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EFFECTS OF OXYGEN SORPTION-DESORPTION ON SUPERCONDUCTIVITY OF HIGH-Tc Bi(Pb)-Sr-Ca-Cu-O

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Abstract Temperature-programmed desorption (TPD) chromatograms revealed that a small amount of oxygen (2.5×10^{-5} mol/g) was desorbed from high-Tc Bi(Pb)-Sr-Ca-Cu-O (BPSCCO) in the temperature range from ca. 350 to ca. 600 °C. The Tc of BPSCCO lowered by 15 K from 111 K to 96 K with the above oxygen desorption below 600 °C, and was restored to the original level when the desorbed oxygen was recovered. As revealed by a temperature-programmed oxidation (TPO) technique, the desorbed oxygen was sorbed reversibly at ca. 100-350 °C in a O_2(5%)-He atmosphere, accompanied with an increase in Tc by 12 K. In these oxygen sorption-desorption processes, no corresponding changes in X-ray powder diffraction pattern were observed.

INTRODUCTION

Since the discovery[1] of a new class of Bi-Sr-Ca-Cu-O (BSCCO) superconducting oxides with a remarkably high Tc, there has been an enormous amount of activities aiming at the structural identification and preparation of the superconducting phases. It has been confirmed that in the BSCCO system there exist three superconducting phase, i.e., 2201 phase with Tc ≃ 10 K, 2212 phase with Tc ≃ 85 K, and 2223 phase (high-Tc phase) with Tc ≃ 110 K. The last one is difficult to obtain as a purely single phase, and the addition of Pb has been shown to be effective for increasing its fraction.[2] The BSCCO compounds appear to be less sensitive to oxygen treatments than $YBa_2Cu_3O_{7-x}$ (YBCO) which has much oxygen vacancies. Very few studies have dealt with the relationship between the superconducting characteristics and the oxygen content for pure 2223 phase in BSCCO, while several have reported that the Tc of 2212 phase shifts downward when its oxygen content increases by annealing under increased O_2 pressure.[3-5]

Previously we reported the temperature-programmed desorption (TPD) chromatograms of oxygen from YBCO samples with various oxygen contents.[6] It has been established that the TPD technique allows highly sensitive, precise detection of even a trace amount of oxygen desorption. In the present work, the same technique was applied to investigate the oxygen sorption-desorption behavior of pure 2223 phase containing Pb (high-Tc BPSCCO) in connection with

its superconductive properties.

EXPERIMENTAL

The sample with a nominal composition of $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_x$ was prepared from the nitrates of Bi, Sr, Ca, Cu and $Pb(CH_3COO)_2 \cdot 3H_2O$. The nitric acid solution dissolving these salts to the nominal composition was evaporated to dryness at a temperature around 350 °C. The resulting powder was calcined at 820 °C for 12 h in air (precalcination). After grinding and pressing into a disc at 210 MPa, the sample was calcined at 845 °C for 60 h in air. To increase the purity of 2223 phase, the final calcination was repeated twice. As shown by the X-ray powder diffraction pattern in Figure 1, the sample thus prepared was composed of only 2223 phase. Electric resistivity was measured for a rectangular prism specimen by means of a conventional four-probe technique. The superconducting transition of the prepared sample reached the onset ($T_{c,on}$) at about 120 K and the zero resistivity ($T_{c,end}$) at 105 K. Magnetization measurements were carried out for powder samples on a SQUID magnetometer (HOXAN, HSM-2000).

TPD experiments were carried out as described before.[6] As the oxygen-adsorption pretreatment, a powder sample was exposed to oxygen (101 kPa) for 1 h at a prescribed temperature (T_{ad}), followed by cooling down to room temperature (RT) in the same oxygen atmosphere. This treatment is abbreviated hereafter as $T_{ox}(T_{ad} \rightarrow RT)$. To obtain a TPD chromatogram the sample was heated in He gas flow at a rate of 10 °C/min. The desorbed gases were monitored with a thermal conductivity detector (TCD) and identified with a quadruple mass spectrometer.

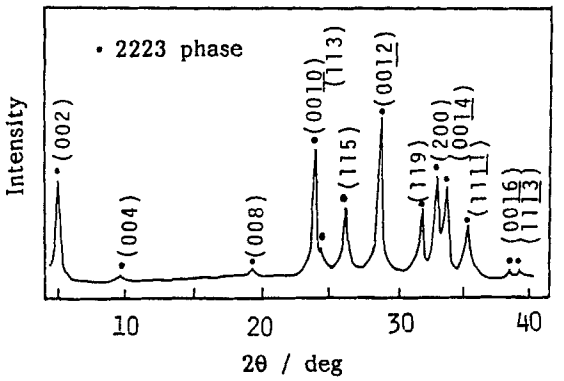

FIGURE 1 X-ray diffraction pattern of the Bi(Pb)-Sr-Ca-Cu-O sample prepared.

RESULTS AND DISCUSSION

Our previous investigation have shown that 2223 BPSCCO undergoes oxygen desorption in two steps, i.e., a small, leading desorption in ca. 350-600 °C and a steep desorption above ca. 600 °C. The latter step was found to result in the decomposition of high-Tc phase.[7] Only the former step is concerned in this investigation.

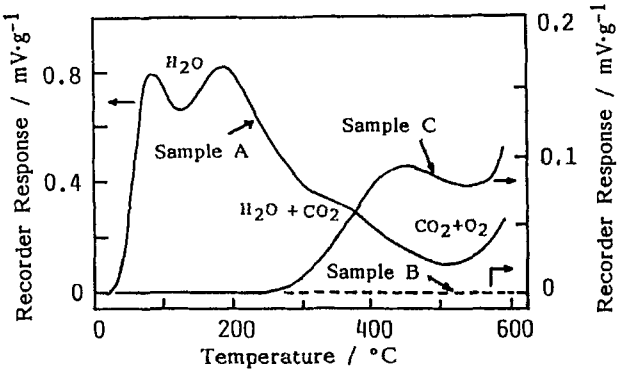

FIGURE 2 TPD chromatograms from 2223 BPSCCO samples. Sample A: as-prepared, Sample B: heated up to 620 °C in He, Sample C: treated with pure oxygen at 600 °C for 1 h after the above He treatment.

Figure 2 shows TPD chromatograms from 2223 phase of BPSCCO. The sample was subjected to three different pretreatments: as-prepared (Sample A), heating up to 620 °C in He (Sample B), and heating up to 600 °C in He followed by an oxygen treatment T_{ox}(600 °C → RT) (Sample C). The mass spectrometric analysis indicated that Sample A was heavily contaminated with H_2O and CO_2. Sample C exhibited only oxygen desorption which started at ca. 350 °C and amounted to about 2.5 x 10^{-5} mol/g up to 600 °C, while no gas desorption was naturally seen from Sample B. The dc magnetization data for the above three samples are shown in Figure 3. Sample A began to be diamagnetic at about 111 K ($T_{c,dia}$), irrespective of the contamination with H_2O and CO_2. These contaminants hardly seem to influence the superconductivity of BPSCCO. On the other hand, Sample B showed a lower $T_{c,dia}$ of 96 K and its magnetization was about half of that for Sample A at 4 K. This means that the small amount of oxygen desorption revealed by the above TPD chromatogram significantly degrades the superconductivity of BPSCCO. Quite interestingly, however, the subsequent oxygen treatment, T_{ox}(600 °C → RT), carried out for Sample C restored almost exactly the same magnetization behavior as that of Sample A, indicating that the change concerned is reversible. Such a reversible change in superconductivity with an oxygen treatment has been also

reported for 2212 phase.[3] In spite of such a difference in magnetization behavior, no significant differences were detected among the X-ray powder diffraction patterns of the three samples (Figure 4).

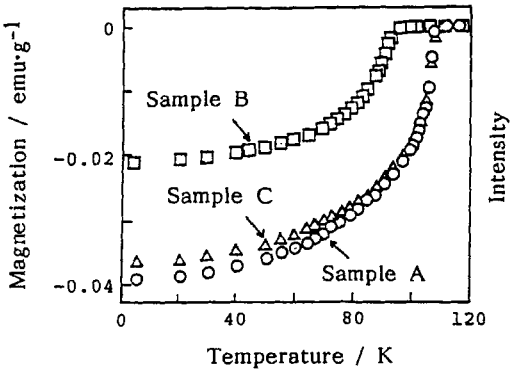

FIGURE 3 Temperature dependence of dc magnetization for Samples A, B, and C at 10 Oe.

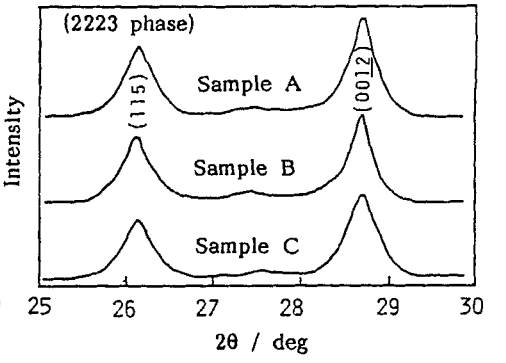

FIGURE 4 X-ray diffraction patterns of Sample A, B, and C.

The oxygen uptake process was investigated by using a temperature-programmed oxidation (TPO) technique. When Sample B was heated up at a constant rate (10 °C/min) in a flow of O_2(5%)-He mixture, oxygen sorption was observed in the range of ca. 100 - 350 °C as shown in Figure 5. The total amount of sorbed oxygen, ca. 2.5 x 10^{-5} mol/g, was comparable to that of oxygen desorbed from Sample C at temperatures up to ca. 600 °C. In the higher temperature range 350-600 °C, a part of oxygen was found to be desorbed under the present TPO condition.

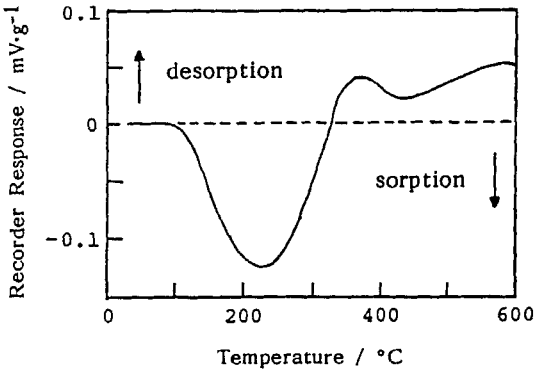

FIGURE 5 TPO chromatogram from 2223 BPSCCO sample treated in He up to 620 °C (Sample B) in O_2(5%)-He.

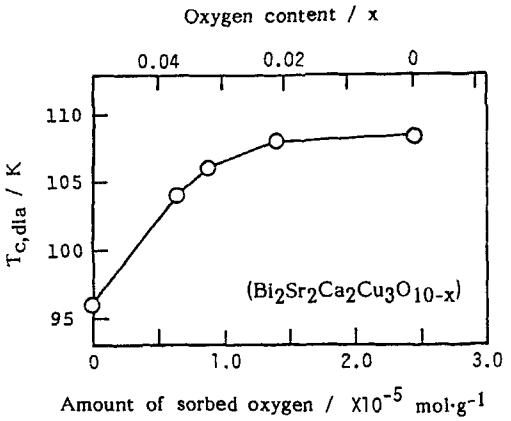

FIGURE 6 Dependence of $T_{c,dia}$ of 2223 BPSCCO sample on the amount of sorbed oxygen (deviation of oxygen content, x).

These findings clearly show that the oxygen sorption-desorption taking place at the lower temperature region below 600 °C has strong relevance to the superconductivity of the high-Tc BPSCCO. As shown in Figure 6, TPO experiments could control the oxygen sorption by the temperature to which the sample was heated up. A steep increase in Tc from 96 K to 106 K resulted from the oxygen sorption of about 0.8 x 10^{-5} mol/g. It is also noted that this tendency of Tc shift is just opposite to that for 2212 phase previously reported.[3-5] The deviation of oxygen content (x) in the expression of $Bi_2Sr_2Ca_2Cu_3O_{10-x}$ was estimated from the sorption data on the assumption that x=0 for the sample heated up to 350 °C. As seen from the figure, $T_{c,dia}$ begins to lower steeply when x exceeds ca. 0.03. The steep lowering as large as 10 K takes place when x increases from 0.03 to 0.05. Such behavior of $T_{c,dia}$ suggests that the superconductivity of 2223 BPSCCO is significantly influenced by a small amount of oxygen defects in the bulk.

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