

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 $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (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 $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$ (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)NbO₃, 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 $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ studied by convergent-beam electron diffraction

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$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ -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 $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ 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 LaB₆ 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)

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Keywords: symmetry, domains, CBED

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The synthesis, crystal structural study and microwave dielectric properties of $\text{Ba}_6\text{WNb}_2\text{O}_{14}$

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Recently, B-site cation-deficient hexagonal perovskites, containing mixed cubic-hexagonal stacking sequences of the AO₃ 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 ($\epsilon_r > 25$). The studies of hexagonal perovskites within the BaO-WO₃-Nb₂O₅ ternary system have revealed that the ternary compound with a nominal composition of

Ba₆WNb₂O₁₄ appears at least in two different polymorphs with the phase transition around 1200°C. The X-ray powder diffraction pattern of high-temperature modification corresponds merely to the niobium homologue of the hexagonal Ba₆WTa₂O₁₄ (ICDD file #35-0187), while the XRD spectra of the low-temperature modification is closely related to the orthorhombic β-Ba₄Nb₂O₉ (ICDD file #35-1155). In order to understand the crystal chemistry governing the formation of Ba₆WNb₂O₁₄, the ceramic prepared by a conventional solid-state reaction, was analyzed by means of X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of microwave dielectric data revealed a low negative coefficient of resonant frequency varying from -25 to -18 ppm/K, dielectric permittivity in the range of 15-20, and the quality factor Qxf distributed over 18 000 GHz.

Keywords: perovskite structures, phase transitions, dielectric materials characterization, TEM, X-ray crystal structure analysis

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Crystallographic direct observation of chemical reactions in a pore

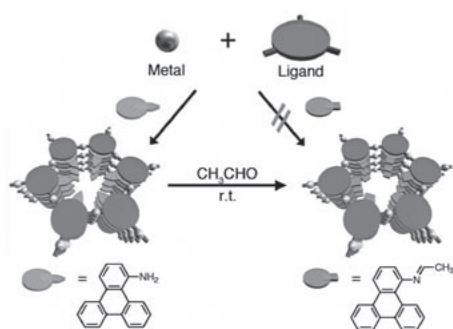
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In-situ preparation of labile compounds in a single crystalline state is a unique and effective method for the crystallographic observation.¹ There are, however, several practical problems in this method. Here we utilize the pores of a coordination network. Thanks to the pseudo-solution state in the pores, even bulky substrates can easily interpenetrate into the crystals with keeping single crystallinity. We examined the reaction of acetaldehyde with amines to form acetaldehyde imines that are, normally, easily hydrolyzed or isomerized into enamines.² The aromatic amines were incorporated in the columnar array of aromatic ligands of an as-synthesized porous network complex.³ We also succeeded in observing several condensation reactions of the aromatic amines to produce acylated products in a pore.

References

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Keywords: *in situ* observations, coordination polymers, reactive intermediates

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Phase behavior of block copolymer/inorganic nanocomposites

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Block copolymers offer as versatile platforms for the fabrication of hybrid composites with ordered phases useful for nanotechnology. Success in this area however requires knowledge on the thermodynamic principles that govern the self assembly of the nanoparticles in the polymer matrix and the resulting morphology and the long range order of the nanocomposites. We carried out a systematic study on the phase behavior of block copolymers with well dispersed grafted nanoparticles enthalpically compatible to one of the domains of the block copolymer. The sequestered nanoparticles in the preferred domain have profound effects on the thermodynamically induced microphase separation of the block copolymers. A number of molecular properties such as polymer molecular weight, segment volume fraction, chi parameter and nanoparticle concentration influence the state of dispersion of the nanoparticles and the degree of segregation of block copolymer morphology. In general, the inorganic nanoparticles tend to weaken the degree of segregation and adversely affect the long range order. We have used a simple method of using small molecular weight homopolymer that can sequester in the same domain as the nanoparticles to overcome the adverse effect of nanoparticles and improve the long range order in the nanocomposites. The basis for this approach is that the small polymers would increase the conformational entropy and swell the preferred domain uniformly which leads to a smoothed interface and improved long range order. The uniform swelling of the preferred domain by the small polymers will also enable higher loading of nanoparticles without losing the long range order. The derived phase behavior will have high impact in the design and fabrication of composites for nanotechnology.

Keywords: block copolymer, nanocomposites, small angle diffraction

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From molecular clusters to nanocrystals - Optical and magnetic properties of metal sulfides

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In this talk, I will discuss the transformation of molecular clusters of molybdenum sulfide and arsenic sulfide into novel nanocrystals with new properties. Bulk molybdenum disulfide is known to be a nonmagnetic material. We have synthesized edge-oriented MoS₂ nanosheet-like films that exhibit weak magnetism (similar to 1-2 emu/g) and 2.5% magnetoresistance effects with a Curie temperature of 685 K. The magnetization is related to the presence of edge spins on the prismatic edges of the nanosheets. Spin-polarized calculations were performed on triangular-shaped cluster models in order to provide insight into the origin of magnetism on the edges as well as