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SUPERCONDUCTING MATERIALS BY AEROGEL PROCESS

B. POMMIER, S.J. TEICHNER, P. LEJAY*, A. SULPICE* and R. TOURNIER*

*Université Claude Bernard, Lyon I, 43 bd du 11 novembre 1918, F-69622
Villeurbanne Cedex, France*

**C.R.T.B.T. (CNRS), 38 avenue des Martyrs, BP 166X, F-38042 Grenoble
Cedex, France*

Résumé - Lorsque les oxydes précurseurs du supraconducteur $YBa_2Cu_3O_{7-x}$ sont sous forme d'aérogel mixte ternaire et non pas d'un mélange mécanique conventionnel, la conversion en céramique supraconductrice, par chauffage sous oxygène, se produit beaucoup plus rapidement, sans l'apparition de la phase eutectique liquide.

Abstract - When oxide precursors of the superconductor $YBa_2Cu_3O_{7-x}$ are under the form of a ternary mixed aerogel and not as a conventional mechanical mixture, their conversion into the superconducting ceramics, by heating under oxygen, is produced much faster, without the formation of the liquid eutectic.

I - INTRODUCTION

The achievement of homogeneous mixing of reactant components in a precursor state to avoid conventional solid state reaction (undesirable) between large and chemically dissimilar particles is an important and fundamental problem in solid-state chemistry and in particular in the generation of high temperature superconducting solids which are formed by chemical interaction between three or more inorganic oxides.

The sol-gel approach in a solvent like water is used successfully to prepare small reactive particles (20 nm or less) of a given reactant (like Al_2O_3). This procedure is difficult to apply for obtaining a chemically homogeneous particle where two or more reactants are present. The aerogel process in an organic solvent for the preparation of mixed oxides /1/ allows to avoid solid state reaction between chemically dissimilar particles. Moreover, the aerogel process leads to amorphous oxides in a highly divided state. These two properties are those required for a high reactivity of the precursors in the dry solid state, at temperatures much lower than conventional firing temperatures used for crystallized precursors.

In the case of $YBa_2Cu_3O_{7-x}$ superconductor the initial precursor is obtained by controlled hydrolysis of organic derivatives of the corresponding elements, dissolved in methanol. The evacuation of methanol in supercritical conditions leads /2/ to a very homogeneous amorphous, highly divided solid, in the form of aerogel.

II - EXPERIMENTAL

1 - Materials

The aerogel containing the oxides of Y, Ba and Cu in the proportions given above is prepared according to the following procedure. In 60 g of methanol containing 9.82 g of ethylacetoacetate are introduced 7.53 g (3 x 0.012586 moles) of Copper(II) acetate monohydrate. After 48 h stirring the initial blue dispersion of powdered copper acetate is converted into a green dispersion of colloidal flakes. In 50 g of methanol, on the other hand, are dissolved 4.255 g (1 x 0.012586 moles) of Yttrium acetate tetrahydrate. Finally, in 85 g of methanol containing 1 g of water are introduced 6.43 g (2 x 0.012586 moles) of Barium acetate. This reactant is not entirely dissolved even after prolonged stirring. However by addition of the methanolic solution of Yttrium acetate a homogeneous solution is obtained. The methanolic dispersion obtained with Copper(II) acetate is now added to this solution of Yttrium and Barium acetates and the system is stirred for 48 h. A green homogeneous solution is then obtained containing the elements in the required proportions, i.e. $YBa_2Cu_3O_x$. This methanolic solution is introduced into an autoclave with an extra amount of methanol, in a

separate vessel, required to achieve the supercritical conditions during the heating. This amount of extra methanol depends on the volume of the autoclave. The autoclave is heated to 270-280°C (above the critical temperature of methanol) which takes 2-3 hours. The pressure is then of the order of 80-100 bars (above the critical pressure of methanol). This pressure is finally gently released (in about 1 hour) and the atmospheric pressure is established. A flow of dry nitrogen during 15 minutes, through the autoclave maintained at 270°C, removes the last traces of methanol. The temperature is then lowered to room temperature (in about 2 hours) and the autoclave is open. The aerogel obtained in this way as a homogeneous, low density powder ($S = 52 \text{ m}^2/\text{g}$), is amorphous to X-Rays with a few lines due to metallic copper (fig. 1).

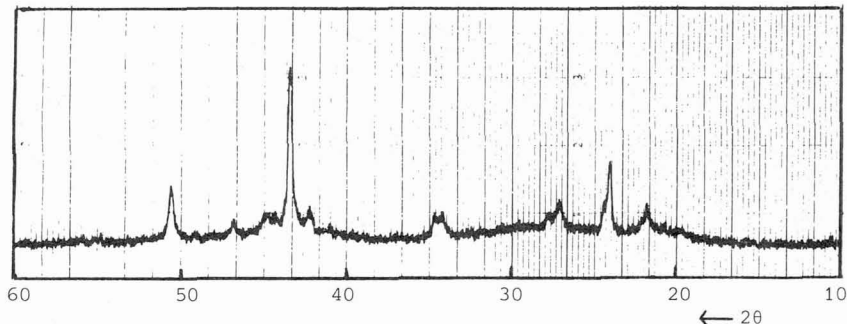


Fig. 1 - Cu K α diffraction pattern of the aerogel precursor.

This aerogel is converted into a crystalline compound of the composition $\text{Y Ba}_2 \text{Cu}_3 \text{O}_{7-x}$ following a procedure, established by the considerations given below. It is known that during the solid state reaction between conventional mixture of crystallized reactants it is formed in each grain a large range of various chemical compositions. The interaction kinetics is controlled by diffusion in the solid state. The various homogenizations between these compositions are also diffusion controlled. Moreover, in the ternary diagram $\text{Y O}_1.5\text{-BaO-CuO}$ an eutectic composition is observed around 900°C /3/, which is close to the nominal composition of the superconductor given previously, which corresponds to the so-called 1-2-3 formula. This liquid eutectic introduces the heterogeneity of composition in the system. The temperatures required for the interaction between the solid reactants should be therefore maintained below the temperature of the eutectic till the state of a perfect homogeneity of the material is achieved. In general, in this type of reactions the preheating requires 12-48 hours with intermediate grindings in order to achieve homogenization of the solid /4/.

In the opposite way, for the reactants in the aerogel form, the sub-micronic dimensions of the particles, their amorphous state and the initial homogeneity of the mixture allow the synthesis of the final solid without various preheatings and the kinetics of the interactions seems to be considerably increased.

The initial amorphous aerogel, of the composition $\text{Y Ba}_2 \text{Cu}_3 \text{O}_n$ starts to crystallize at 750°C. At 950°C, under pure oxygen, without any previous homogenization by preheating and grinding, it gives the final superconductor after 2 hours heating. The solid obtained corresponds to the required crystalline state (see below) with no traces of any undesirable phase, either in the original powder form or as a compressed pellet. It has been observed that the liquid (eutectic) phase is not formed during the heating at 950°C. This is probably due to the homogeneity of the initial material which allows a direct formation (by solid state diffusion) of the desired compound, without the separation of the eutectic. The well known interactions between the liquid eutectic and the material of the vessel are therefore minimized. The cooling is carried out under oxygen with the rate 20°/hour.

2 - Methods

The various physical methods employed in the investigations on superconductors are well described and are only briefly mentioned below.

III - RESULTS AND DISCUSSION

The final solid has the composition $\text{Y Ba}_2 \text{Cu}_3 \text{O}_{7-x}$ with orthorhombic symmetry ($a = 3.821 \text{ \AA}$; $b = 3.885 \text{ \AA}$; $c = 11.676 \text{ \AA}$) whose X-Rays diagram is given on Fig. 2. The splitting of the lines 013 and 103 around $2\theta = 33^\circ$ is characteristic of the formula given above. When x increases the symmetry changes from orthorhombic to quadratic and the splitting of the previous lines vanishes.

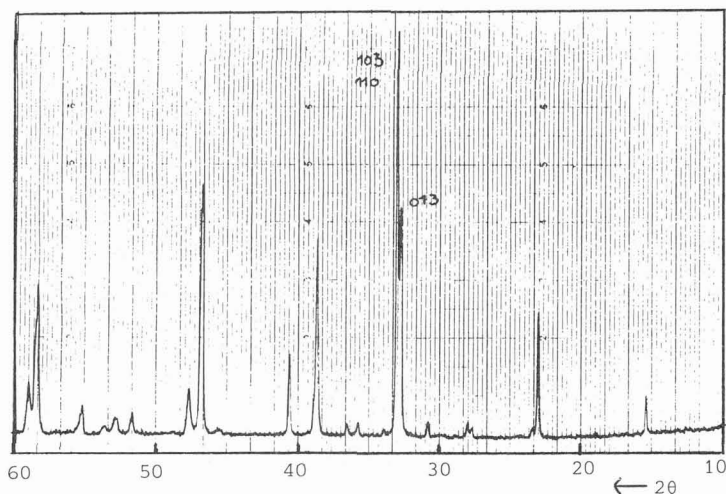


Fig. 2 - Cu $K\alpha$ pattern of the orthorhombic $YBa_2Cu_3O_{7-x}$ superconductor.

Magnetic measurements were performed on a rod cut from a compressed pellet. Figure 3 gives the variation of the magnetization with the magnetic field applied at 4 K. The diamagnetic susceptibility derived from this diagram is 1.43×10^{-2} uem/g. This value corresponds, after the correction of the coefficient of demagnetizing field, to a susceptibility $-1/4\pi$ which corresponds to a superconducting state of the whole sample (no undesirable phases present).

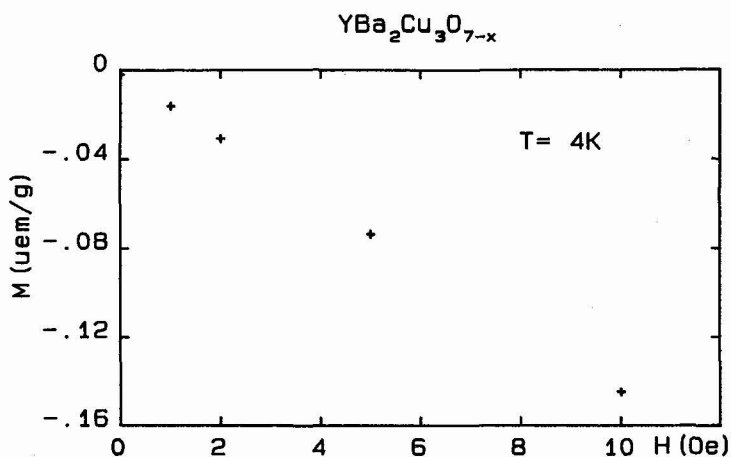


Fig. 3 - Magnetization versus magnetic field at 4 K.

Figure 4 represents the variation of the diamagnetic susceptibility with the temperature in the magnetic field of 10 Oe . Curve a (crosses) is obtained for the sample cooled in the absence of the magnetic field which is applied once the temperature of 4 K is obtained. The susceptibility is then recorded at increasing temperatures. A large screen effect is observed until 80 K and is followed by an abrupt transition achieved around 92 K. Curve b (squares) is obtained for the sample cooled in the magnetic field of 10 Oe . The susceptibility is therefore recorded for decreasing temperatures. The Meissner effect observed represents 10 % of the screen effect. This low value is characteristic of this type of high-pinning superconductors.

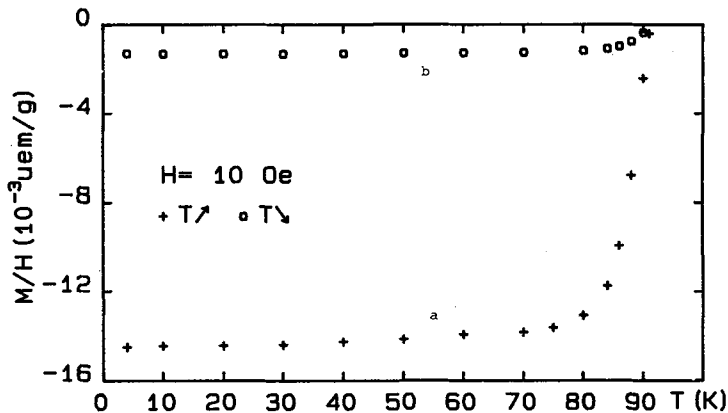


Fig. 4 - Diamagnetic susceptibility versus temperature.

The superconducting properties of the samples derived from the aerogel precursor are thus very comparable to those published earlier in the literature concerning the samples obtained by the conventional solid state reaction with crystallized precursors /5/. Critical current measurements under high magnetic field are now in progress.

IV - CONCLUSIONS

It has been shown that for the amorphous, highly divided, aerogel precursor, the kinetics of the solid state reaction under oxygen, giving orthorhombic $YBa_2Cu_3O_{7-x}$ as a very pure phase, is considerably increased and the parallel undesirable reactions are minimized. The superconducting properties of the samples derived by this method are comparable to those of samples produced by the conventional process involving crystallized precursors.

The sintered pellets of aerogel are bulk superconductors with an abrupt transition at 92 K, as determined by D.C. susceptibility measurements. The highly divided, powdered, aerogel precursor is a very suitable material for the production of very dense ceramics and thick films on certain substrates in order to improve the critical current density in the superconducting state at liquid nitrogen temperature.

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