F. G. Figueiras, et al., Narrow Optical Gap Ferroelectric Bi₂ZnTiO₆ Thin Films Deposited by RF Sputtering

Supplementary Information: Target preparation and characterization

Bulk ceramic pellets with 2 cm diameter were prepared using two different methods: a modified sol-gel and a solidstate route. In the sol-gel method, started from stoichiometric amounts of Bi₂O₃ (Alfa Aesar, 99.99 %), ZnO (Merck, 99 %) and titanium isopropoxide C12H28O4Ti (Sigma, 97 %) as Bismuth (Bi), Zinc (Zn) and Titanium (Ti) sources, respectively. Ethanol:HNO₃ 10:1 mixture is prepared, stirred and heated until the solution became clear, then used to dissolve separately the Bi₂O₃ and ZnO, the Ti precursor was added dropwise to this previous mixture. The solution was stirred at 80°C until a powder is obtained, which will then be grounded in an agate mortar, pestle and calcined in a muffle furnace at 550°C during 1 h. Then it passes through a 38 µm sieve in order to obtain a fine and homogenized powder to be pelletized and sintered at ~850°C during 2 h. In the solid-state method, the stoichiometric amounts of Bi₂O₃, ZnO and titanium isopropoxide were mixed together and milled thoroughly. Then, it was added the appropriate volume of absolute ethanol, in order to obtain a slurry which was stirred during 2 hours. The solution was submitted of a heating process (~ 80 °C) in order to remove the solvent and a yellow pale powder was obtained. This powder was pre-calcined at 300°C during 1 hour, grounded and calcined at 500°C during 5 hours. After re-ground and pelletizing it was sintered at 850°C during 5 hours. For both methods, EDS and geometric analysis of pellets confirm relative densities above 80% and low Bi losses. No adjustments to precursors proportions were found necessary to compensate possible Bi sublimation. Once conferring these results, the sputtering targets of ~5.0 cm diameter were prepared by the above mentioned solid-state method, using a 6.0 cm mould to take into account the ~20% contracting during sintering.

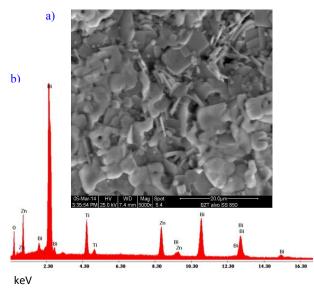


Figure s1: a) SEM image of Target surface and b) respective EDS spectrum.

Scanning Electron Microscopy (SEM) and X-Ray microanalysis of composition (EDS) of target were performed using a *FEI Quanta 400 ESEM/EDAX Genesis X4M*. The surface morphology and composition of the target extend were analyzed through SEM/EDS experiments and typical results are displayed in figure s1. In figure s1a) is possible to observe that the target is mainly comprised of sintered plate-like crystallites reaching up to 10 μ m wide. In figure s1b) is exemplified an EDS spectrogram confirming that target composition consists only of Bi, Zn, Ti and O without traces of contamination elements. Table s1 show information about the target dimensions and averaged atomic Bi:Zn:Ti ratios, which are within a ±2% margin of the intended nominal composition.

Target	Quantity	Units
mass	54.039	g
thickness	4.5	mm
diameter	47.5	mm
density	6.77	g/cm ³
relative density	87.9	%
At. Bi	21.33	%
At. Zn	12.86	%
At. Ti	11.12	%
At. O	54.64	%

Table s1: target specs and composition by EDS

XRD analysis of the ceramic target, shown in figure s2, enables to identify the concomitance of crystallographic phases similar to *I23* (197) $Bi_{12}Ti_1O_{20}$ (PDF# 04-002-1334),¹⁸ Aea2 (41) $Bi_4Ti_3O_{12}$ (PDF# 04-009-5133)¹⁹ and *P6₃mc* (186) ZnO (PDF# 04-008-2750).²⁰ As expected, under ambient pressure, the BZT ceramic target does not sinter into a single phase. Nonetheless, this issue is expected to be overcome in the films, since the control of the thin film phase will be determined by the thermodynamic conditions during deposition in conjunction with the substrate epitaxial effects.

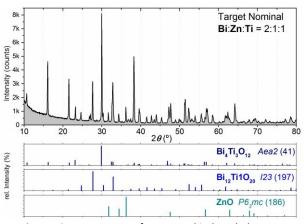


Figure s2: XRD pattern of target and indexed phase.