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## PASSIVATION PROCESS OF HIGH $T_c$ SUPERCONDUCTORS $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ BY FLUORINE GAS TREATMENT

A. TRESSAUD, B. CHEVALIER, B. LEPINE, J. M. DANCE, L. LOZANO,  
J. GRANNEC and J. ETOURNEAU

*Laboratoire de Chimie du Solide du CNRS, Université de BORDEAUX I, 351, cours de la  
Libération, 33405 TALENCE, Cedex, France*

R. TOURNIER, A. SULPICE and P. LEJAY

*Centre de Recherche sur les Très Basses Températures, CNRS — BP 166X — 38042 Grenoble,  
Cedex, France*

The atmospheric degradation of high  $T_c$  superconductors  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  can be prevented using fluorine gas processings around room temperature. A thin layer of amorphous fluorides (and/or oxyfluorides) is formed at the surface of the particles, which passivates the material against hydrolysis and gas-exchange processes. A fluorination mechanism has been proposed, which can account for both fluorine analysis and weight uptake. The superconductivity onset does not seem to be affected by fluorination. Furthermore, an improvement of the shielding effect-Meissner effect cycle to 91% reversibility is achieved when  $\text{F}_2$ -treated oxides are heated at 350°C under vacuum.

### 1. Introduction

The discovery of high temperature superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides has led to intensive activities in the synthesis of new attractive compounds and in the search of technological improvements.

Concerning the potential use of these materials, one of the main drawbacks is their great reactivity vs various reagents. Several researchers have pointed out that major degradation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides occurs in moist air.<sup>1,2</sup> The hydrolysis partly decomposes the oxide and yields  $\text{Ba}(\text{OH})_2$  and  $\text{Y}(\text{OH})_3$  hydroxydes and  $\text{CuO}$  oxide. In a second step, atmospheric  $\text{CO}_2$  reacts with  $\text{Ba}(\text{OH})_2$  to give rise to  $\text{BaCO}_3$ . These mechanisms considerably deteriorate the superconducting characteristics of the ceramics.

The use of these oxides in devices such as Josephson junctions is therefore subject to an efficient protection of the materials against ambient moisture and gas exchange processes.

We have been currently investigating the influence of fluorination on the superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The occurrence of a passivating layer of amorphous fluoride (and/or oxyfluoride) has been confirmed by various

physical techniques: X-ray diffraction, ESR, Auger spectroscopy, magnetic and conductivity measurements.<sup>3</sup>

In the present work, we report the passivation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides using a fluorine gas treatment around room temperature.

## 2. Experimental

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was prepared by thermal treatment of stoichiometric mixtures of  $\text{BaCO}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$ . After a 12hr heating cycle at  $900^\circ\text{C}$  in air, the resulting product was ground and treated again in the same conditions for 24hr. An annealing at  $500^\circ\text{C}$  was performed either in air or in oxygen atmosphere during 24hr, which was followed by a cooling at  $100^\circ\text{C/hr}$  rate.

The oxide has been proved to exhibit an orthorhombic symmetry, with unit-cell constants  $a = 3.824\text{\AA}$ ,  $b = 3.890\text{\AA}$ ,  $c = 11.72\text{\AA}$  in good agreement with those published previously.<sup>4</sup>

Fluorine gas treatments were carried out in a "fluorination line" using handling procedures described elsewhere.<sup>5</sup> The oxide was set as pellets in a nickel boat. The nickel reaction tube was filled with one atmosphere of pure  $\text{F}_2$  gas. The product was kept under a moderate flow of fluorine for 5hr and allowed to stand overnight under 1.3 bar  $\text{F}_2$  atmosphere. When the materials were fluorinated at low temperature ( $T \leq 100^\circ\text{C}$ ) no change in color, nor weight uptake larger than 1% were noticed. No further weight increase was observed even when the pellets were kept for 20 days at room temperature under 1.3 bar  $\text{F}_2$  atmosphere.

The materials were characterized before and after fluorination using X-ray diffraction ( $\text{Cu-K}_\alpha$ ), Auger electron spectroscopy (AES) and electron microprobe techniques. Elemental analyses were carried out at Service Central d'Analyses du CNRS. The temperature dependence of the magnetization was measured at GRENOBLE using a SQUID magnetometer.

## 3. Results and Discussion

Figure 1 showed X-ray patterns of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (a) freshly prepared, (b) after a 4 months exposure to room atmosphere. In the latter spectrum, new peaks can be noted, which are due to the occurrence of baryum carbonate. When the oxide of (a) is previously  $\text{F}_2$ -treated at  $20^\circ\text{C}$ , no change occurs in the X-ray pattern, even when the sample is kept in moist air for long periods (up to 4 months) (c).

For non-treated samples, the observed hydrolysis process appears to be in good agreement with the results of Zhuang Dexin et al.<sup>1</sup>

In order to know whether fluorine has been incorporated during the reaction, an AES study of the surface of a ceramic material has been carried out. Figure 2 shows concentration profiles of carbon, oxygen and fluorine in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (a) before and (b) after the  $\text{F}_2$  treatment. Fluorine and oxygen are both present at the surface of the fluorinated sample and noticeable amounts of fluorine can be

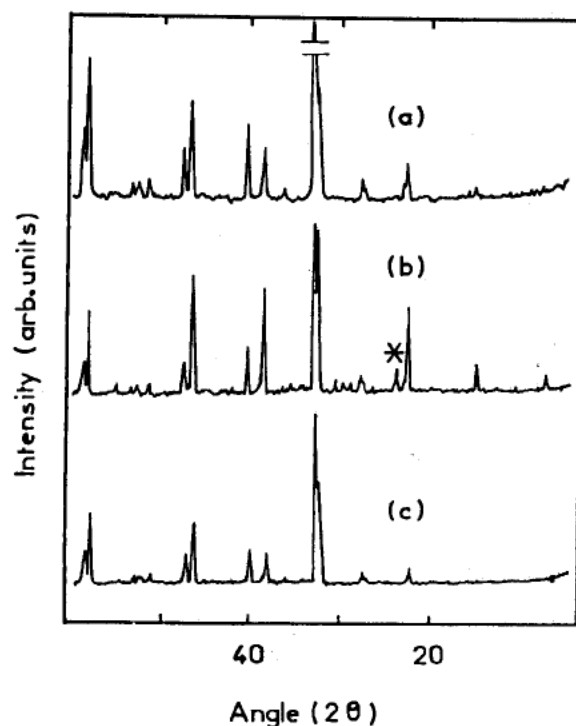


Fig. 1. Part of the X-ray powder spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ : (a) freshly prepared, (b) exposed to the atmospheric moisture for 4 months (\*indicates the  $\text{BaCO}_3$  diffraction peak), (c) treated in fluorine gas at  $20^\circ\text{C}$  and exposed in atmospheric moisture for 4 months.

observed to 200–300 Å deep from the surface. The monotonic decrease of F content and the absence of a plateau with constant F/O ratio tend to confirm the absence of any stoichiometric oxyfluoride at the surface. This study shows that the  $\text{F}_2$  process affects only the surface of the particles. Furthermore, the presence of carbon, which indicates in the case of the pristine oxide the occurrence of carbonate, seems to be totally inhibited in  $\text{F}_2$  treated samples.

O and F analyses carried out on a series of ceramics which had been vacuum treated prior to a  $\text{F}_2$ -treatment at  $20^\circ\text{C}$  are given below [the weight uptake during the fluorination is  $\Delta m = +0.7\%$ ]:

- before  $\text{F}_2$  treatment: 6.7 oxygen atmosphere mole,
- after  $\text{F}_2$  treatment: 0.45 fluorine atom and 6.3 oxygen atoms (by difference) per mole.

Using the assumption that the fluorination mechanism yields amorphous fluorides of bulk composition “ $\text{YBa}_2\text{Cu}_3\text{F}_{13}$ ” with a subsequent oxygen departure, the amount of oxide moles which has been involved in the decomposition process can be calculated from either fluorine analysis or from weight uptake: a value of 3.3% can account for both results.

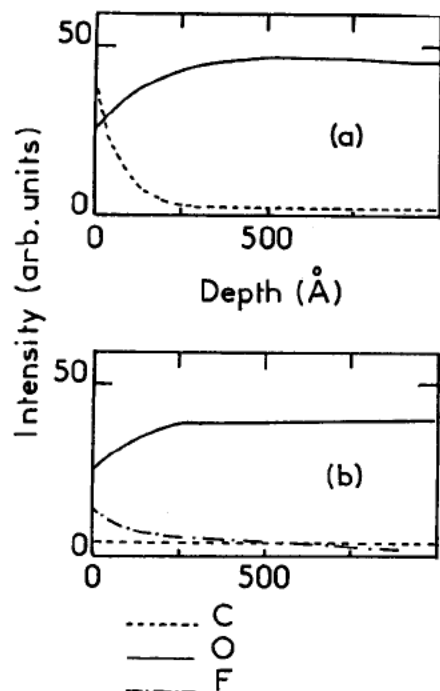


Fig. 2. Concentration profiles of carbon, oxygen and fluorine in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (a) before and (b) after the fluorine gas treatment at  $20^\circ\text{C}$ .

It can be anticipated that the passivation layers obtained at low temperature are amorphous since complete fluorinations of powdered  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples, which occur even below  $200^\circ\text{C}$ , do not yield crystallized materials.<sup>3</sup>

Low temperature  $\text{F}_2$  gas treatment have almost no influence on the superconductivity onset of the starting materials. Figure 3a shows the thermal variation of the magnetization below  $T_c$  in an applied field of 10 Oe for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  before and after a  $\text{F}_2$  treatment at  $20^\circ\text{C}$ . The measurements have been done after a zero-field cooling of the sample (shielding effect) or under an applied field (Meissner effect).

Fluorination treatment does not affect the superconducting volume significantly as can be seen from Fig. 3a, in which the magnetization curves of the materials before and after treatment can be practically superimposed.

When  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides are treated under vacuum, it is well known that the oxygen content is lowered and that a complete disappearance of the superconductivity can even be observed.<sup>4</sup> This behavior is obtained for instance when the starting oxide is heated for 2 hr at  $500^\circ\text{C}$  in secondary vacuum: the superconductivity vanishes completely. On the other hand when the product has been  $\text{F}_2$ -treated previously, an identical processing does not destroy the superconductivity completely, in spite of considerable lowering of both  $T_c$  and

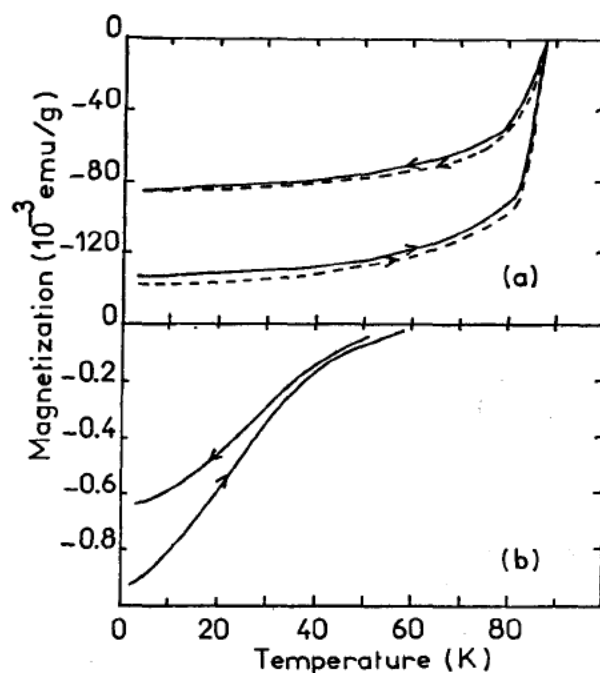


Fig. 3. Magnetization of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  as a function of temperature in an applied field  $H = 10$  Oe before (—) and after (---) the fluorine gas treatment at  $20^\circ\text{C}$  (a) and after the vacuum annealing at  $500^\circ\text{C}$  (b).

diamagnetic signal (Fig. 3b). This result shows that the fluoride layer inhibits the evolution of oxygen during vacuum treatments.

The thermal variation of another  $\text{F}_2$ -treated oxide sample is shown in Fig. 4. At 10 K the ratio: Meissner effect to shielding effect is of 61%. This non reversible property of the diamagnetic signal is well known for this type of oxides and can be

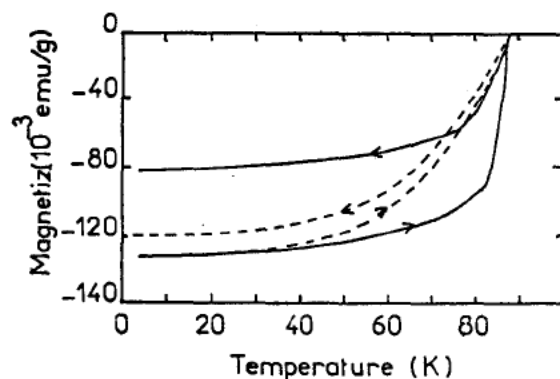


Fig. 4. Magnetization vs temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  treated in a fluorine gas atmosphere before (—) and after (---) the vacuum annealing at  $350^\circ\text{C}$ .

correlated to inhomogeneities: structural defects at the surface can induce an important pinning of the vortex. After a 4hr annealing at 350°C under secondary vacuum, the F<sub>2</sub>-treated oxide still has a superconductivity onset at 89 K but it exhibits a quasi-reversibility of the cycle shielding effect-Meissner effect (Fig. 4). At 10 K, the ratio reaches 91%. It seems clear once more that the fluoride layer treated under appropriate thermal conditions eliminates the surface inhomogeneities of this superconductor.

#### 4. Conclusions

When YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> oxides are treated in a fluorine-gas atmosphere at low temperature, the degradation of the material in moist air is prevented. This curing process can be ascribed to the formation of a layer of amorphous fluoride at the surface of the particles, which passivates the material against hydrolysis. Even after vacuum processing at 500°C, the "fluorinated" oxide still exhibits some superconductivity. An identical procedure carried out at 350°C preserves the superconductivity of the material and improves, moreover, the shielding effect-Meissner effect cycle towards an almost reversibility.

#### 5. Acknowledgment

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