

Microwave plasma oxidation technique for $\text{HoBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic superconductor

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Abstract

A new oxidation technique of high temperature superconducting copper oxides has been invented. The oxidation is performed in a low pressure oxygen plasma generated by a microwave. X-ray and the low temperature alternating current magnetic susceptibility have been used to explore the effect of the oxidation on the superconducting behavior. Also, the measured infrared spectra reveal good dependence of the two copper–oxygen populations. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The ceramic materials $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ (R = rare earth element) [1–5] have a perovskite structure with an ordered series of oxygen vacancies. In general, it crystallizes either an orthorhombic phase (space group Pmmm) [6–9] when $x < 0.6$ or a tetragonal structure (space group P4/mmm) when $0.6 < x < 1$. When this material is orthorhombic, it is a superconductor and when it is tetragonal, it is a semiconductor [9–11]. The orthorhombic–tetragonal transition occurs at elevated temperatures and is confined to the oxygen stoichiometry [12–14] that plays a crucial role in determining the superconducting properties of these materials.

In the limit of $x = 0$, the system is a superconductor around 90 K for all the trivalent rare earth elements R. The structure of the orthorhombic phase, as determined from X-ray [9,10,13], neutron diffraction [7,8,11,12,14] and electron microscopy [15,16] studies shows three weakly coupled Cu–O layers in the unit cell consisting of two quasi-two-dimensional Cu–O₂ planes, Cu(2) and a one-dimensional Cu–O chain, Cu(1). The Cu(2) atoms, in the H_{a-b} plane, are strongly bonded to four oxygen O(2) atoms and O(3) (using the notation of Cox et al. [17]), forming the basis of a pyramid and are weakly bonded to the oxygen atom O(1) at the apex. For the highest critical temperature (T_c) phase, the O(4) site in the chains which run along the b -axis is fully occupied, and the O(5) site

located between the chains is vacant [7,8,11,12,15–17]. When $0 < x < 1$, Beech et al. [18] and Horiuchi et al. [19,20] found that the oxygen vacancies in the structure are always confined to the sites O(4) in the chains. One notable change in the structure as the oxygen atoms O(1) moves away from the Cu–O₂ plane towards the Cu–O chain along the c -axis, so that the Cu-atoms in the chain layer are more isolated and the interlayer coupling between Cu–O₂ plans are further reduced [17,18–22].

The synthesis temperature is a very important factor too. Although, no structure–phase transition occurs in YBCO at low temperature [23]; it has been observed that the total oxygen stoichiometry decreases smoothly with increasing temperature [13] and that the vacancies associated with this decrease involve only the O(4) sites. Shaked et al. [24] observed that at around 700 °C, the position of O(5) at 1/200 are gradually filled and a smooth order–disorder orthorhombic–tetragonal transition occurs. Tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ may become orthorhombic by annealing and cooling in an oxidizing atmosphere [25]. The experimental observations show that an appropriate heat treatment can give YBCO any bulk oxygen content between 6 and 7 [12,26–28]. T_c in YBCO was found to vary smoothly with the oxygen concentration, while still producing sharp superconducting transitions [8,26,27,29–33]. T_c is around 90 K for $0 < x < 0.2$ before decreasing sharply to 60 K where it remains up to $x = 0.5$. Beyond $x = 0.5$, T_c drops sharply and antiferromagnetic order has been observed near $x = 0.7, 0.85$ and 1.0 [8,29–33]. T_c correlates linearly with the reduction of the cell volume [6,8,26,27], as it does also with Cu–O

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bond distance [7,8,11,12,14] and with the carrier density as measured by the Hall effect [34,35]. High temperature X-ray [36] and some other studies [26,27,34,35,37–40] suggest three structural phases associated with the T_c . Two of them are orthorhombic and superconducting and one is tetragonal and non-superconducting. Orthorhombic I has $T_c = 90$ K and $x < 0.25$, orthorhombic II has $T_c = 60$ K and $0.25 < x < 0.6$, while the non-superconducting tetragonal phase has $x > 0.6$. This lower T_c region has been associated with an ordering of the oxygen vacancies in the chains [26,29].

Denisov et al. [41,42] and Rothschild et al. [43] have investigated irradiation of YBCO by a visible laser beam. They have reported a heating effect which can produce a phase change by the changing oxygen content and inducing defects. They also showed that irradiation in N_2 or O_2 atmospheres produced two different non-superconductive states. Repeated irradiation in either O_2 or N_2 transformed the material back and forth between the two states [43–45]. He^+ ion bombardment significantly decreases the T_c as reported by Xiao et al. [46]. Based on the above information, it is important to note that the final oxygen atmosphere treatment is intimately connected to the superconducting properties. Deviations from the ideal oxygen stoichiometry ($x = 1$) influence the copper valence and critically affect all physical properties including the orthorhombic–tetragonal-phase transition. The strong association of the superconductivity with the copper–oxygen planes and chains connects the details of the oxygen sublattice occupation with the superconductivity. In the molecular beam epitaxy deposition technique, a high voltage discharge has been used to grow superconductor films in an ambient of oxygen gas.

2. Experimental

2.1. Sample oxidation

The microwave plasma set-up used by Ismail and El-Magd [47,48] is shown in Fig. 1. The plasma was generated inside a silica tube with an inner diameter of 10 mm and a

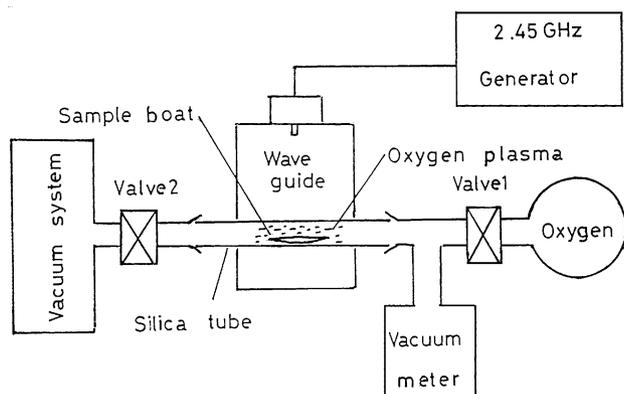


Fig. 1. Experimental set-up of the oxygen plasma device.

length of 200 mm. The microwave source with a frequency 2.45 GHz was coupled to the discharge horizontal tube by an aluminum wave-guide (50/100/200 mm). The plasma tube was fixed perpendicular to the direction of the radiated electric field. The sample was placed in an alumina boat, which was centered inside the plasma tube. In order to reduce the gas impurities, the tube was evacuated and filled with an atmospheric oxygen gas pressure. Then oxygen gas flow is adjusted to keep the pressure value fixed at 1 mbar along the exposure time. The sample was exposed to the oxygen plasma of the power of 200 W for a different duration times (1, 2, 5, and 7 h) at the same condition of oxygen gas flow pressure. For each period, the starting sample is the basic one. At the end of the exposure time, the pressure of the oxygen gas increased to the atmospheric one and the sample was left over night to cool to room temperature.

2.2. Sample preparation

The powder samples of $HoBa_2Cu_3O_{7-x}$ ceramic were synthesized by the co-precipitation technique using Ho_2O_3 ,

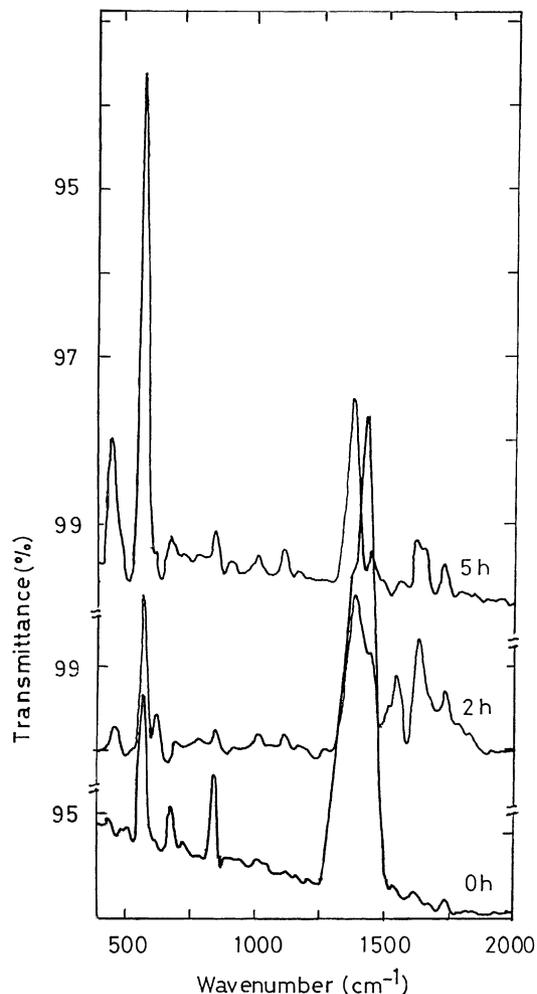


Fig. 2. Effect of the oxygen plasma exposure time on the IR spectra.

BaCO₃ and CuO powders (99.9% purity, Aldrich product) according to the atomic ratio of [Ho]:[Ba]:[Cu] = 1:2:3. The stoichiometric quantities were dissolved separately in HNO₃, and the solutions were mixed together. The resultant mixture was treated with oxalic acid to precipitate out the oxalate followed by drying on a sand bath. The co-precipitated oxalate was then placed in an alumina crucible, heated to 600 °C and calcined for 6 h. The product was then ground and annealed in air at 850 °C for 12 h. It was reground and reheated again at 950 °C for 12 h in air. This process was repeated four times with intermediate grindings to produce a denser and less porous microstructure. The fired material was then ground and divided into six samples equal in weight. Microwave plasma annealing for each sample was done separately with different annealing times in the presence of oxygen flow environment. The final annealing process for the powder form of the samples were done as follows: sample A was un-annealed and used as prepared sample; sample B was microwave plasma annealed in an oxygen flow for 1 h; sample C was annealed in the oxygen microwave plasma for 2 h; sample D was annealed the same way for 3 h; sample E was annealed in the microwave plasma for 5 h; sample F was annealed under the same conditions but for 7 h.

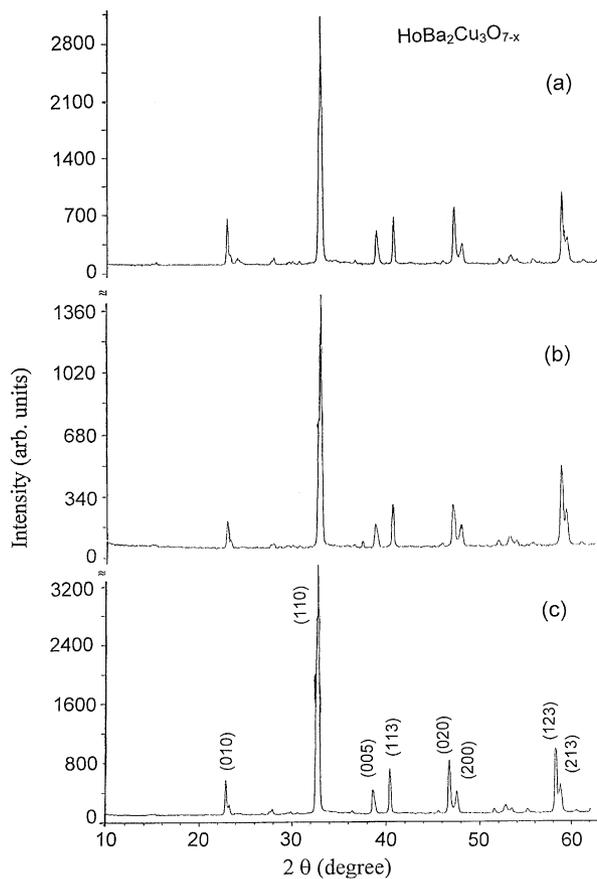


Fig. 3. X-ray diffraction pattern for: (a) unaffected sample; (b) 2 h oxygen plasma exposed sample; (c) 5 h oxygen plasma exposed sample.

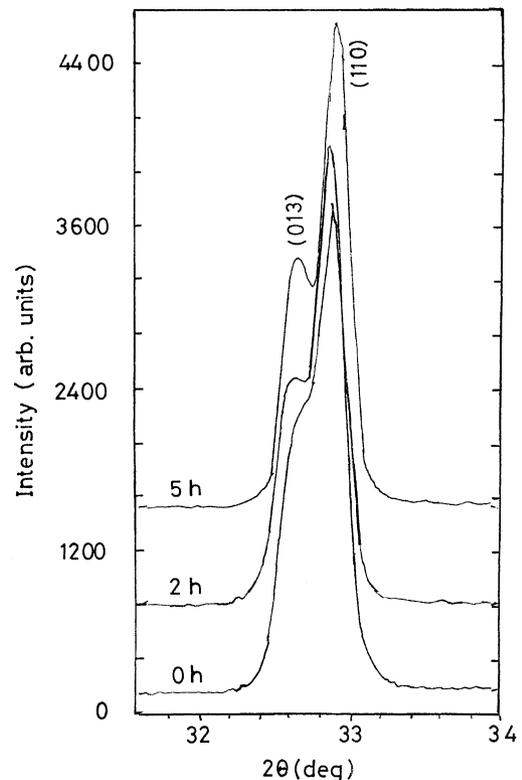


Fig. 4. Influence of the oxygen plasma exposure time on the splitted X-ray peak.

3. Results and discussion

3.1. Infrared (IR) spectra

The IR spectra of the samples were measured using the second derivative from 400 to 4000 cm^{-1} . The behavior of the IR spectra on the oxygen plasma exposure period is shown in Fig. 2. The IR transmittance reflects the existence of three peaks located at 450 and 550 cm^{-1} (Cu–O) and 660 cm^{-1} (Cu–O₂) as found from the correlation IR chart for metal oxides. Also, there is an observable band around 1380 cm^{-1} . The figure illustrates the dependence of the height of the peaks on the oxidation time in the way that the ratio Cu–O/Cu–O₂ increases.

3.2. X-ray studies

The samples were examined by X-ray powder diffraction in the angle range $2\theta = 10\text{--}60^\circ$ at room temperature using a SCINTAG-XGEN4000 diffractometer with the characteristic Cu K α radiation wavelength of 1.54060 Å. The X-ray diffraction pattern is shown in Fig. 3 for the unaffected sample, 2 h oxygen plasma exposed sample and for 5 h exposure time. X-ray of the unaffected sample shows the different ordering planes in crystal structure of the tetragonal phase. Also the splitting between the planes (013) and (110) in the range 32–33° (corresponding to the d

Table 1
Superconducting transition temperature as a function of the plasma exposure time

Dose time (h)	Structure	T_c (K)	X-ray parameters (\AA)
1	Tetragonal	–	$a = b = 3.87, c = 11.75$
2	Orthorhombic II	<80	$a = 3.84, b = 3.86, c = 11.66$
5	Orthorhombic I	92	$a = 3.84, b = 3.86, c = 11.66$
7	Orthorhombic II	<80	$a = 3.86, b = 3.89, c = 11.74$

spacing 2.6–2.7 \AA). The comparison between the X-ray spectra for samples with different oxygen plasma times (0, 2, 5 h) is shown in Fig. 4 at the angle range of 30–35°. The spectrum splitting behavior as a function of the oxygen plasma exposure time reveals the phase transition from the tetragonal to the orthorhombic structure and from the orthorhombic II to the orthorhombic I structure. The dependence of the lattice parameters and its volume on the exposure time is shown in Table 1 and Fig. 5, respectively.

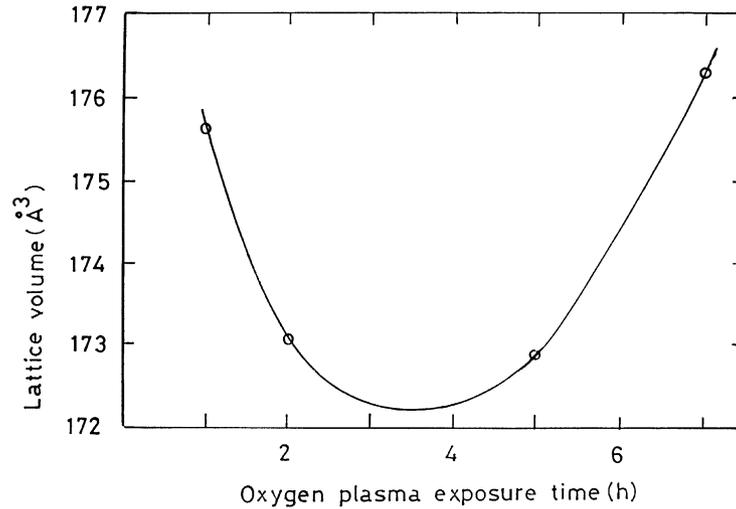


Fig. 5. Lattice volume as a function of the oxygen plasma exposure time.

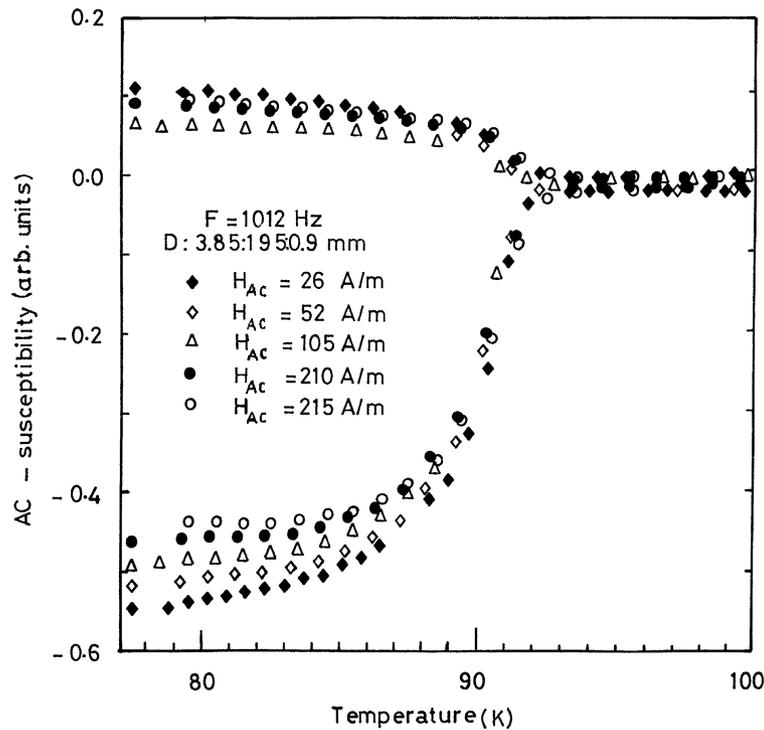


Fig. 6. AC magnetic susceptibility as a function of temperature at different applied magnetic fields (H_{a-c}).

3.3. Alternating current susceptibility

The absolute magnetic susceptibility as a function of the temperature and frequency of the applied field is used to characterize the magnetic properties of the sample with the oxygen plasma exposure time of 5 h, which lies at the minimum lattice volume with respect to the time of Fig. 5. A system of two identical sensing coils oppositely wound and connected in series to detect the variation in the flux created by the sample when its position is in the center of one of them. The resultant signal is measured by a phase-sensitive detector which produces an output voltage proportional to the sample susceptibility. The measured complex of alternating current (AC) susceptibility is illustrated in Fig. 6. The measurements show a characteristic temperature T_c equal to 91 K.

4. Conclusions

Low energy microwave plasma of 100 W is used to oxygenate a polycrystalline ceramic material of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-x}$ in the presence of an oxygen ambient. The variations of the lattice parameters and the unit cell volume as a function of the exposure time of the oxygen microwave plasma are investigated. A correlation of the transition temperature with the plasma doses as well as the oxygen vacancies in the structure has been found. The experimental studies of $\text{HoBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic superconductor show that the microwave oxygen plasma technique is efficient for preparing this type of rare earth superconductors. This method increases the oxygen concentration and gradually induces a transition from the tetragonal to orthorhombic II structure through 2 h exposure time. By increasing this time to 5 h, a second transition from orthorhombic II to orthorhombic I occurs. Increasing the exposure time, a reverse transition from orthorhombic I to orthorhombic II occurs. Also, we can conclude that the proposed technique orders the oxygen atoms to the Cu–O chains more than to their Cu–O₂ plans which reduces the lattice volume. This technique is simple, fast and inexpensive as well as more efficient in producing ceramic superconductors. Further work is in progress.

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