parameters $a_1 = 10.534(2)$, $a_2 = 11.683(2)$, $a_3 = 20.407(4)$Å, $\alpha_2 = 93.33(3)°$. When lowering the temperature from 293 K, a strong attenuation of certain ultrasonic resonances occurs reaching a maximum at 288.4 K. Below this temperature the attenuation of ultrasonic waves, in which the elastic constants c_{11}, c_{22}, c_{12} and c_{66} are involved, is drastically reduced. If the low temperature phase is heated to room temperature, the attenuation reaches a maximum at 291.5 K indicating a hysteresis. This hysteresis is confirmed in DSC measurements, where a transition enthalpy of 2 J/g is observed. In the low temperature phase, domains with several mm thickness parallel to (001) are formed. In the direction [010] the angle of optical extinction of these domains deviates by about $\pm$ 6° from the extinction in the high temperature phase. Both phases exhibit a topotactic structural relation, which however, does not prevent the single crystalline state of the mother crystal to be maintained after the transition. The phase transition is considered to be of weakly first order.

Keywords: nitrilotriacetates, elasticity, phase transition

P.08.06.24
Thermal Transformations of Some Alicyclic β-amino Acid Hydrates
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Alicyclic β-amino acids were recently used for the construction of two-dimensional hydrogen-bond grids that link molecules into bilayer structures [1]. While the crystallization of several β -amino acids yielded the expected bilayer type structures, others (*cis*-2-hydroxycyclohex-4-ene-1-carboxylic acid, all-*cis*-amino-4-hydroxy-cyclohexanecarboxylic acid, *trans*-2-aminocyclopentane-carboxylic acid and 3-*exo*-aminobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid) crystallized as hydrates and did not form the expected grid pattern. These hydrates were analysed by thermogravimety, differential scanning calorimetry, powder and single crystal X-ray diffraction in an attempt to prepare and characterize their anhydrous crystal forms. The results show that each powder loses the hydrogen-bonded solvent before decomposition. The powder patterns of the solvent-free forms show similarity to those of the bilayer structures.

[1] Fábián L., Kálmán A., Argay Gy., Bernáth G., Gyarmati Zs. Cs., *Cryst. Growth Des.*, 2005, **5**, *in press*.
Keywords: thermal analysis, hydrates, hydrogen bonding

P.08.06.25
X-ray Diffraction Study on the Phase Transitions of Barium Titanate
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Structural phase transitions in as-grown single crystal of $BaTiO_3$ were studied by X-ray precession method in the temperature range between 420 K and 90 K. It was found that high temperature cubic phase, designated here as cubic I, is transformed into the room temperature phase (RTP at T_1=403 K), and further into the low temperature phase (LTP at T_2=278 K), in both of which closely related two structures coexist to form domains with a shape of multi-domain 'hybrid' structure. In RTP the coexisting structures are tetragonal I and monoclinic I and in the LTP tetragonal II and monoclinic II. On the other hand, the lowest temperature phase (below T_3=183 K) is in a single domain of a tetragonal III form. These observations are in disagreement with the phase transition sequence, proposed by previous studies, cubic→tetragonal→orthorhombic→rhombohedral.

The lattice constants of the tetragonal I form are a_{TI}=0.4009(10) nm and c_{TI} =0.4048(10) nm, and those of the monoclinic I form are a_{MI}=0.4059(10), b_{MI}=0.4009(10), c_{MI}=0.5700(10) nm and β_{MI}=135.33(10)°at room temperature. Those of the tetragonal II form are a_{TII}=0.4027(10) and c_{TII}=0.3996(10) nm, and those of the monoclinic II form are a_{MII}=0.3994(10), b_{MII}=0.4027(10), c_{MII}=0.5678(10) nm and β_{MII}=134.77(10)°at 233 K. Evolution and crystallographic relationship of the four phases forming the multi-domain 'hybrid' structures are presented.
Keywords: $BaTiO_3$, phase transitions, 'hybrid' structure

P.08.06.26
X-ray and Neutron Scattering Study of *as-grown* Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$ Single Crystals
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Characters of static and dynamic structures of *as-grown* Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$ (PIN) at room temperature (RT) have been investigated by a complementary use of x-ray and neutron scatterings. The PIN crystal has different chemical ordering ($S_2 = 0 \sim 1$) in the arrangement of In^{3+} and Nb^{5+} on the B-site by a different thermal treatment.

The diffuse scatterings showing the relaxor state have been observed in the outer-layer of the crystals, while *h/4 k/4 0* reflections showing the long-range antiferroelectric (AFE) state in the inside [1,2]. Phonon dispersion of the as-grown PIN crystals has also been measured, which is the first time for the PIN series. We have measured two transverse optic modes (TO1 and TO2) at zone center and concluded that the major part of the as-grown crystal at RT is ferroelectric(FE). This is consistent with the dielectric measurement performed on the as-grown PIN crystal [3].

These results show that the degree of B-site order S_2 is widely distributed in the as-grown PIN crystal from $S_2 = \sim 0$ to ≥ 0.7. That is, the AFE grain locates in the FE matrix, while the outer-layer is Relaxor in the as-grown PIN.

[1] Nomura K., et al., *J. Phys. Soc. Jpn.*, 1999, **68**, 39. [2] Nomura K., et al., *J. Phys. Soc. Jpn.*, 1997, **66**, 1856. [3] Ohwa H., et al., *J. Phys. Soc. of Jpn.*, 2000, **69**, 1533.
Keywords: ferroelectric properties, neutron and X-ray scattering, phase transitions
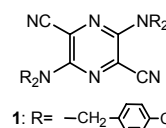
P.08.06.27
Phase Relationship of Two Polymorphs of a Diaminodicyanopyrazine Dye
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2,5-Diamino-3,6-dicyanopyrazine dyes are novel fluorescent dyes for opto-electronic applications [1]. These dyes have been found to have crystal polymorphs with different colours depending on the amino substituents. The colour difference is considered to be ascribed to the different molecular conformation among the polymorphs. In this study, the stability relationship of two polymorphs (red and yellow) of **1** were determined by melting data and correlated with their molecular and crystal structures.

The red phase was found to transform to the yellow phase at room temperature. DSC measurement showed that the yellow phase has a higher melting point than that of the red phase. The heat capacities were also determined by DSC measurement. These results suggest that the red phase and the yellow phase are a monotropic relationship. The phase relationship will be also discussed on the basis of their

molecular and crystal structures.

[1] Matsuoka M., in *Colorants for Non-textile Applications*, Freeman H. S. and Peters A. T. Ed., Elsevier Science, 2000, 339.
Keywords: polymorphism, phase stability, properties and structures relationship

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Phase Transition Sequence in Ferroelectric Aurivillius Compounds

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The high-temperature paraelectric-ferroelectric transformation in Aurivillius materials is not yet well characterized. They are known to be non-polar tetragonal at high temperature and ferroelectric at room temperature, but an intermediate phase has been reported in some cases and explained using ab-initio calculations [1]. This intermediate phase is related with the existence of an additional non-polar anti-ferrodistortive instability. Its independent freezing in this intermediate phase seems a necessary condition for a subsequent continuous or quasi-continuous phase transition into the ferroelectric phase [1]. We present a single-crystal X-ray diffraction investigation of the transition sequence in some representative members of the family as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN). By monitoring specific reflections as a function of temperature, sensitive either to the superstructure formation or to polar displacements, it was possible to check the existence or not of an intermediate phase. This latter was confirmed in SBT, but within experimental accuracy could not be detected in SBN, confirming previous reports [2]. The reason for this different behaviour is unclear and requires further theoretical investigations.

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Keywords: aurivillius, ferroelectric, phase transitions

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New Graphical User Interface for Calculating Structural Distortions Using the ISOTROPY Software

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ISOTROPY (http://stokes.byu.edu/isotropy.html) is a set of computer programs which use group-theoretical methods for solving a variety of crystallographic problems dealing with structural phase transitions in crystalline materials. One of the most useful features is the association of distortions (patterns of atomic displacements) with the reduction of space-group symmetry in a transition. We have designed a new interface for ISOTROPY which guides the user through the process of choosing a distortion mode based on considerations such as initial and final space group symmetry, distortion k-vector, irreducible irrep, etc., and subsequently returns the distorted structure which the user can import into a 3rd-party package for analysis or visualization.

Keywords: structural change associated with phase transitions, group theory, graphical interfaces

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General Method for Determining Atomic Pathways in Reconstructive Phase Transitions: SiC and GaN

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We have developed a general method for determining atomic pathways in reconstructive phase transitions in crystalline materials.

Using a computer program COMSUBS, we first collect a large number of possible pathways under a set of constraints determined by the user. Second, we estimate the enthalpy barrier for each pathway by finding the barrier along pathways which are linear in the structural parameters. Third, we use the bow-function method to calculate the enthalpy barrier for the pathways with the lowest estimated barriers. Fourth, we search for possible ways to lower the barrier even further along each pathway by lowering the symmetry and increasing the number of structural parameters. We have successfully applied this method to the zincblende-rocksalt transition in SiC and the wurtzite-zincblende transition in GaN.

Keywords: structural change associated with phase transitions, group theory, ab-initio calculations

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Phase Transition and Structures of the Phosphate $Zn_{0.50}Ti_2(PO_4)_3$

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Compounds of general formula $M^{II}_{0.5}M^{IV}(PO_4)_3$ with M^{II} = Mg, Mn, Fe, Co, Cu, Cd, Ca, Sr, Pb and M^{IV}= Ti, Zr crystallize with either a Nasicon-type structure or a $Sc_2(WO_4)_3$- type structure, depending on the size of the M^{II} element [1]. Temperature dependent XRD study of $Zn_{0.5}Ti_2(PO_4)_3$ reveals a reversible $\alpha\rightarrow\beta$ phase transition around ~400°C.

Single crystals of the α phase have been obtained with cell parameters, a=14.652(2)Å, b=8.602(1)Å, c=16.930(2)Å, β=125.89(1)° and V=1728.7(1)Å^3. The single crystal structure was solved in the non standard space group $P2_1/a$ (referring to the $Fe_2(MoO_4)_3$ study [2]) with R_1=0.059 and wR_2= 0.090.

Diffraction data of the β phase were collected at 500°C on a Philips PW 1050 equipped with an Anton Paar furnace. X-ray diffraction pattern of this powder can be indexed in the $P2_1/n$ monoclinic cell: a=11.918(5)Å; b=8.610(4)Å, c=8.506(4)Å; β=90.37(3)°; V=873.8(1)Å^3 referring to the $Sc_2(WO_4)_3$ study [1]. This structure type was confirmed by Rietveld refinement (R_B= 0.043, R_{wp}=0.076, R_P=0.053). The α phase can be considered as a superstructure of the β one with an ordering of zinc atoms and vacancies along b direction.

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Keywords: phosphates, phase transition, crystal structures

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Two Phase Transitions in the Low-dimensional Quantum Spin System TiOBr

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Recently, Seidel *et al.* [1] suggested from the susceptibility measurements and LDA(+U) calculation that the new inorganic compound TiOX (X=Cl, Br) is a possible candidate for the new spin-Peierls system. However, nobody can observe the new superlattice reflection originated from the spin-Peierls transition.

We report here on the lattice distortion in the new quasi-one-dimensional spin system TiOBr by x-ray [2] and electron diffractions. Superlattice reflections were observed mainly at around (h, k+1/2, 0) which implies the dimerization along b-axis. The temperature dependence of superlattice reflections shows the two successive phase transitions, a second order transition at T_{c2}=47K and a first order transition at T_{c1}=27K. We will discuss on the key roles of the two successive phase transition of this system.

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