

Preparation of Submicron YBaCuO Powder by Sol-gel Method

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Abstract

The submicron $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder was prepared by the sol-gel method. The particle size is distributed from 0.2 to 1.0 μm , which benefits to eliminate the micro-cracks formed in the $\text{YBa}_2\text{Cu}_3\text{O}_x$ films deposited by electrophoresis. The powder was single phase of $\text{YBa}_2\text{Cu}_3\text{O}_x$ examined by X-ray diffraction. In the sol-gel process the citrate gel was formed from citric acid and nitrate solution of Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ and CuO . When pH values were adjusted to 6.4~6.7, $\text{Ba}(\text{NO}_3)_2$ could be dissolved in the citrate solution completely. Appropriate evaporative temperature of the sol-gel formation is discussed. After the heat treatment the transition temperature(T_c) and critical current density(J_c) of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples made of the submicron powder were measured.

Key Words : YBaCuO powder, sol-gel method, particle size, composition

1. Introduction

Sol-gel method is a very useful way to produce inorganic powder for the material preparations[1-3]. The method has been successfully applied for coatings of glass and oxides as well as powders of function ceramics, especially for the composite oxides and high T_c superconducting materials which is difficult to be synthesized by the conventional methods [4-7]. The sol-gel method uses the liquid chemical agents or dissolves the powders in the solvent, therefore the chemical reactions carry out in homogenous liquid phase. The products are stable gelatinoids without depositions. The method has following advantages:

- (1) The products have high homogeneity in atomic or molecular dimension, especially for the multi-components products;
- (2) The products have high purity. It does not introduce the impurities as in the solid state reaction process in which impurities are lead in from grinding and CO_2 and moisture from ambient;

- (3) The particle size of sol-gel powder is less than 1 μm , nanometer size particles can be reached, if the solution is improved;
- (4) The fine particles have large surface area and do not need diffusive reaction, therefore the sintering temperature is about 100°C lower than the conventional solid sintering.

In the experiment electrophoresis is used for deposition of YBaCuO film on the Ag substrate. It was found that when the conventional sintering powder was used, the micro-cracks appeared in the film due to the big particle size[8]. The surface of the film would be smooth and less crack with decreasing particle size. To make small particle size ($< 1 \mu\text{m}$) of YBaCuO powder is the main purposes of the experiment. After the improvement of the sol-gel process it results in that the particle sizes distribute 0.2~1.0 μm ; the powders are single phase of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and 91K zero resistance super-conductor after post oxygenation; the processing time is shortened.

2. Experiment

The YBaCuO sub-micrometer powder is prepared by sol-gel method. The chemicals Y_2O_3 , $Ba(NO_3)_2$ and CuO , which have the metal atoms ratio of $Y : Ba : Cu = 1 : 2 : 3$, are dissolved in hot nitric acid. Ammonia is used for adjusting the pH to a appropriate value on which $Ba(NO_3)_2$ could dissolve completely. When the solution is added to citric acid, H_3Cit (or $C_6H_8O_7$), the mixed solution becomes blue color. After drying at $90^\circ C$, the solution is concentrates and dark blue. When the dry gel is put in Muff furnace at $300^\circ C$ the solvent evaporates, the gel expands, and after a certain time the dry gel will be spontaneous combustion. The product is black grey powder. The powder is pressed to pellets and sintered at $880^\circ C$ for 3 hours, and then cooled to $400^\circ C$ for oxygenation for 10 hours, the pellets become superconductive.

3. Results and Discussions

3.1 The formation process of the Sol-gel

When $Ba(NO_3)_2$ is solved in the citric acid, Ba^{2+} joins with H_2Cit^- to form BaH_2Cit^+ , which is not stable. If pH is lower or some solvent evaporate Ba^+ will separate out from the solution as $Ba(NO_3)_2$, white deposition. Ammonia, $NH_3 \cdot H_2O$ is used to adjust the pH values. When pH is over 6.5 the white deposition disappears, and the solution become blue transparent solution. In the experiment pH value of 6.4~6.7 is suitable. The citrate solution is put in dry oven at $90^\circ C$, the volume of solution reduces with the drying time and the solution become viscous. After several hours drying the solution become dark blue, some dry gel appears gradually. Because of the low temperature it will take a week if the whole wet gel transfers to dry gel. At lower drying temperature some of ammonia can evaporate, and the pH value of the solution reduces, which causes the white $Ba(NO_3)_2$ to deposit. In order to reduce the transferring time from wet gel to dry gel the drying temperature is increased to accelerate the

evaporation of the solvent.

In table 1 the differences of the sol-gel formation with various temperatures are shown. It was found than the spontaneous combustion of the gel happened at $200^\circ C \sim 250^\circ C$. The product of burning is black grey ash in honeycomb shape. In the experiment $300^\circ C$ is used for the drying temperature, at that temperature expanded volume is not large and the combustion starts fast and the ash after burning is easy to be collected.

Table 1. Differences of the sol-gel formation with various temperatures.

drying temp.	drying time(h)	sol-gel formation
$100^\circ C$	12	white crystal deposition
$200^\circ C$	6~7	white crystal deposition
$250^\circ C$	4~5	blue gel transparent
$300^\circ C$	2~3	blue gel transparent

3.2 Composition of the sol-gel product

The X-ray diffraction pattern of the black grey ash after combustion is shown in figure 1.

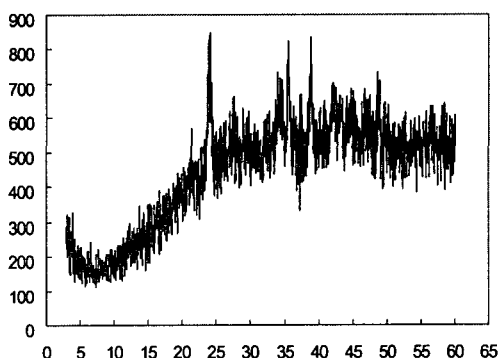


Fig. 1. The X-ray diffraction of combustion ash from YBaCuO sol-gel.

XRD presents the powder is an amorphous mixture which may include Y_2O_3 , BaO , CuO and some $Ba(NO_3)_2$ undecomposed. In the heat treatment at $600^\circ C$ the powder would eliminate

some organic remains and its volume may slightly expand. After grounding the powder was pressed into pellets and sintered at 880°C under oxygen flow. The XRD of the sintered sample is shown in figure 2, in which all diffraction peaks are from $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystal planes and the impurity phases did not present. Therefore the single phase of $\text{YBa}_2\text{Cu}_3\text{O}_x$ can be concluded for the sol-gel powder.

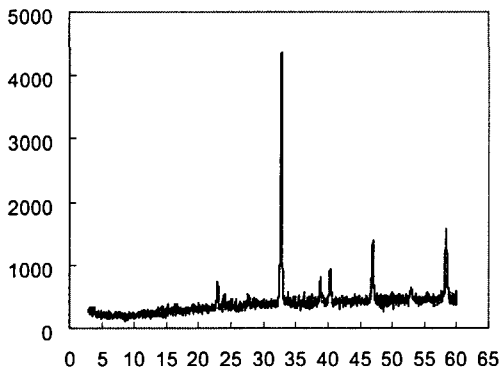


Fig. 2. The X-ray diffraction of YBaCuO powder made by sol-gel, and after sintering at 880°C under oxygen flow.

3.3 The particle size of YBaCuO powder made by sol-gel

The separating technique is very important in the measurement of particle size.

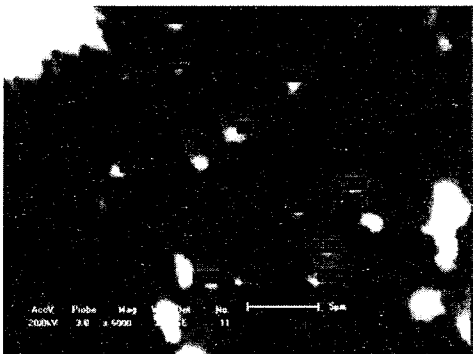


Fig. 3. The SEM picture of YBaCuO superconductor powder.

Figure 3 is the Scanning Electron Microscopy (SEM) picture of sol-gel YBaCuO powder, in which the particles were separated by alcohol.

The particle sizes are in 0.2~1.0 μm. It was found that the ratio of citric acid would affect the particle size, the more citric acid quantity, the less particle size of the sol-gel powder.

3.4 The superconductivity of YBaCuO powder made by sol-gel

The sol-gel powder was pressed into 60 mm × 5mm × 0.5 mm rectangle sample, and the sample was sintered at 900°C for about 5 hours. After sintering the temperature was reduced to 400°C to carry out the oxygenation in oxygen flow for 10 hours. The superconductivities (T_c and J_c) were measured by standard four line method, the results were shown in table 2.

Table 2. The superconductivities of sintered YBaCuO sol-gel powder.

samples	T_c (K)	J_c (A/cm ²)
6#	89	0.26
9#		5.11
10#		28.96
12#	91	11.93
13#	93	5.95

Because the size of the sol-gel particle is very small, in the sample the grain boundaries are much more than that in solid sintering ones, which are the obstacles of superconductivities. Therefore the superconducting samples are random in the sintered samples of sol-gel powder. In order to transfer the sol-gel powder to superconducting material, the post heat treatment needs to be study in detail.

3.5 Electrophoretic Deposition Using Sol-gel $\text{YBa}_2\text{Cu}_3\text{O}_x$ Powder

In the test, the sol-gel submicron $\text{YBa}_2\text{Cu}_3\text{O}_x$ powder was used in electrophoretic deposition. In order to make a comparison of the particle size

effect on the surface state of deposited thick film, the conventional solid sintering powder was applied to deposit $\text{YBa}_2\text{Cu}_3\text{O}_x$ film in the same electroporetic condition. By the observation of optical microscopy it is found that the film deposited from sintering powders, particle size of which was less than $40 \mu\text{m}$, was easy to create the cracks in the film and the adherence of the film on the substrate was poor after the heat treatment. In contrast, the film deposited from the sol-gel submicron powder has smooth surface and strong adherence on the substrate

4. Conclusions

From the study of sol-gel process the advantages of sol-gel powder of YBaCuO can be presented: (1) The sol-gel powder is single phase $\text{YBa}_2\text{Cu}_3\text{O}_x$ compound, the impurity phase can not be seen in the XRD patterns; (2) The sol-gel YBaCuO powder has lower sintering temperature (880°C) in comparing with solid state sintering temperature (950°C); (3) The small particle size (sub-micrometer) can be prepared by sol-gel method. In the experiment pH values from 6.4~6.7 are suitable for $\text{Ba}(\text{NO}_3)_2$ solved in citric acid completely, if $\text{pH} < 6.4$, $\text{Ba}(\text{NO}_3)_2$ will separate out as white crystals. After the 880°C heat treatment and 400°C oxygenation the sol-gel powders are 90K superconductors.

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