuO$_2$ planes of PBCO lattice. Raman spectroscopy is one of the many tools to detect the Cu ion sites of the substituted trivalent or divalent ions.

As shown in Figure 1, the unit cell of PBCO is either tetragonal or orthorhombic, which contains two dimpled Cu (2)–O (2)–O (3) planes (CuO$_2$ planes), separated by a single Pr atom that form a two-dimensional rectangular network. The O (1) atoms along the b-axis direction (y-axis in Figure 1) form the Cu (1)–O (1) chains at the top or bottom of the each unit cell. There are no equivalent oxygen atoms along a-axis direction (x-axis direction in Figure 1) and hence no Cu (1)–O (1) chain in this direction. O (4) oxygen forms a bridge between the Cu (1) and Cu (2) ions. X-ray and neutron diffraction measurements performed on the metal-doped PBCO powder samples, namely, PrBa$_2$[Cu$_{1-x}$M$_x$]$_3$O$_7$
Most $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ compounds are centro-symmetric crystals and have inversion centers [3, 4]. For example, in YBCO and PBCO, the sites of the Y or Pr atom, Cu (1) atom, and the O (1) atom in the Cu-O chains behave as inversion centers. The vibration of both atoms in the Cu-O chain move in the same direction and it is called an odd vibration. Raman spectroscopy involves two odd photons, whose combination is even and couples only to even vibrations. On the contrary, infrared (IR) spectroscopy involves only one photon (odd in dipole approximation) and therefore couples only to odd vibrations. The vibrations of the Cu (1) and O (1) atoms are thus Raman inactive and IR-active. The remaining atoms do not have centers of inversion in the unit cell. They appear as pairs of equivalent atoms connected by the inversion and can give rise to either odd (both atoms moving in the same direction) or even (motion in opposite directions) vibrations.

The atoms of Figure 1 can vibrate along the $z$ as well as along the $x$ and $y$ directions. Even vibrations along $z$-axis appear to be much stronger in the Raman spectra than their $x$–$y$ counterparts. If O (1) atoms of the chains are removed, the unit cell of Figure 1 becomes tetragonal ($D_{4h}$ point group).

For the structure of Figure 1, five $z$-polarized Raman phonon vibration mode exist [4]: vibrations of Ba (115 cm$^{-1}$), Cu (2) (150 cm$^{-1}$), O (2)–O (3) plane oxygens (340 cm$^{-1}$, 440 cm$^{-1}$), and the apical oxygen O (4) (500–520 cm$^{-1}$). The vibrations of the oxygen atoms lie in the 300 cm$^{-1}$–700 cm$^{-1}$ range. The Raman vibration mode at 500 cm$^{-1}$ in YBCO and 520 cm$^{-1}$ in PBCO is due to axial vibration of the apical oxygen atom between the two copper atoms: Cu (1) and Cu (2). It is an $A_g$ mode and has a cc-polarization, which refers to incident radiation polarized along the $c$-axis of the crystal and scattered radiation polarized along the $c$-axis. The 440 cm$^{-1}$ peak is also an $A_g$ mode. It is assigned to O (2)–O (3) in phase binding motion, consistent with cc-polarization.

Theoretically, there are five phonons of $A_g$ symmetry in the orthorhombic phase of PBCO and four $A_{1g}$ and one $B_{1g}$ phonons in the tetragonal phase of PBCO. When the PBCO structure becomes tetragonal, four of the five $A_g$ phonons become $A_{1g}$ and the remaining $A_g$ phonon becomes $B_{1g}$ or $B_{1g}$-like. The difference between $A_{1g}$, $A_{1g}$, and $B_{1g}$ is in their

(\(M = \text{Al}, \text{Co}, \text{Fe}, \text{Ga}, \text{Ni}, \text{and Zn}\) and $x = 0.00, 0.05, 0.10, 0.15$, and 0.20 by our research group showed that the crystalline structure of PBCMOs are of orthorhombic ($P_{mmm}$ space group), same as those for PBCO and YBCO. However, the orthorhombicity of PBCMO was found to be small than that of PBCO. X-ray data indicated no significant second phases for substituting Cu by Al, Co, Fe, and Ga up to 20%.

Raman tensor corresponding to a crystal are described by different point groups as described in [3] and Table 1, which show a tensor representation for orthorhombic and tetragonal space groups. Most RBCO compounds fall into one of these two groups and, a vibrational mode is allowed if the element of the Raman tensor, called the Raman active mode is nonzero. On the contrary, if the element in the Raman tensor is zero, the mode is Raman forbidden, is inactive, and will not show in the Raman spectrum. Vibrational mode of $A_g$ symmetry are observed in the orthorhombic ($D_{2h}$) point group for a parallel polarization of incident and scattered light, for example, $x (z, z)x'$. However, Raman active modes $B_{1g}$, $B_{2g}$, $E_g$, and $F_g$ are observed with crossed polarizations, for example, $y (x, z)y'$. Raman scattering from the $A_g$ symmetry mode in $D_{2h}$ point group is allowed only in $xx$, $yy$, or $zz$ polarization symmetries and the Raman scattering from $B_{1g}$, $B_{2g}$, and $F_g$ symmetries are allowed only for $(xy$ or $yx)$, $(xz$ or $zx)$, and $(yz$ or $zy)$ polarization geometries, respectively.

![Figure 1: A unit cell of PrBa$_2$Cu$_3$O$_{7-\delta}$](image)

**Table 1: Raman Tensor in $D_{2h}$ (orthorhombic) and $D_{4h}$ (tetragonal) point group [3].**

| Orthorhombic structure | $B_{1g}$ | $B_{2g}$ | $B_{3g}$ |
|------------------------|----------|----------|----------|
| $A_g$                   | $(xx,yy)$| $(xy,yx)$| $(xz,zy)$|
| $B_{1g}$                | $(xx,zz)$| $(yx,zy)$| $(zx,zy)$|
| $B_{2g}$                | $(xx,zz)$| $(yx,zy)$| $(zx,zy)$|
| $B_{3g}$                | $(xx,zz)$| $(yx,zy)$| $(zx,zy)$|

| Tetragonal structure | $A_{1g}$ | $B_{1g}$ | $B_{2g}$ | $E_g$ |
|----------------------|----------|----------|----------|-------|
| $A_{1g}$             | $(xx,zz)$| $(zx,zz)$| $(xy,yy)$| $(xy,yy)$|
| $B_{1g}$             | $(xx,zz)$| $(zx,zz)$| $(xy,yy)$| $(xy,yy)$|
| $B_{2g}$             | $(xx,zz)$| $(zx,zz)$| $(xy,yy)$| $(xy,yy)$|
| $E_g$                | $(xx,zz)$| $(zx,zz)$| $(xy,yy)$| $(xy,yy)$|
Raman tensors and therefore in their polarization selection rules. We expect no intensity for the B1g or B1g-like mode in the zz polarization spectra.

Detailed analysis of the Raman scattering of YBCO have been published by various researchers such as Thomsen and Kaczmarczyk [3], Cardona [4], McCarty et al. [5], Pinczuk and Burstein [6], Hemley and Mao [7], Thomsen and Cardona [8], Kakihana et al. [9], Roughani [10], and Bates et al. [11, 12]. Raman scattering studies also on PBCO and metal-doped PBCO have been reported in references [13–15]. In this paper, we present a comprehensive study of Raman scattering on pure and Ga, Al, Fe, Co, Ni, and Zn doped (110)-oriented PrBa$_2$(Cu$_{1-x}$M$_x$)$_2$O$_7$ (PBCO) thin films in which 20% Cu atoms in Cu (1) or Cu (2) sites are substituted by Fe, Co, Ni, Zn, Ga, and Al.

2. Materials and Methods

(110)-oriented PrBa$_2$(Cu$_{1-x}$M$_x$)$_2$O$_7$ (x = 0, 0.2 and M = Fe, Co, Ni, Zn, Ga, and Al) thin films were grown by pulsed laser deposition technique (PLD) as described in [16, 17]. The (110) epitaxy of the films was confirmed using X-ray diffraction.

Raman scattering measurements were performed on these thin films using Horiba Jobin Yvon T64000 Triple Raman spectrometer equipped with a liquid nitrogen cooled charge-coupled device (CCD) and a microscope in conjunction with computer-controlled XYZ stage and an optical cryostat Microstat (Oxford instruments). The 488 nm and 633 nm lines of lasers were used for the excitation at a power of 0.21 mW under the ×100 objective. The spectra were taken with parallel scattering configurations [(001), (001)] = zz or [110, 110] = x’x’ which means that both incident and scattered light polarizations were parallel to either the (zz) or (x’x’) dimension of the substrate.

For the description of the scattering configurations, we followed the convention of Porto notation a (bc) d [18], where the first and fourth letters denote, respectively, the directions of incident and scattered light in a Cartesian xyz system with the axes along the crystallographic directions.

3. Results and Discussion

Raman spectra of our (110)-oriented pure PBCO and Fe, Co, Ni, Zn, Ga, and Al doped PBCO thin films are shown in Figures 2–8 and Table 2.

In the Raman spectrum of the (110)-oriented pure PBCO film, we observed four prominent Raman modes in zz polarization: ∼130 cm$^{-1}$, ∼150 cm$^{-1}$, ∼440 cm$^{-1}$, and ∼520 cm$^{-1}$. These Raman modes are related to Ba, Cu (2), in-phase with O (2)–O (3), and O (4) apical oxygen vibration along c-axis, respectively. Our observed Raman modes in PBCO are in complete agreement with [13–15].

We also observed four prominent A$_g$ lines in zz polarization Raman spectra of our (110)-oriented Ga, Al, Fe, and Co doped thin films. Three of them were at ∼130 cm$^{-1}$, ∼160 cm$^{-1}$, and ∼440 cm$^{-1}$, which belong to Raman vibrational modes of Ba, Cu (2), and O (2)–O (3) along c-axis, respectively. The fourth Raman mode related to the O (4) apical oxygen vibration mode was observed in the frequency regime (485–502 cm$^{-1}$).

Next, we observed B1g-like Raman mode near 300 cm$^{-1}$ in all of our thin film samples. This mode belongs to the “out-of-phase vibrations of the O (2) and O (3) atoms” in c-axis direction [4], and it is allowed only in xx or yy polarizations. Surprisingly, we observed this mode in zz-polarization in our samples. The observation of this B1g-like mode in the zz-polarization Raman spectrum of (110)-oriented PBCO thin film can tentatively be explained by either the presence of small islands with different (e.g., c-axis) orientation or a small misorientation of <001> direction with respect to the substrate edges.

An additional Raman mode near 600 cm$^{-1}$ was observed in the Raman spectra of our Ga, Al, Fe, and Co doped PBCO thin film samples. However, we did not observe this Raman mode in the Raman spectra of pure PBCO and Zn or Ni doped PBCO thin film. We discuss these results in detail below.

3.1. Behavior of Raman Mode Corresponding to Apical Oxygen O (4) Vibrations

The Raman mode corresponding to the O (4) apical oxygen vibration was observed in the frequency regime (485–502 cm$^{-1}$) of the Raman spectra on Ga, Al, Fe, and Co doped PBCO thin films. This is the softening of the Raman mode ∼520 cm$^{-1}$ corresponding to the vibration of the apical oxygen O (4) along c-axis in pure PBCO. This mode behaves in many ways similar to the axial stretching mode of the O (4) apical oxygen against the Cu (1) in YBCO (∼500 cm$^{-1}$). Similar type of Raman mode for the apical oxygen vibration has been reported in [14, 15, 19–22]. On the contrary, we observed no shift in the Raman mode of apical oxygen in the Raman spectra of Ni and Zn doped PBCO samples, again in agreement with Xu [19]. Here, we discuss effect of substituting Fe, Co, Ni, Zn, Ga, and Al with Cu ions in PBCO in the context of the behavior of this Raman mode.

Kakihana et al. [22] have discussed the role of Cu (1)–O (4) and Cu (2)–O (4) bond lengths for the vibrational frequency of apical oxygen on trivalent ions on Al, Fe, and Co doped YBCO, where the vibrational frequency $\omega$ of apical oxygen followed the relation,

$$\omega^2 = \frac{A}{r_{\text{Cu(1)–O(4)}}} + \frac{B}{r_{\text{Cu(2)–O(4)}}},$$

and decreased with the substitution of them with Cu ion in YBCO. On the contrary, the Rietveld refinement of neutron diffraction data showed that all of these ions replaced Cu from Cu (1) ion location. The structural changes occurred in such a way that Cu (1)–O (4) bond length decreased by 0.1 Å per Co atom and Cu (2)–O (4) bond length increased by 0.3 Å per Co atom for 15% Cu substitution. Al ion
Figure 2: \(zz\) and \(x'x'\) polarization Raman spectra of (110)-oriented PBCO thin films.

Figure 3: Continued.
substitution in PBCO also behaved similarly but with a larger change in the bond lengths [23].

Using normal mode calculations, Roughani [10] and Bates et al. [11, 12] described the behavior of the apical oxygen vibrational mode based on the changes in the interatomic force constants and the bond lengths on trivalent and divalent metal doped YBCO. The substitution of Cu (1) by Co in Cu-O chains decreased the Cu (1)–O (4) bond

![Graph](image-url)

**Figure 3:** $zz$ and $x'x'$ polarization Raman spectra of (110)-oriented Al doped PBCO thin films.

![Graph](image-url)

**Figure 4:** $zz$ and $x'x'$ polarization Raman spectra of (110)-oriented Ga doped PBCO thin film.
length but increased the Cu (2)–O (4) bond length causing the softening of the apical oxygen-related Raman vibrational mode.

Based on the behavior of Raman mode corresponding to the apical oxygen vibration along the c-axis on YBCO and looking at the similarity in the lattice structure of YBCO and PBCO, we argue that the trivalent atoms Ga, Al, Fe, and Co substitute Cu ions from Cu (1) site and divalent atoms Zn and Ni substitute Cu from the Cu (2) site of PBCO lattice as well.

3.2. Behavior of Raman Mode at Cu-O Chain Site. The Raman mode near 600 cm$^{-1}$ in the Raman spectra of Al, Ga, Co, and Fe doped PBCO thin film represents the vibration of O (1) atom along the Cu-O chain of the PBCO unit cell. This is a forbidden Raman mode in PBCO by group theory as Cu and O in the Cu-O chains are at the inversion center of the PBCO unit cell. However, since the symmetry is broken in Al, Ga, Co, and Fe doped PBCO due to the substitution of Cu (1) ions with these substituents; this mode has become Raman active.

It is noteworthy to mention the results from the other experiments including the Rietveld refinement on the neutron diffraction measurement of trivalent metal-doped YBCO [22], where these dopants created disorder in Cu-O chain and O (1) was statistically distributed in a less symmetric position ($x$, 1/2, 0). In addition, the neutron diffraction performed by Zolliker et al. on Co doped YBCO showed similar disorder phenomenon in Cu-O chains [24]. Comparing the similarity of the Cu-O chains in both YBCO and PBCO and the appearance of Raman peak near 600 cm$^{-1}$ in our Al, Ga, Fe, and Co doped PBCO thin film samples, we argue that these metal ions substituted Cu (1) of PBCO lattice and destroyed the regular distribution of the oxygen length.
we argue that they did not replace any Cu ion from Cu (2) quency did not change with the Fe, Co, Ga, and Al doping, the PBCO lattice. On the contrary, as the vibrational fre-
argue that Zn and Ni ion substituted Cu at the Cu (2) site of substitution of Cu (2) with Zn and Ni, and therefore, we conclude that trivalent ions Fe, Co, Ga, and Al replace Cu (1) in CuO2 planes of the PBCO lattice structure. These results are in complete agreement with the conclusions of our electrical transport studies on these samples [16, 17].

### 4. Conclusions

We performed Raman scattering measurement on pure and Al, Ga, Fe, Co, Zn, and Ni ion-doped (110)-oriented PBCO thin films and investigated the effects of different ion substitution for Cu (1) or Cu (2) in the lattice of PBCO.

The Raman spectra taken with zz polarization on (110)-oriented pure and Ga, Al, Fe, and Co PBCO films showed three prominent Ag peaks at ~130 cm⁻¹, ~160 cm⁻¹, and ~440 cm⁻¹ and an apical oxygen O (4) vibration-related Raman mode between 480 and 502 cm⁻¹. However, this apical oxygen vibration-related Raman mode remained unaffected in the spectra of Ni or Zn doped PBCO thin films compared to the Raman spectrum of pure PBCO thin film. We explained these results in correlation with Cu (1)–O (4) and Cu (2)–O (4) bond lengths due to the substitution of Cu ions.

In addition, we observed a new Raman mode near 600 cm⁻¹ in the Raman spectra of Ga, Al, Fe, and Co doped PBCO thin films. This forbidden Raman mode became Raman active because of the broken symmetry at the Cu-O chain site when these ions substituted Cu (1) partially. When a divalent Cu (1) was substituted by trivalent ions Ga, Al, Fe, and Co, the symmetry of the PBCO crystal was broken leading to this Raman mode. However, we did not observe this Raman mode in the Raman spectra of pure PBCO and Zn or Ni doped PBCO thin films indicating that Zn or Ni did not substitute Cu (1) at the Cu-O chain site.

On the contrary, the Raman mode at ~440 cm⁻¹ corresponding to “O (2)–O (3) 3 in-phase vibration” in c-axis direction at the CuO2 planes remained unaffected on Fe, Co, Ga, and Al doped PBCO thin films. However, it softened to 430–435 cm⁻¹ on Zn or Ni doped PBCO thin films as the vibration of the oxygen atoms at Cu-O2 plane was influenced by the substitution of Cu (2) with Zn or Ni ions. Therefore, we argue that Zn and Ni ions substitute Cu (2) at CuO2 planes site but Ga, Al, Fe, and Co ions do not.

Based on the analysis of the Raman modes corresponding to the phonon vibrations of “in-phase O (2)–O (3)”, O (4) apical oxygen, and Cu-O chain along b-axis, we conclude that trivalent ions Fe, Co, Ga, and Al replace Cu (1) in CuO2 planes and divalent ions Ni and Zn replace Cu (2) in CuO2 planes of the PBCO lattice structure. These results are in complete agreement with the conclusions of our electrical transport studies on these samples [16, 17].

### Data Availability

Data used in this study are available from the corresponding author upon request.

### Disclosure

The views expressed herein are those of the authors and are not necessarily those of WiSys or UW System.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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