

Synthesis of bulk and film $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ high-temperature superconductor by the sol–gel method

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Bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been prepared by the sol–gel method using metal alkoxide and metal acetate as precursors and ammonia or ethylenediamine as complexing agent. The temperature of the transformation of the gel precursor to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ depended on the type of precursor and the agent used for adjusting the pH. The gel synthesized from precursor alkoxide gives $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at lower temperature (750 °C for 6 h) than with acetate. The gel synthesized by different metal acetates and ammonia produces $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at a lower temperature than the sample prepared from acetate and ethylenediamine. From X-ray diffraction studies it appears that a relationship exists between the reactivity of the gel and the orientation of the corresponding pellet. The preliminary results from a film prepared by painting the gel on alumina and yttria-stabilized zirconia are presented. A high sintering temperature (940 °C for 1 h) was found to be necessary for obtaining superconductor film. The reactions between $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and supports were reduced by using silver as buffer. The T_{on} of the film prepared on the modified alumina support was 91 K and T_{off} was 78 K.

1. Introduction

The discovery of high transition temperature superconductors has triggered a huge amount of research in this area [1, 2]. The most studied ceramic material to date has been $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). This oxide can be synthesized from a mixture of barium carbonate, copper oxide and yttrium oxide. The reaction is slow and several calcination steps, separated by strong grinding, are necessary [3]. This procedure also leads to heterogeneous solids. The decomposition of barium carbonate seems to constitute the rate-limiting step, but calcination under vacuum does not seem to accelerate the process to any great extent [4]. Therefore, other synthesis procedures have been proposed, such as co-precipitation [5], freeze-drying [6], complexation [7], drying-decomposition [8] and the sol–gel method [9]. In the latter method, the one-step synthesis of homogeneous powders and even films is made possible via the formation of a polymeric gel [10–12].

Current density remains relatively low in bulk samples, thus limiting its uses for the moment [13]. For this reason, films are receiving increased attention. The general objective is to produce films exhibiting superconductivity at temperatures substantially exceeding 77 K, with current density of more than 10^4 A cm^{-2} . Several methods can be used for forming such films: chemical vapour deposition (CVD) [14], organo-metallic vapour deposition (OMCVD) [15], pulsed-laser deposition (PLD) [16] and spray pyro-

lysis [17]. In almost all attempts, for making these thin films, physical techniques have been used (CVD, in particular). For thick films, spray deposition with simultaneous pyrolysis on MgO and Al_2O_3 have been mentioned for its superconducting properties [18]. However, these methods require sophisticated equipment and films obtained with these techniques are likely to be costly.

For preparing these films, several substrates can be used: MgO , SrTiO_3 , yttrium-stabilized zirconia (YSZ), LaAlO_3 , Y_2BaCuO_5 , Al_2O_3 and various metals. To date, the best substrate seems to be SrTiO_3 . Even with thin films, this substrate does not react with YBCO at relatively high temperature, whatever the preparation method used. The film is oriented, and current density is higher than 10^5 A m^{-2} [19]. Unfortunately, SrTiO_3 seems too costly for practical applications and its high-loss dielectric constant makes it unsuitable for electronic applications.

Because of its low cost and low-loss dielectric constant, alumina, Al_2O_3 , would constitute an ideal substrate [20]. YSZ would also be acceptable [21]. Unfortunately, the use of Al_2O_3 has not been successful until now, probably, because it readily reacts with YBCO to give BaAl_2O_4 , Y_2O_3 and CuO .

Although, relatively, reactive supports are acceptable for thick films, the sol–gel method gave poor results. This might be attributed to the porosity of the film, the film itself, the film–substrate interaction and impurities such as residual BaCO_3 .

In this paper a simple and reproducible sol-gel procedure for obtaining bulk YBCO of good conducting properties is presented, using acetates or alkoxides as precursors. The results of powders and pellets obtained from these precursors are compared. Starting from the gel, it is possible to prepare partially oriented films on polycrystalline alumina or YSZ. The film is obtained by spreading the gel on the prepared substrate. The superconducting film obtained, after a high sintering temperature (940 °C, 1 h), is smooth and adheres to the substrate. The reaction with the substrate is diminished due to the formation of a transition layer composed of BaAl₂O₄ or BaZrO₃. Silver reduces barium diffusion and improves the electrical properties of YBCO.

2. Experimental procedure

2.1. Precursors and gel preparation

2.1.1. From acetates

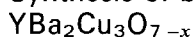
The synthesis procedure followed for precursor acetate is as reported elsewhere [22]. Yttrium, barium and copper acetates were supplied by Aldrich (99.99%). A 200 mM l⁻¹ solution of these elements (Y:Ba:Cu = 1:2:3) in acetic acid/water, 2.5:1, was prepared under agitation at 80 °C. Ammonia or ethylene diamine were used to adjust the pH to pH₀. The solutions were prepared with different initials pH₀: 2.16, 3.36, 4.47, 5.46 and 6.6 and the evolution of these pH values was recorded. The solutions were maintained at 80 °C for 16–24 h until viscous liquids were obtained due to slow evaporation. The transparent gels thus obtained contained a total concentration of 5 g at l⁻¹ metallic elements.

2.1.2. From alkoxides

Copper ethoxide, barium isopropoxide, yttrium isopropoxide were supplied by Alfa Products. Because copper ethoxide Cu(OC₂H₅) is not soluble in ordinary alcohols, the solvent used was a 10:1:2 mixture of isopropanol, acetic acid and water. It will be indicated in the Section 3 that this procedure results in considerable reduction in the reactivity of the alkoxide and thus allows the controlled preparation of a gel.

A solution containing a total of 456 mg at l⁻¹ metals was prepared (Y:Ba:Cu = 1:2:3). The pH, initially at 3.5, was adjusted to a value of 6 and maintained at this value during the whole reaction by addition of ammonia. This was necessary for avoiding segregation of the various constituents. The solution was maintained at 75 °C for 48 h. The final gel was green and viscous.

2.2. Synthesis of bulk and pelleted



The gels obtained from precursor acetate with an initial pH around 6 were compared with the gel obtained from precursor alkoxide.

The gels from both procedures were progressively dried by heating successively at 150, 200, and 250 °C, stirring magnetically. The drying procedure was con-

tinued until the viscous and homogeneous solution was transformed into a black solid. It was then transferred to an oven where it was decomposed at 300 °C for 4 h. The black powder obtained was subsequently calcined for 6 h at 750 or 940 °C in a tubular furnace under a flow of oxygen at 60 ml min⁻¹.

The calcined powders, from both precursors, were pelleted by pressing at 8 tf cm⁻² for 3 min. These pellets were then calcined at 940 °C for 6 h and annealed at 475 °C for 16 h under an oxygen atmosphere (60 ml min⁻¹).

2.3. Preparation of films

Alumina and yttrium-stabilized zirconia were both obtained from Degussa. The original plates were cut into pieces of 10 mm × 5 mm × 3 mm. They were cleaned with concentrated nitric acid and rinsed with acetone. The gel used in the synthesis of films was obtained from the acetate precursors.

2.3.1. Preparation of the film on unmodified support

Alumina and YSZ were heated to 150 °C and several layers of the gel were applied using a glass tube. The temperature was then increased to 250 °C and kept at this temperature for 8 h. This was followed by a calcination at 940 °C for 1 h in a tubular furnace in an oxygen atmosphere (60 ml min⁻¹).

2.3.2. Preparation of the film on modified substrate

Alumina and YSZ were modified by impregnation with a saturated solution of AgNO₃ which was subsequently evaporated by heating at 150 °C. The supports were then calcined at 200 °C for 12 h and several layers of the gel applied as before. The heat treatment allows silver to be produced by decomposition of silver nitrate. These painted supports were then dried at 250 °C for 8 h. This was followed by a calcination in two steps. The first calcination at 700 °C for 3 h produced a film with many cracks. These cracks could be eliminated by gently rubbing the surface of the film. Following this process the films were calcined again at 940 °C for 1 h and annealed at 475 °C for 12 h in an oxygen atmosphere.

Table I lists the supports and AgNO₃-modified supports used in this work.

2.4. Characterization techniques

The X-ray diffraction equipment consisted of a Siemens D-5000 diffractometer using CuK_α and scan of 1°2θ min⁻¹.

TABLE I Types of support

	Support	AgNO ₃	Rubbing
1	Al ₂ O ₃	No	No
2	Al ₂ O ₃	Yes	Yes
3	YSZ	No	No
4	YSZ	Yes	Yes

The measurement of particle size was made possible by a Coulter LS 130 using both laser light scattering and polarized intensity differential scattering. The latter provides the primary size information for particles in the 0.1–0.4 μm range and enhances the resolution of the particle size distributions up to 1 μm . A suspension was prepared by mixing the powder and the surfactant, sodium pyrophosphate, in water. This suspension was placed in an ultrasonic bath for 10 min. Before particle size analysis, the powders were calcined at 300 °C for 4 h.

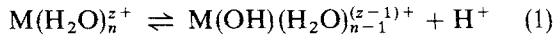
The electrical measurement was realized by the four-contacts method using silver electrodes.

3. Results and discussion

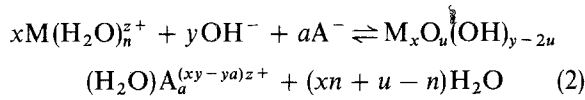
3.1. Gel synthesis

The acetate procedure is quite flexible with respect to pH. $\text{Cu}(\text{OH})_2$ and $\text{Y}(\text{OH})_3$ precipitate above pH 7 and 7.5, respectively. $\text{Ba}(\text{OH})_2$ is soluble in a wide range of pH. The only requirement is to start from a pH lower than 7. An increase of pH is observed during evaporation; but seems limited to a value lower than 7. The gellation rate increases with increase in pH. Table II reports the variation of the pH values after 4 h as a function of initial pH (pH_0) of the solution.

According to Pierre [23], the mechanism for gel formation with acetate precursors consists of two successive reactions.



This is followed by successive associations, leading to polymerization



where A^- represents the associated acetate. An increase of the pH value, by ammonia addition, favours the forward reaction in Equation 1. When the temperature is raised, the evaporation rate increases, leading to polymerization, Equation 2. Similar results are obtained with ethylenediamine.

In the case of alkoxide precursors, the mechanism proposed in the literature is as follows [23]

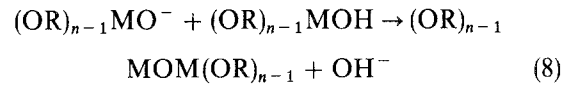
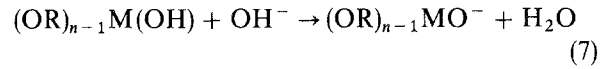


The presence of hydroxide ions facilitates the nucleophilic attack of the alkoxides. The following reactions were suggested by Gao *et al.* [20] in the case of silicate



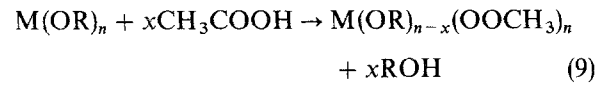
TABLE II pH after 4 h evaporation, as a function of initial pH

	pH_0				
	2.16	3.36	4.47	5.46	6.6
$\text{pH}_{4\text{h}}$	3.1	5.5	5.92	5.72	6.6



However, there is a tendency for the pH to decrease during gel synthesis. So it is necessary to add ammonia to keep the pH at a value of 6. A clear solution cannot be maintained at lower pHs. In fact, when the pH reaches a value of 5, colloidal particles appear in the solution. These particles solubilize with increasing pH. The effect of the hydroxyl is not only a catalytic effect, as shown by these equations, but must be also incorporated into the gel structure in order to explain the decrease in pH.

The use of acetic acid in the solvent mixture avoids the formation of a colloidal gel and promotes that of a polymeric gel in such way that there is no need to protect them with a perfectly dry atmosphere. The essential role of acetic acid is to diminish the hydrolysis rate, thus making the precipitation of hydroxides (principally $\text{Cu}(\text{OH})_2$ and $\text{Y}(\text{OH})_3$) more difficult. The explanation is probably that acetic acid forms a complex with alkoxides and that this complex is more difficult to hydrolyse.



This stable complex leads preferentially to partial hydrolysis and polymerization instead of to the total hydrolysis and segregation of different compounds.

3.2. Decomposition of the gel and formation of YBCO

Fig. 1 presents the X-ray diffraction (XRD) spectra of samples from both precursors calcined at 750 °C for 6 h. The spectrum of the sample obtained from the precursor alkoxide, Fig. 1a, shows all peaks of the orthorhombic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and small peaks attributed to BaCO_3 , CuO and Y_2O_3 . In Fig. 1b, corresponding to a sample obtained from acetate and ammonia, there is a mixture of YBCO and BaCO_3 , CuO and Y_2O_3 . For the sample obtained from acetate and ethylene diamine there is mainly a mixture of BaCO_3 , CuO , Y_2O_3 and very weak peaks corresponding to YBCO.

On comparing the line intensities of the different solids calcined at 750 °C, we may suppose that the alkoxide precursors give a more reactive gel, as indicated by the more developed YBCO XRD lines. Those prepared with the acetates and ammonia are less reactive. The use of ethylene diamine instead of ammonia, leads to the least reactive precursors. This behaviour could originate from the greater number of $\text{M}-\text{O}-\text{M}'$ bonds formed during hydrolysis of the alkoxide in addition to simple oxides (M and M' are the metallic cations). These bond formations reduce the synthesis temperature of YBCO by 200 °C compared to solid-state reaction. However, the presence of ethylene diamine in hydrolysis leads to the formation of

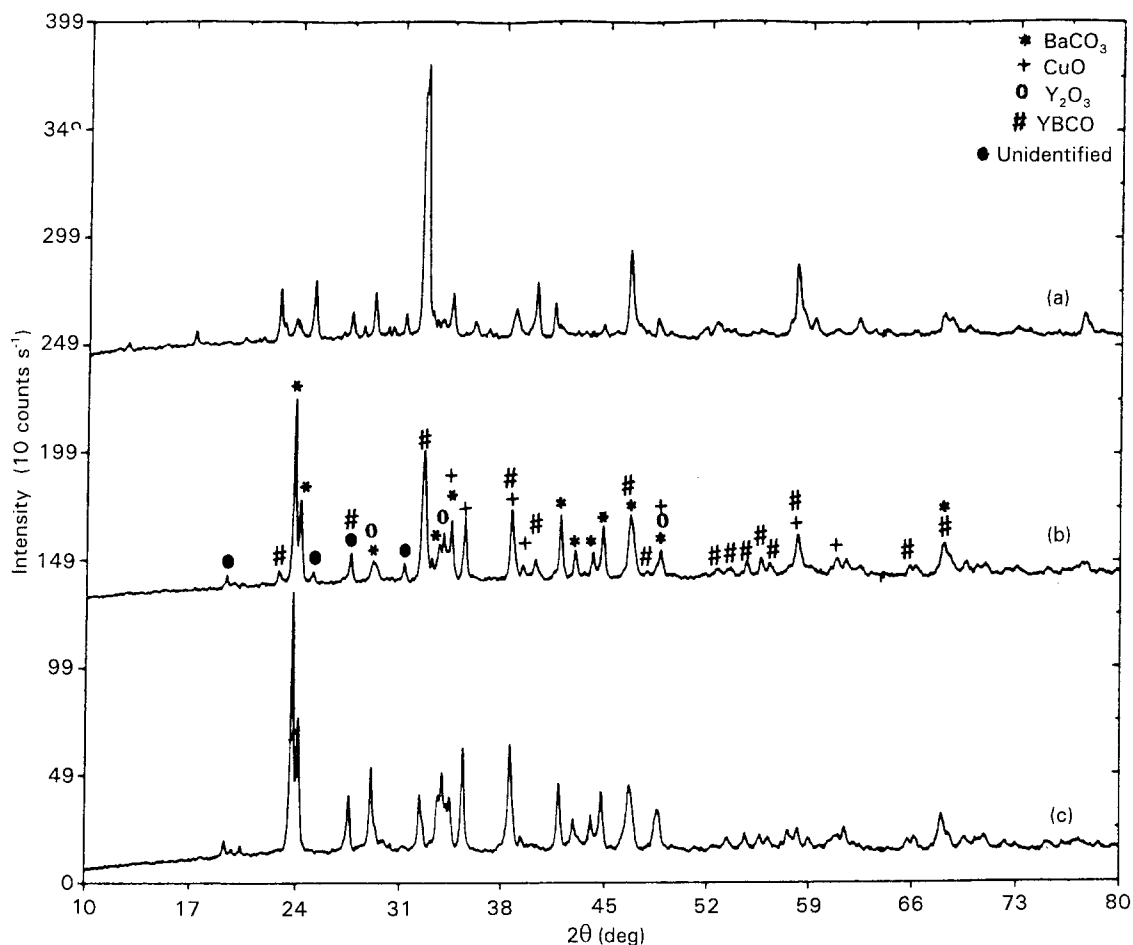


Figure 1 XRD spectra of powder prepared from precursor (a) alkoxide/ NH_3 , (b) Acetate NH_3 and (c) acetate/EDA and calcined at 750°C for 6 h.

many metal–nitrogen bonds— $\text{M}'\cdots\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—}_2\text{HN}\cdots\text{M}$ — and $\text{—M}\cdots\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2\cdots\text{M}$ —. These bonds are stable for hydrolysis and therefore lead to a less-reactive mixture compared to the $\text{M—O—M}'$ bonds formed during hydrolysis of alkoxide. In fact, by decomposition of the gel which was obtained by using precursor acetate and ethylene diamine, Y_2O_3 , CuO and BaCO_3 without any mixed oxides, was the principal mixture of components obtained.

The success of the method certainly rests on the fact that the Y_2O_3 , BaCO_3 and CuO are highly dispersed and intimately mixed, thus facilitating the formation of YBCO which takes place at 750°C and above. Therefore, the presence of barium carbonate in the solid mixture does not limit the synthesis of YBCO to higher temperatures as in solid-state reactions.

It was reported that the reactivity in the mixture oxides is related to particle size of different compounds [24]. The analysis of particle size is presented in Fig. 2. The curves represent the distribution of the cumulative inferior number of the particles. Almost 99% of the particles, prepared using alkoxide, exhibited a size less than $1\ \mu\text{m}$, compared to a particle size of less than $2\ \mu\text{m}$ for samples prepared with acetate and ethylene diamine. These measurements show that both preparations produce submicrometre particles. This difference of particle size is not high enough to explain the reactivity of different precursors. The

measurements also show that both samples prepared have good dispersity.

3.3. Study of the pellets

Fig. 3 presents the XRD spectra of pellets from different precursors. There is no difference observed be-

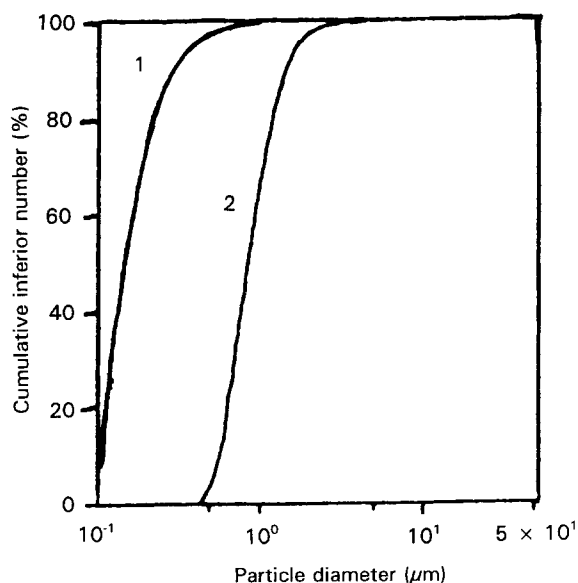


Figure 2 Cumulative inferior number of particle size of gel powder precursor (a) alkoxide and (b) acetate/EDA, both calcined at 300°C .

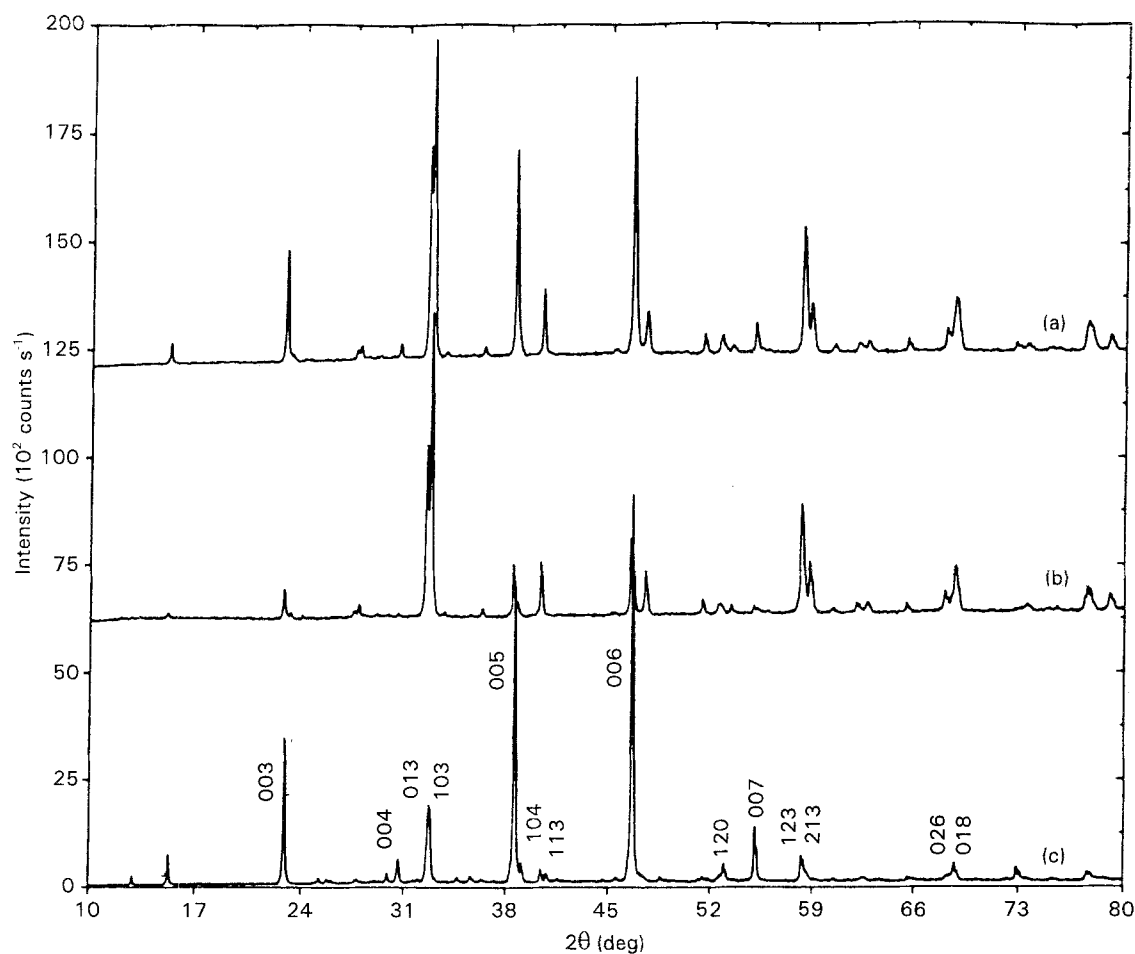


Figure 3 XRD spectra of pellets calcined at 940°C for 6 h and annealed at 475°C for 16 h. (a) Acetate/EDA, (b) acetate/NH₃ and (c) alkoxide/NH₃.

tween the XRD spectra of powder and pelleted samples obtained from acetate precursor and EDA (Fig. 3a). Meanwhile, the XRD spectra of pellets synthesized from both acetate (Fig. 3b) and alkoxide precursors (Fig. 3c) with ammonia, exhibit a (001) plane of greater intensity compared to that of the powder spectra suggesting partial orientation of the oxide particles. The pellets from alkoxide preparation have a (001) plane intensity higher than that of the pellets prepared with acetate and ammonia. The results can be summarized as follows:

pellets from acetate/EDA → no orientation

pellets from acetate/ammonia → partially oriented

pellets from alkoxide/ammonia → highly oriented.

The difference in reactivity and orientation of the prepared samples originates from the kind of gel formed by hydrolysis. In fact, there seems to be a relationship between reactivity of gels and the level of orientation, i.e. YBCO prepared from alkoxide is the most reactive and finally, highly oriented. The sintering of YBCO prepared from precursor alkoxide leads to more aligned particles.

The electrical properties of pelleted YBCO prepared via the sol-gel method are always criticized because of their low critical temperature, compared with pellets from solid-state reaction. Fig. 4 shows the change in resistance with temperature for a typical

pellet. Above the critical temperature the sample exhibits a metallic behaviour. At 93 K the sample begins the transition to the superconductor state. The T_{zero} temperature is 90 K and the difference between the onset and the end of the transition is 1 K. This means that the sample has a high level of purity and oxidation [10, 25].

The results of this section can be summarized as follows.

1. This sol-gel method produces submicrometre particles.

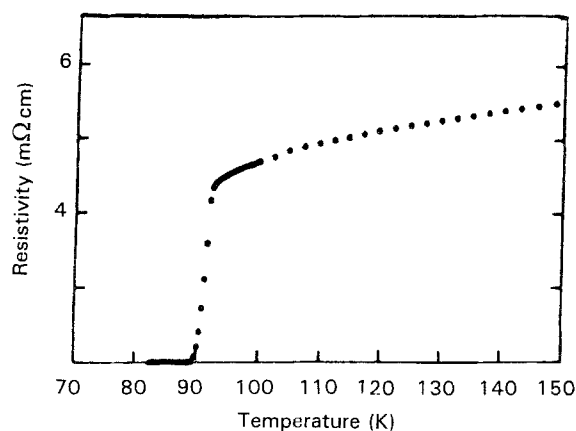


Figure 4 Electrical measurement of a pellet calcined at 940°C and annealed at 475°C for 16 h.

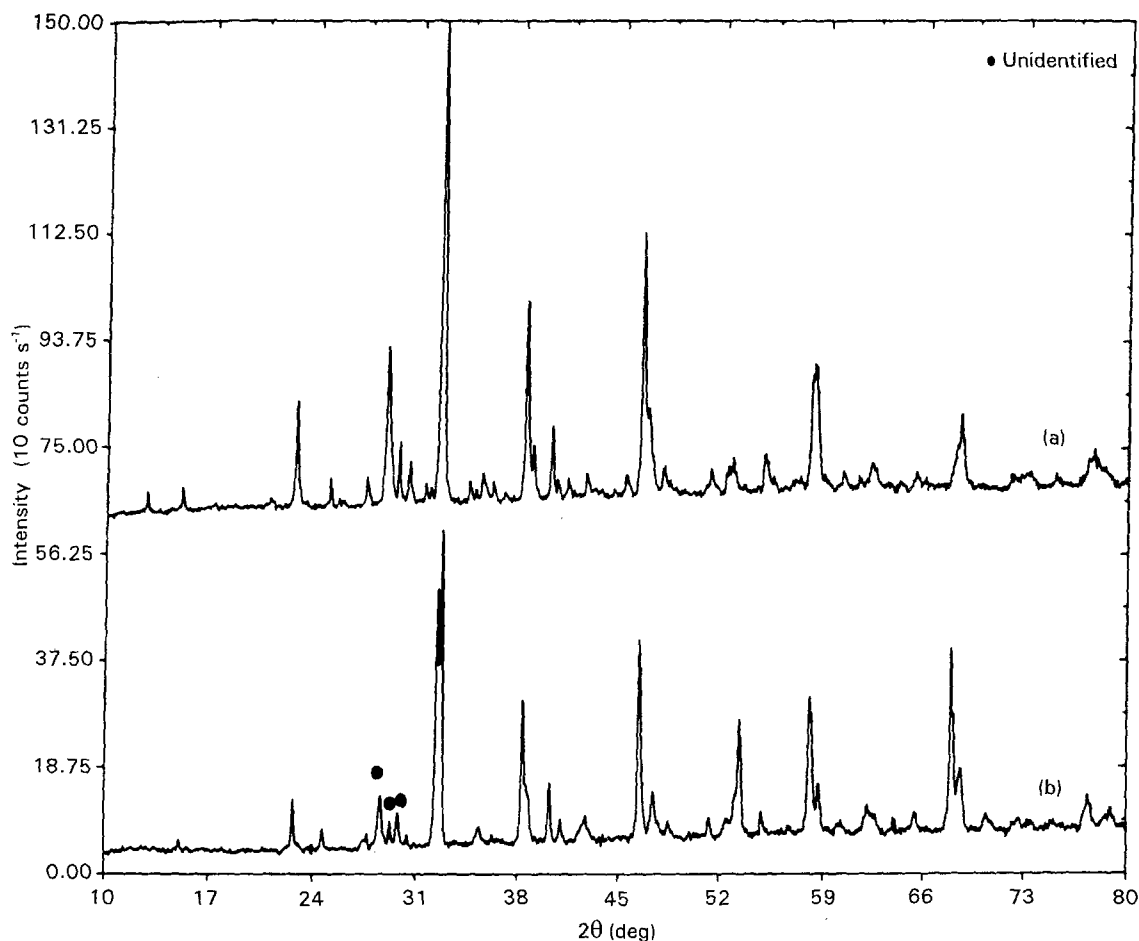


Figure 5 XRD spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film on (a) alumina and (b) YSZ supports, calcined at 940°C for 1 h.

2. The powder precursors are submicrometre sized particles.

3. The reactivity of a gel for obtaining the YBCO depends on both the precursor and the base for adjusting the pH.

4. The orientation of pellets, detected by XRD measurement, is sensitive to synthesis conditions.

5. The pellet has good electrical properties, T_{zero} is 90 K.

3.4. Films

3.4.1. Synthesis of film

Fig. 5 presents the XRD spectra for the film supported on (a) alumina and (b) yttria-stabilized zirconia. It can be seen that the intensities of the (001) lines are higher than those of the powder spectra, indicating that these films are partially oriented. This sol-gel method produces a film without barium carbonate after calcination at 940°C for 1 h even without using an NO_x or ozone atmosphere during calcination. In fact, it was reported that the barium carbonate is present during the synthesis of the film by the sol-gel method [26, 27]. Fig. 6 shows the spectra of the films prepared on modified supports (a) alumina and (b) YSZ. In this figure only the lines of the orthorhombic structure of YBCO can be observed, with some traces of an unidentified phase. There is no preferential orientation of the particles observed by XRD.

This result demonstrates that it is possible to synthesize the film on polycrystalline alumina substrate by the sol-gel method, even if the reactivity of YBCO with this substrate is high. The film formation is controlled by the temperature, time of calcination and thickness of the film. The XRD spectra do not reveal other crystalline impurities in the films. The adhesion of YBCO film on the alumina and YSZ proceeds as follows [28, 29]

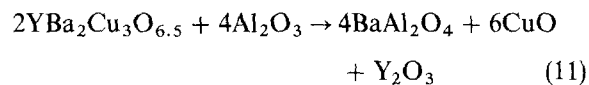
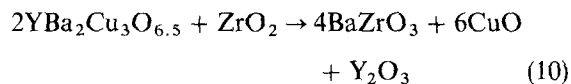


Table III summarizes the resistance at 300 K and T_{on} , in addition to T_{off} for the different films. It can be observed that the film supported on alumina has more resistance than the film prepared on YSZ. This table

TABLE III Resistance at room temperature of different films, beginning and end of transition, T_{on} and T_{off}

Number	Support	$R_{300\text{K}}$ (%)	T_{on} (K)	T_{off} (K)
1	Al_2O_3	190	—	—
2	$\text{Al}_2\text{O}_3/\text{Ag}$	22	91	78
3	YSZ	35	90	—
4	YSZ/Ag	0.1	91	80

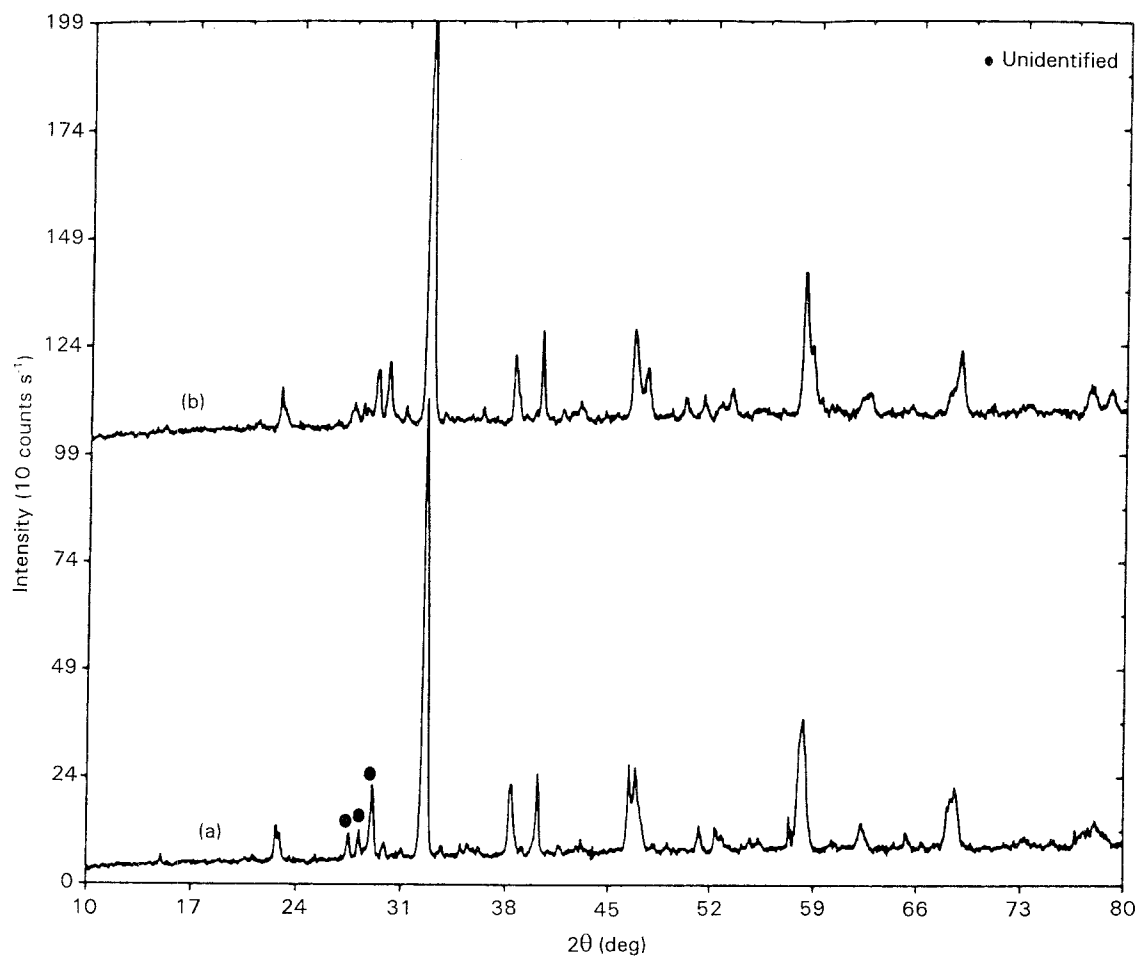


Figure 6 XRD spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film on modified support (a) alumina and (b) YSZ.

also shows the beneficial effect of AgNO_3 impregnation. This impregnation considerably reduces the resistance of the film at room temperature. Actually, AgNO_3 decomposes at high temperature into silver metal and becomes a buffer between the support and the film, thus reducing their interaction. So the silver improves the properties of alumina as a support for YBCO film.

Fig. 7 displays the change in electrical resistance with temperature for the film obtained with and without AgNO_3 . Fig. 7a and b give the electrical measurement of the film prepared on alumina and YSZ, respectively. The resistance at room temperature is high, especially in the case of the alumina support. These films were prepared without any rubbing of the surface. In fact, during the first step of drying and calcination of the gel, there is elimination of organic material. The departure of this volatile material leads to the formation of cracks and porous films. Then, rubbing of the surface of the film is necessary. This allows removal of the cracks and improvement of the contacts between the grains.

The presence of cracks and weak links between grains led to highly resistive films during the electrical measurement (Fig. 7a and b).

Fig. 7c and d exhibit the electrical measurement of the film prepared on alumina and YSZ support modified by silver. The positive effect of rubbing, in addition to silver, is clearly demonstrated. The resistances at room temperature of both films have drastically

decreased, 22 and 0.1Ω for the film prepared on alumina and YSZ modified support, respectively. For the film prepared on YSZ support the electrical resistance starts to decrease linearly when the temperature decreases until 91 K. The transition to superconducting state is observed (Fig. 7d).

For the film prepared on modified alumina support (Fig. 7c) the electrical resistance starts to increase slowly during the decrease in temperature until 230 K. From this temperature, the resistance is constant even when the temperature decreases. At 91 K the transition to the superconducting state is started. The end of the transition is recorded at 78 K.

The films on the modified supports have similar behaviour and T_{on} at 91 K than that of the pelleted sample. This suggests that the film is composed of superconducting particles connected together. The films prepared on non-modified supports exhibit a semiconductor effect during the decrease in temperature. These samples start the transition at 90 K but they cannot reach the superconductor state.

It can be concluded from this part that, for the first time, by painting, alumina can be used as a substrate in the synthesis of superconductor films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with low resistance by the sol-gel method, especially when silver is used as a buffer on the surface of the support.

4. Conclusions

1. The use of acetic acid during the preparation

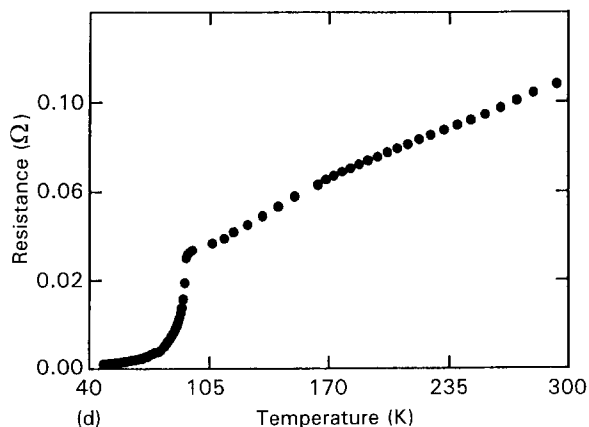
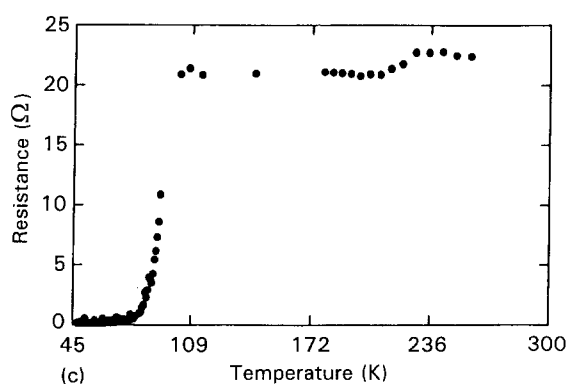
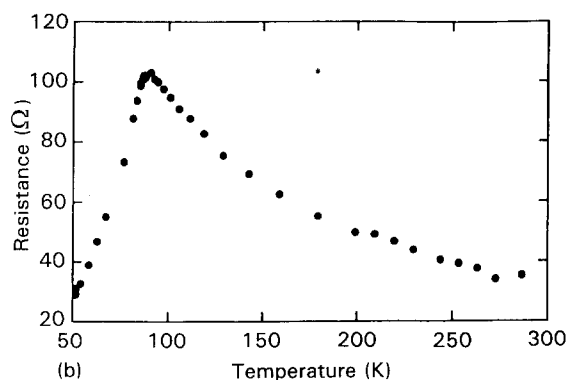
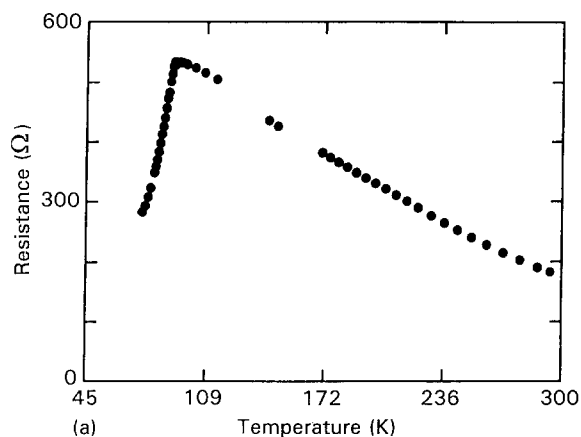


Figure 7 Electrical measurement of the films on (a) alumina and (b) YSZ, both without silver, and (c) alumina and (d) YSZ, with silver.

increases the solubilities and the stabilities of the precursors, especially the alkoxide, in the solution.

2. The particle size obtained by this preparation method is submicrometre.

3. The alkoxide precursors lead to highly reactive gels at 750 °C compared to acetate precursors.

4. The reactivity of the precursor depends not only on the kind of precursor but also on the pH adjuster during the preparation.

5. The orientation, detected by XRD, of pellets depends on the precursors and the synthesis conditions.

6. The preparation of the film by the sol-gel method on the alumina substrate is successful. The film obtained is partially oriented. Furthermore, the resistance at room temperature is low and T_{on} and T_{off} are 91 and 78 K, respectively. However, research must be continued to reduce further the range of transition temperature and to improve the orientation.

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