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Raman studies on the undoped and WO_3-doped Y–Ba–Cu–O system

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Abstract. Undoped and WO_3-doped Y–Ba–Cu–O ceramics have been studied by Raman spectroscopy. The results show that the peak positions at 499 and 338 cm^{-1} have been shifted for WO_3-doped samples compared with those for undoped samples, which reveals that the oxygen contents are different for undoped and WO_3-doped quenched samples in air. It is suggested that suitable WO_3 doping can change the oxygen content and reduce the effect of thermal treatments on the superconductivity of the Y–Ba–Cu–O system.

1. Introduction

It has been found that the gradual removal ($x \simeq 0$ to $x \simeq 1$) of oxygen from the class of high-T_c superconductors of the $YBa_2Cu_3O_{7-x}$ system first leads to a decrease in the transition temperature and finally to complete loss of superconductivity. The crystal symmetry changes from orthorhombic to tetragonal under this transition [1, 2]. Moreover, the oxygen content is strongly affected by the thermal treatment of the sample. Different thermal treatments give different effects on the oxygen contents and superconductivities of the system. As the orthorhombic transformation takes place at a temperature between 600 and 700 °C when a sufficient amount of oxygen is present, an additional heat treatment at 600–700 °C in oxygen or slow cooling in flowing oxygen is required to obtain the orthorhombic superconducting phase [3, 4]. After having studied the properties of the quenched $YBa_2Cu_3O_{7-x}$ system, Zhang *et al* [5] found that the samples quenched from temperatures above 880 °C had a typical tetragonal structure, showing no superconductivity above 4.2 K. On the other hand, impurity doping can change the oxygen content and the superconducting properties of the $YBa_2Cu_3O_{7-x}$ system [6, 7]. It has been found that the addition of WO_3 samples directly quenched from 900 °C in an oxygen atmosphere have a transition temperature of 88 K [6, 8]. The element added forms a second phase at the grain boundaries and exerts a considerable influence on the grain morphology of the materials. The problem remains, however, of what is the effect of the addition of WO_3 on the oxygen content of the $YBa_2Cu_3O_{7-x}$ system. Usually, Raman spectra in the range from 100 to 700 cm^{-1} show the vibrations of Ba, Cu and oxygen and are highly sensitive to the existence of an impurity phase in the $YBa_2Cu_3O_{7-x}$ system. In this work, the Raman spectra of the undoped and WO_3-doped Y–Ba–Cu–O system prepared by two different procedures have been measured in this range.

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It is found that suitable WO_3 doping can change the oxygen content and reduce the influence of thermal treatments on the Y–Ba–Cu–O system.

2. Experiment

The $YBa_2Cu_3O_{7-x}$ powder was fabricated by the coprecipitation method. This powder was then well mixed and ground with dry WO_3 powder in weight ratios $[YBaCuO]:[WO_3] = 100 - x:x$, where $x = 0$, 0.5 and 3. After the mixture was pre-heated at 890 °C in air for 24 h, it was reground, pressed and sintered at 900 °C for 30 h in flowing oxygen. Finally, the samples underwent two different procedures.

(1) They were quenched to room temperature in air.
(2) They were slowly cooled to room temperature at 2 °C min^{-1} in flowing oxygen.

The AC susceptibility measurements showed that the undoped $YBa_2Cu_3O_{7-x}$ sample quenched in air shows no sign of Meissner effects above 63 K; however, the transition temperatures of the doped samples are found to be around 88 K [8]. X-ray diffraction data showed that WO_3 does not enter the $YBa_2Cu_3O_{7-x}$ lattice and form an impurity phase or a second phase [9].

The Raman spectrum experiments were conducted using a Spex-1403 spectrometer of back-reflection geometric layout. The excitation source was an argon laser operating at 5145 Å.

3. Results and discussion

Figure 1 shows the Raman spectra for the samples quenched in air from 900 °C to room temperature. It can be seen that the peaks of Raman spectra appear at 154, 338, 499, 606 and 633 cm^{-1}, besides the sharp lines below 150 cm^{-1} which may be due to laser plasma lines and the Raman spectrum of air [10]. The characteristic lines at 154, 338 and 499 cm^{-1} have been identified as modes of the lattice vibrations of the superconducting phase $YBa_2Cu_3O_{7-x}$ [10–12], and the positions of the latter two lines are directly related to the oxygen content [11, 12]. As seen in figure 1, the peak position at 499 cm^{-1} is a little shifted to a higher frequency while the peak position at 338 cm^{-1} is shifted to a lower frequency for WO_3-doped samples compared with those of undoped samples. We know that the Raman peak associated with Cu–O stretching vibration (502 cm^{-1}) decreases in frequency when oxygen is removed, while the bending–stretching modes of the Cu–O framework (334 cm^{-1}) harden under the same condition [12, 13]. This reveals that the oxygen contents are different for undoped and WO_3-doped samples. The addition of WO_3 can increase the oxygen content in the $YBa_2Cu_3O_{7-x}$ phase. Also, the lines at 606 and 633 cm^{-1} can be attributed to the modes of $BaCuO_2$ [10, 14]. It is found that the intensity of the peak at 633 cm^{-1} increases with increasing W content. This suggests that the amount of $BaCuO_2$ phase has been increased by the addition of WO_3. The W atom may not enter the $YBa_2Cu_3O_{7-x}$ lattice and form a second phase with Y or another element, and the remaining Ba and Cu may form a $BaCuO_2$ phase besides the $YBa_2Cu_3O_{7-x}$ phase.

The Raman spectra for the samples slowly cooled in oxygen are shown in figure 2. The positions of these peaks are similar to those of the specimens quenched from 900 °C in air. The line at 419 cm^{-1} can be attributed to the modes of $BaCuO_2$ [10, 14]. It can be seen, however, that the peak position at 501 cm^{-1} is little shifted for WO_3-doped samples

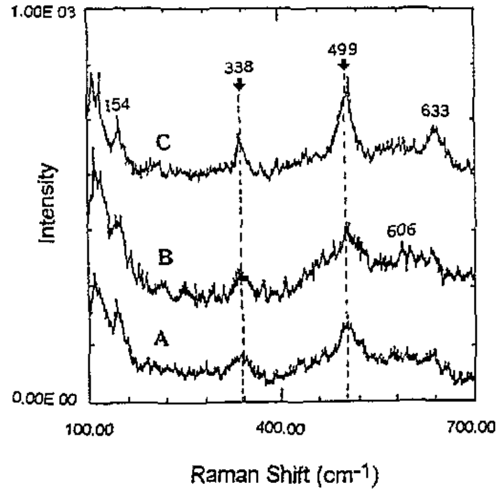

Figure 1. Raman spectra for the quenched samples in air: spectrum A, $YBa_2Cu_3O_{7-x}$; spectrum B, $YBa_2Cu_3O_{7-x}$ + 0.5% WO_3; spectrum C, $YBa_2Cu_3O_{7-x}$ + 3% WO_3.

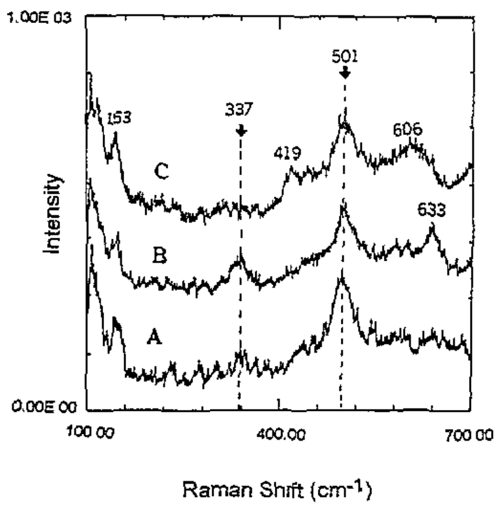

Figure 2. Raman spectrum for the slowly cooled samples in flowing oxygen: spectrum A, $YBa_2Cu_3O_{7-x}$; spectrum B, $YBa_2Cu_3O_{7-x}$ + 0.5% WO_3; spectrum C, $YBa_2Cu_3O_{7-x}$ + 3% WO_3.

compared with those of undoped samples. This reveals that the oxygen content in the undoped sample has changed little after WO_3-doping.

In summary, the addition of WO_3 can increase the oxygen content and reduce the effect of thermal treatments on the oxygen content. In other words, the effect of suitable WO_3 addition can be equal to that of slow cooling in oxygen, which ensures the absorption of a sufficient amount of oxygen. Therefore, it can be inferred that slow cooling is not necessary to obtain the $YBa_2Cu_3O_{7-x}$–WO_3 superconductor with a high critical temperature. We consider that the rate of absorption of oxygen may be improved by the WO_3 addition and therefore the samples quenched in air become superconductors.

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References

[1] Jorgensen J D, Veal B W, Paulikas A P, Nowicki L J, Crabtree G W, Claus H and Kwok W K 1990 *Phys. Rev.* B **41** 1863
[2] Tarascon J M, McKinnon W R, Greene L H, Hull G W and Vogel E M 1987 *Phys. Rev.* B **36** 226
[3] Cava R, Van Dover R B, Battlogg B and Rietman E 1987 *Phys. Rev. Lett.* **58** 408
[4] Hikami S, Hikami T and Kayoshima S 1987 *Japan. J. Appl. Phys.* **26** L135
[5] Zhang Y H, Wang J, Yue Y, Hu J B, Meng G Y, Peng D K and Chao L Z 1989 *Sci. China* **9** 937
[6] Kuwabara M and Kusaka N 1988 *Japan. J. Appl. Phys.* **27** L1504
[7] Wu M K and Liang D C 1990 *Chin. J. Phys.* **28** 9
[8] Feng Y, Zhou L, Du S, Wang J, Zhang P, Shi L and Zhang Y 1994 *Physica C* **235–40** 405
[9] Shi L *et al* 1995 *J. Appl. Phys.* at press
[10] Rosen H, Engler E M, Strand T C, Lee V Yu and Bethune D 1987 *Phys. Rev.* B **36** 726
[11] Hemley R J and Mao H K 1987 *Phys. Rev. Lett.* **58** 2340
[12] Thomsen C, Liu R, Bauer M, Wittlin A, Genzel L, Cardona M, Schönherr E, Bauhofer W and König W 1988 *Solid State Commun.* **65** 55
[13] Starola M, Krol D M, Weber W, Sunshine S A, Jayaraman A, Kourouklis G A, Cava R J and Rietman E A 1987 *Phys. Rev.* B **36** 850
[14] Chang H, Ren Y T, Sun Y Y, Wang Y Q, Xue Y Y and Chu C W 1994 *Physica* C **228** 383