

Raman scattering spectra of high- T_c superconductors based on Bi-Sr-Ca-Cu-O

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The Raman scattering spectra and the temperature dependence of the direct-current resistance and of the diamagnetic screening have been measured for various stoichiometric compositions of the system Bi-Sr-Ca-Cu-O. The spectrum of the nonsuperconducting composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_{11+y}$ contains the bands at 299, 463, 543, and 616 cm^{-1} . The superconducting composition $\text{Bi}_6\text{Sr}_7\text{Ca}_2\text{Cu}_6\text{O}_{24+y}$ ($T_c = 70\text{--}80\text{ K}$) is characterized by oscillations with frequencies of 292, 462, and 626 cm^{-1} .

The discovery of new superconducting materials based on Bi-Sr-Ca-Cu-O (Refs. 1–3) has created the need to optimize the stoichiometric composition of the compound and to identify the conditions under which it can be synthesized.

In the present letter we describe the method used to synthesize ceramic pellets made from Bi-Sr-Ca-Cu-O. We measured the Raman scattering spectra, direct-current resistance, and diamagnetic screening of various stoichiometric compositions.

The samples were synthesized from pure, dry oxide powders: Bi_2O_3 , SrO, CaO, and CuO, which were mixed thoroughly in appropriate proportions. The samples were synthesized in two steps. In the first stage the original mixture was heated to a temperature $T_1 = 830\text{--}860\text{ }^\circ\text{C}$ in air for 20–24 h. The mixture was then pressed into pellets. In the second stage the pellets were placed in flowing oxygen at $T_2 = 850\text{--}870\text{ }^\circ\text{C}$ for 20–24 h and then were cooled in a furnace.

Using the method described above, we have synthesized pellets from two different stoichiometric compositions: $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_{11+y}$ at temperatures $T_1 = 855\text{ }^\circ\text{C}$ and $T_2 = 870\text{ }^\circ\text{C}$ (sample 1) and $\text{Bi}_6\text{Sr}_7\text{Ca}_2\text{Cu}_6\text{O}_{24+y}$ at $T_1 = 830\text{ }^\circ\text{C}$, $T_2 = 870\text{ }^\circ\text{C}$ and $T_1 = 825\text{ }^\circ\text{C}$, $T_2 = 860\text{ }^\circ\text{C}$, respectively (samples 2 and 3).

The electrical resistivity of the ceramic pellets fabricated in this manner was $\rho \approx 10\text{ m}\Omega\cdot\text{cm}$ at room temperature. Sample 1 exhibited a nonmetallic behavior of the resistivity and did not go superconducting. The critical temperature T_c , determined from the dependence $\rho = \rho(T)$ and from the diamagnetic screening signal (Fig. 1), is $\sim 70\text{ K}$ and 80 K for samples 2 and 3, respectively. The measurements of the diamagnetic screening measured at a frequency 29 MHz show that the phase transition is diffuse and that the bulk superconductivity develops gradually at $T < T_c$. There is no clear evidence of the existence of superconducting phases with $T_c > 100\text{ K}$, which were reported by Hazen *et al.*⁴ to be present in samples synthesized by the method described above.

The Raman scattering spectra of the samples described above were measured in

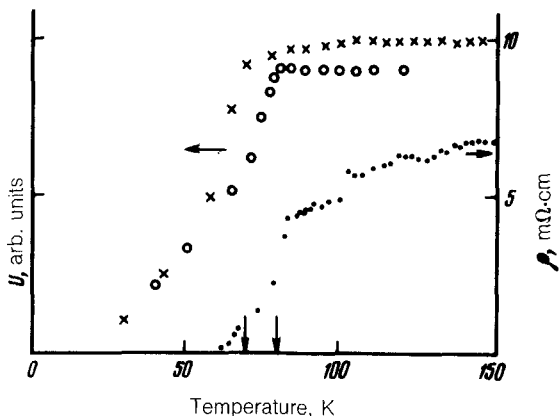


FIG. 1. Temperature dependence of the diamagnetic screening signal U (the scale on the left) for sample 2 (\times) and sample 3 (\circ) and of the resistivity $\rho = \rho(T)$ (the scale on the right) for sample 3 (\bullet).

the region from 60 cm^{-1} to 1100 cm^{-1} . The experiments were carried out at room temperature, using OMARS-89 multichannel spectrometer. The pumping was produced by the 514.5-nm line from an Ar^+ laser (a 50-mW beam was focused into a $50\text{-}\mu\text{m}$ spot. The spectra were measured from a freshly cleaved fracture surface of a polycrystalline sample in a back-scattering geometry. The comparable intensity of the Raman scattering signal of various samples was severalfold higher than that of the previously studied pellets of the $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ composition.⁵

Figure 2 shows the Raman scattering spectra of samples 1–3. These spectra show that the spectral distribution is similar to that reported by Wu and Loo⁶ for the BiSrCuO_{4-y} system. The Raman spectra of all three samples contain bands at 292 (I), 462 (II), and 626 cm^{-1} (III). The spectrum of sample 1 contains an additional band at 543 cm^{-1} , while the shifted bands I and III have maxima at 299 cm^{-1} and 616 cm^{-1} . The widths of the bands lie within the range $25\text{--}40 \text{ cm}^{-1}$. Figure 2 also shows the Raman spectra of Bi_2O_3 and CuO oxides which were used for synthesizing our samples. The structure of the SrO and CaO oxides is of the NaCl type,⁷ for which the first-order Raman scattering of light is forbidden.

The Bi_2O_3 spectrum contains the band at 446 cm^{-1} , which is near band II. The other bands of the same order of the intensity do not have any analogs in the spectra of samples 1–3. The CuO spectrum contains two bands, 284 and 612 cm^{-1} , whose positions are close to bands I and III of the test samples, but they have an inverse intensity ratio.

We have measured the Raman scattering spectra of the possible secondary reaction products: Cu_2O and a ternary system Bi-Cu-O which was synthesized using the method described above. The Cu_2O spectrum contains an intense band at 217 cm^{-1} (Ref. 8) which was not observed in the spectra of samples 1–3. The spectrum of the ternary system Bi-Cu-O contains relatively narrow bands at 298, 345, and 630 cm^{-1} , suggesting that Bi_2CuO_4 compound can be formed.

The Raman spectra of samples 1–3 thus show no evidence of a surplus of oxide

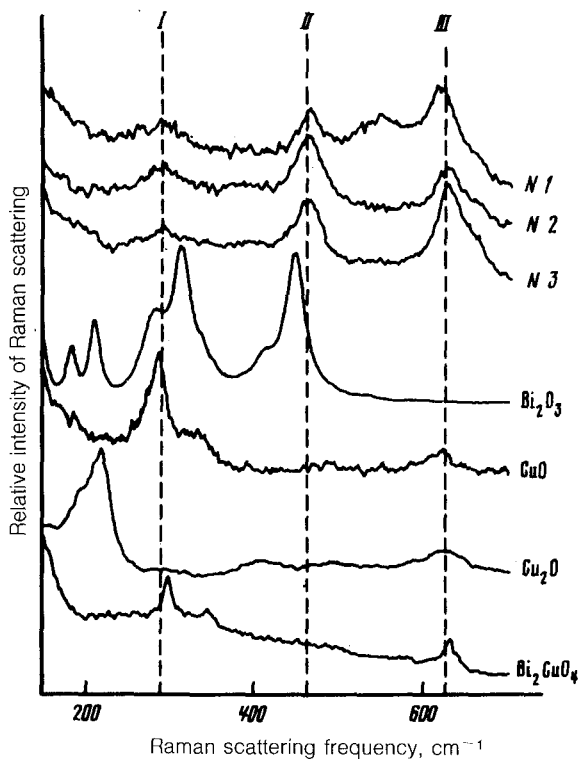


FIG. 2. The Raman scattering spectra of the system Bi-Sr-Ca-Cu-O at 300 K vs the conditions for synthesizing the samples. Also shown are the spectra for several copper and bismuth oxides.

compounds or of the secondary products mentioned above. The 292, 462, and 626 cm^{-1} bands observed in the Raman scattering spectrum characterize the vibrations of the $\text{Bi}_6\text{Sr}_7\text{Ca}_2\text{Cu}_6\text{O}_{24+y}$ compound which undergoes a transition to the superconducting state at $T_c = 70\text{--}80$ K.

As a tentative interpretation, the 626- cm^{-1} vibration can be attributed to the breathing vibration of the CuO_4 group, consistent with the existence in the $\text{Bi}_6\text{Sr}_7\text{Ca}_2\text{Cu}_6\text{O}_{24+y}$ structure of the planes formed by the CuO_4 groups.³ The vibrations of approximately equal frequency are contained in the Raman scattering spectra of BaCuO_2 at 635 cm^{-1} and in the Raman scattering spectra of La_2CuO_4 at 664 cm^{-1} , where they are related to the planar vibrations of CuO_4 in the oxygen octahedra. The band with a frequency 292 cm^{-1} may belong to the structural vibrations of the CuO_4 group. A similar vibration of the $\text{Ba}_2\text{YCuO}_{7-\delta}$ system has a frequency of 340 cm^{-1} (Refs. 5, 9, and 10). The band with a frequency 462 cm^{-1} may belong to the vibrations of the atoms in the Bi-O planes, since the spectrum of the Bi_2O_3 oxide contains a band of approximately equal frequency.

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