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Keywords: silicate, thermal_expansion, powder_diffraction

MS05.P14

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Ordering effects in BiFeO₃-based solid solutions

Pavel Teslenko,^a Anatoly Pavlenko,^b Larisa Reznichenko,^b Olga Razumovskaya,^b Yuri Kabirov,^a ^a*Departament of Physics, Southern Federal University, SFEDU, Rostov-on-Don, (Russia).* ^b*Institute of Physics, Southern Federal University, SFEDU, Rostov-on-Don, (Russia).* E-mail: teslenko_pavel@mail.ru

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In solid solutions of BiFeO₃ multiferroic and KNbO₃ ferroelectric or NaNbO₃ antiferroelectric the different order parameter interactions should occur: magnetic, ferro(-antiferro)electric, and of ferroelastic nature.

X-ray diffraction study in 20≤T≤800°C temperature range of (1-x)BiFeO₃-(x)KNbO₃(BFKNO) and (1-x)BiFeO₃-(x)NaNbO₃(BFNNO) solid solutions systems' samples has allowed to make the (x,T) phase diagrams of the systems. It was established that in BFKNO system the R3c, Pbnm, Pm3m phases' boundaries of pure BiFeO₃ with KNbO₃ doping lessen in transition temperature with the increase of X. The transition temperatures between Amm2, P4mm and Pm3m phases of pure KNbO₃ are also decreased with the decrease of X. The phase boundaries in BFNNO system's solid solutions shift in a similar way.

The comparison of BFKNO and BFNNO phase boundaries shows that in these systems the ferroelectric phase transitions' temperatures of BiFeO₃, KNbO₃ and NaNbO₃ decrease with the increase of secondary component's content. This is also proved by preliminary results of permittivity-temperature dependencies investigations.

Keywords: ferroic, ferroelectricity, X-ray

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Structural study of SrPrMRuO₆ double perovskites by symmetry-mode analysis

Edurne Iturbe-Zabaló,^{a,b} Gabriel J. Cuello,^a Josu M. Igartua,^b ^a*Institut Laue-Langevin, Grenoble (France).* ^b*Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, UPV/EHU, Leioa (Spain).* E-mail: iturbe@ill.fr

The natural way to study the phase-transitions is the use of the symmetry-mode analysis, to understand in a proper way the microscopic mechanisms responsible for the phase-transitions. For that propose we have used the Bilbao Crystallographic Server [1][2][3] together with FullProf Suit [4].

The SrPrMRuO₆ (M=Zn,Co,Mg,Ni) materials have been elaborated by the conventional Solid State Reaction Method. Rietveld analysis of laboratory X-ray Powder Diffraction (XRPD), Synchrotron Radiation Powder Diffraction (SXPDP) and Neutron Powder Diffraction (NPD) shows that these materials are double perovskites with a primitive space group: $P2_1/n$ (No. 14, non conventional setting). In the four compounds Sr²⁺ and Pr³⁺ are totally disordered in A- and A'-sites; whereas M²⁺ and Ru⁵⁺ are completely ordered, in B- and B'-sites, respectively. For the refinements we have used AMPLIMODES for FullProf [3][5-6]. AMPLIMODES carries out a symmetry-mode analysis of a displacive

phase-transition. Starting from the experimental structures of the parent-phase (virtual or real, $Fm-3m$, No. 225 conventional setting) and knowing the metric of the low-symmetry phase ($P2_1/n$), the program determines the symmetry modes compatible with the symmetry break. In the NPD data analysis two modes have been identified as active: the ones responsible to yield the $P2_1/n$ space group: GM_4^+ and X_3^+ . These two modes are related to the rotation of the octahedra (oxygen movements): GM_4^+ generates a rotation around the monoclinic b axis and X_3^+ , around the c axis.

The high-temperature (HT) laboratory XRPD analysis has revealed the following temperature phase-transition sequence [7]: $P2_1/n-R-3-Fm-3m$. HT neutron diffraction data of SrPrMgRuO₆ material has been used to study the phase-transition by the symmetry-mode analysis. According to the theory, the two order parameters actuating in the monoclinic phase are expected to thermally stabilize and become zero at higher temperature. Taking into account that the amplitudes are different, it can be expected that one of them will become zero before the other and, thus, an intermediate phase will appear, before the cubic one. A first order phase-transition has been observed between $P2_1/n$ and $R-3$ (No. 148 conventional setting). None of the amplitudes of the active modes will reach the zero value at the transition temperature. In the symmetry breaking from the prototype cubic phase into the trigonal intermediate (HT) phase a unique active mode has been identified: GM_4^+ , which generates a rotation of the octahedra around the hexagonal c axis.

[1] M.I. Aroyo, J.M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov, H. Wondratschek. *Zeitschrift fuer Kristallographie*, **2006**, 221, 1, 15-27. [2] M.I. Aroyo, A. Kirov, C. Capillas, J.M. Perez-Mato, H. Wondratschek. *Acta Cryst.* **2006**, A62, 115-128. [3] D. Orobengoa, C. Capillas, M.I. Aroyo, J.M. Perez-Mato, *J. Appl. Cryst.* **2009**, A42, 820-833. [4] J. Rodriguez-Carvajal, *Physica* **1993**, B192, 55. [5] J.M. Perez-Mato, D. Orobengoa, M.I. Aroyo. *Acta Cryst.* **2010**, A66, 558-590. [6] A. Faik, J.M. Igartua, M. Gateshki, G.J. Cuello, *J. Solid State Chem.* **2009**, 182, 1717-1725. [7] M. Gateshki, J.M. Igartua, *Mater. Res. Bull.* **2003**, 38, 1893-190.

Keywords: transition-metal perovskites, phase-transitions, symmetry-mode analysis

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High-pressure behavior of high silica ferrierite

Rossella Arletti,^a Simona Quartieri,^b Giovanna Vezzalini,^c ^a*Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, (Italy).* ^b*Dipartimento di Scienze della Terra, Università di Messina, (Italy).* ^c*Dipartimento di Scienze della Terra, Università di Modena, (Italy).* E-mail: rossella.arletti@unito.it

Ferrierite (FER framework topology) is a well-known aluminosilicate zeolite mineral. An understanding of the structure and properties of FER remains important because of its role as a catalyst in commercial reactions. For example, it is important in the petrochemical industry, where it has been used as a shape selective catalyst for the production of isobutene. The thermal behavior of this phase (in its high silica form) was recently studied by Bull et al [1], while its compressibility has never been investigated before.

The high pressure (HP) behavior of synthetic high silica zeolite ferrierite (FER) was investigated by means of in-situ synchrotron X-ray powder diffraction, with the aim to understand the P-induced deformation mechanism. The microporous material was synthesized starting from pure silica and pyridine and propyl-amine as structure directing agents. Here we report the preliminary results on the compressibility of the as synthesized phase. The study of the compressibility of the calcined one will be carried out in the following steps of the project.

The crystal structure of ferrierite is built up of rings of fivecorner-shared SiO₄ tetrahedra (known as five-membered rings or 5MRs) building units, which form layers in the *ab* plane. The layers are connected to form a matrix of 10MR channels running parallel to the *c* axis, which are intersected by 8MR channels running parallel to the *b* axis. Six-membered rings connect the 10MRs along the *c* axis direction.

The HP diffraction experiments were performed at BM01a beamline (ESRF), at the fixed wavelength of 0.71 Å, using a modified Merrill-Basset DAC and a mixture of methanol- ethanol and water (16:3:1) as penetrating P-transmitting medium. The powder patterns were collected from P_{amb} to 6.2 GPa. Some patterns were also measured upon pressure release up to P_{amb}, to check the reversibility of the compression effects. The unit cell parameters were refined by means of Rietveld method.

The main results of this study are:

- 1) No complete X-ray amorphization is observed up to about 6.6 GPa;
- 2) No abrupt change of the elastic behavior is observed in the whole pressure range. Between P_{amb} and 6.2 GPa the reduction of the cell parameter are 4%, 5% and 6% for a, b and c respectively, accounting for a volume reduction of about 14 %.
- 3) The bulk modulus obtained using a second order Birch-Murnaghan equation of state and data weighted by the uncertainties in *P* and *V* was K₀ = 30.1(3) GPa. This compressibility determined in m.e.w. is one of the highest when compared with other natural and synthetic zeolites studied with “penetrating” aqueous media [2], [3].
- 4) The P-induced effects on as-synthesized ferrierite structure are completely reversible.

[1] I. Bull, P. Lightfoot, L.A. Villaescusa, L.M. Bull, R.K.B. Gover, J.S.O. Evans, R.E. Morris, *JACS* **2003**, *125*. [2] S. Ori, S. Quartieri, G. Vezzalini, V. Dmitriev, *Amer. Mineral.* **2008**, *93*, 1393-1403. [3] R. Arletti, S. Quartieri, G. Vezzalini, *Amer. Mineral.* **2010**, *95*, 1247-1256.

Keywords: high pressure, zeolite ferrierite, synchrotron XRPD

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Variable-temperature studies of three polymorphs of 1,3-nitrobenzoic acid

Grażyna M. Wójcik,^a Marek Wołczyrz,^b ^a*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wrocław (Poland).* ^b*Institute of Low Temperature and Structural Research PAN, Wrocław (Poland).* E-mail: grazyna.m.wojcik@pwr.wroc.pl

The reported results concern the multi-disciplinary investigations including: variable-temperature single crystal and powder X-ray diffraction, differential scanning calorimetry (DSC) and IR and Raman spectroscopy.

The thermodynamic relationship between three polymorphs has been elucidated. Three polymorphs can be grown at ambient temperature, two of them as metastable phases. Enantiotropic transformations between polymorphs occur at temperatures above ambient (353 K and 378 K) and are due to thermally enhanced vibrations of the nitro groups. The double hydrogen bonding linking carboxyl groups remains preserved in two polymorphs. One transformation has been also observed as single crystal – single crystal transition.

Structurally two polymorphs differ by the position of nitro groups in the molecular dimers, that is *trans* in the low-temperature form and *cis* in the high-temperature form. As a consequence the interactions involving the nitro groups are different. In the low-temperature form the nitro...nitro intermolecular interactions are observed. In the high-

temperature form the nitro...HC intermolecular weak hydrogen bonds occur. The crystal structure of the third polymorph still remains the subject of our investigation.

The relevant role of the out-of-plane torsional vibrations of the nitro groups for the crystal structure stability is consistent with the thermodynamic properties of the crystals of other nitrobenzene derivatives, able to form strong hydrogen bonds. The crystals exhibit phase transitions above ambient temperature. The transitions are driven by large-amplitude torsional vibrations of the nitro groups while the intermolecular hydrogen bonds remain persistent [1], [2].

[1] G. Wójcik, J. Holband, J.J. Szymczak, S. Roszak, J. Leszczynski, *Cryst. Growth Des.* **2006**, *6*, 274-282. [2] G. Wójcik, I. Mossakowska *Acta Cryst. B*, **2006**, *62*, 143-152.

Keywords: polymorphism, transformation, vibration

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Parametric symmetry mode refinement of the structural phase transition of CuInSe₂

Melanie Müller,^{a,b} Robert E. Dinnebier,^a Susan Schorr,^c ^a*Max Planck Institute for Solid State Research, Stuttgart (Germany).* ^b*University of Trento, Trento (Italy).* ^c*Free University Berlin, Berlin (Germany).* E-mail: m.mueller@fkf.mpg.de

As it is the case for many structural phase transitions, the low symmetry structure of CuInSe₂ can be described as a distorted form of its high symmetry structure by adding a set of symmetry modes to the atomic structure of the high symmetry phase. The decomposition of the structures in terms of symmetry modes can be easily done by web based software packages [1], [2]. Symmetry modes of one given type (e.g. lattice strain, displacement or occupancy) comprise an order parameter according to Landau theory.

This alternative approach to describe the structural evolution during ferroelastic phase transitions can also be applied in Rietveld refinement, simply refining the amplitudes of the symmetry modes instead of refining free atomic positions, occupancies and lattice parameters. To investigate the behaviour of the relevant modes over the phase transition parametric Rietveld refinement [3] offers the possibility to model the characteristics of those modes using power law trends as proposed in Landau theory.

For the structural phase transition of CuInSe₂ from the tetragonal chalcopyrite to the cubic sphalerite structure type the temperature dependence of all symmetry modes influencing lattice parameters, atomic coordinates and occupancies as well as the evolution of the isotropic temperature factors have been modeled with a phenomenological power law behaviour. The results of this study reveal superior statistics and much higher stability of parametric as compared to sequential Rietveld refinement leading to a more detailed understanding of the nature of the phase transition (Figure 1).

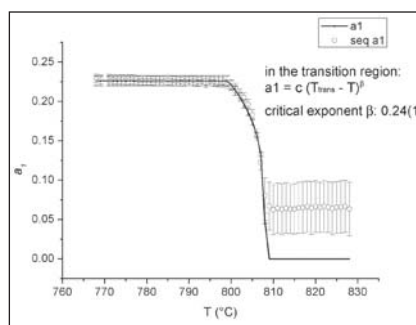


Figure 1: Comparison of the results of traditional sequential refinement (dots) and parametric refinement (line) for the a1 symmetry mode describing the evolution of the x-position of the Se atom.