

Keywords: ferromagnetic, ferroelectric, magnetic entrop

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X-ray diffraction study of the electric-field-induced structural deformations in LiH_2PO_4 . Sebastian Wagner^a, Oleg Schmidt^a, Ullrich Pietsch^a, Ladislav Bohatý^b. ^a*Solid State Physics Department, University Siegen, Germany.* ^b*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 LiH_2PO_4 , which belongs to the space group Pna21 and consists of PO_4 and 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 LiO_4 tetrahedra are by a factor of about 1.7 more sensitive to an external electric field than the PO_4 tetrahedra. In order to explain this bond-selective response of LiH_2PO_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 (ρ_{BCP}) in LiH_2PO_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.:

	PO_4	LiO_4
$\langle \nabla\mu-\mathbf{O} \rangle, 10^{-5} \text{Å}(k\text{Vmm}^{-1})^{-1}$	3.9	5.7
$\langle \rho_{\text{BCP}} \rangle, e/\text{Å}^3$	1.78	0.19
Q, e	4.12	0.87

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A temperature-dependent ^{57}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 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 ($\text{M} = \text{Fe}$, Ga and Al) contains nonmagnetic planes of bismuth oxide which sandwich a M^{3+} metal oxide region providing two types of metal coordination sites, tetrahedral and octahedral. The linear chains of 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 Ga , is studied using ^{57}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 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 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

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Correlation of Microstructure and Catalytic Properties of Gold - Zirconia Core - Shell Nanostructures Arti Dangwal-Pandey^{a,b}, Robert Güttel^a, Matteo Leoni^c, Ferdi Schüth^a, Claudia Weidenthaler^a

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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

catalysts without any sintering effects or changes in the size distribution. However, changes of the microstructure of the gold nanoparticles can be induced by chemical and thermal treatment. The effect of the microstructure properties of gold nanoparticles on the catalytic activity for CO oxidation has been investigated. Line profile analysis of powder diffraction data based on Whole Powder Pattern Modelling (WPPM) approach was used to determine both the domain size distribution and lattice defects present in this two phase system [2]. The different catalysts showed substantial variation in the activity towards CO oxidation depending on their microstructure. Lower dislocation densities and less stacking faults, but higher twin densities result in decreased catalytic activity.

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Keywords: microstructure, catalysts, nanocrystalline structure defects

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Lattice dynamics of multiferroic BiFeO₃. Elena Borissenko^a, Alexei Bosak^a, Pauline Rovillain^b, Maximilien Cazayous^b, Marco Goffinet^c, Philippe Ghosez^c, Dorothee Colson^d, Michael Krisch^a. ^a*European Synchrotron Radiation Facility, Grenoble, France.* ^b*Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot-Paris 7, France.* ^c*Département de Physique, Université de Liège, Belgium.* ^d*Service de Physique de l'Etat Condensé, CEA Saclay, France.*
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Materials with the coexistence of at least two ferroic orders (ferromagnetic, ferroelectric, ferroelastic) are known as multiferroics [1]. These materials represent a strong potential for devices based on the magnetic properties switch by an external electric field and vice versa. Among the multiferroics, Bismuth ferrite belongs to the *class* with the coexistence and coupling between magnetic order and electric polarization (ME: magneto-electric coupling).

This material is one of the most extensively studied multiferroic due to its unique property of ferroelectric and magnetic order at room temperature. Its dynamical properties have been studied by Raman [2, 3] and infrared spectroscopy [4], and have revealed some anomalies in the temperature dependence of the lowest optical phonon, which were interpreted as signature of magneto-electric coupling [2]. Here, we present an experimental study of the phonon dispersion in BiFeO₃ single crystals at ambient conditions by inelastic x-ray scattering. Phonon dispersions were recorded along several high-symmetry directions up to 35 meV. Our results compare favourably with *ab-initio* calculation performed using density functional theory (DFT) within the local-density approximation (LDA). We resolve a recent discrepancy concerning the symmetry of the lowest optical phonon branch observed by Raman spectroscopy [2, 3], determine the energy of the Raman- and infrared silent modes, and derive the elastic constants of BiFeO₃.

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Keywords: BiFeO₃, single crystal, lattice dynamics, Inelastic X-ray Scattering

FA2-MS14-P32

First Single-Crystal Neutron Diffraction Results on PZT Structure. A. M. Glazer^a, D. Phelan^b, X. Long^c, Y. Xie^c, Z. -G. Ye^c, H. Yokota^a, P.A. Thomas^d, P. M. Gehring^b. ^a*Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom.* ^b*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA.* ^c*Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, Canada.* ^d*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom.*
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The outstanding piezoelectric properties of PbZr_{1-x}Ti_xO₃ (PZT) perovskite ceramics have long been exploited in important device applications. The effort to understand the underlying piezoelectric mechanism has inspired a plethora of structural studies spanning decades. However, structure determination of PZT has always been problematic because single crystals have not been available, except for Zr and Ti-rich compositions near the end members PbZrO₃ and PbTiO₃, where the piezoelectricity is weakest. As a result, PZT has been the subject of literally thousands of powder and ceramic investigations. Despite these efforts, no consensus regarding the true PZT crystal structures has been achieved. Here we report the first neutron diffraction study of single-crystal PZT with $x = 0.325$ and 0.460 . Our measurements help to resolve a key debate on the structure of PZT by placing severe constraints on the magnitude of the structure factors of weak superlattice peaks and the splitting of fundamental Bragg peaks.

Keywords: perovskite structures, neutron diffraction, piezoelectrics

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Crystal structure of Li₂B₄O₇. Anatoliy Senyshyn^a, Björn Schwarz^b, Thomas Lorenz^c, Yaroslav Burak^d, Volodymyr Adamiv^d, Jūras Banys^e, Robertas Grigalaitis^e, Hartmut Fuess^a, ^a*Institute of Material Science, Darmstadt University of Technology, Darmstadt, Germany.* ^b*Leibniz-Institute IFW Dresden, Dresden, Germany.* ^c*II. Physikalisches Institut, Universität zu Köln, Köln, Germany.* ^d*Institute of Physical Optics, Lviv, Ukraine.* ^e*Physics Faculty, Vilnius University, Vilnius, Lithuania.*
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The crystal structure of lithium tetraborate Li₂B₄O₇ (mineral name diomignite) at room temperature is tetragonal with the space group *I4₁cd* (point group *4mm*) and with the polar axis along the crystallographic *c*-direction [1]. It is formed by a boron-oxygen network throughout the crystal with lithium atoms in the interstices; the anion B₄O₇²⁻ - the basic subunit of this net consists of four boron atoms, where two of them tetrahedrally and two other are triangularly linked to oxygens.