

investigations. Due to the similar electron count of Sn, Sb and Te, conventional X-ray diffraction does not allow to study the exact element distribution. We obtained high-resolution resonant scattering data at the Sn-, Sb- and Te-edges (29.20 keV, 30.49 keV, 31.81 keV) and at wavelengths far away of the edges which allow for a simultaneous refinement of mixed site occupancies with anisotropic displacement parameters. The enhanced scattering contrast clearly reveals the element distribution in long-periodically ordered structures. For 21R-SnSb₂Te₄, the structure of which has been controversially discussed, a joint refinement of all datasets ($R-3m$, $a = 4.292$, $c = 41.50$ Å, $R1 = 0.028$) including refined dispersion correction terms f' and f'' indicates no significant amounts of Sb-Te or Sn-Te anti-site defects, but mixed site occupancy of cation positions comparable to that in 21R-GeSb₂Te₄. [3] The optimized f' and f'' values were used for the determination of the concentration modulation of the elements in the much more complex 39R-type phases mentioned above. These show interdependent concentration modulations of the site occupancies of anion and cation positions accompanied by positional displacements. Thermoelectric properties of both phases can be correlated with the structural differences between the Ge and Sn containing materials.

Comparable structure-property relationships may be expected for crystalline phases of Ge-Sb-Te phase-change materials. Metastable GeTe-rich single crystals obtained by chemical transport exhibit a pseudocubic average structure with significant temperature-dependent changes of the diffuse intensities present. In situ temperature dependent single-crystal diffraction data obtained at the K-edges of Sb and Te promise further insight into the structural chemistry of this class of materials.

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SAXS INVESTIGATION OF THE SURFACE FRACTAL DIMENSION OF MnO₂ PYROLYTIC THIN FILMS. Skatkov^a, V.Gomozov^b. ^aPCB "Argo", 4/23 Shaul ha-Melekh Str., 84797 Beer Sheva, Israel ^bNTU "KhPI" 21 Frunze Str., 61002 Kharkov, Ukraine. E-mail: sf_lskatkov@bezeqint.net

MnO₂ films which have been prepared by the thermal deposition (pyrolysis) of Mn(NO₃)₂ are important semiconductor materials for application as semiconductor layer in metal (sintered Nb pellet) – dielectric (anodic Nb₂O₅)– semiconductor (MnO₂) MDS electrical capacitors. Earlier reported significant influence of the fractal layer on electrical characteristics of MDS capacitors. This feature are responsible for the interest in investigating the fractal properties of this latter. The surface fractal dimension D have been investigated by small-angle X-ray scattering (SAXS). The theory of scattering by a porous solid was developed by Wong. The main formula of this theory is as follows:

$I(q) \sim \text{constant} \times q^{D-6}$ (1) Here $I(q)$ is the X-ray scattering intensity, q is the wave vector, and D is the surface fractal dimension. The scattered intensity vs wavevector relationship shows the fractal behaviour. Indeed, on the graph the coefficient of the slope of the curved part, which can be closely approximated by a line, is: $-\text{d} \ln I(q) / \text{d} \ln q = 2.87$

As report in [1] in case when $2 < \alpha < 3$, the scattering cause by the **whole volume** of subject and $D = \alpha = 2.87$. The obtained D value coincides with previously found value of surface fractal dimensionality in a sintered niobium powder pellet with high accuracy $D_{(Nb)} = 2.81$ (see formula (1) at $\alpha = 3.19$).

So far, authors are at loss and cannot say whether it is a mere coincidence or the result of some specific features of generation of the capacitor MDS structure. But it as should be noted in [2] in case when $2 < \alpha < 3$ scattering stipulate by the **surface** of sample.

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FA2-MS14-P27

Structural, magnetic, electrical and magnetocaloric properties in Pr_{0.6}Sr_{0.4}MnO₃/BaTiO₃ composites. M. Triki^a, E. Dhahri^a, M.P.F. Graça^b, M.A. Valente^b.

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Composites with varying composition of ferromagnetic Pr_{0.6}Sr_{0.4}MnO₃ and ferroelectric BaTiO₃ have been prepared using a solid-state ceramic method (1-x)(Pr_{0.6}Sr_{0.4}MnO₃)/x(BaTiO₃), with x is the molar ratio and x = 0.0, 0.03, 0.05, 0.10 and 0.30 using conventional ceramic double sintering process. We report the structural, magnetic electrical and magnetocaloric properties of all samples. The presence of the two phases of Pr_{0.6}Sr_{0.4}MnO₃ (PSMO) and BaTiO₃ (BTO) was confirmed by X-ray diffraction (XRD) technique and the structural analysis. Magnetic measurements of magnetization versus temperature and applied field were performed. The temperature dependence of magnetization reveals that the composite samples show paramagnetic to ferromagnetic transition when the temperature decreases at the same Curie temperature as the parent PSMO compound ($T_c \approx 273$ K). The magnetic entropy change $|\Delta S_M|$ has been deduced from the M(H) data by the Maxwell relation. Close to T_c , large change in magnetic entropy has been observed in all samples. The maximum value of the magnetic entropy is $|\Delta S_M^{\max}|$ decreases from 2.88 J.kg⁻¹.K⁻¹ for x = 0 to 1.86 J.kg⁻¹.K⁻¹ for x = 0.3 for an applied magnetic field of 2T. At this value of magnetic field the relative cooling power (RCP) decreases also from 63 J.kg⁻¹ for the parent sample to 38.3 J.kg⁻¹ for x = 0.3. The temperature dependence of the Landau coefficients have been deduced using the Landau expansion of the magnetic free energy, indicating the second order nature of the magnetic transition.

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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
$\langle \Delta\mu\text{-O} \rangle, 10^{-5} \text{ \AA} (\text{kVmm}^{-1})^{-1}$	3.9	5.7
$\langle \Delta_{\text{BCP}} \rangle, e/\text{ \AA}^3$	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