INFLUENCE OF FLUORINE-GAS TREATMENT ON THE STRUCTURAL AND PHYSICAL PROPERTIES OF La_2CuO_4

Bernard CHEVALIER, Alain TRESSAUD, Bruno LEPINE, Catherine ROBIN and Jean ETOURNEAU

Laboratoire de Chimie du Solide du CNRS, Université Bordeaux I, 33405 TALENCE cedex, France.

La_2CuO_4 samples have been treated under pure fluorine gas at temperatures T_{F_2} ranging from 20°C to 300°C. For T_{F_2}=300°C, the starting oxide is completely decomposed in a mixture of LaF_3 and CuF_2, whereas for $T_{F_2} \leq 230$°C the resulting product crystallizes in an orthorhombic distortion of the K_2NiF_4-type structure as La_2CuO_4 starting oxide. After the fluorination process, the weight uptake of the material, the elemental analysis and a noticeable change of the unit cell parameters corroborate the incorporation of fluorine atoms inside the La_2CuO_4 lattice. These oxyfluorides are superconductors below $T_c = 40 \pm 1$K and exhibit a metallic behaviour above T_c. On the other hand the three-dimensional antiferromagnetic ordering observed in starting oxide near $T_N \approx 250$ K appears to be destroyed by the fluorine-gas treatment.

1. INTRODUCTION

At room temperature, La_2CuO_4 oxide crystallizes in an orthorhombic distortion of the tetragonal K_2NiF_4-type structure. Its structural and physical properties are greatly dependent on the method of sample preparation, therefore suggesting the presence of various anionic defects in the material[1]. For instance the orthorhombic-to-tetragonal structural transition, which occurs near 450K when the sample is annealed under 42 bar of O_2 at 500°C, takes place at 550K for vacuum-annealed samples. Moreover, the presence of a sharp peak at $T_N \approx 250$K in the temperature dependence of the magnetic susceptibility is the signature of the three-dimensional antiferromagnetic ordering[2].

Single crystals of La_2CuO_4 annealed in nitrogen at about 600°C exhibit a semiconducting behaviour down to lowest temperatures[3]. On the other hand this same oxide annealed under a flow of oxygen gas at 450°C shows a filamentary superconductivity below T_c=40K with a semiconducting behaviour above T_c [4,5]. The superconducting fraction of the sample increases when the annealing is carried out under high oxygen pressures and this effect has

0022-5088/90/$3.50

been correlated to an incorporation of oxygen species into the structure[4,5,6]. It was reported that below 320K these oxygen-enriched materials consist of a mixture of two orthorhombic phases : the first has a stoichiometry close to La_2CuO_4 and the second, which is responsible for the superconducting properties, contains an excess of oxygen and has been formulated La_2CuO_{4+y} with $y \simeq 0,13$ [6]. Let us note that these samples display both a superconducting behaviour below $T_c \simeq 40K$ and an antiferromagnetic ordering near $T_N \simeq 250K$ [7].

The replacement of lanthanum by strontium or barium allows to synthesize the superconducting oxides $La_{2-x}M_xCuO_4$ (M=Sr,Ba) which crystallize in the tetragonal K_2NiF_4-type structure[8,9]. These compounds exhibit a metallic behaviour above the superconducting transition temperature. In the meantime the three-dimensional antiferromagnetic ordering of the Cu^{2+} ions vanishes in these oxides[2].

Recently, we have reported the incorporation of fluorine atoms in La_2CuO_4 oxide by a fluorine gas treatment at $T_{F_2} = 200°C$ [10]. The resulting compound is superconducting at $T_c = 40K$. An extension of this work is presented here, particularly the influence of the fluorination temperature T_{F_2} on the structural, electrical and magnetic properties of the resulting compound. We compare also the characteristics of these oxyfluorides with those of La_2CuO_4 samples annealed in high pressure oxygen gas.

2. EXPERIMENTAL DETAILS

La_2CuO_4 oxide has been prepared as powders or pellets by thermal treatments as previously described[10]. The fluorination process has been carried out under 1,3 bar of pure F_2-gas for $20°C \leqslant T_{F_2} \leqslant 300°C$ and for duration times of about 20h. Phase analysis has been performed using X-ray powder diffractometry (CuK_α). Lattice parameters have been determined by least-square refinement, based on 5N-silicon as an internal standard.

Magnetic susceptibilities have been measured between 4,2 and 300K using a SQUID magnetometer. Electrical resistivity measurements have been carried out between 4,2 and 300K using a standard four-probe dc technique.

3. RESULTS AND DISCUSSION

3.1. Fluorination process

The reaction between La_2CuO_4 powdered samples and F_2-gas is strongly dependent on the fluorination temperature T_{F_2}. For $20°C \leqslant T_{F_2} \leqslant 150°C$, the X-ray powder pattern of the F_2-treated compound is identical to that of the starting oxide and without any noticeable weight uptake. On the other hand,

a weight uptake $\Delta m/m < 3\%$ is observed when the treatment is carried out at $150°C \leqslant T_{F_2} \leqslant 230°C$. The resulting compound has been identified as a single phase and crystallizes in an orthorhombic distortion of the K_2NiF_4-type structure. The enhancement of the distortion relative to that of the untreated oxide is shown in Fig.1-a and b. For $230°C < T_{F_2} < 250°C$, $\Delta m/m$ increases drastically and the X-ray analysis shows that the resulting product is not a pure phase anymore. For instance with $\Delta m/m \simeq 8\%$, the X-ray pattern shows, beside remaining lines of the orthorhombic oxyfluoride the presence of a new phase deriving from the K_2NiF_4-type structure (Fig.1-c). This latter phase can be indexed in the tetragonal symmetry with $a \simeq 4{,}03\text{Å}$ and $c \simeq 13{,}07\text{Å}$ as unit cell parameters. Above $T_{F_2} = 250°C$ the presence of LaF_3

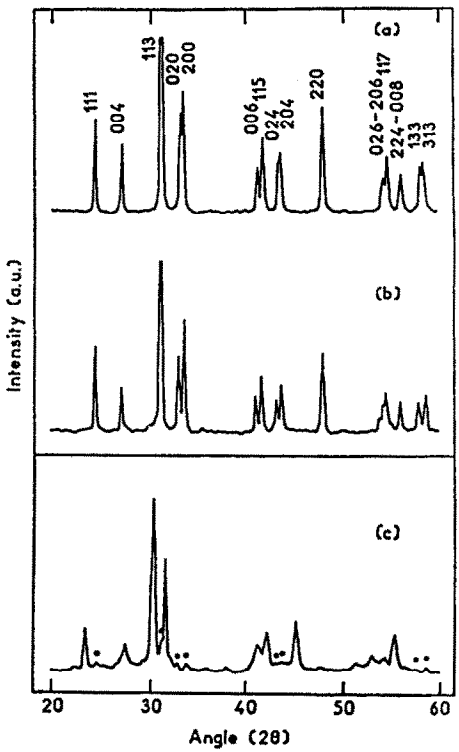

FIGURE 1

X-ray powder pattern of La_2CuO_4 untreated (a) and treated (b) at $T_{F_2} = 200°C$ (b) and 230°C (c) (the lines corresponding to remaining orthorhombic oxyfluoride are noted by).

can be systematically observed. At T_{F_2} =300°C the starting oxide is completely decomposed into a mixture of LaF_3 and CuF_2. At this fluorination temperature, the weight uptake ($\Delta m/m \simeq 20.4\%$) is close to the theoretical value ($\Delta m/m = 21.7\%$) calculated for the complete fluorination mechanism :

$$La_2CuO_4 + 4F_2 \rightarrow 2LaF_3 + CuF_2 + 2O_2\uparrow$$

The T_{F_2}-dependence of the unit cell parameters of the oxyfluorides obtained for $T_{F_2} \leqslant 230°C$ is given in Fig.2. The unit cell volume increases with T_{F_2}. For T_{F_2} = 220°C, the unit cell constants are a = 5.334Å, b = 5.448Å, and c = 13.21Å, which corresponds to an enlargement of the unit cell volume $\Delta V/V_o \simeq 0.55\%$ (V_o = unit cell volume of the starting oxide). These results corroborate the incorporation of fluorine atoms in La_2CuO_4. The elemental analysis of the F_2-treated sample at T_{F_2} = 200°C, for which a weight uptake of 1.95% has been observed, gives the following experimental atomic percentages : La 66.35% , Cu 14.95% , O 15.05% and F 2.55%. These values correspond to the chemical composition $La_2Cu_{0.98}O_{3.96}F_{0.55}$, which is close to that determined from the weigth uptake, i.e. $La_2CuO_4F_{0.41}$. The number of anions (O+F) per formula unit is greater than 4 as observed for oxygen atoms (O) in samples annealed under strongly oxidizing conditions[6].

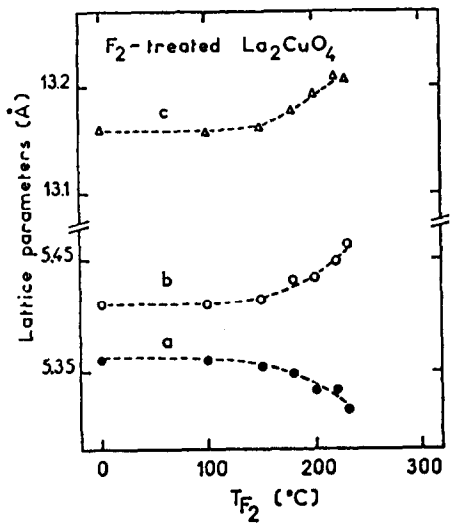

FIGURE 2
T_{F_2} - dependence of the unit cell constants of F_2-treated La_2CuO_4.

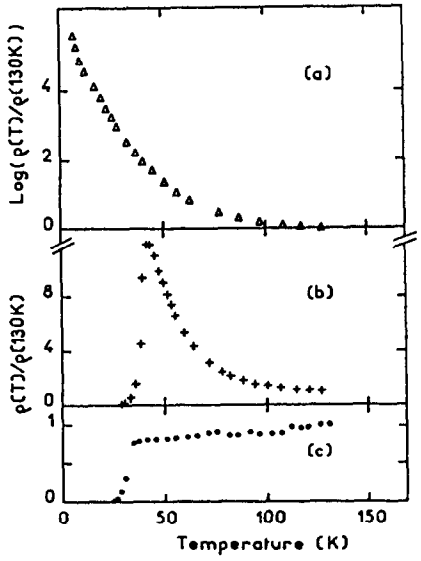

FIGURE 3
Temperature dependence of the resistivity of La_2CuO_4 annealed under Ar (a) or O_2 (b) or F_2-treated at 200°C

3.2. Resistivity properties

Figure 3 shows the temperature dependence of the reduced resistivity of an La_2CuO_4 pellet annealed under a flow of argon gas at 600°C (a), then treated either under 1 bar of oxygen gas at 450°C (b), or under 1.3 bar of pure F_2-gas at 200°C (c). The starting oxide has a semiconducting behaviour at any temperatures above 4.2K. A zero resistance is observed at 25-30K for the O_2- or F_2- treated compound. But only the fluorinated sample exhibits a metallic behaviour above 40K, whereas the O_2 - annealed compound has a semiconducting dependence. This last result is in good agreement with previous works concerning the effect of oxygen-pressure on La_2CuO_4 [4,5]. The metallic behaviour of the F_2- treated sample is similar to that observed for the substituted superconducting oxides $La_{2-x}M_xCuO_4$ (M=Sr,Ba)[8,9].

3.3. Magnetic properties

Above 6K no diamagnetic signal was detected on our La_2CuO_4 starting oxide (Fig.4). On the other hand, for materials F_2- treated at 150°C $\leq T_{F_2} \leq$ 230°C, the magnetic susceptibility becomes negative below 40K, confirming the superconducting behaviour of these oxyfluorides.

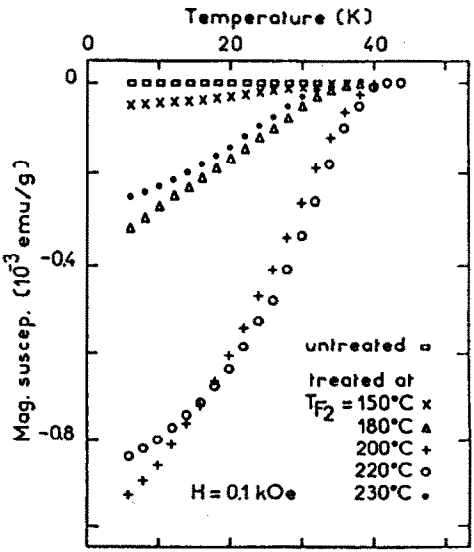

FIGURE 4
Temperature dependence of the magnetic susceptibility of La_2CuO_4 samples treated at various T_{F_2} temperatures.

The 6K-susceptibility increases with increasing T_{F_2} for $150°C \leq T_{F_2} \leq 200°C$, then decreases in the $200°C < T_F \leq 230°C$ fluorination temperature range. For the compound treated at $T_{F_2} = 200°C$ the 6K- susceptibility $M/H = -0.95\ 10^{-3}$ emu/g at 6K corresponds to a fraction of 8% to the theoretical value $M/H = -1/4\ \pi$.

For the La_2CuO_4 starting oxide, the M/H = f(T) curve shows a maximum around 250K (Fig.5). This behaviour indicates that the compound develops a three-dimensional antiferromagnetic ordering below this temperature[2]. The magnetic ordering has been shown simultaneously with the superconducting properties in La_2CuO_4 samples treated under 400-500 bar of oxygen gas[7]. Concerning the susceptibility of the F_2- treated compound, a monotonic decrease is observed above 40K, without any distinguishable anomaly up to 300K. This behaviour is similar to that observed in the $La_{2-x}Sr_xCuO_4$ oxides with x=0.024 - 0.028, where the three-dimensional antiferromagnetic ordering also disappears[11].

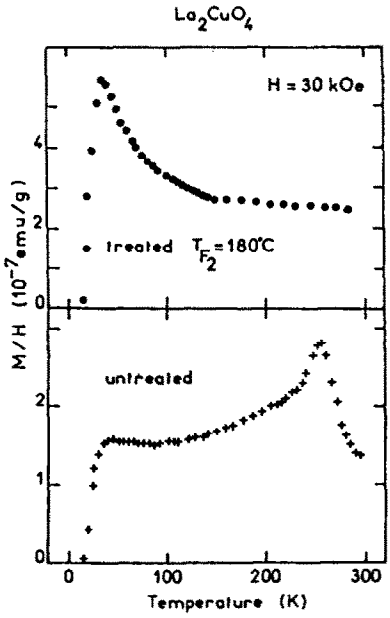

FIGURE 5
Influence of the F_2-treatment on the M/H=f(T) curve.

3.4. Thermal annealings

A mass-spectrometry study of superconducting $La_2CuO_4F_y$ oxyfluoride has shown that the material started to loose oxygen under vacuum at about 250-300°C. No trace of superconductivity is observed in the resulting product, which still crystallizes in an orthorhombic distortion of the K_2NiF_4-type structure. However a structural change is associated with the oxygen loss :a = 5.334Å, b = 5,448Å and c = 13.21Å, before the vacuum annealing and a = 5.369Å, b = 5,459Å and c = 13.18Å after. These last values are different to those determined for the La_2CuO_4 starting oxide and indicate that fluorine atoms are still present in the vacuum annealed compound. Finally the $La_2CuO_4F_y$ oxyfluoride decomposes into a mixture of La_2CuO_4 and LaOF for treatments in argon flow at 600°C.

We have tried to prepare these oxyfluorides by a solid state synthesis method using powdered mixtures of La_2CuO_4 and CuF_2 for molar ratios ranging from 9/1 to 1/1. The experiments have been performed at 200-300°C for ten hours in sealed platinum tubes. A noticeable change in the unit-cell constants of La_2CuO_4 is observed after the reaction and the resulting samples may exhibit superconducting properties below 40K depending on both the chemical composition and the reaction temperature. It can be also pointed out the presence in the X-ray patterns of small amounts of CuO for all compositions and of other phases deriving from the K_2NiF_4-type, especially for molar ratios close to 1/1. A detailed study concerning this fluorination process has been proposed elsewhere[12].

4. CONCLUSIONS

A fluorine-gas treatment of La_2CuO_4 at $150°C \leq T_{F_2} \leq 230°C$ allows to obtain $La_2CuO_4F_y$ oxyfluorides isostructural with the starting oxide. The incorporation of fluorine atoms leads to both an enlargement of the unit cell volume and an increase of the orthorhombic distortion. These compounds are superconductors at $T_c \simeq 40K$ and exhibit a metallic behaviour above T_c. In addition, no three-dimensional antiferromagnetic ordering can be detected below 300K. These materials loose small amounts of oxygen at 250-300°C under vacuum, with a consequent disappearance of the superconductivity. The possibility to incorporate extra anionic species in the K_2NiF_4-type structure has been therefore confirmed by the fluorine-gas treatments of La_2CuO_4 oxide.

ACKNOWLEDGEMENTS

The authors are indebted to L. Lozano for fluorination experiments. This work was carried out with the support of Rhône-Poulenc in the scope of a CNRS project "GS Matériaux Supraconducteurs" and as a part of an European Community Research Program.

REFERENCES

1) D.C. Johnston, J.P. Stokes, D.P. Goshorn and J.T. Lewandowski, Phys. Rev.B, 36 (1987) 4007.

2) S.W. Cheong, J.D. Thompson and Z. Fisk, Physica C, 158 (1989) 109.
3) S.W. Cheong, M.F. Hundley, J.D. Thompson and Z. Fisk, Phys. Rev.B, 39 (1989) 6567.

4) J. Beille, R. Cabanel, C. Chaillout, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J.L. Tholence and R. Tournier, C.R. Acad. Sc. Paris, 304 (1987) 1097.

5) J. Beille, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, O. Laborde, C. Michel, P. Lejay, J. Provost, B. Raveau, A. Sulpice, J.L. Tholence and R. Tournier, Physica B, 146 (1987) 307.

6) J.D. Jorgensen, B. Dabrowski, S. Pei, D.G. Hinks, L. Soderholm, B. Morosin, J.E. Schirber, E.L. Venturini and D.S. Ginley, Phys. Rev. B, 38 (1988) 11337.

7) Y. Oda, M. Yamada, H. Ochiai, K. Asayama, T. Kohara, Y. Yamada, K. Koga, S. Kashiwai and M. Motoyama, Solid State Comm., 73 (1990) 725.

8) J.G. Bednorz, M. Takashige and K.A. Müller, Mat. Res. Bull., 22 (1987) 819.

9) J.M. Tarascon, L.H. Greene, W.R. McKinnon, G.W. Hull and T.H. Geballe, Science, 235 (1987) 1373.

10) B. Chevalier, A. Tressaud, B. Lépine, K. Amine, J.M. Dance, L. Lozano, E. Hickey and J. Etourneau, Physica C, 167 (1990) 97.

11) R. Yoshizaki, N. Ishikawa, M. Akamatsu, J. Fujikami, H. Kurahashi, Y. Saito, Y. Abe and H. Ikeda, Physica C, 156 (1988) 297.

12) A. Tressaud, C. Robin, B. Chevalier, B. Lépine, Mat. Sci. Engin., submitted (1990).