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# Low-Temperature Crystallization of Sol–Gel Processed $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ : Powders and Oriented Thin Films

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**A novel sol–gel process suitable for depositing thin-film lead barium titanate has been developed. X-ray diffraction analysis showed perovskite phase crystallization to occur at a temperature as low as 400°C with single-phase  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  (PBT) resulting at a temperature as low as 500°C. Small concentrations of barium carbonate were evident by X-ray diffraction at 400°C, and indications of minor, carbonate-containing phases were evident by FTIR at 600°C. Deposition of the sol by spin coating on single-crystal and thin-film MgO on silicon resulted in highly oriented PBT films after calcination at 600°C. Mixed (100)/(001) films were obtained on single-crystal MgO, whereas entirely (100) films were obtained on thin-film MgO.**

## I. Introduction

TO USE  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  (PBT) in micro-actuation applications, it is necessary to synthesize highly textured thin films at low temperatures,<sup>1,2</sup> with single-crystal thin films offering the greatest possibilities for actuation. Low-temperature crystallization, furthermore, offers the potential for integration with silicon-based electronic devices. Toward this goal, we examined the possibility of obtaining highly oriented PBT films on MgO using sol–gel techniques. Various acids and alkanolamines have been used as chelating agents for titanium in the synthesis of  $\text{BaTiO}_3$ ,  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT), and  $\text{PbTiO}_3$ ,<sup>3–5</sup> however, only limited studies have been conducted on the PBT system in particular. In an earlier work,<sup>1</sup> it was demonstrated that good-quality films could be produced from solutions in which acetylacetone served as a chelating agent. However, the system was highly sensitive to slight variations in processing conditions, and undesired precipitation often occurred before titanium could be fully chelated. In the present study, we used diethanolamine [ $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$ , DEA] as a chelating agent for the sol–gel synthesis of PBT powders and thin films. DEA is widely used in the sol–gel synthesis of  $\text{TiO}_2$ , and is known to effectively chelate titanium and thereby produce stable sols.<sup>6,7</sup> Recently, it has been used to stabilize PZT and  $\text{PbTiO}_3$  sols.<sup>8,9</sup> We show here that DEA leads to PBT powder crystallization at temperatures as low as 400°C, and to highly oriented films at temperatures as low as 600°C.

## II. Experimental Procedures

From an examination of many possible precursor and solvent systems, the combination of lead nitrate, barium acetate, titanium isopropoxide, ethylene glycol (as a solvent), and diethanolamine

(as a chelating agent) was found to yield a chemically compatible system in which all species remained in solution and from which PBT crystallization occurred at relatively low temperatures. Dissolution of the metals salts (25 mmol lead nitrate and 25 mmol barium acetate) in ethylene glycol (2 mol) was conducted at 60°C using a rotary evaporating system. Separately, titanium isopropoxide (50 mmol) was mixed with diethanolamine (200 mmol), and then added to the lead/barium solution and mixed at 60°C. The resulting solution was cooled to room temperature, and deionized water (in a prescribed molar ratio with titanium, e.g., 4:1) mixed with ethylene glycol (7.2 mL) was added. The solution was divided into two parts, with one part used for spin coating and the other dried at 175°C for several days to form a xerogel. After drying, the xerogels were calcined at  $T_c = 400^\circ, 500^\circ, 600^\circ, 700^\circ\text{C}$  under stagnant air for 2 h. Thin films were prepared by spin-coating the sol onto (100) MgO single crystals, at 4000 rpm for 60 s (KW4-A, Chemat, Northridge, CA). After deposition, each layer was dried at 200°C for five minutes (under stagnant air) to enable deposition of subsequent layers. Calcination was conducted at  $T_c = 550^\circ$  and 600°C for 2 h with a heating rate of 5°C/min and, again, under stagnant air.

The solution chemistry of the sols and the high-temperature decomposition of the organic components were probed by FTIR spectroscopy (Nicolet Magna 860, Madison, WI) over the wavenumber range 4000–400  $\text{cm}^{-1}$ . Thermal decomposition characteristics of the oven-dried xerogel were further studied by simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA; Model STA-449, Netzsch, Exton, PA) at a constant heating rate of 10°C/min under an atmosphere of 4%  $\text{O}_2/96\%$  Ar. Phase formation in both powder and thin-film samples were examined by X-ray diffraction (XRD; Model X'Pert, Philips, Eindhoven, Netherlands). Data from different samples were collected under identical conditions to permit (to first order) comparison of the absolute diffraction intensities.

## III. Results and Discussion

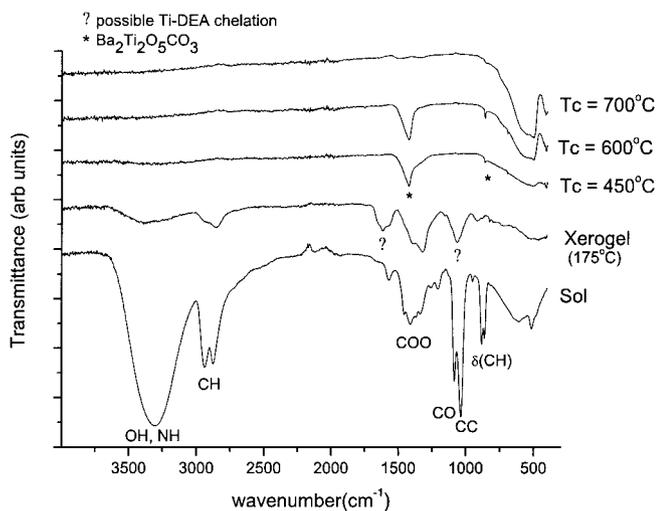
Transparent, colorless PBT precursor sols were obtained for diethanolamine:Ti molar ratios ( $R_A$ )  $\geq 3$ . Because of the extremely hygroscopic nature of titanium isopropoxide, insufficient chelation at lower DEA concentrations resulted in rapid precipitation. Generally, an alkoxide-based system cannot be prepared homogeneously with other metal salts containing high water of hydration.<sup>10</sup> To ensure excess DEA to fully chelate titanium,  $R_A = 4$  was used. The chelated system was stable for more than 2 months for water:titanium molar ratios ( $R_w$ ) as high as 16. At higher water concentrations, in particular  $R_w = 32$ , a precipitate was formed within minutes. XRD studies of powders calcined at 600°C (data not shown) revealed that a pyrochlore phase was formed at very high ( $\geq 6$ ) and very low ( $\leq 2$ ) values of  $R_w$ , whereas intermediate  $R_w$  (e.g.,  $R_w = 4$ ) formed phase-pure PBT. Thus,  $R_w$  was held fixed at 4 in subsequent synthesis. The optimized sol ( $R_A = 4, R_w = 4$ ) had a PBT concentration of 0.35M.

FTIR spectra of the sol, xerogel, and calcined powders are shown in Fig. 1. The sol exhibits peaks due to the presence of the

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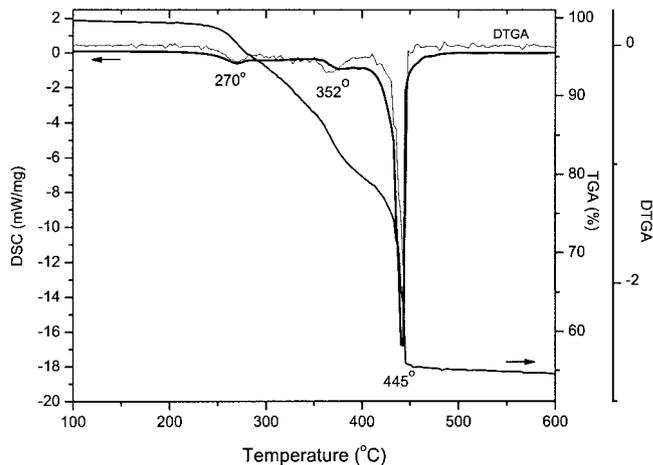
\*Member, American Ceramic Society.



**Fig. 1.** FTIR spectra of the sol, xerogel, and powders calcined at the indicated temperatures.

organic moieties of ethylene glycol, isopropoxide, acetate, and diethanolamine, as indicated on the figure. After drying at 175°C to form the xerogel, most of the organics are removed. The OH/NH [3300–3370  $\text{cm}^{-1}$ ], CH [2900  $\text{cm}^{-1}$  doublet] and  $\delta(\text{CH})$  [875  $\text{cm}^{-1}$  doublet] peaks are greatly diminished in intensity. The COO stretching band (1350  $\text{cm}^{-1}$  broad doublet for symmetric and asymmetric stretching modes) is retained, suggesting that acetate groups remain bound to barium and/or lead ions. Perhaps more significantly, a new peak appears at  $\sim 1620 \text{ cm}^{-1}$ , with a comparable intensity to the peak at 1065  $\text{cm}^{-1}$ . The moieties responsible for these absorptions are not readily identifiable, and the peaks are tentatively attributed to strong chelation of titanium by DEA. On heating to 450°C, only a peak at  $\sim 1425 \text{ cm}^{-1}$  is present, along with a very small peak at  $\sim 855 \text{ cm}^{-1}$ . The spectrum at 600°C is identical, with the exception of the appearance of the Ti-O band at 540  $\text{cm}^{-1}$ . This pair of peaks (1425 and 855  $\text{cm}^{-1}$ ) is likely due to  $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ .<sup>11</sup> An adsorption band at 3000  $\text{cm}^{-1}$ , in addition to that at 1425  $\text{cm}^{-1}$ , would be expected for simple barium carbonate.<sup>12</sup> By 700°C, all trace of organic components is absent, and even the spectrum obtained after annealing at 450°C shows relatively little organic (i.e., oxycarbonate) content. In comparison to these results, preliminary experiments in which lead acetate rather than lead nitrate was used as the lead source indicated retention of the peaks assigned to oxycarbonate to temperatures of at least 800°C.<sup>13</sup>

Thermal analysis of the dried PBT gel samples showed a total weight loss of  $\sim 45\%$ , occurring over three weight loss regions (Fig. 2). Each weight loss event is associated with an exothermic thermal event (and all thermal events are associated with weight loss). Gradual weight loss ( $\sim 9 \text{ wt}\%$ ) occurs over the range 225–325°C, peaking at 270°C and accompanied by a DSC peak of 49 J/g. A second, similarly broad weight loss event of  $\sim 12 \text{ wt}\%$  occurs over the range 325–405°C, peaking at 352°C. The DSC peak for this event is 29 J/g. At 445°C a very sharp peak is evident in both the DSC and DTGA curves. Weight loss over the range 405–480°C is 24 wt% and the DSC signal is 1.9 kJ/g. The first two weight-loss events are presumed to result from the removal of free volatile species, not strongly chelated to any of the metal cations in the gel network (most of which are already removed by the drying process). The sharp weight loss event at 445°C is tentatively assigned to the combustion of DEA, with residual nitrate in the sample as well as oxygen in the atmosphere serving as oxidizers. The FTIR results (Fig. 1) support this interpretation, with only adsorption bands associated with the oxycarbonate remaining at 450°C. Removal of  $\text{CO}_2$ , which is typically an endothermic process, apparently occurs at temperatures  $> 600^\circ\text{C}$  as a result of kinetic constraints. The reaction of barium carbonate



**Fig. 2.** (a) DSC, (b) TGA, and (c) DTGA curves obtained from a  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  xerogel sample.

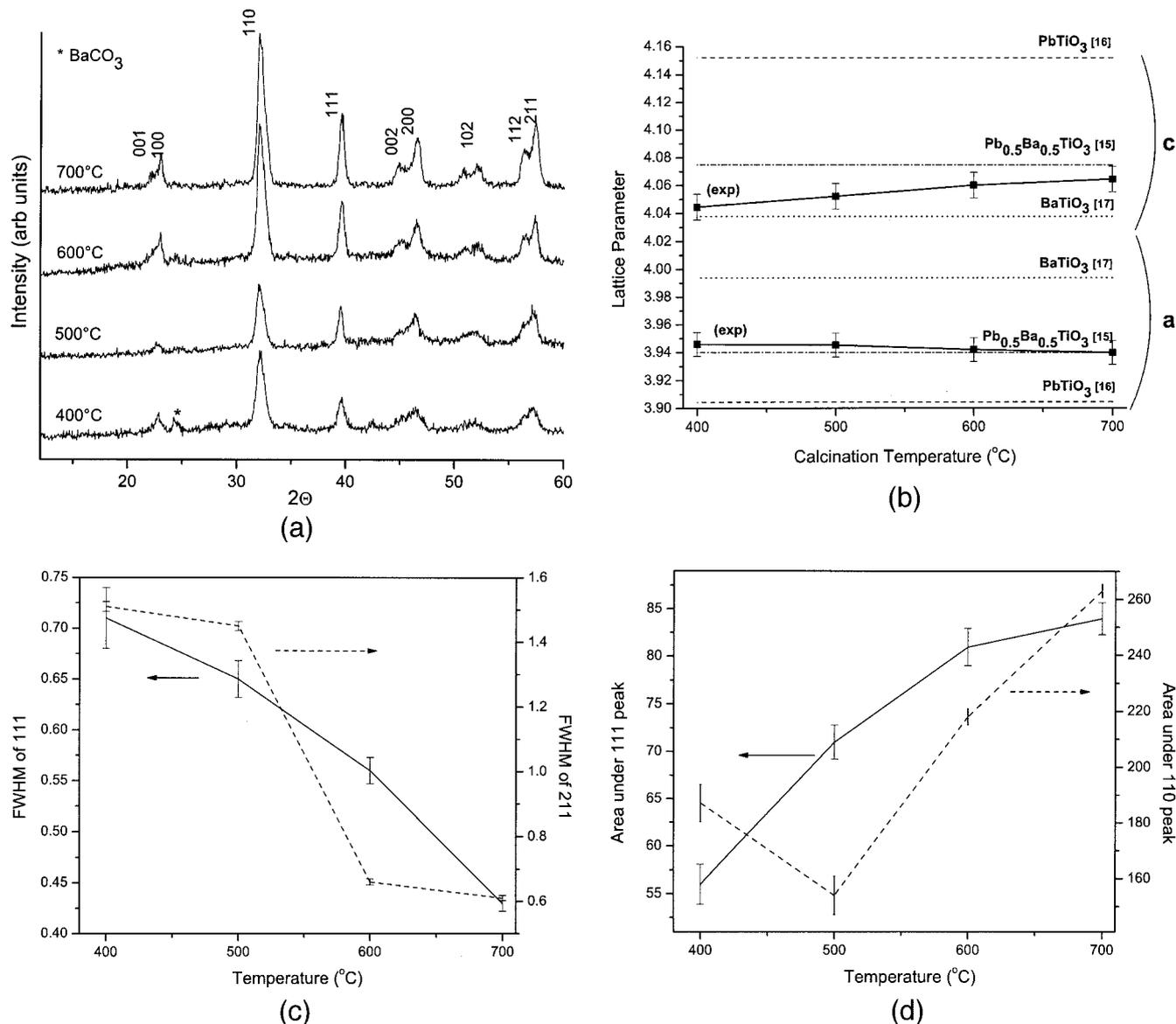
with titanium dioxide, for example, to form barium titanate would occur at  $\sim 370^\circ\text{C}$  under a  $\text{CO}_2$  pressure of 1 atm.<sup>14</sup>

X-ray diffraction studies of calcined powder samples show that the perovskite PBT phase formed at a temperature as low as 400°C, with phase-pure PBT obtained at 500°C (Fig. 3). At 400°C, a small amount of barium carbonate (rather than the barium titanium oxycarbonate indicated by the FTIR results) is present. In addition, although the cell parameters remain essentially constant, sharp changes in overall crystallinity (intensity of peaks and narrowness of peak FWHM) occur between 500–600°C (Figs. 3(b), (c), and (d)). The latter is likely a result of the removal of  $\text{CO}_2$  and crystallization of any previously amorphous carbonate/oxycarbonate material. This is in relatively good agreement with the FTIR and thermal analysis data, which indicate that such a step should occur at slightly higher temperatures, between 600–700°C. The constancy of the  $a$  and  $c$  lattice parameters (as a function of calcination temperature) and their similarity to the values reported for  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  provide strong evidence that a single-phase material of the desired composition has been obtained.<sup>15–17</sup>

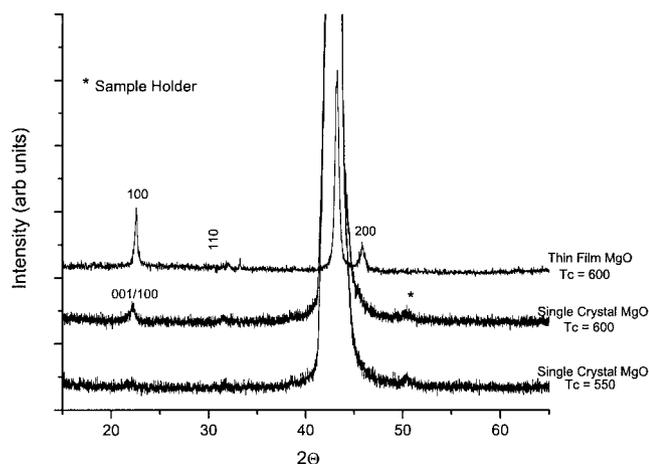
PBT thin films prepared on single-crystal MgO substrates were found to be highly (001)/(100) oriented (Fig. 4), after calcination at 600°C. Each layer is  $\sim 60 \text{ nm}$  thick, as determined by cross-sectional FESEM (not shown). The low intensity of the PBT peaks relative to that of the MgO substrate precludes differentiation between (001) and (100) orientations. Highly oriented films were also obtained on a 25-nm layer of (100) oriented MgO deposited onto Si [ $T_c = 600^\circ\text{C}$ ].<sup>18–19</sup> On both single-crystal and thin-film MgO, PBT crystallized in the absence of any impurity phases. Furthermore, on thin-film MgO, the ferroelectric showed only (100) orientation, with the longer  $c$ -axis parallel to the MgO surface. This is proposed to result from the net tensile stress placed on the PBT by the silicon substrate on cooling from the calcination temperature of 600°C. It is noteworthy that hydroxylation of the MgO surface, as would be expected to occur under the conditions of sol-gel synthesis, apparently improves rather than degrades the degree of PBT orientation, an observation discussed in detail elsewhere.<sup>18</sup>

#### IV. Conclusions

A new sol-gel procedure incorporating diethanolamine as a chelating agent for titanium has been developed for the synthesis of a stable  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  precursor sol. X-ray diffraction studies of the resulting powder showed that perovskite-phase crystallization occurred at a temperature as low as 400°C, albeit in the presence of small amounts of undesired barium carbonate. Highly oriented PBT films were obtained by spin coating on both single-crystal and thin-film MgO, after calcination at 600°C.



**Fig. 3.** (a) XRD patterns obtained from  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  powder samples calcined at the temperatures indicated; (b) comparison of  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  lattice parameters determined with  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , and literature  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ <sup>15–17</sup> lattice parameters; (c) FWHM of 111 and 211 peaks; and (d) area under 111 and 110 peaks.



**Fig. 4.** XRD pattern obtained from  $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  films on single-crystal MgO and thin-film MgO on silicon calcined in air at temperatures indicated.

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