

The crystal structure of ferrierite is built up of rings of fivecorner-shared  $\text{SiO}_4$  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  $P_{\text{amb}}$  to 6.2 GPa. Some patterns were also measured upon pressure release up to  $P_{\text{amb}}$ , 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  $P_{\text{amb}}$  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  $K_0 = 30.1(3)$  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.

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

Grażyna M. Wójcik,<sup>a</sup> Marek Wołczyr,<sup>b</sup> <sup>a</sup>*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wrocław (Poland).* <sup>b</sup>*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.

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### Parametric symmetry mode refinement of the structural phase transition of CuInSe<sub>2</sub>

Melanie Müller,<sup>a,b</sup> Robert E. Dinnebier,<sup>a</sup> Susan Schorr,<sup>c</sup> <sup>a</sup>*Max Planck Institute for Solid State Research, Stuttgart (Germany).* <sup>b</sup>*University of Trento, Trento (Italy).* <sup>c</sup>*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 CuInSe<sub>2</sub> 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 CuInSe<sub>2</sub> 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).

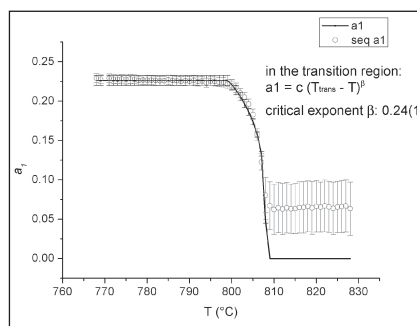


Figure 1: Comparison of the results of traditional sequential refinement (dots) and parametric refinement (line) for the  $a1$  symmetry mode describing the evolution of the  $x$ -position of the Se atom.

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**Parametric XRD profile analysis of SnO<sub>2</sub> crystallite growth**

F. Gispert-Guirado,<sup>a</sup> R.G. Pavelko,<sup>b</sup> E. Llobet,<sup>c</sup> <sup>a</sup>Scientific Resources Service, Univ. Rovira i Virgili, Tarragona, (Spain). <sup>b</sup>Institute of Physical Chemistry, Univ. of Tübingen, Tübingen, (Germany). <sup>c</sup>MINOS-EMaS, Univ. Rovira i Virgili, Tarragona, (Spain). E-mail: francesc.gispert@urv.cat

Simultaneous estimation of lattice strain and crystallite size using sequential profile analysis (SPA) within one TXRD experiment is difficult due to the high correlation between them, especially with short range diffractograms independently fitted to each other. The problem can be resolved without performing additional experiments by applying parametric profile analysis (PPA) [1], where each diffractogram is linked parametrically to the next one. In this case, crystallite size contribution to peak width is calculated using its mathematical function of time with several refinable parameters, which are common for the whole sequence of diffractograms [2].

In this work we report on the comparison of two methods (SPA and PPA) for crystallite size calculation with or without strain contribution. In our previous paper [3] we showed that growth kinetics of SnO<sub>2</sub> crystallites under isothermal annealing can be well described by size-dependent impediment model [4]:  $D(t) = \sqrt{D_0^2 - (D_{lim}^2 - D_0^2) \exp(-2At / D_{lim}^2)}$ , where  $D_0$  and  $D_{lim}$  are the initial and limiting crystallite sizes, and  $A$  – rate constant. In SPA, the kinetic model was used just to fit the already calculated values of crystallite sizes. In PPA the kinetic model was used to calculate the crystallite sizes by fitting simultaneously all diffractograms obtained as a function of annealing time and considering that the evolution of crystallite size obeys the model given.

Three SnO<sub>2</sub> materials (blank SnO<sub>2</sub>, bulk doped SnO<sub>2</sub> with 0.02 wt. % Pd (SnO<sub>2</sub> Pd), and surface doped SnO<sub>2</sub> with 1.2 wt. % Pd (SnO<sub>2</sub> dep Pd)) were analyzed by TXRD under isothermal conditions: at 600, 700 and 800°C. Overall 31 patterns were collected during 32 hours of annealing. Kinetic parameters were calculated for each temperature using SPA, PPA without consideration of lattice strain ( $\epsilon_p$ ) and PPA with consideration of lattice strain according to Gaussian (G) or Lorentzian (L) contribution. The results for 800°C (for the sake of brevity) are shown in the following table.

Material	Method	$D_0$ (nm)	$D_{lim}$ (nm)	$A$ (nm <sup>2</sup> /h)	Mean strain (%)
SnO <sub>2</sub> blank	S P A	2.54 (4)	3.22 (2)	0.76 (9)	-
	PPA w/o strain	2.520 (24)	3.142 (11)	0.857 (69)	-
	PPA w strain (L)	2.606 (87)	3.157 (44)	0.72 (23)	0.0000 (209)
	PPA w strain (G)	3.233 (74)	4.038 (30)	1.99 (35)	0.4940 (202)
SnO <sub>2</sub> Pd	S P A	9.72 (25)	16.0 (9)	2.4 (2)	-
	PPA w/o strain	9.562 (64)	15.697 (33)	28.38 (66)	-
	PPA w strain (L)	9.29 (21)	17.05 (12)	48.7 (3.5)	0.0151 (21)
	PPA w strain (G)	9.635 (92)	16.452 (48)	33.3 (1.1)	0.0667 (44)
SnO <sub>2</sub> depPd	S P A	5.96 (11)	8.70 (4)	6.4 (5)	-
	PPA w/o strain	5.909 (41)	8.657 (19)	6.63 (21)	-
	PPA w strain (L)	5.91 (15)	9.675 (85)	12.4 (1.2)	0.0384 (42)
	PPA w strain (G)	6.032 (65)	9.009 (31)	7.05 (31)	0.0936 (86)

The values obtained without strain consideration, using either SPA or PPA, were found to be quite similar to each other. However, if we take into account lattice strain, the values differ remarkably from the previous ones. The rate constant  $A$  reflects higher discrepancy compared to other parameters, since it is depended on both  $D_0$  and  $D_{lim}$ . The

higher temperature was, the higher the difference was observed, which suggests higher impact of lattice strain at elevated temperatures. This can be explained by the fact that SnO<sub>2</sub> possesses a nonstoichiometric surface which upon heating in air readily loses oxygen. In the case of highly dispersed materials, numerous oxygen vacancies diffuse into bulk, creating defects and increasing lattice strain. The highest values of lattice strain were found for blank SnO<sub>2</sub>.

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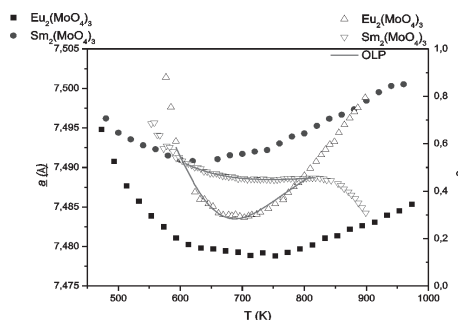
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**Polarons and distortions in rare-earth molybdates at high temperature**

M. C. Guzmán-Afonso,<sup>a</sup> M. E. Torres,<sup>b</sup> C. González-Silgo,<sup>c</sup> E. Matesanz,<sup>d</sup> N. Sabalisck,<sup>b</sup> <sup>a</sup>Departamento de Física Fundamental y Experimental, Electrónica y Sistemas, <sup>b</sup>Departamento de Física Básica, <sup>c</sup>Departamento de Física Fundamental II, Universidad de La Laguna, La Laguna, S/C Tenerife (Spain). <sup>d</sup>C.A.I. Difracción de Rayos X, Universidad Complutense de Madrid, Madrid (Spain). E-mail: mcguzman@ull.es

Light rare-earth (RE) molybdates (RE=La-Eu) can occur in differently ordered scheelite-type (CaWO<sub>4</sub>) structures, where 1/3 of the calcium substituted by the RE are vacancies. At room temperature, are monoclinic with space group  $C2/c$  and  $Z=4$  but the molybdates with RE=La-Nd and RE=Sm-Eu have a volume of nine and three times the volume of the scheelite structure, respectively. In particular, in this work we will study Sm<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> [1] and Eu<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> [2] at high temperature. The study of X-ray diffraction patterns reveals an anomalous behavior of its lattice parameter  $a$  in the range of temperatures from 473 to 973 K (see figure, solid symbol). Rietveld refinements were performed using symmetry adapted modes [3] at 523, 723 and 923 K in order to study the thermal dependence of the distortion from the scheelite structure and to interpret the structural effects that favor the formation of polarons.

We have analyzed the real part of the complex conductivity in the frequency range from 0.1 to 10000 KHz and the temperature range from 550 to 900 K and found that it follows a universal dielectric response [4], [5]. Detailed analysis of the temperature dependence of the adjusted parameters within this model shows that, in the temperature range of 630 to 800 K (see figure, open symbol), the dominant mechanism of electrical transport is by the overlapping large polaron (OLP) model [6].



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