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## PHASE TRANSITIONS IN PEROVSKITE-TYPE RELAXOR FERROELECTRICS

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Relaxor ferroelectrics (relaxors) form a special class of ferroelectric materials of which the understanding remains a challenging problem. Most technologically important relaxors crystallize in the so-called $ABO_3$ perovskite-type structure; between those $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) which are considered as model relaxor ferroelectrics. From an application point of view, relaxor-based materials have been reported to exhibit near structural phase boundaries outstanding electromechanical properties, which point to a potential revolution in electromechanical transduction for a large range of applications. As a consequence, the potential impact of thin-film relaxor ferroelectrics has stimulated a fast growing interest. Although it has been realized that strain effects at the film-substrate interface modify dramatically their physical properties, there is incomplete understanding of the responsible mechanisms. In this presentation we will mainly focus on two innovative approaches towards the understanding of phase transitions of the relaxors PMN and NBT: on the one hand temperature-dependent birefringence imaging and on the other hand first-time high-pressure investigations of relaxor ferroelectrics by Raman spectroscopy, diffraction and diffuse scattering. As a matter of fact, the observed pressure-dependent transitions are very unusual and point, among other things, to new relaxor-specific spectral signatures and to important pressure-induced changes of the local structure and order. We further show that an external pressure of several GPa, as can be met in thin films, alters fundamentally the structural and polar properties in relaxor ferroelectrics, suggesting that intrinsic instabilities towards pressure play an important role in the unwished reduction of dielectric properties in application-designed relaxor thin films.

**Keywords: PHASE TRANSITION, RELAXOR FERROELECTRICS, HIGH-PRESSURE**

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## PHASE TRANSITIONS IN pB($Zr_xTi_{1-x}$)$O_3$ CERAMICS: SOME RECENT DEVELOPMENTS

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We report the results of some recent structural, dielectric and piezoelectric investigations on highly homogeneous Pb(ZrxTi$_{1-x}$)$O_3$ (PZT) ceramics prepared by a novel semi-wet route. It is shown that the room temperature structure of PZT is tetragonal (T) for $x < 0.520$ but changes abruptly to a pseudo rhombohedral phase for $x > 0.525$. Careful analysis of the x-ray diffraction profiles have revealed that the structure of PZT on the Zr- rich side ($x > 0.525$) of the morphotropic phase boundary (MPB) is not truly rhombohedral, as hitherto believed for decades, but may instead be monoclinic (M(HT)). We show that the monoclinic (M(HT)) and tetragonal (T) phases coexist at room temperature for x = 0.52 and 0.525 due to a first order phase transition between these two phases occurring around 265 and 483 K, respectively. Piezoelectric and dielectric measurements as a function of temperature for x = 0.515 to x = 0.550 have revealed two anomalies corresponding to T to M(HT) and M(HT) to M(LT) transitions discovered by Noheda et al [Phys. Rev. B 61 (2000) 8687] and Ragini et al [Phys. Rev. B 64 (2001) 054101], respectively. Neutron and electron diffraction data are presented to show that the M(HT) to M(LT) transition discovered by Ragini et al is an antiferrodistortive cell-doubling transition associated with phonon instability at the R-point of the cubic Brillouin zone. We show that space group of the M(LT) phase is Pc.

**Keywords: PZT CERAMICS PHASE TRANSITIONS MORPHOTROPIC PHASE BOUNDARY**

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## NUCLEATION AND RELAXATION IN FERROELASTIC PHASE TRANSITIONS

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We have studied theoretically the statics and dynamics of domain patterns in tetragonal-orthorhombic (TO), hexagonal-orthorhombic (HO) and cubic-tetragonal ferroelastics. Despite the analogy responsible for the very name ferroelastic, these patterns differ strikingly from those seen in ferromagnets and other conventional Ginzburg-Landau systems. The coherence requirement in ferroelastics adds two new features. The strains must satisfy the compatibility relations; these produce a subtle frustration. The wall that join the variants also rotate them, and so disclinations form when walls collide. Using nonlinear elasticity theory alone, we solved numerically the equations of motion for the displacement field, thus satisfying the compatibility relations. Our patterns reproduce the variant narrowing, tip splitting, wall wobbling, islands and other features seen in the TO ferroelastic $YBa_2Cu_3O_7$. In the HO case, we found stars (nested and unnested), fans and other low-angle disclinations, trapped high-temperature phase and defects in the nodes, all as seen in related materials like lead orthovanadate, Mg-Cd alloys and Mg-cordierite. The same theory makes unusual predictions for the early stages of the transformation from the parent phase. After a quench into the unstable region, the expanding nucleus is not the compact object found in time-dependent Ginzburg-Landau theory; for example, the a-b projection of the TO nucleus has an X shape, with twinned arms in the 1,1,0 and -1,1,0 directions.

**Keywords: FERROELASTICS DOMAIN PATTERNS DISCLINATIONS**

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## GENERAL PROCEDURE FOR OBTAINING MICROSCOPIC MECHANISMS OF RECONSTRUCTIVE PHASE TRANSITIONS IN CRYSTALLINE SOLIDS

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In a reconstructive phase transition, the symmetries of the two phases do not have a group-subgroup relationship. Instead, the transition often takes a path through an unstable and unobservable intermediate structure which is a common subgroup of the two phases. We describe a general procedure which finds such subgroups common to two crystalline structures. Each of these subgroups is a possible intermediate structure which describes the atomic displacements and strains that take place in a reconstructive phase transition between those two structures. We have implemented this procedure in a computer algorithm, COMSUBS ('common subgroups'). Depending on the search parameters, COMSUBS can in principle provide an exhaustive list of intermediate structures. The application of COMSUBS to a number of well-known reconstructive phase transitions will be discussed.

**Keywords: PHASE TRANSITIONS RECONSTRUCTIVE SYMMETRY**