of these materials. For low concentration of $PbTiO_3$ for which a strong dielectric dispersion is observed, we will show the progressive destruction of the relaxor state when the size of the grains reaches typical sizes (below 30 nm) of the polar nanoregions responsible of this effect. On the contrary a size-driven relaxation will be discussed in morphotropic concentration of $PbTiO_3$ i.e. the appearance of a relaxor state below 200 nm, associated to a destruction of the ferroelectric domains state towards polar nanoregions in a paraelectric matrix. The rotation of the polarisation with concentration of $PbTiO_3$ will be compared in micro and nanosized samples of PMN-PT and related systems.

Keywords: piezo- and ferroelectric materials, nanoparticles thin films and multilayers, dielectric relaxation

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Thermal motion of atoms in cubic structure of perovskites and ferroelectric phase transitions

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Pb-based perovskite solid solutions $PbZr_{1-x}Ti_xO_3$ (PZT) are well known as piezoelectric ceramics. However, all PZT do not show the high piezoelectric performance. PZT with a morphotropic phase boundary (MPB) composition ($x \approx 0.5$) possesses the prominent piezoelectric properties. In relaxor ferroelectrics $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PZN-PT), the excellent properties are also outstanding near the MPB compositions. Hence, it is essential to understand the formation mechanism of MPB for designing new piezoelectric ceramics. High-energy synchrotron-radiation powder-diffraction experiments were performed at BL02B2 in SPring-8 to investigate the relationship between the crystal structure of the perovskite solid solutions in the cubic phase and the emergence of MPB. Thus far, every crystal structure of the paraelectric phase has generally been considered to be isomorphous to the classical perovskite with a cubic symmetry. Our precise structure analyses using the maximum entropy method/Rietveld method have showed clear evidence that the Pb atoms in PZT and PZN-PT are disordered around the cubic corner site and the thermal motions significantly change near the MPB composition, while no anomaly on the thermal parameters are revealed for the *B*-site atoms. Hence, we consider that the appearance of MPB is strongly related to the changes in local environment around the Pb atom originated from the changes in tolerance of perovskite structure caused by the *B*-site substitution. Similar relation is also revealed in the Pb-free system (K, Na)NbO_3, where the anharmonic thermal motions of the K/Na atoms in the cubic phase change significantly around the composition with the high electromechanical coupling constant.

Keywords: perovskite structures, ferroelectric piezoelectric crystals, synchrotron powder diffraction

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The system of $PbZr_{1-x}Ti_xO_3$ studied by convergent-beam electron diffraction

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$PbZr_{1-x}Ti_xO_3$-ceramics are widely used ferroelectric material. They exhibit the highest values in piezoelectric constants close to the morphotropic phase boundary (MPB). At this boundary the crystal structure changes with composition and the material contains minute domain structures that may affect x-ray diffraction patterns [1]. To analyse the crystal symmetry of $PbZr_{1-x}Ti_xO_3$ over the MPB Convergent-Beam Electron Diffraction (CBED) was used. CBED enables us to determine local symmetries of a few nm-size specimen areas within single domains. Samples with compositions x = 0.40, to x = 0.48 were investigated. Experiments were mainly conducted using a transmission electron microscope equipped with LaB_6 cathode and a spot size of 10 nm. Further experiments include a heating experiment with a sample of composition x=0.46 and with a field emission gun (FEG) and a spot size of 0.5 with few compositions and the pure $PbTiO_3$. Based on the patterns obtained with spot size of 10 nm the symmetry within microdomains can be described by tetragonal, monoclinic and rhombohedral cells depending on composition. Monoclinic to tetragonal transition was observed with increasing temperature for x = 0.46. Contrast variations in images and the comparison to the results obtained with a FEG and a spot size of 0.5 nm give evidence that the symmetry may vary on a local scale within some domains. For rhombohedral side of the MPB a lower intensity of the First Order Laue Zone reflections is observed for [111] compared to the <11-1> zone axes. This can be explained by anisotropic thermal ellipsoids for the lead ion or additional random displacements perpendicular to the threefold axis [2].

[1] Schoenau *et al.* PRB **75** (2007)
[2] Corker *et al.* Condens. Matter **10** (1998)

Keywords: symmetry, domains, CBED

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The synthesis, crystal structural study and microwave dielectric properties of $Ba_6WNb_2O_{14}$

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Recently, B-site cation-deficient hexagonal perovskites, containing mixed cubic-hexagonal stacking sequences of the AO_3 layers along $[0001]_H$ have started to attract attention due to their low microwave dielectric losses (Q > 5,000 between 5 - 10 GHz), near zero temperature coefficient of resonant frequency ($\tau_f < 0 \pm 5$ ppm/K) and relatively high permittivity ($\varepsilon_r > 25$). The studies of hexagonal perovskites within the BaO-WO_3-Nb_2O_5 ternary system have revealed that the ternary compound with a nominal composition of