

THERMOGRAVIMETRIC AND MICROGRAVIMETRIC STUDIES OF THE SURFACE PROPERTIES OF A HIGH-TEMPERATURE SUPERCONDUCTOR

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Abstract

This paper presents possible applications of thermal analysis, sorptometric and microgravimetric methods for the study of surface adsorption and porosity properties via the programmed thermodesorption of liquid from the sample. The thermodesorption of liquids under quasi-isothermal conditions demonstrates that the adsorption layers on a high superconductor surface possess non-continuous properties. The degradation of the superconducting properties of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor sintered in a CO_2 -containing atmosphere has been revealed. It is known that atmospheric contaminants such as CO_2 and H_2O can strongly influence the transition temperature, the critical current density, and the width of the superconducting transition of the YBCO superconductor. Similarly to other liquids adsorbed on solid samples, water induces changes in the physicochemical properties at the interface. A good correlation was obtained between the adsorption and porosimetric, thermal analysis and sorptometric findings. The results prove the applicability of these findings for determination of the adsorption capacity.

Keywords: high-temperature superconductor, surface properties

Introduction

The adsorption and porosity properties of high-temperature superconductor samples are not well known. Investigation of the adsorption properties of these materials towards different liquids, and especially water, seems to be of great interest. A few publications have appeared on this subject. It has been reported that water is adsorbed on superconductor surfaces in accordance with a mechanism of physical and chemical adsorption, and the time dependence has been studied [1, 2]. The chemically adsorbed multilayer of water molecules stimulates the exchange of ions between the surface and the bulk of the crystal lattice. Physical adsorption does not change the elemental composition of the surface layer. It is presumed that ion exchange is stimulated by an electric field in ordering the water dipoles in the multilayer.

At liquid nitrogen temperature and in high fields, the intrinsic current-carrying properties of YBCO are superior to those of the Bi, Tl and Hg superconducting phases [3], and from this point of view it is the preferred material for both thin-film and bulk applications at this temperature. As concerns thin-film superconductor devices, the most progress has been made with the fabrication of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, Josephson junction and microwave devices. Knowledge of the chemistry and thermodynamics of the superconducting oxides is essential not only for prediction of the optimum processing conditions for the different forms of the materials, but also for an understanding of the origins of defects.

It is known that atmospheric contaminants such as CO_2 and H_2O can have strong effects on the transition temperature, the critical current density and the width of the superconducting transition of YBCO superconductors [4–16]. For practical applications of high- T_c superconductors, it will be necessary to make long, continuous superconductors in a variety of shapes. It is therefore important to know the extent to which YBCO decomposes in the presence of CO_2 and H_2O and to establish whether the decomposition of YBCO can be prevented by careful control of the furnace atmosphere. In this paper, we report on the adsorption, the surface porosity properties and the degradation of the superconducting properties of an YBCO superconductor sintered in CO_2 -containing atmospheres.

Experimental

The thermodesorption of polar and non-polar liquids from the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was studied to obtain information on the adsorbed liquid films and the porosity of the sample. The sample was dried at 200°C . The thickness of adsorbed liquid layers on the surface can be controlled by the mode of immersion of the solid samples. The immersion of the sample in liquid vapour in a vacuum desiccator, with $p/p_0=1$, blocks all the active adsorption centres, and the surface and capillary forces of the sample studied [17]. The studies were made with a simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary) [18]. Water, benzene and *n*-octane thermodesorption measurements were carried out under quasi-isothermal conditions in the temperature range $20\text{--}250^\circ\text{C}$ at a furnace-heating rate of 6°C min^{-1} . The Q-TG and Q-DTG curves were registered digitally under the control of the program Derivat running on a PC. The specific surface area, pore size and volume of the high-temperature superconductor sample were calculated from the low-temperature nitrogen adsorption isotherms measured by means of a Sorptomatic 1800 automated apparatus (Carlo Erba, Milan).

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was prepared by the direct solid-state reaction of oxides of at least 99.99% purity. The first and second calcinations were carried out at 930 and 970°C for 24 h each, with intervening grinding at 600°C for 4 h in an oxygen flow. The powder sample was then ground and pressed into pellets. Rectangular pellets of a size suitable for resistivity measurements were made and sintered in an oxygen flow at 980°C for 20 h and then furnace-cooled to room temperature.

The sample was characterized by powder X-ray diffraction, using a Stadi P (Stoe) diffractometer with a position-sensitive detector operating with CuK_α radiation. The oxygen content was measured by iodometric titration with a reproducibility of at least 0.02. DC four-probe resistivity measurements were performed on pellets to which copper contacts were attached by using silver paint. Thermogravimetric analyses (TG) were performed by using a Cahn RG ultramicrobalance system [19], with heating in vacuum and controlled environments at a rate of $10^\circ\text{C min}^{-1}$ in order to study mass uptake or loss at higher temperature.

Blank runs were used to determine disturbances affecting the accuracy of weighing in vacuum or in a controlled atmosphere [20], so as to correct the data obtained during the kinetic runs. The apparent mass changes did not exceed $\pm 40 \mu\text{g}$. As the measurement accuracy was better than $\pm 40 \mu\text{g}$, estimation of the oxygen content in the sample was possible at a level of at least ± 0.01 atom per chemical formula. To ensure a constant grain size distribution, the small samples used in the measurements were always taken from a larger portion of an original preparation. In order to examine the reaction between YBCO and CO_2 in detail, pellets were sintered for 6 h at 1000°C in flowing ($\approx 1\text{atm}$) O_2/CO_2 gas mixtures.

Results and discussion

The results of Q-TG and Q-DTG analysis of water, benzene and *n*-octane thermodesorption from a sample of YBCO are presented in Figs 1–3. The characteristic inflections in the Q-DTG curves correspond to the individual stages of thermodesorption of the liquids from YBCO.

From the data presented in Fig. 1, it is clear that there are two peaks in the Q-DTG curve corresponding to the desorption of water. Figure 2 presents the results of benzene

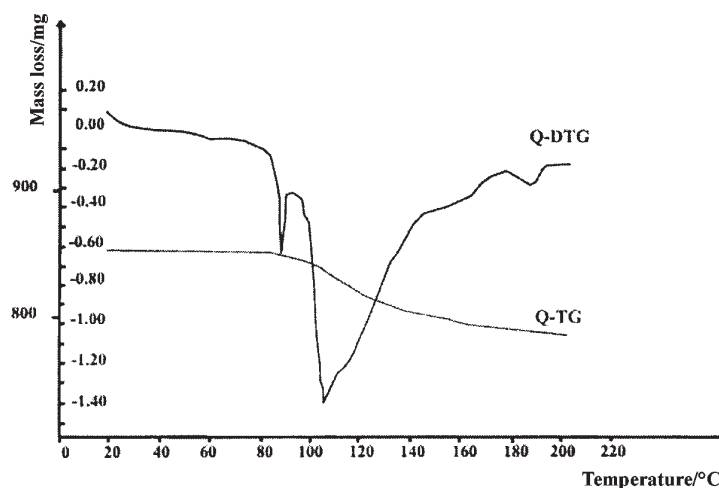


Fig. 1 Q-TG and Q-DTG curves of thermodesorption of water from YBCO

thermodesorption. It is seen that the desorption of benzene molecules from the YBCO surface is characterized by three peaks. However, the desorption of *n*-octane furnishes one large peak (Fig. 3). These peaks correspond to liquid desorption in the capillary condensation range, from the pores and active centres [21].

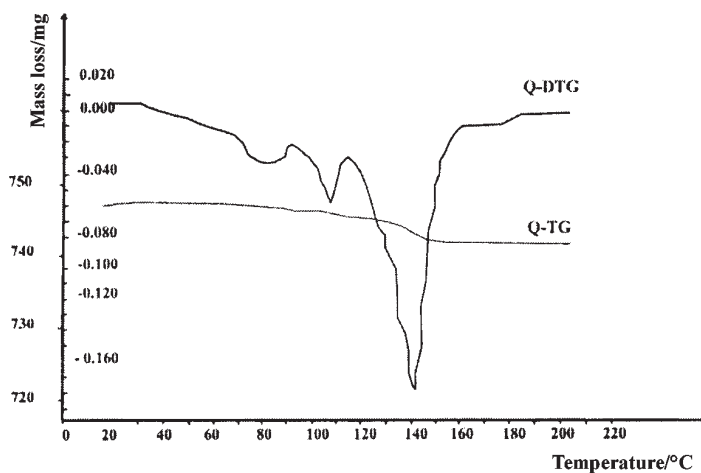


Fig. 2 Q-TG and Q-DTG curves of thermodesorption of benzene from YBCO

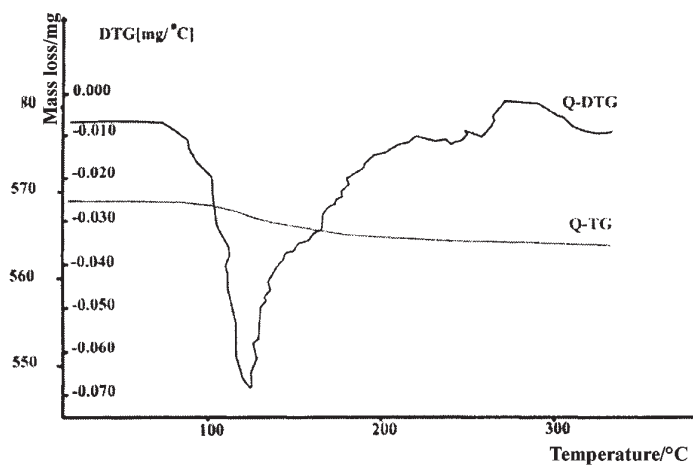


Fig. 3 Q-TG and Q-DTG curves of thermodesorption of *n*-octane from YBCO

The calculated data reveal that the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is characterized by a large adsorption capacity. The statistical number of monolayers is larger than 100 for water, but much smaller for the non-polar liquids. The degree of coverage and thermodesorption of water and benzene demonstrate that the investigated superconductor has a polar surface. However, the superconducting phase is decomposed by water (reaction 1) [22–24] and loses its superconducting properties.

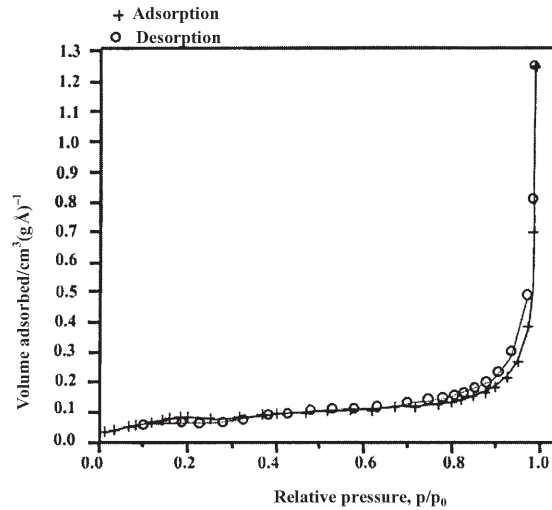


Fig. 4 Low-temperature nitrogen adsorption-desorption isotherms for YBCO

The specific surface area, pore size and volume of the high-temperature superconductor were calculated from the low-temperature nitrogen adsorption-desorption isotherms (Fig. 4).

Figures 5 and 6 present the pore area and volume distribution functions for YBCO. From the data presented in Figs 5 and 6, it appears that there is one peak of Gaussian type. It has been confirmed that the YBCO sample surface has one kind of pores, only. The mean pore radius and pore volume of the high-temperature superconductor sample were calculated from the BJH desorption isotherms to be 145.5 Å and 0.002 cm³ g⁻¹, respectively (Table 1). The specific surface area was calculated from the Langmuir isotherm to be 0.53 m² g⁻¹. From Table 1, it appears that there is a

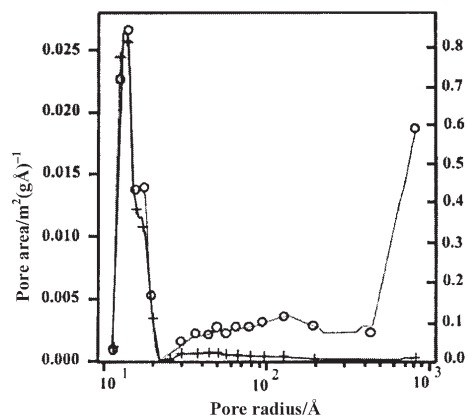


Fig. 5 Pore area distribution function for YBCO

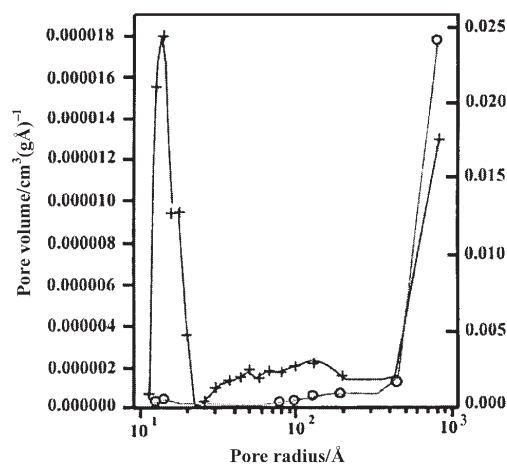


Fig. 6 Pore volume distribution function for YBCO

good correlation between the BJH pore volumes obtained from the sorptomatic ($0.0019 \text{ cm}^3 \text{ g}^{-1}$) and thermal analysis methods ($0.002 \text{ cm}^3 \text{ g}^{-1}$).

Table 1 Pore structure parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor calculated from nitrogen adsorption-desorption isotherms and thermal analysis method

Parameter	Unit	Value
Sorptomatic method		
Single point surface area at $p/p_0=0.2$	$\text{m}^2 \text{ g}^{-1}$	0.2829
BET surface area	$\text{m}^2 \text{ g}^{-1}$	0.341
Langmuir surface area	$\text{m}^2 \text{ g}^{-1}$	0.5261
BJH adsorption cumulative surface area for 8.5–1500 Å pores	$\text{m}^2 \text{ g}^{-1}$	0.2783
BJH desorption cumulative surface area for 8.5–1500 Å pores	$\text{m}^2 \text{ g}^{-1}$	0.2662
Single point total pore volume for $<382 \text{ Å}$ pores	$\text{cm}^3 \text{ g}^{-1}$	0.000588
BJH adsorption cumulative pore volume for 8.5–1500 Å pores	$\text{cm}^3 \text{ g}^{-1}$	0.001949
BJH desorption cumulative pore volume for 8.5–1500 Å pores	$\text{cm}^3 \text{ g}^{-1}$	0.001936
Average pore radius ($2V/A$ by BET)	Å	34.5
BJH adsorption average pore radius ($2V/A$)	Å	140.07
BJH desorption average pore radius ($2V/A$)	Å	145.49
Thermal analysis		
Pore volume of benzene	$\text{cm}^3 \text{ g}^{-1}$	0.002

Figure 7 shows the dependence of the critical temperature T_c on the oxygen deficiency for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The oxygen content dependence of T_c exhibits a typical plateau at about 90 and about 60 K [25], the length of which was found to be affected by the ionic radius of the substituted RE (rare earth) atom [26]. T_c can also be influenced by partial substitution of the RE atoms or the Ba atoms by atoms of lower or higher valence [27].

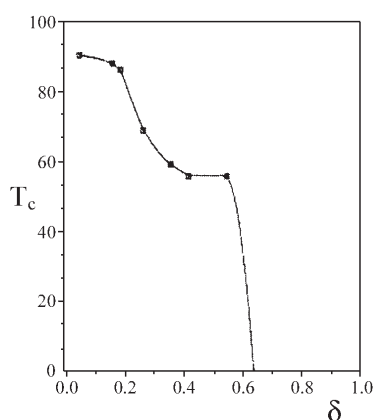


Fig. 7 Dependence of critical temperature T_c on oxygen deficiency δ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Figure 8 reveals that, when the CO_2 partial pressure in the sintering atmosphere was increased, the resistivity decreased and the material was semiconductive. Resistivity data are given for two samples fired at 1000°C , one a superconducting sample processed in 100% O_2 and the other a semiconductive sample processed in 0.5% CO_2/O_2 . These results suggest that CO_2 reacts with YBCO in a thin layer of non-superconducting second phase at the grain boundaries, but does not degrade the interior of the superconducting grain.

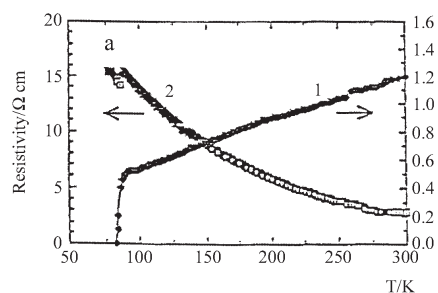
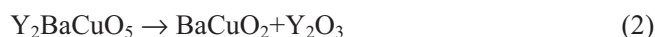
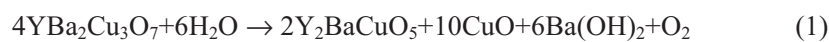


Fig. 8 Resistivity vs. temperature for two samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ fired at 1000°C . Sample 1 was fired in 100% O_2 and was superconducting. Sample 2 was fired in 0.5% CO_2/O_2 and was semiconductive

The X-ray data show the grain boundary material consists of BaCuO_2 and $\text{Y}_2\text{Cu}_2\text{O}_5$. The majority of the grain boundaries appear quite sharp, with no obvious evidence of a second phase. The YBCO surface degrades in air. This degradation occurs via the reactions



There is a strong thermodynamic driving force for most alkaline earth compounds to form hydroxides and carbonates. This means that degradation reactions such as those above are an inherent problem with most high-temperature superconducting materials.

Degradation of the surface of high-temperature superconductors in air is a widely recognized problem. It is a major factor in the difficulties encountered in early attempts to characterize these materials, such as irreproducible tunnelling measurements and the failure to detect a Fermi edge in XPS measurements of the valence bands. It is involved in the growth process itself and may result in non-superconducting surface phases, e.g. the Y-rich surface observed on some *o*-YBCO single crystals, with stoichiometry appropriate for Y_2BaCuO_5 with a smaller amount of $BaCO_3$. Transmission electron diffraction studies of *o*-YBCO crystals have demonstrated that, near the surface, the crystal structure differs from that of the bulk by being less orthorhombic [28], which is evidence of an oxygen deficiency [29].

Summary

The liquid mass loss Q-TG and differential Q-DTG curves consist of steps and inflections that are associated with the liquid-liquid and liquid/high-temperature superconductor surface interactions. They yield information on the adsorption capacity, pore volume and discontinuous change in the adsorbed layer properties. The programmed thermodesorption investigations of the liquids have provided evidence that the YBCO has a polar surface. The high- T_c superconductor samples display a very large affinity for the adsorption of polar liquids. The adsorption of water molecules destroys the porosity of the surface. This is stimulated by electric fields in ordering the water dipoles in the multilayers. YBCO samples have only one kind of pores, as confirmed by sorptomatic measurements. The specific surface area values are typical of those for mesopore adsorbents.

The YBCO reacts strongly with CO_2 at high-temperatures, leaving superconducting grain interiors encased in non-superconducting grain boundary phases. At high partial pressures of CO_2 , YBCO completely decomposes to $BaCO_3$, Y_2BaCuO_5 and CuO . The degradation of high-temperature superconductor surfaces in air, which is particularly rapid for those materials containing alkaline earth elements, and the possible formation of non-superconducting species during the growth process, necessitates some form of surface cleaning for many applications.

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