

Order-disorder in ferroelectric-relaxors

Thesis directors

B. Hehlen

Laboratoire des Colloïdes, Verres, et Nanomatériaux (LCVN)

J. Rouquette

Institut Charles Gerhardt (ICG)

Ferroelectric materials exhibit large dielectric susceptibility (ϵ'_r) and piezoelectric properties (d_{ij}) due to their great polarisability. The origin of the high ϵ'_r in ferroelectric perovskite of general formula ABO_3 is the cooperative displacement of the B ions from the centre of symmetry of their octahedral sites below a critical temperature T_c ; these spontaneous displacements create local dipoles that are aligned parallel to one another in order to give a permanent dipole moment by application of an electric field E . “Relaxors” can be distinguished from “classic ferroelectrics” by a diffuse ferroelectric-paraelectric phase transition where ϵ'_r reaches a broad high peak value with a strong frequency dispersion (the temperature at the maximum T_m increases with frequency). Additionally, the spontaneous polarization P_s is not suddenly lost at T_m , but decays more gradually to zero (at T_{Burns}) with increasing temperature. Finally, no evidence of optical anisotropy is observed below T_m , what is characteristic of the absence of a macroscopic symmetry change to a polar phase ($PbMn_{1/3}Nb_{2/3}O_3$). On cooling from high temperatures, relaxors transform from a paraelectric state to a state with ferroelectric nanodomain fluctuations in a paraelectric matrix and possibly, to a disordered low-temperature polar phase ($PbZn_{1/3}Nb_{2/3}O_3$). The existence of polar Nano-Regions (PNR) which can be associated to local lattice deformations with respect to the average structure can be linked by the presence of diffuse scattering in diffraction experiments. Perovskite relaxors found particular attention since the discovery of $(1-x)PbZn_{1/3}Nb_{2/3}O_3-xPbTiO_3$ (PZN-PT) materials, in which solid solutions have been performed between a relaxor ($PbZn_{1/3}Nb_{2/3}O_3$) and a classic ferroelectric ($PbTiO_3$). Giant electromechanical coupling can be obtained with a relatively modest applied electric field, due in part to the single crystal form of this material.

Dielectric susceptibility and piezoelectric properties are dependent from 3 variables: the applied electric field, the temperature and the mechanical stress σ_{ij} . The original purpose of this project consists in the study of the ferroelectric relaxor solid solutions PZN-PT as a function of hydrostatic pressure ($\sigma_{ij}=\delta_{ij}P$). This latter parameter enables to modulate the crystalline structure by varying only the interatomic interactions and the balance between long- and short-range forces without changing the chemical composition or thermal agitation. Thus, pressure-induced changes in atomic bond lengths are directly correlated to changes in physical properties. In spite of the high sensibility of the physical properties of ferroelectric/relaxors to hydrostatic pressure, its particular effect found much interest only recently. But large stress fields can be observed for example by the miniaturization of components or in ferroelectric dots. Therefore, the pressure behaviour of these materials has a great importance from both fundamental and technological point of view.

In this thesis proposal, complementarities of competences of the Institut Charles Gerhardt (ICG) and of the Laboratoire des Colloïdes, Verres et Nanomatériaux (LCVN) would be investigated to study the $PbZn_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$ solid solutions (PZN-PT). The main goal of this work will be to better understand the different mechanisms governing ferroelectricity, thus allowing for the design and optimization of such higher-performances materials. Therefore, the experimental project will be based on the use of multi-scale

characterization methods in order to improve our understanding of the different electrical, structural and dynamical processes which take place at the nano-, micro- and macro-scopic levels: 1) X-Ray and neutron diffraction [J. Rouquette *et al*, Phys. Rev. B, 2005], 2) dielectric and piezoelectric measurements, 3) Raman and hyper-Raman spectroscopy [B.Hehlen *et al.*, Phys. Rev. B, 2007], and 4) EXAFS.