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Ethanol-based Tape Casting Process of the Textured $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-$BiFeO_3$ Ceramics

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ABSTRACT

The rheological and tape casting behavior of ethanol-based $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-7 mol% $BiFeO_3$ (BNKT-BF) slurries was investigated. The effect of sintering temperature profile on texture development with a preferred <001> orientation was also studied. A 50 MPa pressure assisted three step sintering profile promoted extensive texture development together with densification. The role of BF as a sintering promoter has been discussed.

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1. INTRODUCTION

Currently, lead-free piezoelectric materials have attracted great attention from the standpoint of environmental compatibility [1]. The (1-*x*)$Bi_{0.5}Na_{0.5}TiO_3$-*x*$Bi_{0.5}K_{0.5}TiO_3$ (BNKT*x*) solid solutions with morphotropic phase boundary (MPB) are promising environmentally friendly piezoelectric ceramics [2, 3]. The MPB BNKT*x* (*x*=0.16-0.20) ceramics having rhombohedral and tetragonal ferroelectric phases, exhibit optimized performances [2].

$BiFeO_3$ (BF) with a rhombohedral structure has a high Curie temperature (T_C) of 830°C and is a stable perovskite at ambient conditions [4, 5]. In our previous work, we found that although BF is a ferroelectric ceramic, its addition into BNKT*x* tended to disrupt ferroelectric ordering accompanied by a decrease in coercive field and no effect on grain size [6]. Therefore, it is expected that BNKT-BF should trigger exaggerated grain growth (EGG) and a much larger grain size, promising for texturing, as tailored sintering condition is applied.

Tape-casting is a low cost method mainly suitable for the fabrication of thin (10 to 500 μm) flat components. It allows producing a wide variety of controlled morphologies such as porous, dense and oriented microstructure [7, 8]. Textured BNKT ceramics with developed properties have been processed by tape casting method. The growth of template grains is responsible for the highly textured samples. The increase in the degree of orientation is in proportion to the grain growth during sintering [9, 10]. However, the effect of additives on densification and microstructure of BNKT ceramics via templated grain growth (TGG) process have not been investigated.

The first and most important step in tape-casting is the fabrication of slurry with controlled colloidal properties using various additives [11, 12]. The rheology of the slurry has the key role when tape casting is applied for TGG process, because the degree of texture is dependent on the homogeneity, stability, good dispersion of the templates and optimized viscosity of the slurry [13-15]. Organic and/or inorganic additives are added to the powder to form slurry. A variety of

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organic solvents, such as, methyl ethyl ketone-ethanol, toluene-ethanol and xylene-ethanol [9, 10, 16, 17] are commonly used to prepare highly concentrated BNKT suspensions with reproducible rheological properties and drying behavior. In recent years, the environmental and health aspects of the tape casting process have received special attention. Organic solvents like toluene are toxic and harmful to the environment and human health. Therefore, the possibility of using ethanol as solvent, which is environmentally friendly and easily available, is promising [18].

In this work, textured BNKT-BF ceramics were fabricated by TGG method with platelet $Bi_4Ti_3O_{12}$ (BIT) particles as template in combination with tape casting of ethanol-based slurries. The influence of the loading of BNKT-BF powders, the dispersant, binder and milling time on the rheological properties was investigated. In addition, the effect of nano-sized $BiFeO_3$ as a liquid phase, promoting agent and its effects on densification and microstructure of BNKT ceramics via TGG process was also studied.

2. EXPERIMENTAL PROCEDURE

Plate-like $Bi_4Ti_3O_{12}$ (BIT) particles were prepared from Bi_2O_3 (99.9%, Aldrich) and TiO_2 (>99%, Aldrich) via molten salt synthesis method at 1100 ^oC for 1 h, using 1:1 molar ratio of NaCl (99%, Aldrich) and KCl (99%, Aldrich) mixture with 1:1 weight ratio of oxides to salt [19]. The product was washed with hot deionized water for several times to remove residual salts. The obtained BIT particles had a plate-like shape with an average diameter of about 5-10 μm and thickness of about 0.4 μm. Figure 1 shows a SEM micrograph of the BIT particles. The platelet BIT particles were mixed with the raw materials (Na_2CO_3 (99.95%, Aldrich), K_2CO_3 (>99.0%, Aldrich), and nano-sized TiO_2 (Degussa-75% Anatase, 25% Rutile) to form BNKT. $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$ with 7 mol% nano-sized $BiFeO_3$ powder was synthesized by solid state method, details of the procedure was reported in literature [6].

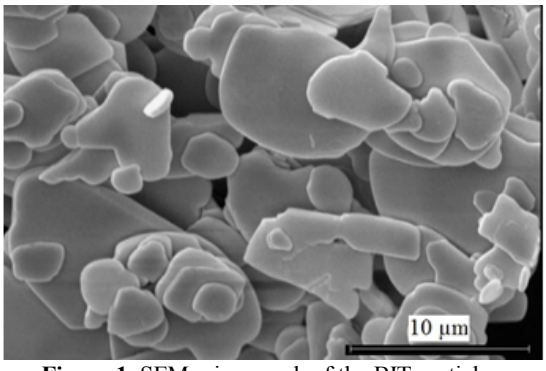

Figure 1. SEM micrograph of the BIT particles.

Suspensions were prepared in absolute ethanol (99.7% grade, Panreac, Barcelona, Spain) using different quantities of a polymeric dispersant that is soluble in ethanol (Hypermer KD6, Uniqema, Wirrall, UK). Solid loading 14 vol% was dispersed inside the solution via rotary ball-mill with zirconia milling media for different times, up to 24 h. For preparing the tape-casting slurries, poly (vinyl butyral) (PVB; Aldrich, St. Louis, MO) and benzylbutyl - phthalate (BBP; Merck - Schuchardt, Hohenbrunn, Germany) were used as binder (B) and plasticizer (P), respectively. The different amount of binder system (B+P) was added to the suspensions with relative ratio of B/P=1. The slurries were ball milled again in a rotary mill for 1 h and after that in a high-energy mill for another 1 h. For TGG method, 5 vol% (referred to solids) BIT particles as templates was added to slurry and stirred for 1 h previous to the tape casting. The rheological behavior of the suspensions and slurries was studied using a rheometer (Model RS50, Thermo Haake, Karlsruhe, Germany).

Tape casting procedure was carried out with a single blade system with a silicone-coated Mylar (R. E. Mistler Inc., Yardley, PA). The blade height was fixed at 200 μm and the casting speed at 5 cm/s. Therefore, viscosity values are reported at shear rate of 250 s^{-1}. The tapes were dried at room temperature for 24 h. Finally, tapes were cut, stacked, and laminated using 50 MPa uniaxial pressures. Organic materials were burned out at 500 ^oC for 1 h, with heating/cooling rates of 1 ^oC/min, which are sluggish enough to inhibit cracking and delamination. The different temperature profiles were applied for sintering of the samples. At the first and second temperature profile (namely, TP1, TP2), the samples were heated at 1150 ^oC and 1200 ^oC, respectively for 10 h, using heating/cooling rates of 5 ^oC/min. At the third temperature profile (namely, TP3) the sample was first heated at 800^oC for 4 h to initiate the in-situ reaction between the matrix powders and the templates, and then heated at 1200 ^oC for 10 h with heating/cooling rates of 5 ^oC/min for the development of the texture. The last temperature profile (namely, TP4) had three steps; first the sample was heated at 800 ^oC under 50 MPa pressure for 1 h. After cooling the sample to room temperature, then heating procedure was continued at 1200 ^oC for 10 h, heating/cooling rates for all steps was 5 ^oC/min. The green samples were previously buried with BNKT powder to prevent bismuth and alkalis volatilization. Density of ceramics was calculated from their weight and dimensions.

X-ray diffraction (XRD) was carried out on the sintered ceramics using Siemens D500 (Munich, Germany) diffractometer with Cu-K_α radiation. A 2θ range from 20 to 50^o was scanned in steps of 0.05^o with a counting time of 3 s/step. The texture was estimated by the Lotgering method based in the relative intensities of the peaks. The degree of <001> orientation of a

sample is determined from $f=(P-P_o)/(1-P_o)$, where $P=\sum I_{(00l)}/I_{(hkl)}$ and I are the intensities of the peaks, whereas P_o and P are for non-textured and textured materials, respectively. Lotgering factor can be used as an estimation of the degree of grain orientation in a textured material [20].

The microstructure was characterized by SEM (Stereo Scan 360-Leica Cambridge) on cross-sections perpendicular to the casting direction.

3. RESULTS AND DISCUSSION

Rheological measurements were used to characterize stability and flow behavior of the suspensions and also to study the interaction between constituent materials in the suspension. Both the deflocculant (Hypermer KD6) content and the milling time were optimized for the binder-free 14 vol% suspension in ethanol. Figure 2 shows flow curves of 14 vol% suspensions with different amount of deflocculant after ball milling for 2 h. For a concentration of 5 wt% KD6 (referred to solids) a milling time of 2 h is sufficient to stabilize the slip and the flow curve shows a lower viscosity and thixotropy. The slips with 3, 4, and 6 wt% KD6 after 2 h milling time present the higher viscosity and also more thixotropy. According to these results, 5 wt% KD6 was selected as the optimum dispersant content to obtain stable slips.

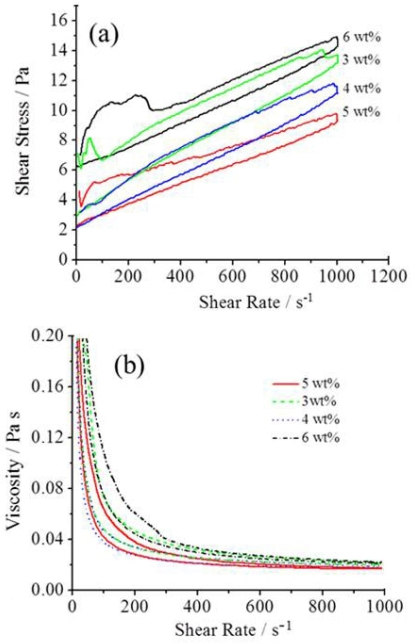

Figure 2. (a) Flow curves and (b) viscosity curves, of 14 vol% suspensions with different deflocculant content after 2 h of ball milling.

A minimum viscosity of 24.5 mPa.s was obtained for the best suspension at a shear rate of 250 s^{-1}. The deflocculant content does not affect thixotropy markedly. However, from the flow curves in Figure 3, the suspension with 5 wt% KD6 after milling time for 2 h allows to the deaggolmeration and the lowest viscosity. This suspension shows more thixotropic behavior with increasing milling times. A minimum viscosity of 21.5 mPa.s was obtained after 2 h of milling, which means that a dispersed state of particles have obtained. This milling time was effective in breaking up the soft agglomeration and in ensuring adsorption of dispersant on the powder surface. The viscosity of the slips increased after 24 h milling time, due to reagglomeration of the particles [21]. As the result, 5 wt% of KD6 and 2 h of milling time were selected as the best dispersing conditions with the lowest viscosity and thixotropy conditions.

Figure 4 shows the effect of the binder system (B+P) on the rheological behavior of the suspensions. The viscosity curves of slips with solid loading of 14 vol% with an 18, 20, and 22 wt% of B+P (referred to solids) was investigated. After addition of 22 wt% of P+B, the suspension with the highest viscosity was obtained. Since, the adhesion process between particles and polymers must be higher than the adhesion between the tape and the carrier film (silicon-coated Mylar) [21], the slip with 22 wt% of P+B allowed an easy remove of the dry tape; hence the 22 wt% binder system was chosen.

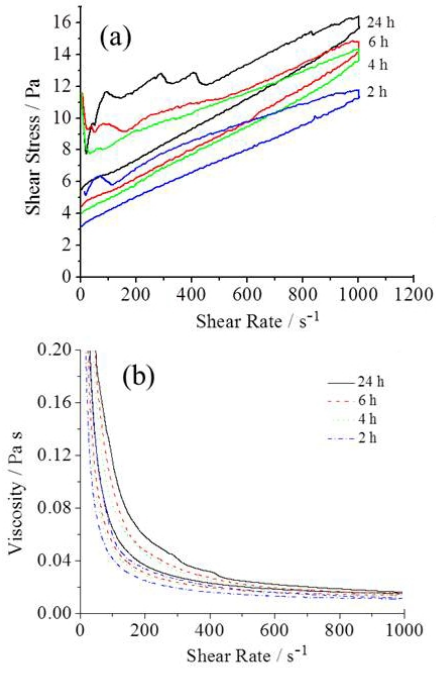

Figure 3. (a) Flow curves and (b) viscosity curves with 5 wt% dispersant content and different milling times.

Generally, all the prepared suspensions showed Bingham behavior due to the effect of the binder system. The slurry showed a Newtonian behavior on high shearing rate.

Therefore, high shear rates promote the orientation of the platelet template particles without changes in rheological properties of the suspensions. The shear forces of the tape casting process make it possible to align plate like BiT particles to obtain a highly textured ceramic. Homogenous green tape with thickness about 44 μm and relative density of 54% were obtained. Figure 5 shows SEM micrographs of the cross-section of green tape, which reveals a matrix with uniform, smaller grain size, and densely packed microstructure, the BIT templates were aligned in the planar direction, which is the casting direction. This obviously shows that the tape casting method has been done effectively to align the template particles.

The tape cast samples were sintered using four different temperature profiles (TPs) as plotted in Figure 6. Figure 6(a) shows that heating at 1150 °C, which led to the formation of the cubic-shaped BNKT particles. No obvious crystallographic orientation can be observed at this sintering temperature (TP1).

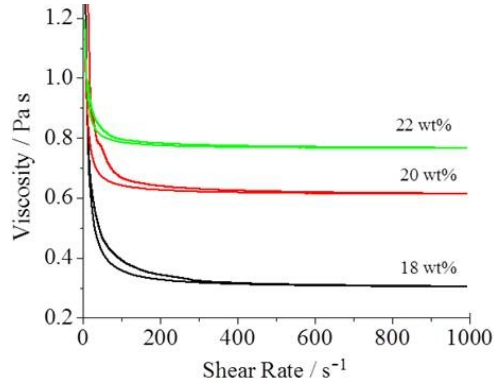

Figure 4. Viscosity curves of slips using the binder system.

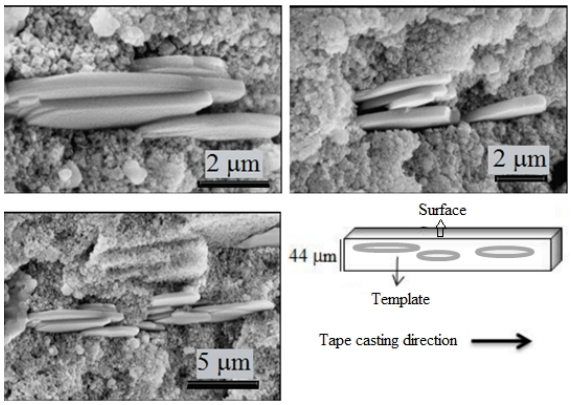

Figure 5. SEM micrographs of the cross section of green tape cast samples.

The sample in Figure 6(b) was sintered at the temperature of 1200 °C. The size of BNKT grains evidently increased with increasing temperature (TP2). Moreover, no distinction could be made between the matrix and BIT particles (Figure 6(b)). These results indicate that the inter-diffusion of small matrix grains and template platelets results in uniform cubic-shaped grains without a pronounced texture [9]. Two step sintering profiles (TP3) and (TP4) were employed for the samples seen in Figures 6(c) and 6(d). The sample in Figure 6(c) was initially soaked for 4 h at 800 °C and then sintered at 1200 °C. The new temperature profile caused better densification of the sample in Figure 6(c) as compared with Figure 6(b). In the final temperature profile (TP4), the sample was initially heated at 800 °C for 1 h under 50 MPa pressure and then cooled down to room temperature. It was then sintered in air at 1200 °C with no applied pressure as in the case of previous samples. This last profile is evidently quite effective in providing a texture microstructure.

The selected additive, bismuth ferrite, with a perovskite-type crystal structure is expected to provide a solid solution with BNKT [6]. On the other hand, the presence of BF with low melting point temperature favors a liquid phase sintering mechanism. The liquid phase content during grain growth also influences texture development in many systems [22].

Figure 7 shows SEM micrographs of the cross section of ceramics with different sintering profiles. The sintering profiles TP1, TP2 and TP3 apparently did not produce the desired texture, whereas simultaneous use of pressure and temperature at 800 °C resulted in the formation of textured samples. Figure 8 shows the XRD patterns of the all samples with the different sintering profiles. All samples possess a pure perovskite structure, indicating that a homogeneous solid solution between matrix and template particles were formed.

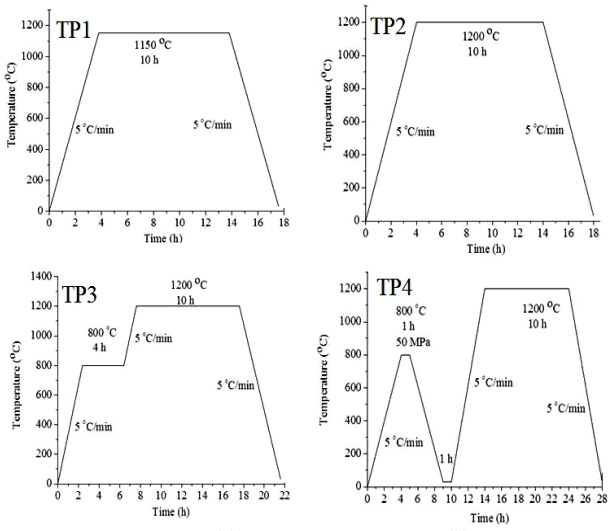

Figure 6. Different temperature profiles.

Figure 8 shows the XRD patterns of the all samples with the different sintering profiles. All samples possess a pure perovskite structure, indicating that a homogeneous solid solution between matrix and template particles were formed. In addition, after the densification process, bismuth ferrite as a liquid phase may either enter the perovskite lattice or remain at the grain boundaries. The intensity of (100) and (200) peaks of the textured sample (TP4) was higher than that of the non-textured ones. The density and the degree of orientation of the all samples are tabulated in Table 1. The degree of orientation of the samples shows a strong dependence on the sintering profile. During sintering process, when Na_2CO_3, K_2CO_3 and TiO_2 were used as reactants, the BIT to BNKT conversion occurred at 600-800 ^oC, and the converted perovskite type platelet template with preserved orientation developed at the expense of matrix particles above 1000 ^oC [23]. According to our results applying 50 MPa pressure at 800 ^oC is evidently quite effective in providing a texture microstructure.

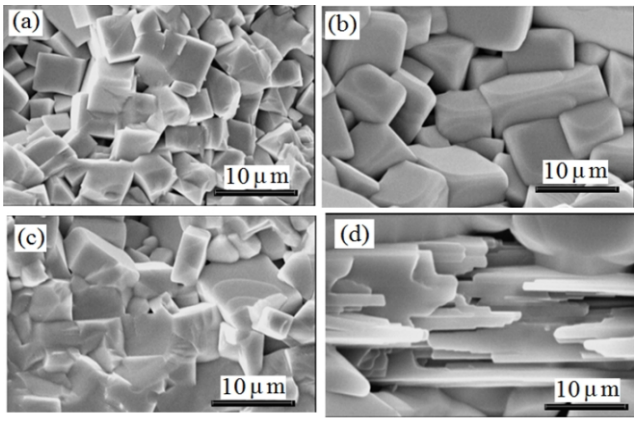

Figure 7. SEM micrographs of the cross section of ceramics with different sintering profiles heating at (a) 1150 ^oC for 10 h, (b) 1200 ^oC for 10 h, (c) 800 ^oC for 4 h then 1200 ^oC for 10 h, and (d) 800 ^oC with 50 MPa pressure for 1 h then 1200 ^oC for 10 h.

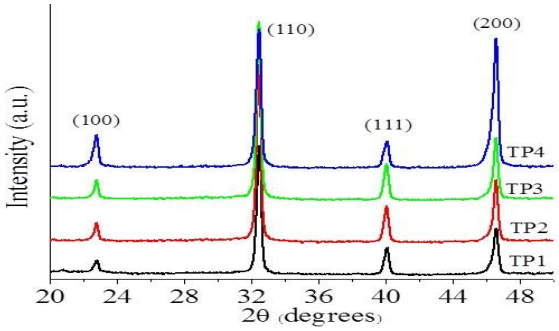

Figure 8. X-ray diffraction patterns of the ceramics with the different sintering profiles (a) 1150^oC for 10 h, (b) 1200^oC for 10 h, (c) 800^oC for 4 h then 1200^oC for 10 h, and (d)800 ^oC with 50 MPa pressure for 1 h then 1200 ^oC for 10 h.

TABLE 1. Relative densities and Lotgering factor of ceramics with different sintering profiles.

Sintering profile	TP1	TP2	TP3	TP4
Relative density (%)	87	86	90	91.5
Lotgering factor	0.15	0.14	0.17	0.92

4. CONCLUDING REMARKS

Ethanol-based homogeneous slips of BNKT-BF powder with addition 5 wt% of a polymeric dispersant and 14 vol% of a solid loading were prepared. A 22 wt% of binder and plasticizer (B/P=1) was added to obtain suitable slips for tape casting process. Platelet BIT templates were added to the optimized slurries to develop of extensive texture. The effect of different types of sintering temperature profile was investigated to obtain highly textured ceramics. The degree of grain orientation increased with three step sintering along with 50 MPa pressure. In addition, after the densification process, bismuth ferrite as a liquid phase may either enter the perovskite lattice or remain at the grain boundaries.

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چکید

در این پژوهش رفتار رئولوژیکی دوغاب‌های حاوی ذرات پیزوالکتریک بدون سرب، بر پایه تیتانات بیسموت سدیم پتاسیم به همراه ۷ درصد مولی نانو ذرات فریت بیسموت با فرمول شیمیایی $Bi_{0.5}(Na_{0.80}K_{0.20})_{0.5}TiO_3$-7 mol% $BiFeO_3$ (BNKT-BF) مورد بررسی قرار گرفت. نانو ذرات فریت بیسموت به همراه ذرات BNKT به کمک روش ریخته‌گری نواری به همراه ذرات صفحه‌ای شکل تیتانات بیسموت($Bi_4Ti_3O_{12}$(BIT، به عنوان شابلون، برای رسیدن به ریزساختار بافت‌دار استفاده شدند. ریزساختار بافت‌دار با رشد ترجیحی ذرات، توسط برنامه‌های تف جوشی متقاوتی بررسی و سرانجام با اعمال فشار ۵۰ مگاپاسکال در دمای $^{\circ}C$ ۸۰۰ و حرارت دهی مجدد در دمای $^{\circ}C$ ۱۲۰۰ به مدت ۱۰ ساعت ریزساختار بافت‌دار حاصل شد.

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