Nanostructured ferroelectric ceramics ground states: Structural and physical properties

J.M. Kiat[1,2*], M. Anoufa[1], G. Thorner[1], C. Bogicevic[1], B. Hehlen[3], A. Al-Zein[4]
[1] Laboratoire Structures, Propriétés et Modélisation des Solides, Ecole Centrale Paris, CNRS-UMR8580, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France
[2] Laboratoire Léon Brillouin, CE Saclay CNRS-UMR12, 91991 Gif-sur-Yvette Cedex, France
[3] Laboratoire Charles Coulomb (LCC), CNRS-UMR 5221, Université Montpellier II - CC 069 Place E. Bataillon, 34095 Montpellier, France
[4] European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, BP220, Grenoble Cedex, 38043 France
*e-mail: jean-michel.kiat@ecp.fr

Ferroelectric nano-objects display a rich variety of shapes, among them nanocubes (bulk or hollow), nanospheres, nanotori etc with fascinating morphogenesis mechanisms[1]. Structural and physical consequences of ferroelectric downsizing to form nanopowders or nanoceramics are very important both from applicative and fundamental point of view (see ref. 2 for a good review). Indeed many interesting effects have already been reported such as diminishing of permittivity and increase of diffusivity[2,3], cancelation of dielectric relaxation in relaxors[3,4], lowering of ground states, increase and rotation of polarization in relaxors and morphotropic compounds[3,5] etc. In order to explain these experimental results, one must take into account not only size and microstrains effects but also existence of core-shell structure[2,5-8]. Modeling also shows that there is optimal nanostructurations to maximize energy storage[6] and electrocaloric effect[8]. Calculations also show the possibility to form new phases in which vortices of polarization compete with homogeneous polarization[8] or in which homogeneous hypertoroidization of nanotori coexists with axial homogeneous toroidization[10]. After a survey of these effects, we will give new experimental results observed in $SrTiO_3$ showing at small size decoupling of oxygen octahedra tiltings and distortion, strong shift of ferroelastic critical temperature[11,12] and lowering of the tetragonal structure towards orthorhombic ground state. Possible connection with a core-shell structure will also be discussed.

1. Morphogenesis mechanisms in solvothermal synthesis of $BaTiO_3$ from titanate nanorods and nanotubes, Bogicevic C., Thorner G., Karolak F., Haghi-Ashtiani P. and Kiat J.M., Nanoscale, Accepted Manuscript, DOI: 10.1039/C4NR06266C (2015).
2. Dielectric Grain-Size Effect in High-Permittivity Ceramics, Petzelt J., Ferroelectrics, 400: 1, 117 (2010).
3. Low-symmetry phases and loss of relaxation in nanosized lead scandium niobate PSN, Kiat J.M., Bogicevic C., Karolak F., Dezanneau G., Guiblin N., Ren W., Bellaiche L. and Haumont R., Phys.Rev B. 81, 144122 (2010).
4. Size-driven relaxation and polar states in PbMg1/3Nb2/3O3-based system, Carreaud J., Gemeiner P., Kiat J. M., Dkhil B., Bogicevic C., Rojac T. and Malic B. , Phys.Rev. B., 72, 174115 (2005).
5. Monoclinic morphotropic phase and rotation of polarisation induced by reduction of grain size in PMN-PT, Carreaud J., Kiat J.M., Dkhil B., Algueró M., Jiménez R. and Jiménez B., Holc J. and Kosec M., Appl. Phys. Lett. 89, 252906 (2006).
6. Dielectric evidences of Core-shell-like effects in nanosized relaxor PbMg1/3Nb2/3O3 (PMN), Carreaud J., Bogicevic C., Dkhil B. and Kiat J.M., Appl. Phys. Lett., 92, 242902 (2008).
7. Energy harvesting in core-shell ferroelectric ceramics: theoretical approach and practical conclusions, Anoufa M., Kiat J.M., Kornev I., Bogicevic C., J. of Appl. Phys. 113, 054104 (2013).
8. Vortices of polarization in $BaTiO_3$ core-shell nanoceramics: Calculations based on ab-initio derived Hamiltonian versus Landau theory, Anoufa M., Kiat J.M., Kornev I., Bogicevic C., Phys. Rev. B 88, 144106 (2013).
9. Tailoring electrocaloric properties in core-shell ferroelectric nanoceramics. : this conference
10. Axial hypertoroidal moment in a ferroelectric nanotorus: A way to switch local polarization, Thorner G., Kiat J.M., Bogicevic C. and Kornev I, Phys.Rev. B 89, 220103(R) (2014).
11. Structural investigation of Strontium Titanate nanoparticles and the core-shell model, Kiat J.M., Bogicevic C., Gemeiner P., Al-Zein A., Karolak F., Guiblin N., Porcher F., Hehlen B., Yedra L., Estradé S., Peiró F., Haumont R., Phys. Rev. B 87, 024106 (2013).
12. Soft-mode dynamics in micrograin and nanograin ceramics of strontium titanate observed by hyper-Raman scattering, Hehlen B., Al-Zein A., Bogicevic C., Gemeiner P., and Kiat J.M., Phys. Rev B 87, 014303 (2013).