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Texture evolution in tape cast lead metaniobate

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Abstract

Lead metaniobate ceramics were tape cast with inclusions of acicular seed particles. The effects of seed particle concentration, slurry viscosity, and casting velocity on the shear behavior of the tape cast slurry were quantified based on a model using the ratio of pressure driven forces to viscous driven forces. Texture was quantified using a combination of X-ray diffraction with the Lotgering factor and neutron diffraction with Rietveld refinement. The shear behavior of the individual slurries was linked to the amount of texture that is induced from given slurry.

Keywords: Tape casting; Lead metaniobate; $PbNb_2O_6$; Piezoelectrics; Texture

1. Introduction

Tape casting ceramic powders with inclusions of shaped seed particles is a convenient way to induce crystallographic textures. While highly anisotropic ceramics can be created in this way, most investigations in this area focus on either the seed particle shape or the concentrations of seed particles in the slurry.[1–4] While these two parameters do influence the degree of preferred orientation developed, there are other parameters related to the slurry rheology and operating conditions of the tape casting process that may effect the degree of developed texture. In this paper, the relationship between the rheology of the tape casting slurry and the conditions of the casting process used will be examined in relation to the amount of preferred orientation induced in a tape cast lead metaniobate ceramic.

Recently, Kim and coworkers conducted a model for tape casting Newtonian fluids with several simplifying assumptions.[5] They employed a parameter, Π, to quantify the ratio of pressure forces to viscous forces acting on a tape cast slurry during deformation under a doctor blade. Utilizing all process conditions and slurry viscosity, it is possible to calculate Π and estimate whether a casting operation will be dominated by pressure flow or shear flow. From Kim's work, Π is given by the equation:

$$\Pi = \frac{\Delta PH^2}{2\mu LU} \qquad (1)$$

where ΔP is the pressure exerted by the slurry head ($\Delta P = \rho_{\text{slurry}} g H_{\text{slurry}}$), H is the blade gap used, μ is the slurry viscosity, L is the length of the doctor blade, and U is the casting velocity.[5] The ratio of the pressure force to shear force determines the flow characteristics and the wet tape thickness for tape casting. Since a viscous force is more favorable than a pressure force for particle alignment, variations to the tape casting process that gives lower Π values should result in a higher degree of texture.[5]

In the present study, lead metaniobate ceramics were tape cast with acicular seed particles that serve as templates for subsequent grain growth with a preferred orientation. Lead metaniobate is a ferroelectric ceramic that is isostructural with orthorhombic tungsten bronze where the polar axis is parallel to the crystallographic *b*-direction.[6] When subjected to an electric field, the material develops a *b*-type texture relative to the poling direction.[7] Previous researchers have shown that the relatively weak piezoelectric response of lead metaniobate can be increased by processing the ceramic with preferred orientation prior to electrical poling.[1,8] Granahan and co-workers showed that the piezoelectric properties could be improved by tape casting lead metaniobate slurries containing acicular seed particles.[1] However, the effects of tape casting itself on the orientation developed have not been examined with systematic consideration of tape casting variables. In this study, preferred orientation developed through a tape casting process similar to Granahan's will be examined. The link between tape casting variables including variations in seed particle concentration, slurry viscosity, and casting velocity will be linked to varia-

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tions in the degree of preferred orientation developed during processing.

2. Experimental procedure

2.1. Tape casting with acicular seed particles

Acicular seed particles were grown from a melt following the method proposed by Li and co-workers for lead metaniobate of the stoichiometry $PbNb_2O_6$.[9] These particles (Fig. 1) are single crystals of orthorhombic lead metaniobate with an elongated "box" shape. The long axis of these particles is parallel to the crystallographic *c*-axis with the *a*- and *b*-axes parallel to the shorter sides. The ceramic powder used was unfired K81 (Piezo Technologies, Indianapolis, IN). K81 is a modified lead metaniobate, which contains a modest amount of an alkali dopant. When fired, the crystal structure exhibits the ferroelectric, orthorhombic structure with elongated *a*- and *b*-axes relative to the *c*-axis (*a*: 17.63 Å, *b*: 17.92 Å, and *c*: 3.87 Å).

Two generalized slurries based on tape casting of PZT were used in this study. The two slurry compositions are shown in Table 1.[10] The solvent used was a 67/33 by weight mixture of methyl ethyl ketone (M209-4, Fisher Scientific, Waltham, MA) and ethanol (A407-4, Fisher Scientific, Waltham, MA). The binder and plasticizer used were polyvinyl butyral (Butvar B-98, Tape Casting Warehouse, Yardley, PA) and butyl benzyl phthalate (S-160, Tape Casting Warehouse, Yardley, PA), respectively. In addition, two different dispersants were used. Slurries designated PE employed a phosphate ester dispersant (PE-1168, Huntsman, The Woodlands, TX) while slurries designated HYP used hypermer KD-1 dispersants (KD-1, Tape Casting Warehouse, Yardley, PA).

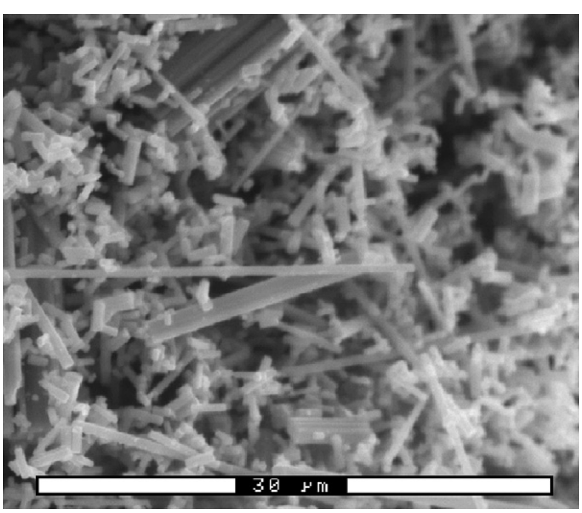

Fig. 1. SEM micrograph of $PbNb_2O_6$ acicular seed particles grown from a molten salt synthesis procedure. The particles are of a $PbNb_2O_6$ stoichiometry with the long axis parallel to a crystallographic *c*-direction.

Table 1
Breakdown of the PE and HYP slurries used in the present study

	Ceramic	Solvent	Binder	Plasticizer	Dispersant
PE	64.7	22.4	5.7	6.7	0.5
HYP	65.8	22.8	4.1	6.8	0.5

Numbers are given in wt%.

The powder (K81), solvent, and dispersant were ball milled for 24 h, at which time the binder and plasticizer were added. This mixture was then ball milled for 23 h, followed by the incorporation of the required amount of seed particles. After 1 h of ball milling, the slurry was de-aired under vacuum. Slurry viscosities were measured using a Brookfield viscometer (Dial Reading Viscometer, Brookfield Engineering, Middleboro, MA) over a range of shear rates. The equivalent shear rate is calculated using the spindle size and speed accompanied with conversion information provided from the manufacturer.

Seed particle concentrations were varied by weight of K81 powder. The HYP slurries were cast with concentrations of 0, 5, 10, 15, and 20 wt% seed particles. The PE slurry was cast solely with 5 wt% seed particles. Casting velocities were 20 and 80 cm/min for the HYP slurries containing 10 wt% seed particles. All other slurries were cast at a velocity of 20 cm/min. After casting, tapes were dried for 24 h at room temperature. Green tapes were cut and laminated into stacks of 10–20 sheets. Care was taken to keep the orientations of the green tapes consistent during lamination. Laminates were pressed at 6.9 MPa with heated platens at 38 °C. After lamination, samples were bisque fired and sintered at 600 and 1240 °C, respectively.

2.2. Texture evaluation from diffraction experiments

Directions discussed in this paper are designated as the tape casting direction (TCD), tape casting normal (TCN), and transverse direction (TD), shown in Fig. 2. After firing, samples were polished to a fine grit (1 μm) on the tape cast normal (TCN). To examine texture, two diffraction experiments were employed. Cu Kα X-ray diffraction (D500, Siemens, Germany) was performed over an angular range of 20–50° in 2θ to examine differences in the diffraction patterns relative to a random sample. X-ray diffraction patterns taken on the TCN of each sample were used to quantify the development of preferred orientation using the Lotgering factor.[11] Accounting for the *a*–*b* texture occurring during layered manufacturing of lead metaniobate, Hagh and coworkers proposed the equation:

$$f = \frac{p_{\text{tex}} - p_{\text{o}}}{1 - p_{\text{o}}} \times 100, \quad p_{\text{tex}} = \frac{\sum I_{h\,k\,0}}{\sum I_{h\,k\,l}} \tag{2}$$

to quantify the *a*–*b* texture arising during texture processing.[8] However, significant peak overlap inhibits the use of all of the

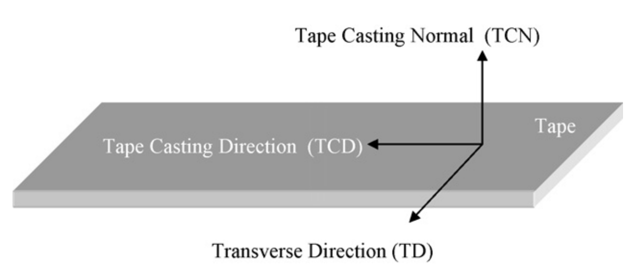

Fig. 2. Directions relative to the present tape casting setup.