Bull. Mater. Sci., Vol. 10, No. 3, May 1988, pp. 241–243. © Printed in India.

Chemical stability of the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}^{+}$

A K GANGULI and N Y VASANTHACHARYA*

Solid State and Structural Chemistry Unit, *Department of Physics, Indian Institute of Science, Bangalore 560 012, India

MS received 16 January 1988

Abstract. $YBa_2Cu_3O_{7-\delta}$ samples stored in different environments have been studied over a period of 30 days employing TGA, electrical resistivity and X-ray diffraction measurements. Oxygen content and T_c do not change significantly in samples stored in the normal laboratory environment, in a sealed tube or in a vacuum desiccator. Superconductivity is lost only in samples stored in a very humid atmosphere around 320 K.

Keywords. $YBa_2Cu_3O_{7-\delta}$; superconductivity.

1. Introduction

Evidence of high temperature superconductivity in the Y-Ba-Cu-O system (Wu *et al* 1987) and subsequent identification of the phase responsible for superconductivity as the perovskite related oxide, $YBa_2Cu_3O_{7-\delta}$ (Rao *et al* 1987a) have led to extensive research on this oxide material. Superconducting $YBa_2Cu_3O_{7-\delta}$ crystallizes in an orthorhombic structure containing Cu-O-Cu chains or corner linked CuO_4 units (David *et al* 1987). Oxygen stoichiometry has been found (Rao *et al* 1987b; Rao 1988) to play a crucial role in determining the structure and superconductivity in $YBa_2Cu_3O_{7-\delta}$. Considering the immense potential of this oxide for various applications, it was of interest to study its chemical stability. We have studied this problem by examining samples stored over a period of time in different environments. There have been some investigations of environmental effects using electron microscopy and other techniques (Hyde *et al* 1987). In the present study we have tried to study systematically the effect of ageing under different atmospheric conditions by a combined use of thermogravimetry, four-probe resistivity and X-ray diffraction.

2. Experimental

Orthorhombic $YBa_2Cu_3O_{7-\delta}$ was prepared by heating an appropriate mixture of Y_2O_3, $BaCO_3$ and CuO at 1200 K for 20 h in air. This was ground pelletised and again heated at 1200 K for 20 h. The samples, annealed in O_2 at 775 K for 20 h, had no measurable impurities such as $BaCuO_2$, $Y_2Cu_2O_5$; and not more than 5% Y_2BaCuO_5. They were then stored in different conditions as shown in tables 1 and 2. Thermogravimetry of the samples in H_2 was carried out to determine the oxygen content at regular intervals. The samples were also characterized by X-ray diffraction and four-probe resistivity studies.

+Contribution No. 508 from the Solid State and Structural Chemistry Unit.

Table 1. Chemical stability of $YBa_2Cu_3O_{7-\delta}$ at 300 K.

Days	Oxygen content[+]	X-ray data	T_c(onset)	T_c(zero)
(a) Open to laboratory atmosphere				
Fresh	6·90	Orthorhombic	90	85
4	6·90	Orthorhombic	90	85
30	6·83	Orthorhombic	90	85
(b) Stored in vacuum desiccator				
30	6·80	Orthorhombic	91	84·5
(c) Stored in a sealed tube				
30	6·78	Orthorhombic	91·5	85

[+]determined by TGA.

Table 2. $YBa_2Cu_3O_{7-\delta}$ stored in an atmosphere saturated with water vapour at 320 K.

Days	Oxygen content[+]	X-ray data	T_c(onset)	T_c(zero)
Fresh	6·98	Orthorhombic	91	83
4	6·98	Orthorhombic	91	83
8	6·98*	Orthorhombic and $BaCO_3$ (~2%)	91	82·5
30	6·97*	Orthorhombic and $BaCO_3$ (~10%)	Semiconducting	

*Corrected values (after removing weight loss due to water and $BaCO_3$); [+]determined by TGA.

3. Results and discussion

Table 1 gives the results on $YBa_2Cu_3O_{7-\delta}$ kept open in the normal chemical laboratory atmosphere ($T \simeq 300$ K). We find that the oxygen content remains essentially constant up to 30 days. The sample also remains orthorhombic with no additional phases after 30 days as observed by X-ray diffraction. There is no change in T_c (onset) and T_c (zero). Thus using bulk characterization techniques it appears that there are no significant changes in the superconducting properties when the samples are exposed to normal chemical laboratory condition. Results of our studies on $YBa_2Cu_3O_{7-\delta}$ stored in a vacuum desiccator and in a sealed tube lend support to this result (table 1).

Table 2 shows the results obtained on samples mounted in a humid chamber (saturated with water vapour) at ~320 K. Up to about four days, there was no observable degradation of the sample and the T_c as well as the oxygen content did not change significantly. We see an increasing proportion of $BaCO_3$ after 8 days as shown by X-ray diffraction; T_c is also affected and the sample becomes semiconducting after 30 days. TGA also shows the presence of appreciable amount of water or hydroxyl groups.

From the present study we establish that $YBa_2Cu_3O_{7-\delta}$ is quite stable in normal atmospheric conditions and its superconductivity is not affected over a period of one month. There is no appreciable change in oxygen content in these samples over this period. The presence of water vapour leads to degradation of the samples, $BaCO_3$ being formed in the process. Superconductivity is lost when appreciable amount of $BaCO_3$ is observed.

Acknowledgements

The authors thank Prof. C N R Rao, for valuable discussion and advice. Thanks are also due to the University Grants Commission and the Department of Science and Technology, Government of India for support of this research. One of the authors (AKG) thanks the CSIR for a fellowship.

References

David W I F, Harrison W T A, Gunn J M F, Moze O, Soper A K, Day P, Jorgensen J D, Beno M A, Capone D W, Hinks D G, Schuller I K, Soderholm L, Segre C U, Zhang K and Grace J D 1987 *Nature (London)* **327** 310

Hyde B G, Thomson J G, Withers R L, Fitzgerald J G, Stewart A M, Bevan D J M, Anderson J S, Bitmead J and Paterson M S 1987 *Nature (London)* **327** 402

Rao C N R 1988 *J. Solid State Chem.* (in print)

Rao C N R, Ganguly P, Raychaudhari A K, Mohan Ram R A and Sreedhar K 1987a *Nature (London)* **326** 856

Rao C N R, Ganapathi L and Mohan Ram R A 1987b *Mater. Res. Bull.* (in print)

Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908