Structural and optical properties of bismuth zinc niobate pyrochlore thin films

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Pyrochlore and pyrochlore-related oxide system Bi₂O₃-ZnO-Nb₂O₅ (BZN) has received special attention in last years due to its high dielectric constants (E), low dielectric losses, and compositionally tunable temperature coefficients of the capacitance (TCC). These properties, allied to the low sintering temperatures (less than 950 °C), make these compounds attractive candidates for capacitor and high-frequency multilayer structures co-fired with metal electrodes [1]. Two basic phases of the BZN system, the cubic-pyrochlore-structure composition Bi_{1.5}ZnNb_{1.5}O₇ (α-phase), and the low-symmetry-structure with composition $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (β -phase) have been most studied. Their electrical properties are quite different for each phase (TCC is about -400 ppm/°C for the α-phase and +200 ppm/°C for the β-phase), what is attractive for manufacturing of controllable temperature coefficient of capacitance devices [2]. BZN-based dielectrics ceramics have been systematically prepared by the solid state reaction, which is known to yield large sized particles and local chemical heterogeneity. Commonly this route leads to multiphase powders [3]. Alternatively chemical methods have been employed to achieve smaller sized particles with chemical homogeneity. Nanocrystalline materials obtained by the solution-based chemical methods are normally chemically homogeneous, with a narrow size distribution of particles and lead to low crystallization and sintering temperatures. In this work, bismuth zinc niobate pyrochlore was prepared by the polymeric precursor method. The films were deposited by dip coating the chemical solution on FTO-coated glass, Si(100) and Pt/Ti/SiO₂/Si(100) substrates. The films deposited on FTO-coated glass were annealed at temperatures ranging from 400 to 550 °C, and those deposited on Si(100) and Pt/Ti/SiO₂/Si(100) substrates, from 500 to 800 °C. Atomic force microscopy images revealed the surface morphology of films as a function of the annealing temperature. X-ray diffraction detected the pyrochlore structure in films treated above 450 °C, with full crystallization at 700 °C. No peaks due to intermediary or secondary phases were ever observed in XRD, independently of the substrate. At lower temperatures, the films deposited on Pt/Ti/SiO₂/Si(100) are polycrystalline and highly [222] oriented, as well as the films deposited on Si(100) (in a lower extension). The optical measurements for films on FTO-coated glass revealed an average optical band gap $E_g = 3.9 \forall 0.1$ and reactive index (n) varying in between 1.9 - 2.1.

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^[2] J. Wei, L. Zhang and X. Yao, J. Am. Ceram. Soc, 82, 2551 (1999).

^[3] J. C. Nino, M. T. Lanagan and C.A Randall, J. Mater. Res., 16, 1460 (2001).