

YBa₂Cu₃O₇ superconductor as a mild, deep oxidation catalyst

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Abstract. Several Y-Ba-Cu-O compositions including the superconducting YBa₂Cu₃O₇ are scanned for their oxygen uptake using low temperature oxygen chemisorption (LTOC) technique as the principal probe at 195 K. BET surface area and pore size distribution were also determined. The results indicate their potential for use as mild, deep oxidation catalysts even under ambient and sub-ambient conditions.

Keywords. YBa₂Cu₃O₇ superconductor; oxidation; chemisorption; catalyst.

1. Introduction

The triple perovskite structure adopted by the 90 K superconductor YBa₂Cu₃O₇ is essentially oxygen-deficient, leading to mixed valency of Cu. This property makes the 123 compound a potential oxidation catalyst. A complete characterization of the latter involves determination of O₂ uptake, surface area and pore size distribution, necessitating an oxygen adsorption study (i.e. both physisorption and chemisorption).

The low temperature oxygen chemisorption (LTOC) technique involving both chemisorption and physisorption was considered to be the most appropriate (Chary *et al* 1986) technique for this investigation. In chemisorption the molecules of the adsorbate form a chemical bond with the adsorbent (Yavorsky and Detlaf 1975) so that changes produced in bulk of the sample by chemisorption are expected to be at subgrain level and can thus be related to structural parameters. Schwartz *et al* (1989) show that the amount of O₂ loss by reduction at ambient correlates with the X-ray diffraction data which suggests a bulk reduction rather than surface reduction or decomposition. Our belief that this reduction could take place at sub-ambient temperatures as well motivated us to take up the oxygen chemisorption studies on the 123 superconductor.

We have screened the superconducting YBa₂Cu₃O₇ and other non-superconducting Y-Ba-Cu-O systems and the results are presented.

2. Experimental

Samples used in this study were in the form of polycrystalline powders crushed from pellets of (i) YBa₂Cu₃O₇, (ii) Y₃Ba₄Cu₅O₁₄, (iii) YBa₂Cu₂O₇ and (iv) YBaPbCu₃O₇. These compounds were synthesized from intimate mixtures of reagent grade Y₂O₃, BaCO₃ and CuO by a two-time solid-state reaction at 900°C (15 h) in air with

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intermediate grinding followed by final sintering in the form of pellets at 950°C (15 h) with furnace cooling, all in static air. The samples were characterized by X-ray ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$) diffractometry, electrical resistivity and Meissner effect. Samples (i) and (ii) show magnetic levitation at 77 K and sample (i) has a T_c of 92.3 K ($R = 0$). The indexed X-ray pattern and the dc resistivity plot for the sample (i) are shown in figure 1. The XRD patterns of all except samples (i) and (ii) show the presence of minor phases. They do not show levitation and possess room temperature resistivities of the order of a few $\text{k}\Omega$.

The oxygen chemisorption experiments at -78°C (195 K) were performed on samples of known weight employing a specially designed cell (Chary *et al* 1986) connected to a static high vacuum system. Purified oxygen from a storage bulb connected to the high vacuum manifold was allowed to enter the sample chamber with a known dead space. An initial quick fall in the pressure was followed by levelling off within about 10 min and the equilibrium position was noted. This process was repeated at different equilibrium pressures and the first adsorption isotherm representing both chemisorbed and physisorbed oxygen was generated. The sample chamber was then evacuated at -78°C (195 K) for 1 h to 10^{-6} torr to remove the physisorbed oxygen and the second isotherm representing only physisorbed oxygen was generated in an

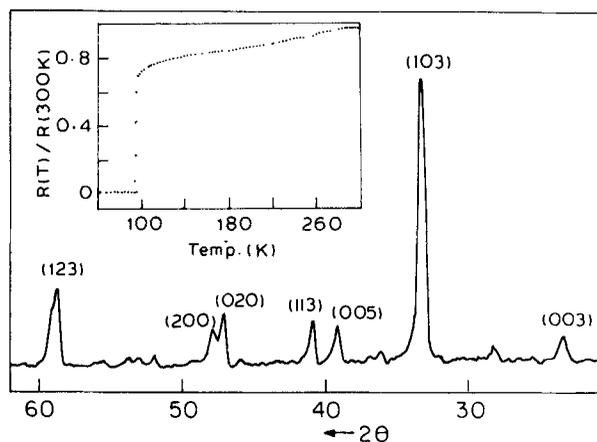


Figure 1. XRD pattern and dc resistivity plot (inset) of $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample used in the LTOC experiment.

Table 1.

Sample	Lattice parameters			Porosity	LTOC O_2 uptake ml/g
	<i>a</i>	<i>b</i> (Å)	<i>c</i>		
$\text{YBa}_2\text{Cu}_3\text{O}_7$	3.8565	3.8386	11.6746	0.228	0.78
$\text{Y}_3\text{Ba}_4\text{Cu}_5\text{O}_{14}$	3.9031	3.8618	11.7709	0.272	0.68
$\text{YBa}_2\text{Cu}_2\text{O}_6$	3.8599	3.861	11.7366	0.230	0.24
$\text{YBaPbCu}_3\text{O}_7$	3.7543	3.9608	11.7751	0.49	0.36

Table 2.

Oxidation catalyst	LTOC O ₂ uptake ml/g	BET surface area m ² /g	Reference
V ₂ O ₅	0.87	11.5	Nag <i>et al</i> (1984)
Cr ₂ O ₃	2.0	29.0	Rama Rao <i>et al</i> (1986)
YBa ₂ Cu ₃ O ₇	0.78	2.0	Present work
YBa ₂ Cu ₃ O ₇	—	0.1	Hansen <i>et al</i> (1988)
CuO	—	0.5	Kryukova <i>et al</i> (1988)

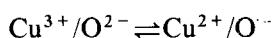
identical manner. It is important to stress at this point that only physisorbed oxygen can be thus removed from the system but not chemisorbed oxygen. The volume of the chemisorbed oxygen was eventually calculated from the difference in the heights of these two linear and parallel isotherms.

The BET surface area was determined by nitrogen adsorption method at 77 K (liq. N₂ temp.). Porosity was calculated from bulk and X-ray density measurements.

3. Results and discussion

All the results are presented in table. 1. The X-ray parameters suggest the formation of basic triple perovskite structure in all the compounds. According to Hansen *et al* (1988) the differences in the *c* parameter can be used to estimate the oxygen content in the sample. The superconducting samples (i) and (ii) (which have shown levitation at 77 K) have shown high O₂ uptake values of 0.78 ml/g and 0.68 ml/g clearly reflecting their oxygen deficiency. In the other two samples (which did not show levitation at 77 K) the O₂ uptake values are of the order of 0.14 ml/g showing their stoichiometric nature (that is almost without oxygen vacancies). Table 2 compares the O₂ uptake values and the surface area of our 123 compound with those for conventional catalysts. BET surface area of 2 m²/g observed by us for YBa₂Cu₃O₇ at 77 K is very high when compared with Hansen *et al*'s (1988) value of 0.1 m²/g at 400 K. Also, since surface area increases with increase in temperature up to 500 K, we can expect a much higher value for our sample at room temperature. The maximum uptake of O₂ by the 123 compound suggests its application as a mild and deep oxidation catalyst. Qiu *et al* (1988) reported that the 123 compound can be modified by water at cryogenic temperatures, and suggested that OH⁻ species may be incorporated in the superconductor which most probably reacts with oxygen vacancies and modifies both Ba and Cu electronic environments. They also observed that most of the water desorbs between 160 K and 210 K.

The 0.78 ml/g oxygen uptake by 123 and hence its oxidation capability suggest the presence of unusual valence state, Cu³⁺. A recent XPS study on YBa₂Cu₃O₇ by Schlogl *et al* (1989) established the preponderance of divalent copper but with a significant contribution of trivalent copper, the latter giving rise to peak asymmetry at higher binding energies. According to this work the oxidation capability may find its origin in the equilibrium condition



which requires the simultaneous presence of trivalent copper and anion p band holes (O^- ions). They also showed that oxygen desorption sets in only at $T > 380^\circ\text{C}$. This oxygen is diffused out of the bulk.

4. Conclusions

Our oxygen adsorption experiments on the 123 superconductor show that this material is a good oxidation catalyst even at ambient and sub-ambient temperatures. Most significantly the low temperature oxygen chemisorption (LTOC) technique provides us with both a basic and an applied tool to study the surface phenomenon and to conduct quantitative tests on several of the newly developed superconductors for catalytic activity. It also provides an indirect method for the determination of oxygen stoichiometry in high T_c superconducting ceramics.

Acknowledgements

One of the authors (YSR) gratefully acknowledges the award of a fellowship by CSIR, New Delhi.

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