

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<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBT) and SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (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.

[1] Perez-Mato J.M., et al., *Phys. Rev. B*, 2004, **70**, 21411. [2] Snedden A., et al., *Phys. Rev. B*, 2003, **67**, 092102.

**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<sub>0.50</sub>Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>**

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Compounds of general formula M<sup>II</sup><sub>0.5</sub>M<sup>IV</sup>(PO<sub>4</sub>)<sub>3</sub> with M<sup>II</sup> = Mg, Mn, Fe, Co, Cu, Cd, Ca, Sr, Pb and M<sup>IV</sup> = Ti, Zr crystallize with either a Nasicon-type structure or a Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>-type structure, depending on the size of the M<sup>II</sup> element [1]. Temperature dependent XRD study of Zn<sub>0.5</sub>Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> reveals a reversible α→β 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<sup>3</sup>. The single crystal structure was solved in the non standard space group P2<sub>1</sub>/a (referring to the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> study [2]) with R<sub>1</sub>=0.059 and wR<sub>2</sub>=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<sub>1</sub>/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<sup>3</sup> referring to the Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> study [1]. This structure type was confirmed by Rietveld refinement (R<sub>B</sub>=0.043, R<sub>wp</sub>=0.076, R<sub>p</sub>=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.

[1] Jouannaux A., Verbaere A., Piffard Y., Fitch A. N., Kinoshita M., *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 683. [2] Chen H. Y., *Mat. Res. Bull.*, 1979, **14**, 1583.

**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-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<sub>c2</sub>=47K and a first order transition at T<sub>c1</sub>=27K. We will discuss on the key roles of the two successive phase transition of this system.

[1] Seidel A., et al., *Phy. Rev. B*, 2003, **67**, 020405(R). [2] Sasaki T., et al., *Cond-Mat*, 0501691.

**Keywords:** spin-peierls, superlattice reflection, phase transition

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#### Phase Transition in Li-Mn Spinels; *in situ* XRD and Impedance Spectroscopy Analysis

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Lithium-manganese stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  undergoes upon cooling phase transformation. In the present work stoichiometric and  $\delta$ -spinels synthesized by sol-gel technique [1] and commercially available ones were studied at -25 to +100<sup>0</sup> C by *in-situ* XRD and impedance spectroscopy (in freq. Range 0.1Hz to 10 MHz). Rietveld as well as separate peaks (400) analysis were performed for phase and structure identification. The correlation of the XRD profile parameters and conductivity was demonstrated. Additional phases in commercial objects seemingly containing only one phase were found and described. The lattice parameters of the regular and orthorhombic phases were determined. Accurate values of the phase transition temperatures for stoichiometric and  $\delta$ -spinels were found. The change in the elementary cell volume was found to be less than 0.5%, distortion which should not influence the working parameters of battery electrodes. Appearance of electric polarization and decrease of the dc conductivity was explained by ordering of electronic charges between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in distorted spinel.

[1] Lisovytskiy D., Kaszukur Z., Baumer N.V., Pielaszek J., Molenda M., Dziembaj R., Marzec J., Molenda J., Dygas J.R., Krok F., Kopec M., *Molecular Physics Reports*, 2002, **35**, 26-30.

**Keywords:** spinel, phase transitions, refinement

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#### Isosymmetric Phase Transitions in the Solid State

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The discontinuous transformations in crystalline solids without change of space symmetry, at high temperature and high pressure, attract special interest. It is convenient to attribute them to isostructural (isomorphous) phase transitions. However, the coincidence of the space groups on the both sides of the transition point is a necessary but not sufficient condition for such an attribution. The analysis of specific anomalies in the pressure/temperature-induced evolution of the certain parameters and their functional form should complement the identification procedure.

Different types of isosymmetric phase transitions, such as isostructural, anti-isostructural etc., will be defined and assigned to different non-symmetry breaking and symmetry breaking mechanisms. The role of the anharmonism of these mechanisms, and the coupling between them will be investigated.

The characteristic phase diagrams corresponding to every type of isosymmetric transformations will be presented. I will show specific details of the crossover between different transformation regimes and identify the corresponding critical points; these are the critical end point of the liquid-gas type and the Landau point.

Examples of isosymmetric transformations in rare-earth and transition metals, intermetallic compounds and oxides will be analyzed in the framework of a rigorous classification scheme.

**Keywords:** phase transition, phase diagram, critical point

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#### Synchrotron Powder Diffraction Study of Phase Transitions in Rutile Type Halides

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The structures of  $\text{CaBr}_2$ ,  $\text{CaCl}_2$  and  $\text{CrCl}_2$  have been investigated, using high-resolution synchrotron X-ray powder diffraction methods, at temperature of up to 800 °C. At room temperature all have an orthorhombic  $\text{CaCl}_2$ -type structure ( $Pnmm$   $Z=2$ ). Heating  $\text{CaBr}_2$  through 560 °C results in a continuous transition to a tetragonal rutile type structure ( $P4_2/mnm$   $Z=2$ ). Investigation, via either spontaneous strain or octahedral tilt angle, suggests that the transition is close to second order in nature, although the contribution from the sixth order term in the Landau potential cannot be neglected [1].  $\text{CaCl}_2$  shows a very similar transition, albeit at the lower temperature of 240 °C. By contrast the structure of  $\text{CrCl}_2$  remains orthorhombic to 800 °C, and even at this temperature shows no signs of reversion toward the higher symmetry rutile structure. We observe strongly anisotropic thermal expansion in this material and, surprisingly, an increasing distortion of the  $\text{CrCl}_6$  octahedron with increase in temperature.

[1] Kennedy B.J., Howard C.J., *Phys. Rev. B*, 2004, **70**, 144102.

**Keywords:** synchrotron X-ray diffraction, structural phase transitions, rutile-type halides

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#### Displacive Transition Revisited by Coherent X-ray Diffraction

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The perovskite oxide  $\text{SrTiO}_3$  undergoes a prototypical example of structural phase transition, which stabilizes below  $T_c=110$  K a antiferrodistorsive modulation at the  $(1/2,1/2,1/2)$  reduced wave vector. However, this transition has been the first example where, in addition to the usual Lorentzian component in the critical x-ray scattering profiles, a sharp Lorentzian-squared component has been observed close to  $T_c$ . This sharp component was later found to be quite general in the class of structural phase transitions<sup>1</sup>, and believed to correspond to a surface phase transition (10 to 100  $\mu\text{m}$  depth), exhibiting a different critical behavior from the bulk (a second length scale) but the same transition temperature.

We show that the use of Coherent X-ray Diffraction (CXD) allows one i) to separate the different critical behaviors ii) to give evidence of the static character of the second length scale fluctuations and iii) to confirm it takes place in the near surface close to defects.

Beyond this experiment, we show that CXD is a valuable new tool to study phase transitions and defects in the low temperature ordering<sup>2</sup>.

[1] Cowley R.A., *Physica Scripta*, 1996, T66, 24. [2] Le Bolloc'h D., et al., *in preparation*.

**Keywords:** phase transition, critical phenomena, perovskite oxide

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#### Bifurcation and Metastable States in Phase Transitions of Nucleotide Hydrates

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The understanding of phase transitions of molecular crystals is