

I series existed at RT in polar orthorhombic phase are isostructural to BW at  $0 < x < 0.6$  and BM at  $0.7 < x < 1$ . Part of solid solutions at  $0 < x < 0.3$  and  $0.8 < x < 1$  transforms into monoclinic phase through intermediate unpolar orthorhombic phase. The transition temperatures depended considerably on doping level and heating rate. The only reconstructive transition into monoclinic phase without intermediate phase was observed at  $0.4 < x < 0.7$ . The restricted solid solutions in series II with the polar BW structure ( $0 < x < 0.3$ ) have also exhibited two transitions. The monoclinic phase based on BM exists in series II at  $x > 0.3$ . Obtained results have shown that the BW and BM compounds, which existed in polar phase at RT, at heating are similar in respect of numbers and sequences of their transition phases.

Keywords: phase transitions, Aurivillius phases, solid solutions

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#### Structural investigations of crystallization processes in amorphous rare earth borates

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Calcite, vaterite and aragonite phases are well known for rare earth borate system. As a rule, different phases in thermodynamic equilibrium states are observed for different rare earth elements. For example,  $\text{YBO}_3$ ,  $\text{YbBO}_3$  and  $\text{GdBO}_3$  are crystallized in vaterite phase while  $\text{ScBO}_3$  is crystallized in calcite phase only. At the same time  $\text{LuBO}_3$  could be crystallized in the both calcite and vaterite phases. Our studies showed that the structures, which do not exist in equilibrium phase diagram, can be obtained during the crystallization of amorphous borates in non-equilibrium conditions. By non-equilibrium conditions a quick heating up to high temperature and subsequent quench is implied. Moreover by means of this method we have produced the x-phase for  $\text{ScBO}_3$  with so far unknown structural type. Two methods have been used for amorphous borate synthesis. These are thermolysis of the solution-melt and precipitation from the solution. We found that the synthesis method influences considerably on the phase states of the material upon further treatment. Considering this feature we have undertaken the studies of the borate phase crystallization from different starting material under different crystallization conditions such as starting temperature, heat rate, annealing time at final temperature. By this report crystal structure data of the obtained phases and possible routes of the x-phase-vaterite-calcite transformations will be presented.

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#### Structures and transitions in praseodymium at high pressure

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The trivalent lanthanide elements exhibit a range of different close-packed structures as a function of increasing 4f occupancy (hcp  $\rightarrow$  Sm-type  $\rightarrow$  dhcp  $\rightarrow$  fcc) [1]. The same series of structures is also accessible in individual lanthanides by the application of pressure. Two further phases can also be accessed on compression. The first, the distorted fcc phase (d-fcc), has a structure that is closely related to the fcc structure, while the second phase, with the alpha-Uranium structure, arises from the delocalisation of the 4f electrons and marks the end of the sequence of close-packed structures. Despite numerous X-ray diffraction studies dating back 30 years, the structure of the d-fcc phase remains ambiguous. Here we present details of our own structural studies of d-fcc Pr made using powder diffraction methods. In Pr, the d-fcc phase, previously reported to be stable between 9 and  $\sim 20$  GPa, is found to comprise two different structures. Between 9 and 14 GPa, we find the structure to be rhombohedral [2], and can rule out previous reports of a C-centred monoclinic structure. At 14 GPa, we find a structural transition to a second phase, the structure of which does not agree with that reported recently [3]. Further studies reveal that this second phase also exists in Nd, suggesting that there may be a new high-pressure phase in the general lanthanide phase-transition sequence.

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Keywords: lanthanide, distorted FCC, high pressure

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#### Phase transformations induced by point defects studied by group-subgroup relationships

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Symmetry determination for new compounds, structural relations between crystal structures, phase transition paths and new phases generated by point defects, are some of the structural aspects that can be performed by mean of group-subgroup relationships. This work is focused in the analysis of phase transformations induced by point defects *v.gr.* vacancies, interstitial or substitutional impurities. For instance, in monoclinic hydroxylapatite ( $P112_1/b$ , No.14) defects are created in the Wyckoff position  $6h$  for phosphorus substituting the  $\text{PO}_4^{3-}$  by  $\text{CO}_3^{2-}$ ; and the symmetry changes to give the hexagonal hydroxylapatite ( $P6_3/m$ , No.176). Since direct structural relations cannot be established in going from  $P112_1/b$  to  $P6_3/m$ , a common subgroup between these two space groups was considered, *i.e.* the non-centrosymmetric space group  $P2_1$  (No.4) reported for monoclinic chlorapatite under the action of a weak electric field [1]. In the phase transformation from  $\text{YPO}_4$  ( $P4_1/amd$ , No.141) to  $\text{YPO}_4$  ( $Fddd$ , No.70), the orthorhombic phase is induced by  $\text{Li}_2\text{CO}_3$  during the reaction process, its transformation can be described by a translationengleiche subgroup of index 2. The last case considered, was the  $\alpha$ -quartz type germanium oxide ( $P3_121$ , No.154), which phase transformation to  $\text{GeO}_2$  stishovite type ( $P4_2/mnm$ , No.136) was promoted, doping the phase with vanadium. In this phase

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.

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

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

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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 separate 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