

Electrophoretic deposition of SrBi₄Ti₄O₁₅ thick films on Al₂O₃ substrate

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Abstract Electrophoretic deposition (EPD) is a powerful route to obtain thick films onto conductive substrate. In this work, ferroelectric SrBi₄Ti₄O₁₅ films up to 15 μm were prepared by EPD using submicrometer SrBi₄Ti₄O₁₅ (SBT) powders. The ethanol was used as the solvent with addition of HCl and PVB (dispersant). The zeta potential of SBT powder in ethanol is low compared to some other ceramics such as PZT, so it tends to flocculate and is more difficult to be deposited. With addition of PVB, the suspension was then stabilized. The deposition kinetics and the effect of additives were observed and discussed using DLVO theory. From SEM and XRD observation, the films obtained were crack-free and grain-oriented.

Keywords EPD · Thick films · Dispersant

1 Introduction

Colloidal processing is a useful method in the processing of nano-structured films including ferroelectric and piezoelectric films. But the usually used sol–gel process has been proved to be difficult in preparing thick films, and films from 1 to 20 μm are needed for sensor and actuator application. Electrophoretic deposition (EPD) is a colloidal process wherein films are shaped directly from a stable colloid suspension by a dc electric field [1], and it's easy to prepare films above 1 μm. The EPD process also has the

advantages such as simple processing, low-cost facility requirement, and easy to be deposited onto complex shapes. Nonaqueous suspensions are usually preferred for EPD to avoid the electrolysis of the solvent and obtain a bubble free deposit [1].

There has not been any previous work reported on the EPD of bismuth layer structure ferroelectrics (BLSFs) which have many properties such as fatigue-free property, high temperature use, and lead-free [2]. They have different structures with perovskites such as PZT [3], BaTiO₃ [4] which have been prepared by EPD in the past, so it is worth to study the EPD behavior of BLSFs. SrBi₄Ti₄O₁₅ (SBT) belongs to BLSFs. In this work, we successfully obtained crack-free SBT thick films. As sub-micrometer powders are easy to agglomerate, hence difficult to be deposited, some researchers used dispersant such as PEI, PVA [5] to stabilize the suspension in aqueous medium, but in organic medium dispersant is rarely used. Here we use poly(vinyl butyral) (PVB) to prevent particle agglomeration. It was found that the addition of PVB accelerates the deposition rate at early stage but with the process of deposition the rate slows down more quickly than that without PVB addition. We tried to find out the reasons by DLVO theory. We also found the sintered films were grain-oriented.

2 Experimental procedures

The SBT powder was prepared by calcinations of component powders (Bi₂O₃, TiO₂ and SrCO₃). Particle size was measured to be about 450 nm (using a laser particle size analyzer, Zeta Plus, Brookhaven Instruments Corp.).

Suspension of ~1 wt% SBT in ethanol was prepared by dispersing the SBT powders in ethanol with addition of HCl and PVB. They are ball-milled for 4 h. The zeta

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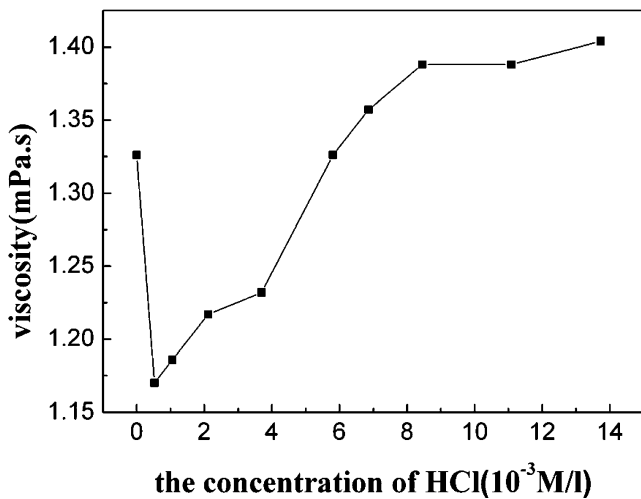


Fig. 1 Viscosity vs concentration of HCl

potential (Zeta plus, Brookhaven Instruments Corp.) and viscosity of suspensions were measured. Before deposition, 10–20 h were allowed for the sedimentation of larger particles and let particles be fully electricized. The concentration of suspensions were controlled at about 0.40 wt% when deposition started.

The films were formed on 1.2×1.2 cm² alumina substrates which were sputtered with Pt. The distance between two electrodes was constantly 10 mm. The voltage source was a DC power supply. Some green films were heated up to 700°C to remove PVB for calculation of deposited weight, and other green films were scraped off and analyzed using FT-IR (Thermo Nicolet Nexus Instrument). The films were sintered at 1080°C. A few SBT ceramics were also made and sintered at 1175°C using the same powder. The phase identification of both films and ceramics were analyzed using a Rigaku D/MAX.B X-ray diffractometer with Cu K radiation. The morphology was investigated by a scanning electron microscopy (SEM)

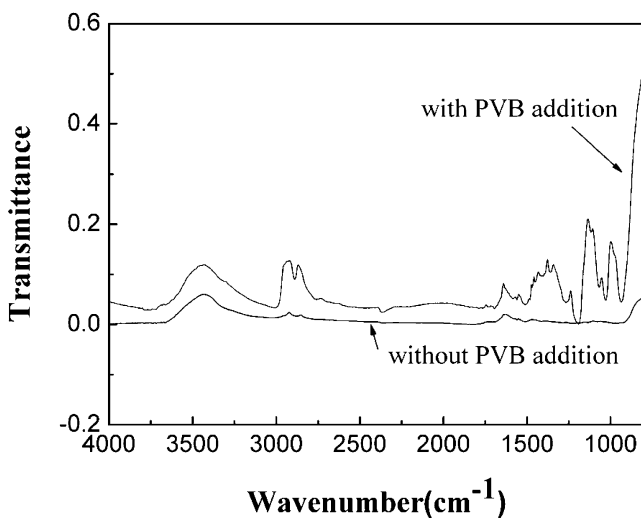


Fig. 2 FT-IR spectrum of as-deposited SBT

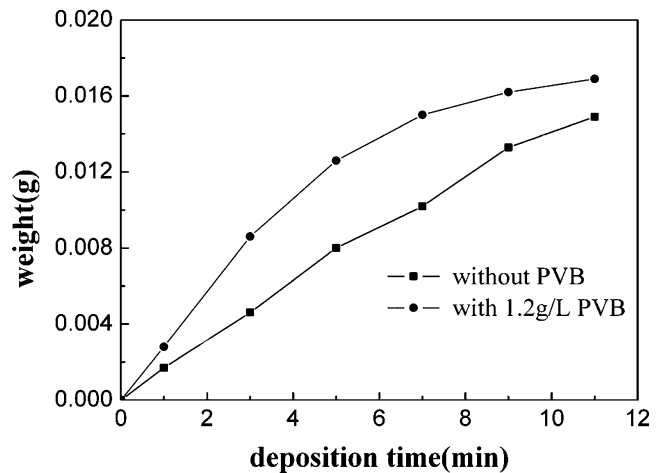


Fig. 3 Deposited weight as function of time

(HITACHI S-570). All of the experiments were carried out at room temperature.

3 Results and discussion

The zeta potential of SBT in ethanol was very low (below 30 mV) and difficult to measure accurately (the data was not shown here). Relative large positive zeta potential exhibited at pH=4~5. Figure 1 shows the viscosity vs. HCl concentration of the suspension. There is a minimum value (1.17 mP·s) in the diagram, at this concentration the pH is about 4 just the point when zeta potential is relatively high. Tang et al. [6] believed that high zeta potential and low viscosity are required for electrophoretic deposition. The addition of PVB also changes the suspension viscosity. In this work, suspensions have the lowest viscosity (1.16 mP·s, slightly lower than 1.17 mP·s) and sedimentation rate when pH equals 4 and 1.2 g/l PVB is added. From

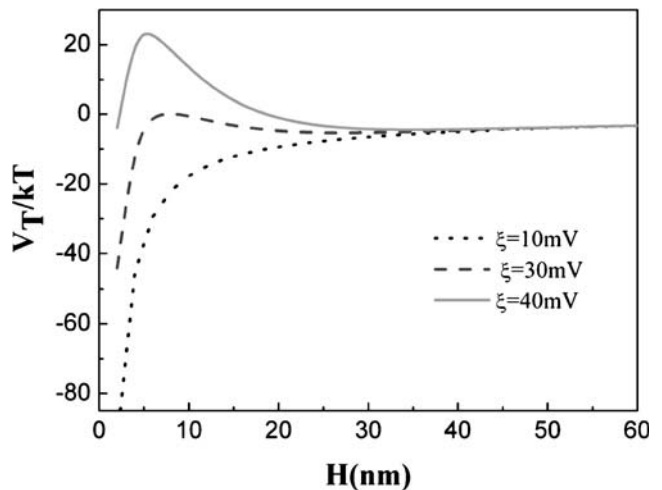
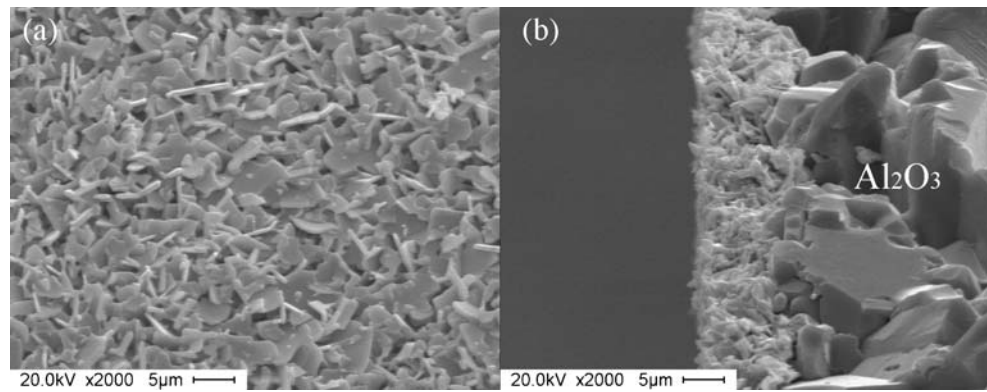


Fig. 4 Total interaction potential between two particles with different zeta potential

Fig. 5 Micrographs (SEM) of the surface (a) and cross section (b) of SBT films, 1080°C sintered



above discussion, proper amount of PVB would stabilize the suspension. If too much PVB is added the superfluous polymers will stay in the solution and inhibit the adsorption of H^+ ions, then a deleterious effect on the stability of the dispersion system is taken [7].

Figure 2 shows the FT-IR spectrum of as-deposited SBT both with and without PVB addition. There are apparent differences between two curves. So it is reasonable to consider that the PVB covered the SBT particles and moved together with them toward the electrode.

The kinetic equation of EPD was given by [1]

$$dw = \frac{fs\varepsilon V \zeta c(t)}{6\pi\eta d} dt \quad (1)$$

where w represents the weight deposited, s the depositing area, V the voltage applied, ζ the zeta potential, ε the dielectric constant, η the viscosity, d the distance between two electrodes, $c(t)$ the concentration of particles at time t and f the possibility of the particles reaching the electrode to settle down onto the electrode.

The voltage applied was 30 V. Because the process was carried out within a few minutes, and the change of concentration was very small, so $c(t)$ can be considered as constant. There are only three parameters that are different between suspensions with and without PVB. From above discussion, we know η_n (no PVB addition) $\approx \eta_p$ (with PVB addition), and it is also reasonable to suggest that ξ_n is not smaller than ξ_p as PVB will compete with H^+ for adsorption sites, thus slightly lowering the ξ . If two f are the same, then the deposition rate of the suspension without PVB will be a little faster than that with PVB addition. But the fact is the formation rate of films with PVB is absolutely higher than that without PVB at the early stage of deposition (see Fig. 3). So here PVB not only enhanced the stability of the suspension, but also acts as binder that forces the particles reaching the cathode to deposit, that is to say f_p is larger than f_n . From the diagram, the slope of curve with PVB addition decreases with time quickly. This is because the green films act as resistant layers [1], and the actual electric field between two electrodes become smaller. The denser

films will have larger resistance [5]. So we can deduce that the films deposited with PVB is denser than those without PVB.

To find out the reasons, we calculated the interaction energy between particles using DLVO theory. According to this theory, the total interaction energy is the sum of ionic repulsion, V_R , and van der Waals attraction, i.e.,

$$V = V_R + V_A \quad (2)$$

The repulsive energy as a function of particle separation, H , is given by [8]

$$V_R = 64\pi a n^0 kT \left(\tan h \frac{ze\psi_0}{4kT} \right) \frac{1}{\kappa^2} \exp(-\kappa H) \quad (3)$$

where κ is the Debye parameter. For symmetrical electrolytes, κ is given by [8]

$$\kappa = \left(\frac{2e^2 n^0 z^2}{\varepsilon_0 \varepsilon_r kT} \right)^{\frac{1}{2}} \quad (4)$$

where ε_r is the relative dielectric constant of the suspending medium (ethanol), n^0 the bulk ion (H^+) concentration with valence z (+1) and ψ_0 the electrostatic potential at the particle surface, for organic media, ψ_0 equals ζ (zeta-

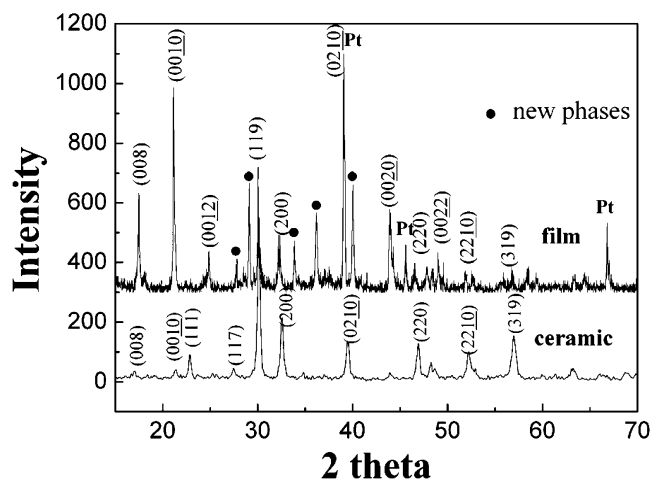


Fig. 6 XRD pattern of the SBT films and ceramics, sintered at 1080°C and 1175°C respectively

potential). ϵ_0 , e , k , T have their usual meanings. In Eq. 3, only ζ and H are unknown (or variable).

The van der Waals energy of attraction for spheres of radius a , with center-to-center distance r is [9]

$$V_A = -A_{131} \frac{1}{6} \left(\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \frac{s^2 - 4}{s^2} \right) \quad (5)$$

where $s = r/a = 2 + H/a$ and A_{131} is the effective Hamaker constant, and is given by [9]

$$A_{131} = \left(A_{11}^{1/2} - A_{33}^{1/2} \right)^2 \quad (6)$$

A_{11} , A_{33} are the Hamaker constants of the SBT particle and ethanol. Using the data from [10], we can calculate $A_{131} \approx 4 \times 10^{20}$ J.

The total interaction potential against surface distance H between two particles with different ζ is computed and plotted in Fig. 4. When ζ is under 30 mV, the potential barrier between two SBT particles is very small compared to 15 kT, the lower limit for colloidal stability [11]. In our suspension, the ζ is under 30 mV, so the electrostatic force arising from H^+ adsorption is not enough to stabilize the particles. When particles move to the cathode under electric field, the concentration near the cathode increases with double layers distortion and thinning [1]. This makes them even unstable. Many of the particles reaching cathode cannot deposit on it, but agglomerate, so f_n is small. When PVB is added, it provides steric repulsion that makes the particles stable, and particles reaching the electrode will deposit on it under electric field. From SEM investigation (Fig. 5), they are dense and crack-free.

Figure 6 shows the XRD patterns of films and ceramics from which we can see clearly that in the curve of films all (0 0 l) reflections have increased compared to the ceramics, indicating that most grains grow with their a–b plane parallel to the substrate. The reasons will be discussed later. Besides the peaks of SBT and Pt, there are some other phases. This may be explained by the reaction of platinum with component element of SBT. Those phases will

deteriorate the property of films, so further work is needed to solve this problem.

4 Conclusions

The optimum conditions for EPD of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ were determined through zeta potential and viscosity measurements. SBT have different structure with perovskites and relative lower zeta potential compared to PZT et al.. The addition of PVB helped to stabilize the suspension and accelerated the formation rate of films at early stage of deposition. The DLVO theory is used to explain the effect of PVB on the depositing speed. This work revealed that EPD method is one of the promising methods for preparation of ferroelectric thick films, and application of appropriate dispersant is helpful.

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