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Hydrothermally synthesized BaTiO₃ textured in a strong magnetic field

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Abstract

Hydrothermally synthesized BaTiO₃ was colloidally consolidated by slip casting and by electrophoretic deposition in a high strength magnetic field of 17.4 T. Textured BaTiO₃ was successfully prepared by both processing techniques, with the {001} plane aligning normal to the direction of the magnetic field. The initial alignment in the green powder compact was preserved and enhanced after sintering from 1400°C to 1500°C. The sintering temperature hardly influenced the degree of texture in slip cast samples but did influence the grain size of all BaTiO₃ ceramics and the degree of texture in the electrophoretically deposited samples. The BaTiO₃ ceramics processed in the strong magnetic field showed crystallographic texture but not morphological, so the microstructure did not show any anisotropy. The highest Lotgering factor (0.85) was measured for the ceramics made by electrophoretic deposition and sintered at 1500°C.

Introduction

Dielectric materials with superior ferroelectric and piezoelectric properties are extensively used in electronic applications, such as multilayer capacitors, sensors, actuators and electronic components [1]. Nowadays, due to environmental concerns, there is a strong need to substitute lead containing materials, like PZT, which exhibit the highest ferroelectric and piezoelectric properties. BaTiO₃, with a high Currie temperature ($T_c \sim 120^\circ\text{C}$) and a d_{33} coefficient equal to 190 pC/N, is a very good potential candidate [2]. However, the ferroelectric properties of BaTiO₃ need to be enhanced in order to compete with PZT. Ceramic texturing has been reported to be a potential route to improve the

physical and mechanical properties of materials, effectively. Various techniques like tape casting [3], hot forging [4, 5] or pressing [6] and templated grain growth [2, 7] are commonly used to produce textured ceramics. Textured ceramics were mainly obtained by templated grain growth. Grain oriented BaTiO₃ ceramics have been prepared by templated grain growth, showing highly anisotropic properties. Park et al. reported that [001]-poled orthorhombic BaTiO₃ crystals at 0°C exhibited a d_{33} of over 500 pC/N and a k_{33} of over 85% [8]. For a [110] grain oriented BaTiO₃, the piezoelectric constant d_{31} was almost constant at -50 pC/N, while the d_{33} increased with increasing orientation up to a maximum of 788 pC/N at a Lotgering factor of 84.6%, almost equal to that of PZT [9].

Another method to achieve texture is by aligning the suspended particles in a strong magnetic field during colloidal processing and retaining this alignment in the green body. Because of the recent availability of strong superconducting magnets, the alignment of feeble magnetic particles, with an equiaxed shape and non-cubic crystal structure, becomes possible [10, 11]. The principle of the orientation process is that a crystal with an anisotropic magnetic susceptibility will rotate to an angle to minimize the system energy when placed in a magnetic field. The driving force of the magnetic alignment is the energy of the crystal anisotropy ΔE , expressed for a crystal with $\chi_a = \chi_b$ as:

$$\Delta E = \Delta\chi VB^2 / 2\mu_0 \quad (1)$$

where $\Delta\chi = |\chi_{a,b} - \chi_c|$ is the anisotropy of the magnetic susceptibility, with $\chi_{a,b}$ the magnetic susceptibility along the crystallographic a, b -axes and χ_c the magnetic susceptibility along the crystallographic c -axis, μ_0 is the permeability of vacuum, V is the volume of each particle and B is the applied magnetic field. The crystal will be aligned to the most stable state having the lowest magnetic energy when the energy of the crystal anisotropy overcomes the energy of the thermal motion (2):

$$\Delta E > k_B T \quad (2)$$

with k_B , the Boltzmann constant and T , the absolute temperature [12, 13]. It follows from equations (1) and (2) that the alignment will be more easily attained for larger particles and in the strongest possible fields as shown recently for zirconia [14].

However, as far as we know, there have been very few reports on highly textured perovskite ceramics fabricated by this method [15]. For BaTiO₃ in particular, various attempts have been made to achieve alignment by colloidal processing in a strong magnetic field [16-17]. However it is not clear yet which is the easy magnetization axis of BaTiO₃ (which axis aligns parallel to the direction of the B-field). The very low crystallographic anisotropy of BaTiO₃, derived from the c/a ratio which is equal to 1.0065, and concomitant low anisotropy in magnetic susceptibility, is responsible for the difficulty to

align this material in a magnetic field. In fact little is known about the diamagnetic susceptibilities of tetragonal BaTiO_3 . It should also be mentioned that once tetragonal particles have been aligned by processing at low temperatures, the green compact will be sintered in the cubic form and the tetragonal form will reappear upon cooling but not necessarily in the original orientation.

The degree of texture so far achieved in published work has been rather weak. More specifically, Özen *et al.* [16] investigated the grain alignment of hydrothermally prepared BaTiO_3 slip cast in 9.4 T magnetic field. They succeeded in obtaining textured BaTiO_3 with the $\{100\}$ and $\{001\}$ planes aligning normal to the magnetic field, with a Lotgering factor of 0.25, but this alignment was only observed on the surface of the sintered samples. Wada *et al.* [17] performed electrophoretic deposition (EPD) and slip casting of nano-sized BaTiO_3 in a strong magnetic field of 12 T. They did not observe any preferential orientation in the green compacts. However at the as-sintered surfaces they obtained strong alignment along the $[111]$ direction which was not attributed to the high magnetic field, since the ceramics prepared outside the magnet for reference, showed strong texture along the $[111]$ direction, too. After polishing though, the BaTiO_3 ceramics prepared by slip casting at 12T were randomly oriented and the ones prepared by EPD had a weak preferential orientation along the $[110]$ direction. The Lotgering factor was 0.25 at the surface perpendicular to the direction of the magnetic field.

Hence there is clear confusion in the literature regarding the crystallographic direction that will align preferentially with the magnetic field. As equation 1 shows, the energy of crystal anisotropy changes with the square of the magnetic field strength. By using a field of 17.4 Tesla this energy is doubled with respect to the 12 Tesla which is the highest field yet used to date.

Hence the goal of this work is to investigate the influence of a high magnetic field of 17.4 T on texturing BaTiO_3 ceramics, study the magnetic alignment and compare the results with literature data using lower strength fields. Hydrothermally synthesized BaTiO_3 powder, which was reported to show some texture in a 9.4 T magnetic field (Lotgering factor equal to 0.25), was used [16]. Colloidal processing was done both by slip casting and by electrophoretic deposition (EPD).

Experimental Procedure

BaTiO_3 powder was synthesized by the hydrothermal method. An amorphous precursor material was prepared by the peroxo-hydroxide method described elsewhere [18]. The amorphous precursor was hydrothermally treated in a stainless steel reactor in a 10 M NaOH solution at 200°C for 24 hours. After washing with demineralized water, the powder was washed in an acetic acid solution with pH 5.5 in order to remove the carbon (BaCO_3) contamination and calcined at 950°C for 1 hour to remove the hydroxides and to improve the tetragonality of BaTiO_3 [19]. Due to calcination, the powder was

strongly agglomerated, as shown in Fig. 1(a). However particles need to be single crystals if the alignment mechanism described above is to apply. Bead milling with small beads was reported to be a very effective de-agglomeration technology [20]. In this study, the powder was bead milled (Dispermat SL, VMA Getzmann GmbH, Germany) in ethanol at 4000 rpm for 2 hours using zirconia beads (TZ-3Y, Tosoh Co., Japan) with an average size of 1 mm, and afterwards dried and sieved to break the soft agglomerates. The particle morphology after bead milling is shown in Fig. 1(b). The mean particle size of the powder after bead milling is 0.27 μm , as measured by laser diffraction (Mastersizer Microplus, Malvern). The BaTiO_3 powder was consolidated by slip casting and electrophoretic deposition in a strong magnetic field of 17.4 T (High Field Resistive DC Magnet, Bore diameter 170 mm, LNCMI, Grenoble) and outside the magnet for reference.

For slip casting, 10 vol% of the BaTiO_3 powder was dispersed in demineralised water. 0.5 wt % ammonium polymethacrylate (Darvan C-N, Vanderbilt Minerals, LLC) was used as a dispersant. Ammonia was added to adjust the pH of all suspensions to 10.5. The suspensions were prepared by magnetic stirring for 1 hour followed by ultrasonic agitation (Ultrasonic processor UP400S, Hielscher Ultrasonics GmbH, Germany, 400 watts, 24 kHz) for 15 minutes to disperse soft agglomerates. The suspensions were cast on a plaster mould in a vertical 17.4 T magnet at room temperature. The top and bottom surfaces of the powder compacts were perpendicular to the magnetic field direction.

To prepare a stable suspension for electrophoretic deposition (EPD), 4 vol% of BaTiO_3 was dispersed in ethanol with 1 wt% (relative to the powder mass) phosphate ester (JP-506H grade, Johoku Chem. Co. Ltd, Japan) as charging agent and binder. 1.1 wt% (relative to the powder mass) poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, Sigma-Aldrich Corp., USA) was also added as binder and 0.03 wt% (relative to the powder mass) polyethyleneimine (PEI, Sigma-Aldrich Corp., USA) as surface charging agent and stabilizer in order to form a thick and crack-free deposit [21]. EPD was performed at 100 V for 1 hour at room temperature with an electrode distance of 3.5 cm. The deposition electrode is made of a conductive polymer (POM-ELS) and has a rectangular shape (5.3 cm $\times$ 3.5 cm) with a 3 cm diameter deposition surface. A vertical magnetic field of 17.4 T was applied to the suspension during EPD at room temperature with magnetic and electric field directions perpendicular to each other. In other words, the deposition electrode was placed vertically and parallel to the magnetic field direction.

The green compacts with a diameter of 30 mm of both processing methods were dried outside the magnet and sintered in air at 1400°C, 1450°C and 1500°C for 2 hrs, with a heating and cooling rate of 5°C/min and 10°C/min, respectively (Nabertherm, Germany). The grain alignment of green and sintered ceramics was characterized by X-ray diffraction (Seifert 3003, Siemens, Germany). Based on the XRD spectra, the Lotgering factor, a semi-quantitative technique to evaluate the degree of

texturing, was calculated. The Lotgering factor f is defined as [22]:

$$f = (P - P_0) / (1 - P_0) \quad (3)$$

where $P = (I_{h00} + I_{00l}) / \sum I_{(hkl)}$ was calculated from the sum of the h00 and 00l reflections over that of all the hkl reflections from the specimen's surface normal to the direction of the field, and P_0 was calculated from the JCPDS card number 05-0626 according to the same formula. $I_{(hkl)}$ is the peak intensity of the hkl reflection over a 2θ range of 20-60°. The f factor of a sample without anisotropy is 0, which is actually the case for a sample prepared outside of the magnet, while $f = 1$ for a fully oriented material in one direction [22]. The Lotgering factor is calculated based on the cubic and not on the tetragonal crystal structure, due to the fact that BaTiO₃ undergoes a phase transformation from tetragonal to cubic above the Curie temperature (120°C). Hence, both (h00) and (00l) planes will be textured during sintering. After the phase transformation to tetragonal during cooling, this alignment is preserved. So the Lotgering factor is calculated from the sum of the (h00) and (00l) reflections. For the specimens consolidated via slip casting, Lotgering factors are calculated from XRD patterns from the surfaces normal to the magnetic field, using the formula mentioned above. However, for electrophoretically deposited samples, the surface normal to the magnetic field could not be measured due to the fact that the discs were very thin and it was difficult to achieve high accuracy in cutting the sample. Hence, we measured the surface parallel to the magnetic field where only {hk0} reflections are expected if a perfect fiber texture is formed with the <001> fiber axis parallel with the field. Accordingly, the formula (3) is used, where:

$$P = (I_{\{100\}} + I_{\{110\}} + I_{\{120\}}) / \sum I_{(hkl)} \text{ and } P_0 \text{ is re-calculated according to the same formula.}$$

The microstructure of the powder and polished surfaces of sintered and thermally etched ceramics was analyzed by SEM (XL30-FEG, FEI, The Netherlands). The average grain size was determined from SEM micrographs using Image-pro Plus software, measuring an average of 200 grains. The density of the sintered ceramics was measured according to the Archimedes method in ethanol.

Results and Discussion

The XRD patterns of the BaTiO₃ powder compact slip cast inside and outside the magnetic field and the reference pattern of the starting powder are compared in Fig. 2. The compact cast in the absence of a magnetic field has an identical pattern as that of the powder, implying it has a random orientation. The XRD pattern of the surface perpendicular to the direction of the magnetic field of the green body slip cast in the magnetic field however has stronger 00l peaks than the one cast at 0

T. This confirms that the longer c-axis aligned parallel to the magnetic field. The Lotgering factor of the surface perpendicular to the magnetic field, as shown in Fig 2c, of the green compact processed inside the magnet, calculated for the (00l) plane, is $f = 0.09$. XRD on green powder compacts made by EPD was not possible due to the fact that they were thin and very fragile.

This alignment in the slip cast ceramics evolved after sintering at 1400, 1450 and 1500°C, as illustrated in Fig 3. In the present case, texture enhanced during sintering at high temperature, proving that the orientation factor increases with grain growth [23]. In the green state (prior to sintering), it is more likely for big particles to align with the magnetic field, due to their larger crystal anisotropy energy (eq. 1), the larger the volume (V) of the particles the larger the crystal anisotropy energy (ΔE). The finer particles remain randomly oriented, a fact that explains the low Lotgering factor in the green specimen. During sintering though, the larger grains act as templates and grow intensively, retaining their initial orientation, by consuming the finer surrounding particles. Through this mechanism of discontinuous grain growth, a well textured material is developed. The intensity of the 101 and 111 peaks of the textured ceramics cast at 17.4 T are lower than for the ceramic cast outside the magnet, which has random orientation. The sintering temperature only slightly influences the degree of texture, with the highest alignment obtained when sintering at 1450°C. The Lotgering factor of the ceramics slip cast in the magnetic field and sintered at 1400, 1450 and 1500°C is 0.58, 0.67 and 0.61, respectively, as reported in Table 1.

The XRD patterns from the surface parallel to the magnetic field of the ceramics made by electrophoretic deposition inside and outside the magnet are compared in Fig. 4. The (h00) and (00l) planes are highly textured for all ceramics deposited in the magnetic field. On the surface parallel to the B-field we also expect the {110} and {102} reflections, since we have the so-called ‘fiber texture’. The {110} and {102} reflections, as stated before, also contribute in the calculation of the Lotgering factor. What determines the degree of texture is the low intensity of the {111} and {112} reflections, which can clearly be seen after sintering at 1450 and 1500°C. The 111 peak disappears almost completely when sintering at 1500°C. The sintering temperature influences the degree of texture more than in the case of slip casting, with the highest alignment obtained when sintering at 1500°C. The Lotgering factor of the samples deposited in the magnetic field and sintered at 1400, 1450 and 1500°C is 0.52, 0.74 and 0.85, respectively, as summarized in Table 1.

The XRD results clearly show the strong influence of the high magnetic field on the alignment of the BaTiO₃ powder. Özen et al. [16] reported a Lotgering factor of 0.25 for hydrothermally synthesized BaTiO₃, slip cast at 9.4 T. The higher degree of texture in the current work is attributed to the much higher intensity of the applied magnetic field. The limited crystallographic anisotropy of BaTiO₃, derived from the c/a ratio which is equal to 1.0065, is responsible for the difficulty in aligning perovskite particles in magnetic fields ≤ 12 T. Wada et al. also obtained weak preferential crystallographic orientation of 25% along the [110] direction but only with EPD of BaTiO₃ at 12 T. Slip casting did not lead to any texture [17]. Additionally, Chen et al. succeeded in aligning some BaTiO₃

particles by magnetic force in the green compact, but texture was not maintained after sintering. [24]. The degree of texture achieved in the current work is much higher than any reported in previous published works, which proves that a strong magnetic field of 17.4 T is indeed highly improving the alignment of BaTiO₃ ceramics.

The microstructures of the BaTiO₃ ceramics were investigated by SEM. The average grain size of the ceramics increased with increasing sintering temperature from 1400°C to 1500°C, as shown in Table 1. Figure 5 shows the microstructure of the ceramic cast inside the magnetic field and sintered at 1500°C. The shape and the size of the grains from the surfaces parallel and perpendicular to the magnetic field is almost identical. This fact reveals that there is no anisotropy in the microstructure of the ceramics cast in the magnetic field, regardless of the high degree of crystallographic texture, as discussed earlier. The same trend was observed for the ceramics prepared by electrophoretic deposition at 17.4 T. As shown in Figure 6, the microstructure does not show any anisotropy despite the strong crystallographic anisotropy of the ceramics deposited in the magnetic field and sintered at 1450 °C. Residual porosity is also observed in the microstructure, which is mainly intergranular, with some intragranular. The ceramics are not fully dense as demonstrated in Table 1. The sintered compacts made by EPD are slightly less dense than those made by slip casting. The relatively low bulk density is attributed to the discontinuous grain growth of the BaTiO₃ ceramics.

Conclusions

Textured BaTiO₃ was successfully prepared by slip casting and electrophoretic deposition in a strong magnetic field of 17.4 T using hydrothermally synthesized BaTiO₃ starting powder. A fiber texture is obtained with the <001> fiber axis aligning parallel to the direction of the magnetic field. Compared to literature data, the use of such a high field is demonstrated to be essential in order to achieve highly textured BaTiO₃. The texture of the green powder compacts processed at 17.4 T, limited to a Lotgering factor of 0.09, was substantially improved during sintering at 1400-1500°C due to discontinuous grain growth. The influence of the sintering temperature was limited when slip casting was used, but did play a role in the alignment of ceramics made by electrophoretic deposition. Maximum Lotgering factor of 0.67 is obtained when sintering slip cast samples at 1450°C. Maximum Lotgering factor of 0.85 is obtained when sintering samples made by electrophoretic deposition at 1500°C. The influence of texturing on the properties of BaTiO₃ is presently under study.

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References

- [1] Aksel E, Jones JL. Advances in Lead-Free Piezoelectric Materials for Sensors and Actuators. *Sensors-Basel*. 2010;10:1935-54.
- [2] Messing GL, Trolrier-McKinstry S, Sabolsky EM, Duran C, Kwon S, Brahmaroutu B, Park P, Yilmaz H, Rehrig PW, Eitel KB, Suvaci E, Seabaugh M, Oh KS. Templated grain growth of textured piezoelectric ceramics. *Crit Rev Solid State*. 2004;29:45-96.
- [3] Lecomte-Nana G, Mokrani A, Tessier-Doyen N, Boussois K, Goure-Doubi H. Texturation of model clay materials using tape casting and freezing. *Ceram Int*. 2013;39:9047-53.
- [4] Sakata K, Takenaka T, Shoji K. Hot-Forged Ferroelectric Ceramics of Some Bismuth Compounds with Layer Structure. *Ferroelectrics*. 1978;22:825-6.
- [5] Kellett BJ, Lange FF. Hot-Forging Characteristics of Fine-Grained ZrO₂ and Al₂O₃/ZrO₂ Ceramics. *J Am Ceram Soc*. 1986;69:C172-C3.
- [6] Ma YC, Bowman KJ. Texture in Hot-Pressed or Forged Alumina. *J Am Ceram Soc*. 1991;74:2941-4.
- [7] Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T, Nakamura M. Lead-free piezoceramics. *Nature*. 2004;432:84-7.
- [8] Park SE, Wada S, Cross LE, Shrout TR. Crystallographically engineered BaTiO₃ single crystals for high-performance piezoelectrics. *J Appl Phys*. 1999;86:2746-50.
- [9] Wada S, Takeda K, Muraishi T, Kakemoto H, Tsurum T, Kimura T. Preparation of [110] grain oriented barium titanate ceramics by templated grain growth method and their piezoelectric properties. *Jpn J Appl Phys* 1. 2007;46:7039-43.
- [10] Suzuki TS, Sakka Y, Kitazawa K. Orientation amplification of alumina by colloidal filtration in a strong magnetic field and sintering. *Adv Eng Mater*. 2001;3:490-2.
- [11] Morikawa H, Sassa K, Asai S. Control of precipitating phase alignment and crystal orientation by imposition of a high magnetic field. *Mater T Jim*. 1998;39:814-8.
- [12] Sugiyama T, Tahashi M, Sassa K, Asai S. The control of crystal orientation in non-magnetic metals by imposition of a high magnetic field. *Isij Int*. 2003;43:855-61.
- [13] Sakka Y, Suzuki TS. Textured development of feeble magnetic ceramics by colloidal processing under high magnetic field. *J Ceram Soc Jpn*. 2005;113:26-36.
- [14] Vriami D, Beaunon E, Vanmeensel K, Vleugels J, Van der Biest O. Texturing of 3Y-TZP zirconia by electrophoretic deposition in a high magnetic field of 17.4 T. *J Eur Ceram Soc*. 2014;34:3879-85.
- [15] Miwa Y, Kawada S, Kimura M, Higuchi Y, Takagi H, Suzuki TS, Uchikoshi T, Sakka Y. Textured PbTiO₃ Based Ceramics Fabricated by Slip Casting in a High Magnetic Field. *Key Eng Mat*. 2010;421-422:395-8.
- [16] Ozen M, Mertens M, Schroeve M, Snijders F, Cool P. Preparation of barium titanate powders and colloidal processing in a strong (9.4 T) magnetic field. *Mater Lett*. 2012;67:154-7.
- [17] Wada S, Kita T, Fujii I, Nakashima K, Takei T, Kumada N, Suzuki T, Uchikoshi T, Sakka Y, Miwa Y, Kawada S, Kimura M, Kuroiwa Y. Preparation of Barium Titanate Grain-oriented Ceramics by Electrophoresis Deposition Method under High Magnetic Field using Single-domain Nanoparticles. *Electroceramics in Japan Xvi*. 2014;582:27-31.

- [18] Ozen M, Mertens M, Luyten J, Snijkers F, D'Hondt H, Cool P. Hydrothermal synthesis of carbonate-free submicron-sized barium titanate from an amorphous precursor: Synthesis and characterization. *Ceram Int.* 2012;38:619-25.
- [19] Hennings DFK, Metzmacher C, Schreinemacher BS. Defect chemistry and microstructure of hydrothermal barium titanate. *J Am Ceram Soc.* 2001;84:179-82.
- [20] Choi JJ, Hahn BD, Park DS, Yoon WH, Lee JH, Jang JH, Ko KH, Park C. Low-temperature sintering of lead zinc niobate-lead zirconate titanate ceramics using nano-sized powder prepared by the stirred media milling process. *J Am Ceram Soc.* 2007;90:388-92.
- [21] Doudgaw S, Uchikoshi T, Noguchi Y, Eamchotchawalit C, Sakka Y. Electrophoretic deposition of lead zirconate titanate (PZT) powder from ethanol suspension prepared with phosphate ester. *Sci Technol Adv Mat.* 2005;6:927-32.
- [22] Lotgering FK. Topotactical Reactions with Ferrimagnetic Oxides Having Hexagonal Crystal Structures .1. *J Inorg Nucl Chem.* 1959;9:113-&.
- [23] Zhu XW, Sakka Y. Textured silicon nitride: processing and anisotropic properties. *Sci Technol Adv Mat.* 2008;9.
- [24] Chen WW, Kinemuchi Y, Tamura T, Miwa K, Watari K. Fabrication of textured ferroelectric ceramics by magnetic alignment via gelcasting. *J Eur Ceram Soc.* 2007;27:655-61.

Figures

Figure 1: Microstructure of hydrothermally synthesized BaTiO₃ powder before (a) and after bead milling (b).

Figure 2: XRD pattern of the BaTiO_3 powder (a) and green powder compacts slip cast outside (b) and inside (c) the magnetic field.

Figure 3: XRD pattern of the BaTiO_3 compact slip cast without magnetic field (a) and compacts slip cast at 17.4 T and sintered at 1400 °C (b), 1450°C (c) and 1500°C (d).

Figure 4: XRD pattern, from surfaces perpendicular to the electric field, of the BaTiO₃ compact EPD without magnetic field (a) and compacts EPD at 17.4 T and sintered at 1400°C (b), 1450°C (c) and 1500°C (d).

Table 1: Density, grain size and Lotgering factors of the BaTiO₃ ceramics made by slip casting and electrophoretic deposition inside and outside the magnetic field.

Sintering temperature (°C)	Magnetic field strength (T)	Density (% T.D.)	Grain Size (μm)	Lotgering Factor
<u>Slip casting</u>				
1400	0	93.5	92.5	0.01
1450	0	93.7	76.5	0.01
1500	0	94.2	121.5	0.02
1400	17.4	95.4	76.8	0.58
1450	17.4	94.2	102.8	0.67
1500	17.4	94.8	115.1	0.61
<u>Electrophoretic deposition</u>				
1400	0	93.0	97.2	0.02
1450	0	92.9	124.9	0.02
1500	0	94.0	154.3	0.02
1400	17.4	94.0	87.7	0.52
1450	17.4	93.4	99.2	0.74
1500	17.4	94.3	120.6	0.85

(a)

(b)

Figure 5: Microstructure of the BaTiO₃ ceramics slip cast at 17.4 T and sintered at 1500°C. Cross-section perpendicular (a) and parallel (b) to the magnetic field direction.

(a)

(b)

Figure 6: Microstructure of the BaTiO₃ ceramics EPD at 17.4 T and sintered at 1450°C. Cross-section perpendicular (a) and parallel (b) to the magnetic field direction.