

Raman spectroscopic evidence of site-selective isotopic substitution of oxygen in $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ and mode assignments of oxygen vibrations

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The site-selective substitution of ^{18}O for ^{16}O in $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ has been investigated by Raman spectroscopy. Three prominent Raman bands are observed at 297, 464, and 623 cm^{-1} . They all shift to lower wave numbers as the ^{18}O content increases. The bands at 297 and 464 cm^{-1} shift at similar rates but the band at 623 cm^{-1} shifts at a slower rate. These results show that all three bands are due to the vibrations involving oxygen atoms, and that the rate of oxygen substitution is site dependent. Based on these experimental results, tentative mode assignments have been made assuming a tetragonal symmetry: 623 $\text{cm}^{-1} \rightarrow \text{O}_{\text{pl}}(A_g)$, 464 $\text{cm}^{-1} \rightarrow \text{O}_{\text{ap}}$, and 297 $\text{cm}^{-1} \rightarrow \text{O}_{\text{Bi}}$.

Though many Raman spectroscopic studies on the Bi-based high- T_c cuprate superconductors ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$) have been reported,¹⁻⁸ there is still much controversy over the mode assignments of the Raman spectra. Most of the mode assignments in the literature were made primarily on the analogy of those of other compounds having similar structure. The mode assignments based on direct experimental evidence are required.

Recently the site-selective isotopic substitution of oxygen in Y-based high- T_c cuprate superconductors ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) was identified by Raman spectroscopy.^{9,10} For Bi-based high- T_c cuprate superconductors, recent extended x-ray absorption fine structure (EXAFS) studies^{11,12} suggested the site-selective detachment of oxygen atoms. Site-selective substitution of oxygen is also expected for Bi-based high- T_c cuprate superconductors. If we identify the site-selective substitution of oxygen in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ by Raman spectroscopy, it is possible to obtain information on the mode assignments of the Raman spectra.

In this paper, we report on the results of the site-selective substitution of oxygen in 91.6-K $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{O}_{8+\delta}$, obtained by combining the gas-solid exchange technique and Raman spectroscopy. We also report on the mode assignments based on these results of the site-selective substitution.

Starting material with composition of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8.21}$ ($T_c = 91.6$ K) was synthesized by the polymerized complex method.^{13,14} The sample was pre-heated in 2.67×10^4 Pa (200 mmHg) of $^{16}\text{O}_2$ atmosphere at 600 °C for 24 h. The Raman spectrum of the 72-h heat-treated sample was exactly the same as that of

the 24-h heat-treated sample, showing that the equilibration between the sample and the ambient gas had been established already within 24 h. This pre-heat-treatment prevented the variation of oxygen content during the exchange experiment. The oxygen content after this pre-treatment was thought to be different from that of the starting material, but we did not measure the oxygen content. So we use the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ hereafter, instead of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8.21}$. After evacuating the whole exchange apparatus by a mechanical rotary pump, the $^{18}\text{O}_2$ - $^{16}\text{O}_2$ mixed gas (91.2% in ^{18}O content) was introduced to 2.67×10^4 Pa (200 mmHg). The temperature was then raised to 600 °C, and the ^{16}O - ^{18}O exchange reaction was made to take place for a given exchange time. Details of the experimental setup and the procedure have been described elsewhere.¹⁵

For Raman measurements, $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ powder was uniaxially pressed at 3×10^7 Pa into a pellet of 2 mm in diameter after the ^{16}O - ^{18}O exchange reaction. The Raman spectra were measured using conventional back-scattering geometry, with a Dilor XY Raman spectrometer (Dilor, France), which consists of a triple polychromator and an intensified photodiode array detector. The excitation source was an Ar-ion laser (514.53 nm). The exposure time was 90 sec. The laser powder was lowered to 2 mW at the sample point to prevent the heating of the sample. It was found that when the laser power exceeded 5 mW, the ^{16}O - ^{18}O exchange reaction took place between the oxygen atoms in the air and those in the sample during the Raman measurement.

Figure 1 shows the Raman spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$, with different exchange times. Because of the strong scattering at the surface, it was not

TABLE I. Mode assignment of Raman spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

	Raman shift (cm^{-1})		
	~ 297	~ 464	~ 623
Present work	O_{Bi}	O_{ap}	$\text{O}_{\text{pl}} (A_g)$
Stalova <i>et al.</i> (Ref. 1)	$\text{O}_{\text{pl}} (A_g \text{ or } B_g)$	O_{ap}	Cu- O_{pl} stretching
Burns <i>et al.</i> (Ref. 2)	Sr	O_{ap}	O_{Bi}
Sugai and Sato (Ref. 3)	Cu- $\text{O}_{\text{ap}} (x-y)$	O_{ap}	O_{Bi}
Boekholt and co-workers <i>et al.</i> (Refs. 4-6)	O_{Bi}	$\text{O}_{\text{pl}} (B_g)$	O_{ap}
Liu <i>et al.</i> (Ref. 7)	O_{Bi}	O_{ap}	O_{Bi}

possible to measure the Raman spectra below 160 cm^{-1} . For the unreacted sample, three prominent Raman bands are observed at 297, 464, and 623 cm^{-1} . The band at 623 cm^{-1} has a broad shoulder at $\sim 650 \text{ cm}^{-1}$, but this is disregarded in further analysis for simplicity. In order to determine accurate Raman shift values, the raw spectra were fitted to Lorentzian curves assuming stepwise base-

lines.

Figure 2 shows the Raman shifts thus obtained at various exchange times. All the three bands shift to a lower wave number as the exchange time and hence the ^{18}O content increases. This result indicates that all the three peaks are due to the vibrations involving oxygen atoms.

Figure 3 is a plot of the relative Raman shift,

$$\text{relative Raman shift} = \frac{\text{Raman shift of } \text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2(^{16}\text{O}-^{18}\text{O})_{8-\delta}}{\text{Raman shift of } \text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2^{16}\text{O}_{8-\delta}} \times 100 (\%),$$

vs the square root of the exchange time. While the two bands at 297 and 464 cm^{-1} shift to a lower wave number at similar rates, the band at 623 cm^{-1} shifts at a slower rate as the exchange time increases. The Raman shift

after 100 min of the exchange time corresponds to the complete substitution of ^{18}O for ^{16}O ($[m_{^{16}\text{O}}/(0.91m_{^{18}\text{O}} + 0.09m_{^{16}\text{O}})]^{1/2} \approx 0.948$). These results show that the degree of oxygen substitution is site dependent: the oxygen atoms responsible for the bands at 297 and 464 cm^{-1} are more easily substituted by ^{18}O than those responsible for the band at 623 cm^{-1} .

X-ray- and neutron-diffraction studies show that the crystal structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is a complicated superlattice of orthorhombic subunits ($Bbmb$ or D_{2h}^{20}), which have $12A_g + 7B_g$ Raman active modes.¹⁶ These orthorhombic subunits can be approximated by a body-

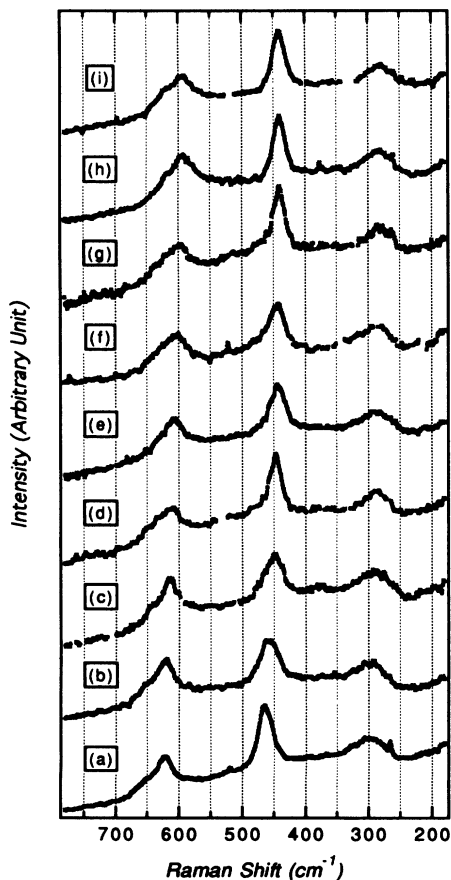


FIG. 1. Raman spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ with different exchange times. Exchange times are 0 (a), 1 (b), 4 (c), 9 (d), 16 (e), 36 (f), 100 (g), 225 (h), and 400 mins (i).

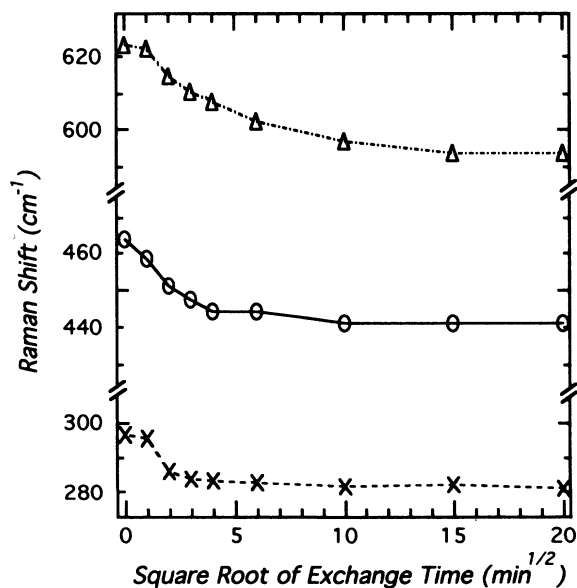


FIG. 2. Plot of the observed Raman shift vs the square root of the exchange time. The 623-cm^{-1} band (Δ), the 464-cm^{-1} band (\circ), and the 297-cm^{-1} band (\times).

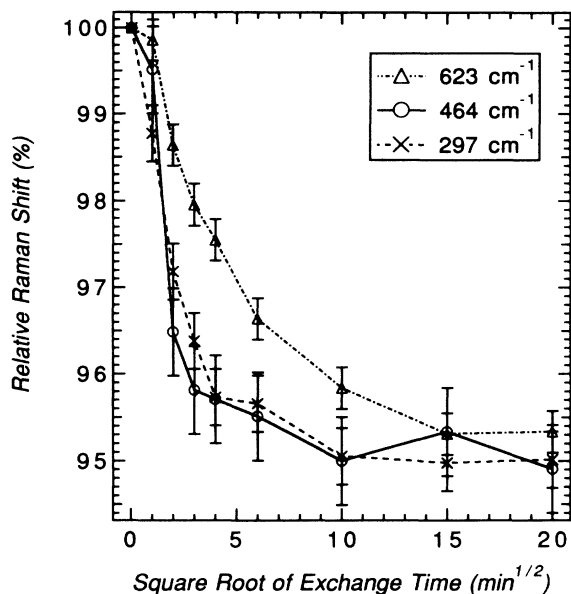


FIG. 3. Plot of the relative Raman shift vs the square root of the exchange time. See text for the meaning of the relative Raman shift. The 623-cm^{-1} band (Δ), the 464-cm^{-1} band (\circ), and the 297-cm^{-1} band (\times).

centered-tetragonal structure ($I4/mmm$ or D_{4h}^{17}), which have $6A_g + 1B_g$ Raman-active modes. The deviations from the tetragonal symmetry are small and the splitting of the phonon frequencies seems to be small or negligible.^{1,2,17} Therefore, the tetragonal symmetry is assumed in further analysis.

There are three inequivalent sites for oxygens in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$: O_{pl} in the basal plane of the CuO_5 pyramid, O_{ap} at the apex of the CuO_5 pyramid, and O_{Bi} in the BiO layer. Six A_g modes are the vibrations of Bi, Sr, Cu, O_{ap} , O_{Bi} along the z axis, and that of O_{pl} in phase out of plane, and one B_g mode is the vibration of O_{pl} out of phase out of plane. Polarized Raman spectra of single crystals^{1,3,4,6,7} show that all the three Raman bands observed in this study have A_g symmetry. By combining these results of polarized Raman spectra and the present experimental results that all the three Raman bands observed are due to the vibrations of oxygen atoms, it is

natural to consider that the three Raman bands observed are due to the vibrational modes of O_{ap} and O_{Bi} along the z axis, and that of O_{pl} in phase out of plane. The modes involving metal atoms are believed to be located below 160 cm^{-1} because of their larger mass.

The metal-oxygen interatomic distance in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ increases in the order of Cu-O_{pl} (~ 1.9 Å), $\text{Cu-O}_{\text{ap-Bi}}$ (~ 2.2 Å), and $\text{Bi-O}_{\text{Bi-Sr}}$ (~ 2.9 Å).¹⁸ It is most likely that the metal-oxygen bonding weakens in the same order. In fact, recent EXAFS studies^{11,12} have shown that the oxygen atoms at the O_{ap} and the O_{Bi} sites are more easily detached than those at the O_{pl} site. The oxygen sites from which the oxygen atoms are more easily detached are believed to be more liable to the isotopic substitution. Hence, we assign the Raman band at 623 cm^{-1} , which shows the slowest rate for the substitution, to the vibration of the oxygen atoms at the O_{pl} site, even though this band has been assigned mostly to O_{Bi} by the other authors.^{2,3,7}

The remaining two bands can be assigned to the oxygen vibrations at the O_{ap} and O_{Bi} sites. From the observed isotopic frequency shifts, $464\text{ cm}^{-1} \rightarrow 441\text{ cm}^{-1}$ and $297\text{ cm}^{-1} \rightarrow 282\text{ cm}^{-1}$, we see that these two vibrations are pure oxygen vibrations. The symmetry requires that they are the stretching vibrations along the fourfold (z) axis. Then, the frequency of these vibrations directly reflects the metal-oxygen stretching force constants, which have monotonic dependence on the metal-oxygen interatomic distance. We therefore assign the higher-frequency band at 464 cm^{-1} to the oxygen vibration at the O_{ap} site and the lower-frequency band at 297 cm^{-1} to that at the O_{Bi} site.

In summary, we have observed the site-selective isotopic substitution of oxygen in $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Y}_{0.2}\text{Cu}_2\text{O}_{8+\delta}$ by Raman spectroscopy, from which tentative mode assignments of Raman bands have been made. Under the assumption of a tetragonal symmetry, the bands at 623 , 464 , and 297 cm^{-1} are assigned to the vibrations of O_{pl} (A_g), O_{ap} , and O_{Bi} , respectively. In Table I, we compare these assignments with those in the literature. Though the agreement among different investigations is rather poor, we believe that the present assignments are better grounded than all the others.

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