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Keywords: protein tyrosine phosphatase families, MAP kinase families, focused structural proteomics

MS.85.5*Acta Cryst.* (2008). A64, C144**Focused structural proteomics of protein synthesis systems**

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Protein synthesis is performed by a large number of proteins and RNAs. We have been doing structural proteomics focused on protein synthesis in bacteria, archaea, and eukarya. The crystal structures of tRNAs, aminoacyl-tRNA synthetases, translation factors, and the ribosomal subunits will be discussed to describe the process of protein synthesis.

Keywords: protein synthesis, tRNA, ribosome

MS.86.1*Acta Cryst.* (2008). A64, C144**Complex perovskites: Chemical order, crystallographic distortions and physical properties**Patrick M Woodward¹, Graham M King¹, Rebecca A Ricciardo¹, Susana Garcia-Martin²

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This contribution surveys our studies of complex perovskites with a particular emphasis on atomic ordering over various length scales and its impact on the structural distortions and physical properties of these materials. I will show some examples of perovskites where cation ordering is critical for properties and applications. In the A_2MnMO_6 systems the coupling between orbital ordering (cooperative Jahn-Teller distortions) and octahedral tilting is demonstrated and exploited to control the magnetic properties of double perovskites. Next I will discuss $AlnMM'O_6$ ($A = Li^+, Na^+, K^+$, Ln = rare-earth cation) perovskites where strong coupling between A-site ordering, B-site ordering and second order Jahn-Teller distortions of the B-site cations are all closely linked. Some of these materials show a fascinating periodic phase separation. They also exhibit coupling between magnetic ordering of transition metal and lanthanide ions that is promising for multiferroic behavior. Finally time permitting I will discuss our studies of oxynitride perovskites, AMO_2N ($A = Ba, Sr, Ca$; $M = Ta, Nb$), where novel dielectric behavior (high, nearly temperature independent permittivity) is closely linked to the details of the anion order.

Keywords: perovskites, magnetic oxides, oxynitrides

MS.86.2*Acta Cryst.* (2008). A64, C144**Local and long-range structure in LLTO perovskites with Li^+ superionic mobility**

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LLTO ($Li_xLa_{2/3-x}TiO_3$) is an excellent Li^+ ion conductor at room temperature ($10^{-3} S cm^{-1}$ for $x=0.3$), of interest as solid electrolyte in electrochemical devices. Structural studies by neutron powder diffraction showed perovskite superstructures with $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$ tetragonal ($x>0.24$) and $2a_p \times 2a_p \times 2a_p$ orthorhombic ($x<0.24$) unit-cells, and $P4/nbm$ and $Cmmm$ symmetries. A partial La-Li ordering according to (001) layers is coupled to anti-phase octahedral tilts $a^0a^0c^0$ and $a^0b^0c^0$ for the tetragonal and orthorhombic cases. Li is heavily disordered within the A-type cage, accounting for the high ionic mobility. The local Li environment was studied by ab initio periodic quantum-mechanical simulations of selected ordered structural models. The phases $Li_{1/8}La_{5/8}TiO_3$ ($2a_p \times 2a_p \times 2a_p$, $Z=8$) and $Li_{5/16}La_{9/16}TiO_3$ ($2a_p \times 2a_p \times 4a_p$, $Z=16$) were considered, with Pm or PI symmetry, to represent the Li-poor and Li-rich compositions. Several different La-Li-vacancy ordering patterns within the (001) layers of A cages were devised. The structures were optimized by energy minimization, so as to localize the preferred lithium sites for each ordering scheme. It was found that the Rietveld-refined most populated Li site, close to the O_4 windows separating adjacent A cavities in the layer, corresponds to La-poor local configurations, and is actively involved in the ion migration process. The second populated site is related to La-rich local environments, and is a trapping location less favourable to ionic transport. By combining NPD results (long-range Li disorder) and ab initio simulations (local Li order), one- and two-dimensional atomistic pathways are proposed for Li^+ ion diffusion within the perovskite framework, including the prediction of activation energy barriers for ionic hopping.

Keywords: solid electrolytes, *ab-initio* calculations, neutron powder diffraction

MS.86.3*Acta Cryst.* (2008). A64, C144-145**Size and strain effects in nanostructured relaxor and morphotropic compounds**Jean-Michel Kiat^{1,2}

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The field of morphotropic systems with giant dielectric and piezoelectric properties is very active, and many interesting results have been obtained, in particular in lead based-systems. However up to now, only very few papers have addressed the question of grain size reduction and its effect on the physical and structural properties of these materials. We will report results obtained in nanocrystalline powders and ceramics with controlled grain size from 15nm up to micrometric sizes, as well in thin films with several thicknesses from 40nm and different substrates, in $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$, $PbSc_{1/2}Nb_{1/2}O_3$ - $PbTiO_3$, and $BiScO_3$ - $PbTiO_3$ systems. The consequences on the dielectric properties and on the rotation of polarisation will be discussed and compared with the situation in bulk materials. In particular it will be shown that changing the grain sizes provides an easy way to tailor the direction of the polarization

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 $\langle 11-1 \rangle$ 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 $\text{Ba}_6\text{WNb}_2\text{O}_{14}$

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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