Multifunctionality in ferroic perovskite systems

PhD. Student Elena Mirabela Soare

PhD. Advisor Prof. Adelina Carmen Ianculescu

Abstract

In advanced electronics, the ferroelectric perovskite ceramics, especially $BaTiO_3$ (BT) and its solid solutions, play a major role due to their high dielectric permittivity, spontaneous polarization, positive temperature coefficient of resistivity (PTCR), piezo- and pyroelectric effects, and high endurance under a DC field. In microelectronic devices, the progressive miniaturization and integration have emphasized the requirement of nanostructured materials that present good thermal stability, higher energy density, and tunable characteristics. The grain size reduction and compositional modifications through substitution on A-site (Ba-site) or B-site (Ti-site) in the barium titanate lattice have emerged as crucial strategies for modulating dielectric, ferroelectric, and energy storage performance due to tailored functional properties via nanostructuring. BT-based solid solutions like $Ba_{1-x}Sr_xTiO_3$ (BST) and $BaTi_{1-x}Hf_xO_3$ (BTH) represent two of the lead-free systems derived from BT, underexplored in nanostructured ceramics. The aim of this work is to provide a systematic investigations of the influence of the grain size and dopant content on the structural, microstructural, dielectric, ferroelectric, and energy storage performance of several nanostructured BST, BTH and particularly $BaTi_{0.90}Hf_{0.10}O_3$ ceramics consolidated via spark plasma sintering (SPS). Therefore, the specific goals are represented by the (i) examination of the influence of the grain size downscaling on ferroelectric-paraelectric phase transitions and understanding the ferroelectric - relaxor behaviour; (ii) the correlation of the local structural distortions and phase coexistence with the functional characteristics and (iii) clarifying the compositional effects induced by A-site and B-site substitutions on dielectric, ferroelectric properties.

BST nanopowders were prepared using "acetate" route of the sol-gel method, while the $BaTi_{1-x}Hf_xO_3$ powders were synthesized by modified- Pechini method to guarantee uniform particles morphology and controlled stoichiometry, followed by the consolidation of the nano-powders through conventional sintering (CS) and SPS technique, obtaining dense nano-ceramics. Phase identification was performed by X-ray diffraction (XRD) with Rietveld refinement, microstructural features using scanning electron microscopy (SEM) coupled with field emission gun (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). To investigate the local structural disorder and phase coexistence, Raman spectroscopy was employed. Electrical characterizations, including impedance spectroscopy, ferroelectric hysteresis (P-E) loop measurements, tunability under high dc electric fields, and energy storage performance, were performed.

All compositions investigated of $Ba_{1-x}Sr_xTiO_3$ (x = 0.2 and 0.4), $BaTi_{1-x}Hf_xO_3$ (x = 0, 0.05, 0.1, 0.2), and particularly $BaTi_{0.90}Hf_{0.10}O_3$ ceramics indicated that the grain size influences the modification of dielectric and ferroelectric properties.

Solid solutions of BTH exhibit a complex phase coexistence (tetragonal and orthorhombic for x=0.05; rhombohedral and cubic for x=0.10 and 0.20) and a compositional crossover from ferroelectric to relaxor behavior as Hf content increases. This also results in a linear decrease of the Curie temperature (T_C), decreasing from 385K to 275K. Meanwhile, the transition temperatures between orthorhombic-tetragonal and rhombohedral-orthorhombic phases increase simultaneously. This causes a single, "pinched" and diffuse ferroelectric-paraelectric phase transition, which inhibits grain growth. Also, with

increasing the Hf content, a reduction of the grain boundary resistivity takes place. At nanoscale grain size, the maximum permittivity is significantly flattened, which indicates a relaxor behaviour. The relaxor character is also confirmed by the polarization value diminishing progressively, hysteresis loops becoming narrower and tilted with increasing Hf concentration, and the tunability being reduced. In particular, the influence of the grain size on electrical properties in $BaTi_{0.90}Hf_{0.10}O_3$ ceramics prepared by alternative sintering techniques were studied. In this case, a clear ferroelectric-relaxor transition was obtained with the decrease of the average grain size. These results are linked to a slight decrease in the ferroelectric-to-paraelectric phase transition and an increase in diffuseness as the grain size increases. The maximum permittivity is flattened, which involves a lower value than in the coarse-grain ceramics, and lower dielectric losses indicate a good thermal stability induced by decreasing the grain size and increasing the density of grain boundary states in nanocrystalline samples. The correlation between the dopant content and grain size results in the presence of multiphase polymorph coexistence, involving rhombohedral, orthorhombic, tetragonal, and cubic phases. Using the spark plasma sintering as a consolidation technique combined with nanopowder synthesis by Pechini or sol-gel methods inhibits the grain growth and induces local distortions and internal stress fields. This leads to suppressing the Curie temperature, the phase transition becomes broadened, the dielectric loss decreases, and the ferroelectric-realaxor crossover appears. All these effects take place due to the substitution of the B-site (Hf^{4+}) and A-site (Sr^{2+}) of the $BaTiO_3$ lattice, which improves thermal stability and energy storage efficiency.

In the case of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics, increasing the average grain size, a lower degree of diffuseness of the maximum permittivity in the submicron range of the specimen in comparison to nanoscale samples was observed. The tetragonality is enhanced, and the maximum permittivity increases as the grain size increases. The Curie temperature remains nearly invariant, unlike the usual reports for $BaTiO_3$ ceramics with comparable grain sizes. Therefore, the Curie constant and Curie-Weiss temperature decrease as the grain size is reduced, suggesting a general reduction in the ferroelectric active volume. Ferroelectric switching was observed in all chosen fine-grained BST ceramics, both at the nanoscale and macroscopic levels. Dense $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics present submicronic grain sizes, with well-defined faces and edges and a cubic structure at room temperature. Varying the SPS parameters, the grain size decreased and a highly diffuse phase transition appears near 280K. Lower values of dielectric permittivity, tunability, and polarization are obtained after the decrease of the grain size from submicron to the nanoscale range. The energy storage efficiency is diminished progressively due to the reduction of the grain size. The obtained characteristics of $Ba_{0.6}Sr_{0.4}TiO_3$ nanostructured ceramics confirm the appearance of the relaxor tendency by nanostructuring.

We also study the structural, microstructural, and optical characterization of cerium-doped BT ($Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$) thin films prepared via a modified acetate-based sol–gel process combined with spin coating. The films exhibited a polycrystalline pseudocubic structure with uniform nanometric grains, dense microstructures and smooth, defect-free surfaces. Spectroscopic ellipsometry indicated that the refractive index of the films increased with wavelength while extinction coefficients remained low, confirming good optical transparency. Overall, the behaviours of the obtained materials can be used for specific applications in MLCC, tunable microwave devices, sensors and energy storage performance.