

**Keywords:** ferromagnetic, ferroelectric, magnetic entrop

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**X-ray diffraction study of the electric-field-induced structural deformations in  $\text{LiH}_2\text{PO}_4$ .** Sebastian Wagner<sup>a</sup>, Oleg Schmidt<sup>a</sup>, Ullrich Pietsch<sup>a</sup>, Ladislav Bohatý<sup>b</sup>. <sup>a</sup>*Solid State Physics Department, University Siegen, Germany.* <sup>b</sup>*Institute of Crystallography, University Cologne, Germany.*  
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An external electric field applied to a piezoelectric crystal induces both, a change of the crystal lattice parameters and a shift of the atomic positions within the unit cell (internal strain). Although both phenomena are well studied on the macroscopic level, there is still a poor understanding of their origin on the atomic scale. Since the last few years the internal strain of different crystals is under intensive investigation using methods of precise X-ray structure analysis for measuring the tiny differences of Bragg diffraction intensities with and without an applied external electric field. From the study of the relative change in the integrated intensities of different X-ray reflections it is experimentally possible to obtain the information about the induced atomic displacements within the unit cell [1]. At the same time the macroscopic homogeneous deformation of the crystal is visible as a small shift of the rocking curve positions [2].

The present study was done with piezoelectric  $\text{LiH}_2\text{PO}_4$ , which belongs to the space group Pna21 and consists of  $\text{PO}_4$  and  $\text{LiO}_4$  tetrahedra linked together by oxygen atoms. The measurements were performed by periodically applying a four-step modulated high voltage ( $U_+ = 3 \text{ kV}$ ,  $U_0$ ,  $U_- = -U_+$ ,  $U_0$ ) to thin crystal plates. As a result, we obtained that the  $\text{LiO}_4$  tetrahedra are by a factor of about 1.7 more sensitive to an external electric field than the  $\text{PO}_4$  tetrahedra. In order to explain this bond-selective response of  $\text{LiH}_2\text{PO}_4$ , we considered the electron density (ED) properties of this crystal that were calculated based on the density functional theory with the program WIEN2k [3]. The characterization of the chemical bonds and the calculation of the pseudoatomic charges were performed by means of the Bader formalism. The ED in the bond critical points ( $\rho_{\text{BCP}}$ ) in  $\text{LiH}_2\text{PO}_4$  and the pseudoatomic charges are given in Table 1. Accordingly, the average ED in the Li-O bond critical points is 10 times smaller than for the P-O bonds. At the same time the Bader atomic charge of P is 5 times larger than the corresponding value for Li. Considering that the external electric force deforming the bond lengths in a crystal is proportional to the atomic charges and the resistivity of a bond is proportional to the bond strength, one may conclude that the observed effect has its origin in the much weaker ionic Li-O bonds compared to the covalent P-O bonds.

Table 1.:

	$\text{PO}_4$	$\text{LiO}_4$
$\langle  \nabla(\mu-\text{O})  \rangle, 10^{-5} \text{ \AA}(\text{kVmm}^{-1})^{-1}$	3.9	5.7
$\langle  \nabla_{\text{BCP}}  \rangle, e/\text{ \AA}^3$	1.78	0.19
$Q, e$	4.12	0.87

[1]O. Schmidt, S. Gorfman, L. Bohatý, E. Neumann, B. Engelen, U. Pietsch, *Acta Cryst. A* 65, 267-275 (2009). [2] S. V. Gorfman, O. Schmidt, U. Pietsch, P. Becker, L. Bohatý, *Z. Krist.* 222, 396-401 (2007). [3] P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka, J. Luitz, *WIEN2K*, TU Wien (2001).

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#### FA2-MS14-P29

**A temperature-dependent  $^{57}\text{Fe}$  Mössbauer Study of Mullite-Type  $\text{Bi}_2(\text{Fe}_x\text{M}_{1-x})_4\text{O}_9$  with  $\text{M}=\text{Al}$  and  $\text{Ga}$ .** S.-U. Weber, O. Bartels, K.-D. Becker. *Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Braunschweig, Germany.*  
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The  $\text{Bi}_2\text{M}_4\text{O}_9$  structure ( $\text{M} = \text{Fe}$ ,  $\text{Ga}$  and  $\text{Al}$ ) contains nonmagnetic planes of bismuth oxide which sandwich a  $\text{M}^{3+}$  metal oxide region providing two types of metal coordination sites, tetrahedral and octahedral. The linear chains of  $\text{M}^{3+}$  containing octahedra in c-direction constitute the relevant criterion for the mullite-type structure. In the present work, the local structure of the solid solutions  $\text{Bi}_2(\text{Fe}_x\text{M}_{1-x})_4\text{O}_9$  ( $0.1 \leq x \leq 1$ ) with  $\text{M} = \text{Al}$  and  $\text{Ga}$ , is studied using  $^{57}\text{Fe}$  Mössbauer spectroscopy.

Oxides of the chemical composition  $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$  ( $0.1 \leq x \leq 1$ ) have been investigated by Mössbauer spectroscopy in the temperature range between 293 K and 1073 K. The spectra have been fitted with two doublets for tetrahedrally and octahedrally coordinated  $\text{Fe}^{3+}$  ions, respectively. Their area ratio has been used to determine the distribution of iron on the tetrahedral and octahedral sites. The site occupancy does not exhibit any significant preference of iron for the octahedral or tetrahedral sites, neither as a function of temperature nor in dependence of the chemical composition of the solid solutions. Also the mullite-type system  $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$  ( $0.1 \leq x \leq 1$ ) has been investigated by Mössbauer spectroscopy in dependence of the chemical composition and in the temperature range between 293 K and 1073 K. The site occupancy of this system shows an increasing preference of Fe for the octahedral site with increasing Ga content caused by the preference of  $\text{Ga}^{3+}$  for the tetrahedral site. Temperature dependent Mössbauer measurements indicate no change of site occupancy with temperature.

**Keywords:** Fe Mössbauer , Bi-Mullites, site occupancy

#### FA2-MS14-P30

**Correlation of Microstructure and Catalytic Properties of Gold - Zirconia Core - Shell Nanostructures** Arti Dangwal-Pandey<sup>a,b</sup>, Robert Güttel<sup>a</sup>, Matteo Leoni<sup>c</sup>, Ferdi Schüth<sup>a</sup>, Claudia Weidenthaler<sup>a</sup>

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Detailed microstructure studies of gold nanoparticles encapsulated into crystalline zirconia hollow-spheres are presented. Gold nanoparticles are known to be excellent candidates for low temperature CO-oxidation. One important requirement for high catalytic activity is to keep the size of the catalyst particles small. The stability of the gold nanoparticles can be increased by encapsulation of gold into porous zirconia shells [1]. The hollow-shells with diameters of about 125 nm consist of nanosized zirconia and contain single 15 nm gold particles. The thickness of the shell is about 10 nm. Thus, the gold nanoparticles are well separated from each other. This allows thermal and chemical treatment of the