

Barium titanate doping on superconducting perovskite YBCO

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Abstract

This paper reports a newly developed sol-gel process to synthesize dense YBCO thick films with BaTiO_3 additives using electrophoretic deposition and metal alkoxide sol/particle suspension, which we successfully produce dense YBCO+ BaTiO_3 ceramics at a rather low temperature, compared with the sintering temperature used in conventional methods. The thick films of HTS were prepared by electrophoretic deposition, using pre-sintered powder with barium titanate addition in the form of $\text{BaTi}(\text{OR})_6$ solution in suspension for electrophoresis. The conditions for applied voltage and deposition times for electrophoretic deposition of HTS thick films were studied in detail.

Keywords : perovskite, addition, thick film, HTS

1. Introduction

There have been many investigations in an attempt to fabricate dense HTS films by electrophoresis. Most of the investigations placed their aim mainly on the preparation of monodispersed powders and high stability of organic suspension, and film processing to obtain green compacts with as high a density as possible. On the other hand, there have been few studies that dealt with powderless processing to obtain dense perovskite ABO_3 ceramics or films from monolithic gels. In general, it has been recognized that starting with alkoxide derived powders offers greater advantages for the preparation of ABO_3 ceramics than starting with monolithic gels, since monolithic gels show a relatively slow densification behavior with sintering temperature due to their inherent large porosity [1-2].

Many ceramic system are sintered with the aid of liquid-forming additives, and it is important for the densification properties and the final sintered microstructure that these sintering additives are

blended with the major component particles as homogeneously as possible. In most of these methods, the additives are supposed to coat the particle surfaces. The chemical techniques can be divided into two chief groups. In the first group, the coating is applied by hydroxide precipitation techniques from inorganic salts in aqueous solutions, in the second group, the coating process is based on metal alkoxides in nonaqueous solvents [3].

We have developed an electrophoretic deposition method to prepare a variety of oxide coatings, such as YBCO [4-5]. BaTiO_3 [6-7] on various substrates of different shapes. These oxide coatings showed excellent physical properties, i.e., superconductivity or ferro-electricity. The advantages of this method include: 1) obtaining a uniform and dense coatings, 2) controlling easily the coating thickness by the deposition voltage and deposition time, 3) obtaining various shape and size coatings on various substrates. In the case of YBCO good superconductor coatings were obtained from the acetone bath. Other worker have also investigated this method [8-9].

The goal of the present work was to investigate techniques for preparing superconducting films. This paper reports a newly developed sol-gel process to synthesize dense YBCO thick films with BaTiO_3

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additives using electrophoretic deposition and metal alkoxide sol/particle suspension, which we successfully produce dense YBCO+BaTiO₃ ceramics at a rather low temperature, compared with the sintering temperature used in conventional methods. We used small (10–20nm) colloidal sol particles which electrostatically adsorbed on the submicrometer YBCO particles. This technique has several advantages: it is simple, is conducted in organic solvent, and, at a certain amount of sol added, the sol particles have a stabilizing effect on the slip. Colloidal suspension rheology is influenced by many well-known factors such as surface chemistry, concentration, size, and shape of the suspended particles. The sol-gel precursor solution chemistry, aggregation mechanisms, and gel structure obtained by the present procedure have been discussed in great detail in [6–7], and our particular interest here is to investigate the correlation between processing, microstructure, and crystallographic orientation.

2. Experimental Procedure

A schematic diagram of the sol-gel synthesis of thin films can be divided into three steps: precursor solution synthesis, deposition of this solution on a substrate, drying and pyrolysis to form the final HTS film.

The raw materials used were quite simple and commercially available. Equimolar amounts of barium ethoxide (Ba(OC₂H₅)₂, High Purity Chemicals Laboratory, Osaka, Japan, purity > 99 %) and titanium isopropoxide (Ti - iso(OC₃H₇)₄, High Purity Chemicals Laboratory, purity > 99.999 %) were dissolved in a mixed solvent of dehydrated isopropanol (iso-C₃H₇OH) at room temperature with stirring for 48h. (This mixture of the alkoxides is referred to hereafter as Ba, Ti alkoxide). The synthesis process of Ba, Ti alkoxide precursor solutions was performed in a dry nitrogen atmosphere. CO₂ - free distilled water (molar ratio H₂O:Ba=1:1) was added by spraying into the alkoxide precursor solution to hydrolyze with stirring at room temperature. Finally, the hydrolyzed solution (colloidal sol of Ba-Ti) was added to the YBCO particle iso-butanol, ethanol suspension. All suspensions were prepared by sonication using a Branson sonifer B-30. The sol contained colloidal particles with diameters of 10–20 nm. The concentration of BaTiO₃ was from 1.0 to 9.0 wt.% of the YBCO suspension. The high-purity textured YBCO powder had a median diameter of 2–3 μm.

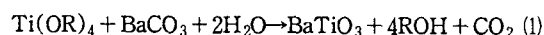
Coating were produced by electrophoretic deposition on Ag wire. The substrate after being ultrasonically

cleaned in acetone (or cleaned by ultrasonication in a 0.1 M solution of HCl for 5 min, followed by the same treatment in distilled water and then in acetone), were kept parallel to the anode (in the form of a cylinder or plate, depending on the shape of the substrate) with a separation distance of 1 cm. A constant DC voltage density ranging from 100 to 200V/cm was applied across the electrodes for a coating time between 0.25 to 3.00 min. Once a coating was applied, the sample was withdrawn from the suspension at a rate 0.5 cm/s. After wet thick films were dried at room temperature during 2–5h and at 90°C during 1h. The films were then fired at 1~10°C/min up to 600°C~900°C for 10min~10h in air. The formation of BaTiO₃ nanocrystals in the dry films was confirmed by X-ray diffraction (XRD) analysis. Microstructural developments of the films were studied by scanning electron microscopy (FE-SEM, JEOL, JSM-840 F).

3. Results and Discussion

Thermal analysis in air the electrophoresis derived films was resulted in four different decomposition steps: (1) evaporation of the solvent below 150°C, (2) removal of the alcohol group from the alkoxide compound from 250 to 300°C, (3) decomposition of some organic residues around 600°C, and (4) decomposition of BaCO₃ around 750°C.

The small amount of material involved in thin films makes it difficult to obtain good-quality XRD spectra, so the crystallization of films was first studied using samples in the form of powders. These powders were synthesized by pyrolyzing a dried gel, obtained by hydrolysis of the precursor solution, at 500, 700, 800, and 900°C in oxygen. The sample fired at 500°C is amorphous. At 700°C it has started to crystallize. All of the peaks can be attributed to the YBCO-123 phase. The fact that the spectrum of the sample pyrolyzed at 900°C for 10h exhibits only YBCO peaks suggests that no phase degradation is taking place even for prolonged firing time. The film crystallization takes places by the following mechanism:



The crystallization of the films was studied by the electrophoretic deposition on Ag substrates and firing them at 600, 700, 800, 900°C for 5min and performing XRD and SEM analysis on these films. At 600°C, SEM shows no evidence of grain boundaries and the corresponding XRD spectrum exhibits only

two broad peaks from substrate. At 700°C, the film processes a grainy microstructure showing that the crystallization took place between 600 and 700°C. This is confirmed by the XRD spectra which reveal the presence of some peaks. As the temperature increases to 800 and 900°C, the average grain size increases from approximately 0.05 μ m (at 700°C) to 0.1 μ m (at 800°C) and 0.3 μ m (at 900°C). At 800 and 900°C, the XRD spectra exhibit more peaks with bigger intensities than at 700°C. Because of the low signal-to-noise ratio caused by the small quantity of film diffracting, it is difficult to know whether the crystallization is still taking place above 700°C or only grain growth. The appearance of new diffraction peaks, normally attributed to crystallization, could be explained in the present case by the increase in all the peak intensities, as a result of grain growth, which makes some peaks emerge from the noise.



Fig.1. An example of YBCO suspended grain coated with BaTiO₃.

After pyrolysis of a mixture of YBCO and BaTi(OR)₆ powders the powder surface was coated with an Ba, Ti, C containing material. In the present case BaTi(OR)₆ sol-particles were suspended in a YBCO/alcohol suspension. It was expected that after the evaporation of the alcohol solvent the metal alkoxide will be deposited on the surface of the YBCO particles. Pyrolyzing at 900°C leads to the formation of BaTiO₃/YBCO layer and pin-hole structure.

Fig. 2 gives a dramatic indication of how the liquid forms and helps to densify a compact. It is obvious from the photographs that a liquid phase is present even at the lowest sintering temperature (950°C). The uneven level of the liquid phase at the lower temperatures and the residual porosity show that the fluid was quite viscous. Some minute residual pores can also be seen at the highest sintering temperature. This is not surprising considering that the liquid phase is likely to be very rich in carbide forming elements such as Ti and Ba. This also means that the larger the pores the more difficulty there will be in filling them completely. The appearance of the particles in relation to the liquid phase suggests that the liquid phase is formed through a general

melting of the surface layers analogous to the melting of an ice cream cone. There is no indication of any surface feature that show fragmentation along grain boundaries within individual particles as has been speculated in literature [10]. Our observation [7] supports the prevailing viewpoint that full density sintering of barium titanate thin films through formation of liquid phase.

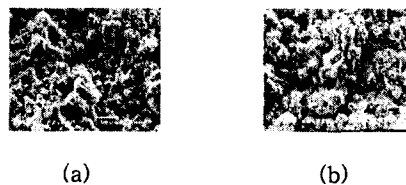


Fig.2. SEM micrographs of (YBCO+BaTiO₃) films with melted structures : (a) YBCO + iso-BuOH + 1% BaTi(OR)₆ ; V=100V, T=60s (fresh), (b) YBCO + iso-BaOH + 1% BaTi(OR)₆ ; V=100V, T=60s (after 48h)

But in present case the presence of the liquid phase is however, not a sufficient condition to achieve full density. We can proposed that fine particles of metal alkoxide melt preferentially to form a small quantity of liquid phase. Melting also occurs over the surfaces of the larger particles and to some extent at grain boundaries within particles. In the optimum sintering range, the liquid phase is very viscous. The densification very likely occurs through rearrangement with substantial contribution by particle deformation as the matrix will be quite low in strength at this temperature. Further work is need to verify this hypothesis about the contribution of particle deformation to densification.

The processing parameters studied were solution chemistry, aging time, pyrolysis atmosphere, and firing time. The influence of the solution chemistry on the final film morphology was studied by electrophoresis solutions with BaTi(OR)_n 1 wt.%; 5 wt. %; 9,0 wt. % addition to YBCO powders and firing the resulting films at 950°C for 10h (Fig.3).

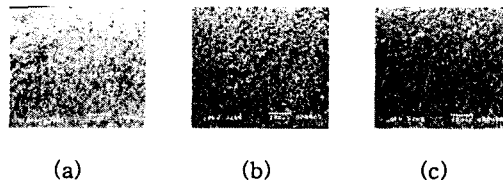


Fig.3. SEM micrographs of films electrophoretically deposited on Ag and fired in air at 10°C/min up to 950°C with 1 (a), 5 (b), 9 (c) wt. % additives.

Solution 1 and 3 lead to stoichiometric and uniform layers. As we will see, the similarity between the micrographs and the small difference in the average grain size can be attributed to the difference in the thickness between the two films.

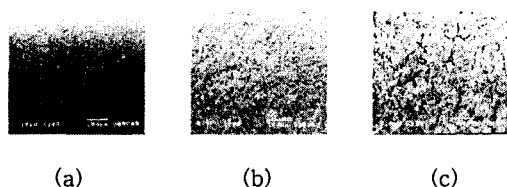


Fig.4. SEM micrographs of films synthesized from solution with 1 % additive; (a) deposition time 15 s and fresh sol, (b) deposition time 60s, (c) deposition time 15s (aged sol =48h)

The influence of the solution aging was studied by electrophoresis from solution with 1 % additive 0,5 and 48h after the sintering, then pyrolyzing them for 10h at 900°C. We know that the aging time affects the compounds of solutions. The difference in grain size could be attributed to the difference in the film chemical composition (Fig.4).

The influence of the firing time on the film microstructure was studied by firing films at 90 0°C for 1, 5 and 10 h. As the firing time increases, the average grain size increases from 0.1µm (for 1h) to 0.2µm (for 10h) with some grains as big as 0.5µm. The average pore size also increases from 50 nm (1h) to 200 nm (10h) with some pores in the 500 nm range. This suggests that in parallel to the grain growth process, a pore coarsening mechanism is taking place.

To summarize, the aging time of the solution affects the grain size: the longer the solution is aged, the bigger the grains. Prolonged firing times produce larger grains and pores, suggesting that grain growth and pore coarsening take place at the same time.

4. Conclusious

Dense and crack-free thin films of HTS were synthesized by sol-gel process. BaTiO₃ phase is formed by reaction (1). The films crystallize between 600 and 700°C, followed by grain growth at higher temperature. Prolonged firing times produce larger grains and pores, but no significant variation of the refractive index was observed, so the total porous volume remains unchanged.

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