

transformation, a direct relation or a common subgroup with physical or chemical sense through group-subgroup relationships cannot be established [2]. How to deal with disruptive phase transformations using symmetry concepts is an open question very interesting to study.

[1] Elliot, J.C. & Young, R.A. (1968) Bull. Soc. Chim. France. (No. special), 1763.

[2] Ulrich Müller, private communication.

Keywords: group-subgroup relationships, phase transitions and structure, point defects

## P08.06.32

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### Phases and structures of $K_xNa_{1-x}NbO_3$ (KNN) at the high sodium end

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Sodium potassium niobate  $K_xNa_{1-x}NbO_3$  (KNN) is a possible lead-free piezoelectric material to substitute for lead zirconium titanate (PZT), which is the leading material in piezoelectric applications. However, the presence of Pb in PZT makes it toxic, and it is for this reason that lead-free piezoelectrics are sought after. This newer lead-free material is united with PZT in that there is a region in their phase diagrams where there appears to be a sudden change in crystal structure. This region has been termed the Morphotropic Phase Boundary (MPB) and appears to coincide with the maximum piezo-response. Of particular interest in  $K_xNa_{1-x}NbO_3$  (KNN) is the presence of three morphotropic phase boundaries (MPB) that occur at  $x = 0.18$ ,  $x = 0.35$ , and  $x = 0.48$ . The phases of sodium potassium niobate over the whole concentration range at various temperatures have been studied, especially at the high sodium end near the phase boundary at  $x=0.18$ . Several neutron diffraction experiments at room temperature and low temperatures were made at the ILL, Grenoble and the phases and structures were carefully refined. X-ray powder diffraction experiments and birefringence measurements of single crystals were carried out in the University of Oxford to complement the neutron work and to complete the phase diagram.

Keywords: morphotropic phase boundary, sodium potassium niobate, neutron and X-ray scattering

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### Transparency and structure of eye lens studied by high-pressure small-angle X-ray scattering

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Short range, liquid-like order of the crystalline proteins, especially  $\alpha$ -crystalline, accounts for eye lens transparency. On concentrating cytoplasmic crystalline proteins, it was reported that eye lens became transparent and that its scattering showed decreasing at low  $S$  as well as more pronounced side maxima at  $0.007 \text{ \AA}^{-1}$  of  $S$ , *i.e.*, typical

character of structure factor of DLVO potentials. Applying high pressure less than 100MPa is not supposed to unfold  $\alpha$ -crystalline, rather to perturb particle interactions by diminishing hydrophobic and increasing electrostatic interactions. High pressure is therefore an important tool to characterize protein-protein interaction on physicochemical basis. We measured in situ high pressure transition of rat eye lens nucleus at post natal days (PND) 14 to 20 by high pressure small-angle scattering (HP-SAXS) as well as light absorption. All HP-SAXS data were collected at RIKEN beamline BL45XU/SPring-8. At  $15^\circ\text{C}$  on ambient pressure they were turbid. Applying high hydrostatic pressure, eye lens got transparent over ca. 80 MPa and turbid again upon decompression, which was found to be reversible. Upon compression the scaled HP-SAXS curves decreased at small  $S$  and interestingly, side maxima  $0.007 \text{ \AA}^{-1}$  of  $S$ , feature of DLVO potentials, became less pronounced. In transparent eye lens at high pressure environment, the structure order of eye proteins seems uniform. We will report further on the basis of structure parameter changes obtained by HP-SAXS.

Reference

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H. Bloemendal et al., *Progress in Biophysics & Molecular Biology* (2004) 86, 407-485.

F. Skouri-Panet et al., *Biochimica et Biophysica Acta* (2006) 1764, 372-383.

Keywords: high pressure small-angle scattering, protein protein interaction, structure order

## P08.06.34

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### Structure and phase transition in a lead-based inorganic-organic perovskites $C_5H_{10}NH_2PbI_3$

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$C_5H_{10}NH_2PbI_3$  has a lead-based inorganic-organic perovskites structure consisting of semiconducting parts which are composed of one-dimensional chains of face-sharing lead-iodide octahedra and barrier parts composed of  $C_5H_{10}NH_2^+$  molecules. The lead-iodide chain is isolated by the organic molecules to be a quantum wire, so this material can be regarded as a naturally self-organized one-dimensional system. The crystal structure at room temperature is orthorhombic with space group of  $C222_1$ . It has been shown by Raman scattering, DSC and optical absorption measurements that the structure undergoes temperature-induced successive phase transitions: phase IV at room temperature, phase III for 255.5K to 284.5K, phase II for 250K to 255.5K and phase I below 250K, which involve rotational/orientational ordering of the organic  $C_5H_{10}NH_2^+$  parts. However, its precise structure has not been determined yet. We have been studying structure and phase transition in this material by combining the data obtained by neutron and x-ray single crystal diffraction, and found drastic structural changes take place in the successive phase transitions. The lattice parameters shows step-like changes at the transition temperatures with considerable large contraction of lattice  $b$ . Below 285K, 400 peak is found to separates in two indicating that the crystal lattice changes from orthorhombic to monoclinic below 285K. The angle between the splitting peaks increases linearly with decreasing temperature down to 255K and decreasing again up to room temperature without any hysteresis. Below 255K, diffuse peaks appear at the reciprocal points at which reflection is forbidden in the  $C$ -centered lattice. These results show

that the large structural changes are accompanied with the successive phase transitions.

Keywords: inorganic organic compounds, neutron X-ray scattering, structural phase transitions

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#### Powder neutron diffraction studies of inorganic ferroelectric phase transitions

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We shall present some of our recent results on the nature of the ferroelectric-paraelectric and other phase transitions in a variety of inorganic systems, as studied by variable temperature powder neutron diffraction. Examples will include the contrasting behaviours of the Aurivillius family of layered perovskites including  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{Bi}_2\text{WO}_6$ ; the former involves simply 'octahedral tilt' type transitions, whereas the latter involves a reconstructive transition from corner-shared to edge-shared octahedra. Other examples will include the unusual layered oxyfluoride  $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ , which exhibits a remarkably high TC for a fluoride ( $\sim 800\text{K}$ ), and which shows 3 ferroelectric phases below TC. Finally, the important multiferroic  $\text{BiFeO}_3$  has been studied, and we will comment on its structural behaviour versus temperature, especially around TC, and including the possibility of a cubic paraelectric phase.

Keywords: ferroelectric, powder neutron diffraction, phase transitions

### P08.06.36

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#### Structural phase transitions in *trans*-1,2-diaminocyclohexane derivative

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*trans*-1,2-Diaminocyclohexane, a rigid molecule of  $C_2$  symmetry and two equatorial C-N bonds, was used as a chiral element of hydrogen-bonded networks and also as a bidentate ligand for chiral catalysts. We reported the synthesis and room temperature crystal structure of *trans*-(1*R*,2*R*)-*N*-acetyl-*N,N'*-di-(4-bromophenyl)-1,2-diamino cyclohexane [1]. Quite unexpectedly we have found out two reversible phase transitions in the temperature range 100-295K. The previously published room-temperature crystal structure is monoclinic  $P2_1$ , with  $Z'=1$ . The structure is disordered: one of the bromine atoms occupies two alternative positions with equal probability (s.o.f.'s are 0.5). The anisotropic refinement of bromine atoms in both positions was very stable and led to perfectly reasonable geometries and  $U_{ij}$  values. On cooling down, below ca. 250K, the crystal undergoes the continuous phase transition to another monoclinic  $P2_1$  phase, with a doubled value of the  $c$  unit-cell parameter, and two symmetry-independent molecules ( $Z'=2$ ). The attempts were made to refine either the room temperature structure in the low temperature unit cell or vice versa, but none of these refinements led to reasonable results. Of course room temperature structure could be refined in a bigger unit cell, but the final effect was inferior to the original one. Above all, the new refinement did

not lead to the ordering of bromine atoms, and some displacement parameters became non-positive determined. Below 160K another phase transition takes place, this time to the triclinic  $P1$  space group with two molecules in the unit cell (i.e.,  $Z'=2$ ). Both phase transitions are reversible; we were able to use the same crystal many times and observe the same diffraction patterns.

[1] M.Kwit et al., *Pol.J.Chem.* 77 (2003) 1669.

Keywords: phase transitions, intermolecular interactions, disorder

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#### Order parameters for phase transitions to structures with incommensurate modulations

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Given the  $k$  vector for a distortion in a parent crystalline structure, what resulting space-group symmetries are possible? We have answered this question (Stokes, Campbell & Hatch, 2007, *Acta Cryst.* A63, 365) for the case of one-dimensional incommensurate modulations where the resulting symmetries are described by (3+1)-dimensional superspace groups. Most recently, we have extended our group theoretical methods to the general case of any arbitrary set of  $N$  modulations where the symmetries are described by (3+N)-dimensional superspace groups.

Keywords: phase transitions in solids, incommensurate modulated structures, group theory

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#### Spontaneous strain in superconductors

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Recently, the change in the orthorhombicity of the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  at the superconducting transition temperature  $T_c$  could be clearly detected by accurate lattice parameter measurement [1]. The introduction of a new critical exponent was considered necessary for explaining the result. The very small anomaly of the lattice parameters of intermetallic superconductor  $\text{MgB}_2$  was also clearly observed near  $T_c$  [2]. This anomaly was considered to be independent of the superconductivity onset. We could also clearly detect the change in the lattice parameter of the high-temperature superconductor  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  at  $T_c$  [3]. For the first time, we showed that the change can be attributed to a spontaneous strain in the superconducting phase caused by the coupling between a superconducting order parameter and the strain. We indicated that the anomaly in  $\text{MgB}_2$  can also be understood on the basis of the same coupling. Similar experiments on conventional superconductors are necessary to clarify whether such a phenomenon is common to all superconductors. We carried out powder X-ray diffraction experiments on  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ , which is a well-studied conventional superconductor with a simple cubic perovskite structure. The diffraction patterns were analyzed by the Rietveld