Aging and Environmental Effects on $YBa_2Cu_3O_{6.95}$ Superconductor

S.A. Siddiqi, Z.M. Pirzada, and A. Mateen

The effect of aging and environmental degrading on a $YBa_2Cu_3O_{6.95}$ ceramic superconductor has been studied by x-ray diffraction, scanning electron microscopy, infrared spectroscopy, and electrical resistivity measurements. The superconductor prepared by solid state reaction was well characterized and then exposed to the normal laboratory environment for more than three years. The material showed substantial microstructural degradation with a small decrease in the transition temperature from normal to superconducting state (T_c). IR spectroscopy reveals the presence of water and carbonate. The damage in oxygen content can be restored by reannealing in oxygen for about six hours at 470 °C, but the restoration of exactly the same microstructural and electrical characteristics is not possible.

Keywords

aging, cuprates, high-temperature superconductors, x-ray diffraction

1. Introduction

THE DISCOVERY of superconductivity in cuprates and especially in the Y-Ba-Cu-O system at about 90 K has generated an unprecedented interest among scientists all over the world. Apart from the scientific interest, the high-temperature superconductors offer many potential applications (Ref 1). However, some technical limitations have to be solved before their use can be promoted commercially.

One of the main drawbacks of these materials is their environmental degradation (Ref 2-6). An understanding of the environmental behavior of these oxide materials is of significant importance in order to determine the stability of the superconducting phase. Degradation of $YBa_2Cu_3O_{7-\delta}$ occurs by water and many organic solvents (Ref 2-6). Most of these studies were carried out under accelerated conditions, which may not give a true picture of the damage being done. Therefore, in the present study, a $YBa_2Cu_3O_{6.95}$ superconductor prepared by the standard solid state reaction between oxides of Y and Cu, and carbonate of Ba and well characterized for its oxygen content, transition temperature, differential resistance, and critical current behavior (Ref 7-9) was exposed to open laboratory atmosphere for more than three years. Changes that occurred due to aging and environment were studied by x-ray diffraction (XRD), scanning electron microscopy (SEM), infrared (IR) spectroscopy, and temperature-dependent resistivity measurement. The observations made under this study are reported in this paper.

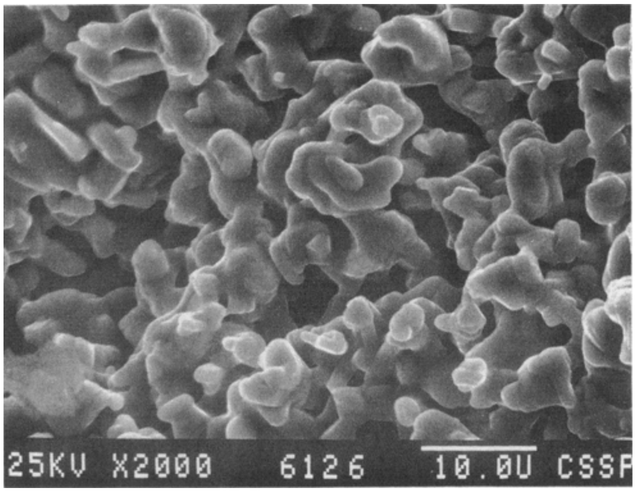
S.A. Siddiiqi and **Z.M. Pirzada,** Centre For Solid State Physics, The Punjab University Lahore-54590, Pakistan.; A. Mateen, Institute of Chemical Engineering and Technology, The Punjab University Lahore-53590, Pakistan

2. Experimental Methods

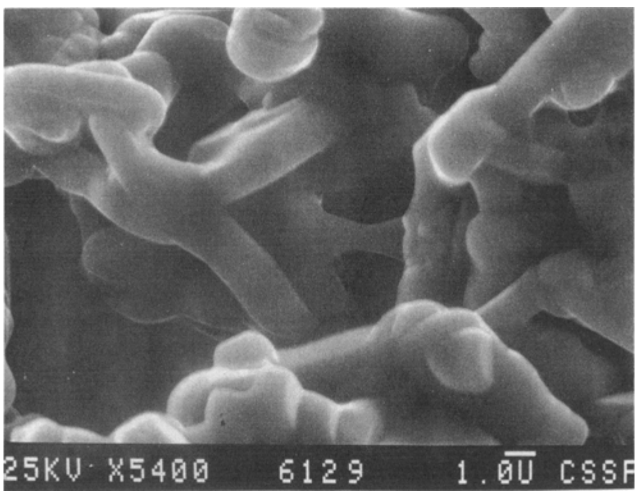
Superconducting $YBa_2Cu_3O_{6.95}$ was prepared from powders of Y_2O_3, CuO, and $BaCO_3$ with purity better than 99.9 at%. The mixture of these powders in their appropriate proportion was well ground and mixed in an agate mortar and pestle. The pellets were made from this mixture before calcining in a tube furnace at 900 °C for 6 h. The product was ground and pelletized for second heating at 940 °C for 24 h in air. The product after second heating was reground and pelletized into 16-mm-diam pellets and heated up to 940 °C in flowing oxygen for 4 h, then slowly cooled to 470 °C at a rate of 1°C/min where it was annealed for 6 h in oxygen and then slowly cooled to room temperature. The material was characterized by XRD on either a Rigaku XRD-D/Max 11A diffractometer (Rigaku-USA, Inc., Danvers, MA.) or a Siemen diffractometer (Siemen AG, Karlsruhe, Germany.) All the measurements were made at room temperature using Cu Kα radiation. Transport critical current density (J_c) and differential resistance ($dv/dI = df$) of the samples were measured in the temperature range 77 to 91 K and in the weak magnetic fields ($H \leq 150$ Oe). The details of this measurement were published (Ref 9). The $YBa_2Cu_3O_{6.95}$ specimen was then exposed to normal open atmosphere for more than three years after performing the first set of characterization experiments. The changes that occurred due to aging and open atmosphere were then monitored by XRD, resistivity-temperature (R-T) four-probe measurements, IR spectroscopy, and SEM. For IR spectra of the samples, the authors used a Bruker IFS88 Fourier Transform IR Spectrometer (Bruker Instruments Inc., Danvers, MA.). The spectra were obtained in the standard manner with the material ground in a small amount of dried KBr and pelletized to form a thin transparent disk. The degraded or aged sample was reannealed in flowing oxygen for 16 h at 470 °C and recharacterized by the same techniques mentioned earlier.

3. Results and Discussion

Figures 1 and 2 show the scanning electron micrographs of the freshly prepared and the aged sample of $YBa_2Cu_3O_{6.95}$ su-

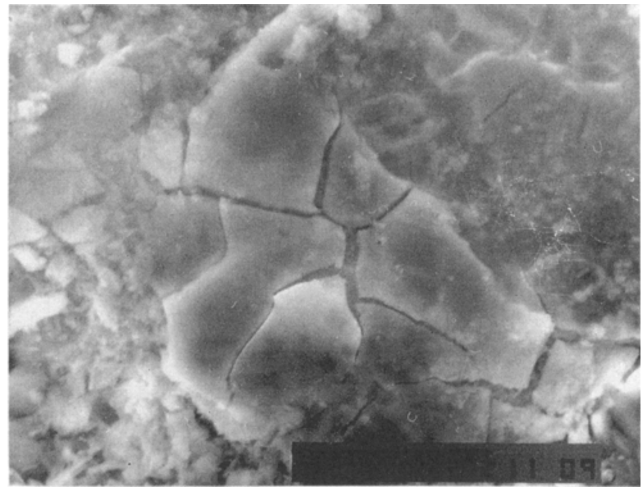


(a)

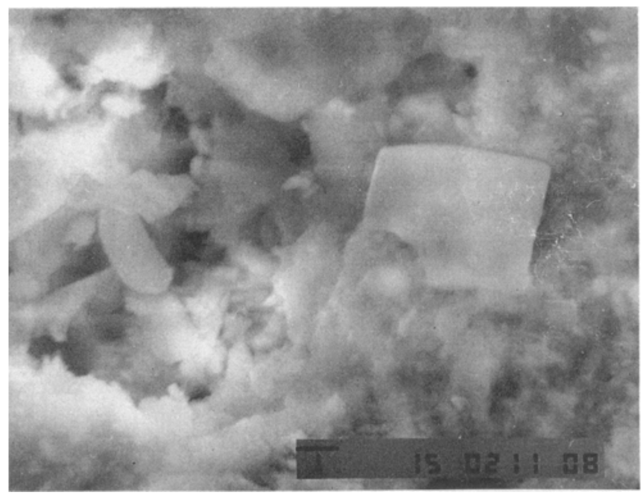


(b)

Fig. 1 Scanning electron micrographs of freshly prepared $YBa_2Cu_3O_{6.95}$ superconductor. (a) General morphology. (b) Cross-links of rod-like crystals.



(a)



(b)

Fig. 2 Scanning electron micrographs of aged $YBa_2Cu_3O_{6.95}$ sample. (a) Severe morphological degradation and crack growth. (b) Breaking of some large-sized rod-like crystals and surface

perconductor, respectively. The micrograph of the freshly prepared specimen reveals nearly uniform grain size distribution occasionally containing some large-size rod-like crystals with 2 to 3 μm diameter. The grains are connected with low contact area. SEM also reveals that the material has about 30% porosity. After three years, the material has undergone severe atmospheric degradation. The surface has corroded from many places, and the grains have broken into individual pieces with very small contact area. Also many cracks can be seen passing through the material. The large, rod-like crystals have broken into small segments as shown in Fig. 2(b).

IR spectrum for the aged $YBa_2Cu_3O_{6.95}$ is shown in Fig. 3. The spectrum shows the presence of $BaCO_3$ and water. Note that a very weak $BaCO_3$ peak was also observed in the freshly prepared sample. However, the relative intensities for CO_3 after aging has increased, and the presence of carbonate peak in the freshly prepared sample indicates that there was some remnant barium carbonate left in the product. It appears that on longer exposure to open atmosphere, the material reacts with water vapor and CO_2 according to the reaction:

$$2YBa_2Cu_3O_{7-\delta} + 3H_2O + 3CO_2 \rightarrow Y_2BaCuO_5 + 5CuO + 3BaCO_3{\cdot}3H_2O + 2O_\delta \quad \text{(Eq 1)}$$

Therefore, the IR spectrum of the aged sample shows stronger peaks due to carbonates and water.

The XRD patterns given in Fig. 4 show the presence of Y_2BaCuO_5, CuO, and $BaCO_3$ in the aged $YBa_2Cu_3O_{6.95}$. Note that trace amounts of these impurity phases are normally present in the freshly prepared $YBa_2Cu_3O_{7-\delta}$ superconductors prepared by solid state reaction. The relative intensities of these

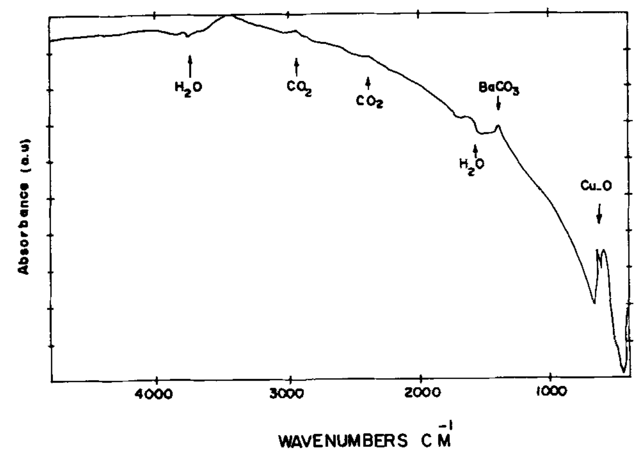


Fig. 3 IR spectrum of the aged $YBa_2Cu_3O_{6.95}$ showing the presence of $BaCO_3$ and H_2O.

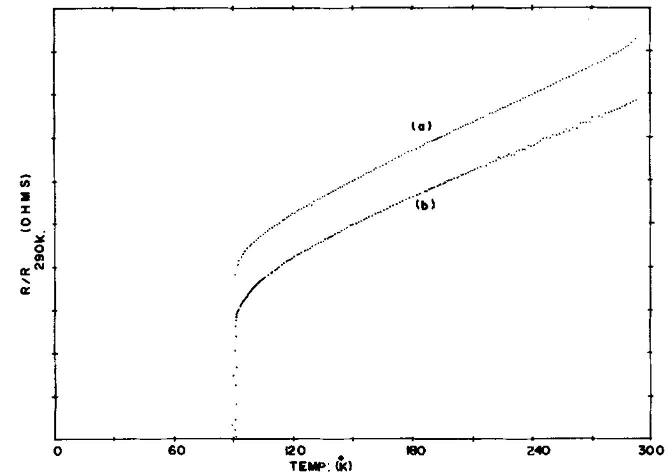


Fig. 5 *R-T* curves for (a) aged and (b) restored $YBa_2Cu_3O_{6.95}$ samples.

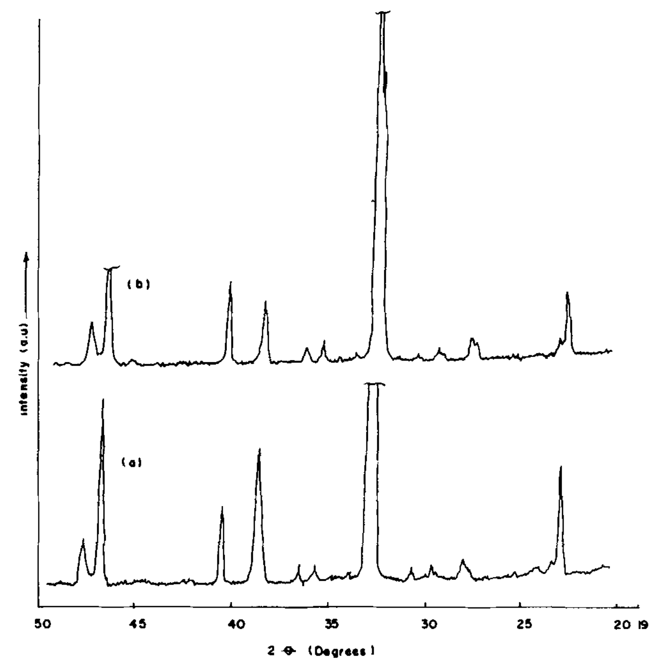


Fig. 4 XRD patterns of (a) the aged and (b) the restored $YBa_2Cu_3O_{6.95}$ samples.

impurity phases have increased with aging and exposure to open atmosphere.

The XRD pattern of the aged sample, which was reheated at 940 °C and annealed at 470 °C in flowing oxygen, is shown in Fig. 4(b). The pattern does not show any significant change in the intensities of the impurity phases. The only noticeable difference lies in the reversibility of the intensities of the (005) and (113) reflections around $2\theta = 40°$, which is indicative of oxygen absorption in the material. The variation in $BaCO_3$ content in the aged sample is more prominent in the IR spectrum rather than in the XRD pattern.

Resistivity measurements of the aged and restored samples are shown in Fig. 5. The T_c zero value and the room temperature resistivity improves slightly after annealing the aged sample. The curve shows that the T_c value does not decrease drastically due to environmental degradation.

Summarizing the above results, $YBa_2Cu_3O_{6.95}$ or any other ceramic superconductor with similar composition but slightly different oxygen content prepared from oxide powders by solid state reaction undergoes slow degradation due to humidity and CO_2 present in the atmosphere. The annealing steps can be helpful to restore the lost oxygen and improve the resistivity, but it may not be possible to repair the microstructure of the original material. Therefore, a method is needed to coat a protective layer on the surface, or a suitable preparation method, which provides environmental stability (Ref 10), is needed.

Acknowledgments

One of the authors (S.A.S.) is grateful to ICTP, Trieste, Italy, for providing a one-year postdoctoral fellowship under Italian Lab. Programme. The author also gratefully acknowledges the unforgettable company and help given by the late Dr. Carlos Infante (on leave from the University of Chile, Santiago, Chile), who was also present at ICTP.

References

1. J.R. Ashburn, and C.J. Tong, *Phys. Rev. Lett.*, Vol 58, 1987, p 908
2. K.G. Frase, E.G. Liniger, and D.R. Clarke, *Adv. Ceram. Mater.*, Vol 2 (No. 3B), 1987, p 698
3. J.G. Thompson, B.G. Hyde, R.L. Withers, J.S. Anderson, J.D. Fitz Gerald, J. Bitmead, M.S. Paterson, and A.M. Stewart, *Mater. Res. Bull.*, Vol 22, 1987, p 1715
4. J. Wang, R. Stevens, and J. Bultitude, *J. Mater. Sci.*, Vol 23, 1988, p 3393
5. B.S.B. Karunaratne and M.H. Lewis, *Br. Ceram. Trans. J.*, Vol 88, 1989, p 33
6. H. Yang, W. Liu, M. Wu, and Y. Fu, *Chin. J. Low Temp. Phys.*, Vol 12 (No. 2), 1990, p 140
7. S.A. Siddiqi and K. Hussain, *J. Nat. Sci. Math*, Vol 28 (No. 1), 1988, p 19

8. E. Babic, M. Prester, Z. Marohnic, T. Car, N. Biskup, and S.A. Siddiqi, *Solid State Commun.*, Vol 72 (No. 8), 1989, p 753

9. E. Babic, M. Prester, Z. Marohnic, and S.A. Siddiqi, *Phys. Rev. B*, Vol 41 (No. 10), 1990, p 6278

10. S.M. Arora, V.H. Desai, and K.B. Sundaram, *J. Mater Sci.*, Vol 28, 1993, p 454