

Thermal Analysis of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ Oxide Superconductor

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Thermogravimetry and powder X-ray diffraction measurements have been made for the title superconductors to show a marked discontinuity in the slope of oxygen content vs. c cell dimension plots at 810 °C (T_2), other than at about 400 °C (T_1). The oxygen content at T_2 increases with increasing Fe doping content.

In order to produce substantial changes in the superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ with the purpose of clarifying the nature and mechanism of the high-temperature superconductivity, a systematic substitution of 3d-transition and other metallic elements for copper has been performed in previous studies.¹⁻⁵⁾ It was concluded from the results that the long-range ordering of oxygen which forms linear Cu-O chains (Cu1) sandwiched between Ba layers is not crucially required for the occurrence of superconductivity.¹⁾ In this work, we will present the results of thermogravimetric analysis (TGA) and powder X-ray diffraction analysis at high temperatures, which further characterize the effects of chemical doping. It is well known that the oxygen content, 7-y, in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ critically affects the superconducting properties.⁶⁾ However, there have been relatively few such studies on the oxygen stoichiometry in the metal doped materials, which strongly depends on the processing conditions (heat treating time, temperature and ambient).⁴⁾ By heating the undoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, oxygen is removed from the Cu1-O chains whereas the content of oxygen in quasi-two-dimensional Cu-O planes (Cu2) between Y and Ba layers is retained.⁶⁾ It is expected that the replacement of copper atoms in the Cu1 site by other metals strongly affects the removal of oxygen because of the difference in the strength of the M-O bonds between copper and the doped metals. However, the content of oxygen in the Cu2-O planes should be reduced before the structure of the planes collapses (at about 1035 °C⁷⁾). We used the iron doped material, $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$, to examine such a temperature dependence of oxygen content in the planes as a function of the doping content, x.

Samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ for $0 \leq x \leq 0.085$ were prepared by solid state reaction of Y_2O_3 , BaCO_3 , CuO, and Fe_2O_3 powders, each 99.99%. Appropriate amounts of the powders were mixed thoroughly, pressed into pellets, and sintered

in air at 900 °C initially for 30 h, then for 52 h, and finally at 920 °C for 38 h followed by annealing at 550 °C for 3 h and then at 380 °C for 34 h. Between each sintering the samples were cooled slowly (in 12 h) to room temperature before being removed from the furnace, reground, and reformed into pellets. Powder X-ray diffraction patterns of all the resulting samples were taken between room temperature and 900 °C by using an automated Rigaku RAD-IIC diffractometer with Cu K α radiation. The data demonstrates no impurity peaks. A transition from orthorhombic to tetragonal symmetry is observed at a composition, $x = 0.02 - 0.03$, as reported previously.^{1,3)} The superconducting transition temperatures, T_c , were determined by both the electrical resistivity using a dc four-probe method and the magnetic susceptibility of powdered samples with an ac field of 3 Oe at a frequency of 400 Hz. As shown in previous works,^{1,3)} T_c decreases monotonously with x and there is no drastic change of T_c at $x = 0.02 - 0.03$, although strong destruction of the Cu1-O chains occurs at this composition. The parent samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ with $x = 0, 0.015, 0.035, 0.060$, and 0.085 have oxygen contents, determined iodometrically with a precision of ± 0.01 in y , of 6.91, 6.93, 6.94, 6.97, and 7.01, respectively. A similar increase in the oxygen content with x is reported for the Fe doped materials by Tarascon, et al.⁵⁾ The dependence of the oxygen content on temperature was investigated by thermogravimetry. The thermal effects during several successive heating and cooling cycles (120-900 °C) of the same sample in air were recorded on a Sinku-Riko TGD-3000-RH thermogravimetric analyzer with an IR image furnace. Heating and cooling rates of 2.5 or 5 °C min⁻¹ and a powdered sample weighing about 50 mg with a grain size smaller than 25 μm were employed in each run. The TGA curves at heating and cooling rates of 2.5 °C min⁻¹ are in good agreement with the corresponding curves at the rates of 5 °C min⁻¹.

Figure 1 shows typical changes in the oxygen content, determined by TGA of the samples on cooling at a rate of 2.5 °C min⁻¹ from 900 °C in air: A discontinuity in the slope of each curve is found around the temperature, $T_2 = 810$ °C and then the oxygen uptake continues until around $T_1 = 400$ °C. On cooling back to 120 °C the oxygen content of each sample is close to that of the corresponding parent sample, although complete oxygen absorption is not observed at these cooling rates. When heated again, the subsequent oxygen desorption is substantially more reversible. Another pronounced discontinuity in the slope for the undoped or 1.5% Fe doped compound which is orthorhombic at room temperature is observed around 620 or 600 °C, respectively: This change may be ascribed to the tetragonal to orthorhombic phase transition

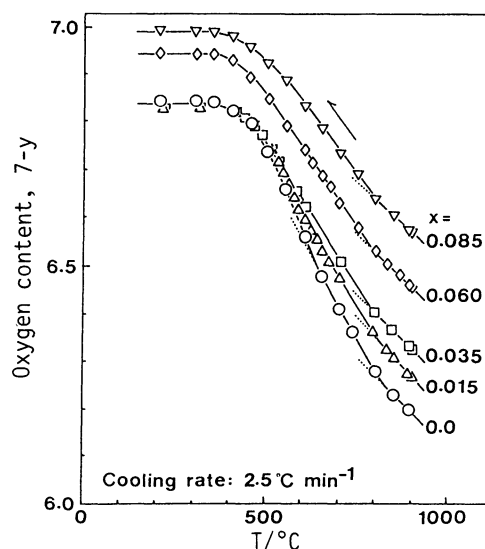


Fig. 1. Relations between oxygen content and temperature for $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ in air (Al_2O_3 crucibles).

(which corresponds to a respective oxygen stoichiometry of about 6.5 or 6.6), shown by the X-ray diffraction study at high temperatures.¹⁾

We found that the values of the oxygen content determined by TGA for the samples mounted in platinum crucibles were systematically low compared to those for the samples mounted in α -alumina crucibles. As shown in Fig. 2, the values for the undoped sample in TGA measurements using Al_2O_3 crucibles at various temperatures are almost identical with those determined by neutron diffraction analysis.⁸⁾ On the other hand, the larger oxygen loss in TGA measurements has been reported for the undoped sample contained in a platinum crucible on heating up to 800 or 900 °C in a stream of 21% O_2 -Ar gas mixture,⁹⁾ in agreement with that observed here (Fig. 2). Remarkable increases in the discrepancy with temperature are observed above 400 °C for all the samples but the discrepancy becomes constant at temperatures higher than about 800 °C. Moreover, the TGA results also provide evidence for substantial reversibility of the discrepancy in the oxygen desorption-absorption cycles. The discrepancy behavior seems to be related somewhat to the oxygen desorption-absorption process but needs to be investigated further. In this paper, we will mainly present the data in Al_2O_3 crucibles, although the main conclusions are not affected by the difference.

Figure 3 illustrates the relation between oxygen content and c cell dimension-

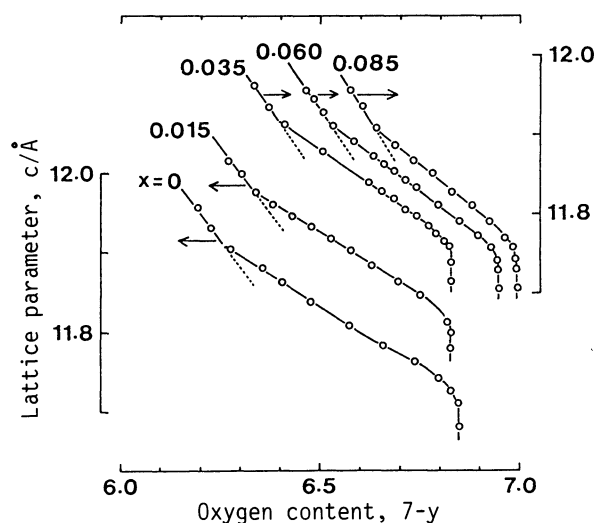


Fig. 3. Relations between the c cell dimension and oxygen content for $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ at high temperatures.

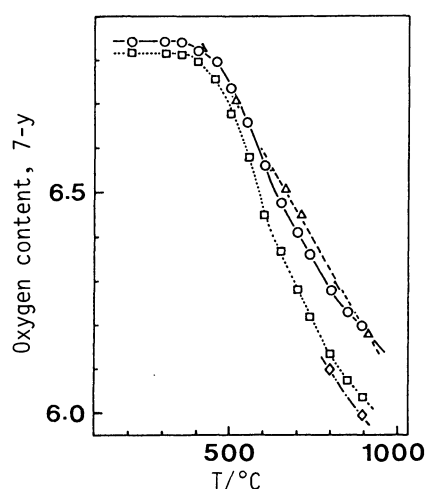


Fig. 2. Oxygen content vs. temperature for samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ in air (\circ : Al_2O_3 crucibles; \square : Pt crucibles). \triangle : Data in Ref. 8. \diamond : Data in Ref. 9.

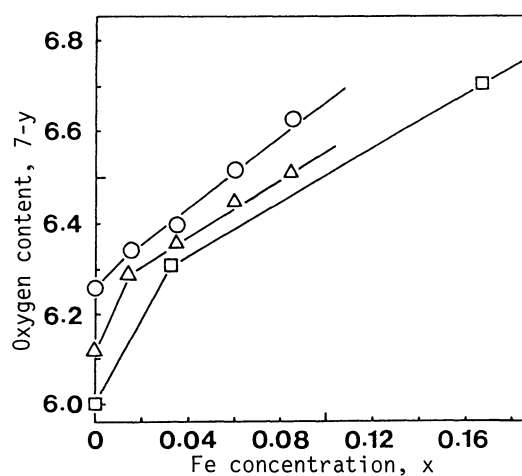


Fig. 4. Variation of oxygen content with x in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-y}$ for the samples at 810 °C in air (\circ : Al_2O_3 crucibles; \triangle : Pt crucibles). Data (in argon) in Ref. 5 are analyzed (\square).

sion at high temperatures for the samples used here. There are marked discontinuities in the slope of each plot at two different oxygen contents: One at a higher oxygen content occurs around T_1 above which these compounds lose oxygen and the other at a lower oxygen content, which increases with x , occurs at 810°C for any x , which corresponds to the above change observed at T_2 . Since both T_1 and T_2 are independent of the Fe concentration, it is reasonable to assume that these signify the changes in dynamics of the oxygen release from Cu-O bonds, rather than Fe-O bonds. The oxygen loss which occurs above T_2 can be attributed to the liberation of oxygen from Cu-O bonds other than in the plane of the Cu_1 site, probably from the Cu_2 -O bonds, which results in an enhanced slope of the plots or an enhanced expansion of the c cell dimension (Fig. 3). The amount of removable oxygen decreases remarkably with increasing dopant content as reported by Tarascon et al.⁵⁾ The TGA results clearly show that the Fe ions (+3 or +4) strongly bond to the oxygen. The difference in oxygen content at T_2 between the undoped and doped samples increases with the Fe concentration as shown in Fig. 4. The TGA curves for the Fe doped compounds reported by Tarascon et al.⁵⁾ are also analyzed for Fig. 4. The data shows that almost one oxygen atom per formula unit can be removed within the undoped phase by heating in argon; the composition is close to $7-y = 6.0$ at the T_2 . Moreover, the oxygen content at T_2 increases rapidly with increasing Fe concentration for x less than 0.033, in agreement with that observed here for the samples mounted in Pt crucibles even in air, as shown in Fig. 4. These results can be explained if we assume that the Fe atoms are substituted mainly for the Cu_1 atoms and that each iron ion is surrounded by 4 oxygen atoms in the plane of the Cu_1 site all the way up to T_2 . For x greater than 0.033, the change becomes less dramatic, suggesting that the substitution occurs on both Cu sites.

In summary, the previous assumption that the Fe substitutes exclusively into the Cu_1 site at low x is confirmed by the present results.

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