

the use of *in situ* method on X-ray diffractometer. The phase changes observed may be explained in the following way: at low synthesis temperatures and relatively short-time calcinating (2 hours) the generation of KNbO₃ as least(possibly nano) particles. This supposal is proved by the fact that known ferroelectrics (BaTiO₃, PbTiO₃ etc.) in nanocrystal condition are characterized by the increased cell sizes and lessened values of spontaneous deformation. The increased cell volumes could be the consequence of large concentrations of defects. On increase of calcinating temperatures, the reduce of the cell volume might be the consequence of either increase of crystalline sizes or of the reduce of defects number. Until now the phenomenological study of ferroelectric phase conditions was observed from the point of view of outer effects(temperatures, pressures, electric fields) that's why including the parameters of real conditions of objects into complete theoretical observation.

Keywords: ferroelectrics, phase transitions, synthesis

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Modulated crystal structure of RE_{1.67}AE_{0.33}NiO₄ in charge ordering state

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Stripe-type charge ordering (CO) [1], as found in some layered perovskite-type transition-metal oxides, is a typical example of self-organized electrons and also responsible for novel electric properties, such as the colossal magnetoresistance and electroresistance that are expected to be applied to the next generation memories [2]. Therefore, investigation of the CO structure is important for material design in layered transition metal oxide systems [3]. In this work, we report on the modulated crystal structure associated with the CO in the single-layered nickelates RE_{1.67}AE_{0.33}NiO₄ (RE and AE are rare-earth and alkaline-earth ions, respectively). The relation between A-site cations and CO structure has been investigated systematically by means of transmission electron microscopy (TEM). Long-range ordered charge stripes with a commensurate modulation wave number along the b-axis (the longer axis in the ab plane) are observed in the orthorhombic single crystal Pr_{1.67}Ca_{0.33}NiO₄ with minimal disorder effect. Change of A-site combination to Sm and Sr, the CO correlation along the b-axis becomes short-range. An abrupt decrease of the CO correlation length along the c-axis with the increase of disorder revealed that the charge stripe ordering collapses via the stacking faults of the charge stripes, indicating that the quenched disorder affects the CO structure in the layered nickelates.

Keywords: modulated crystals, transition-metal oxides, TEM

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Investigation of differently synthesized Co-Ni-Al spinels and precision of the crystallographic data

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Spinelns comprise a large group of compounds with high importance in industry. Our investigations focus on the influence of different synthesis methods on both, the crystallization path and on the crystal chemistry of the spinel product. Additionally to the materials aspects, the precision and reproducibility of the crystallographic analyses are of major interest. (Co,Ni)Al₂O₄ spinels with four different Ni:Co ratios were synthesized by 4 different methods: from impregnated carbons, by sol-gel methods, and by calcination of oxides and of salts. Samples were calcined at temperatures between 550°C and 1300°C. All samples were measured in Bragg-Brentano geometry with Cu-K α radiation. Additionally, selected samples were analyzed in Debye-Scherrer geometry with Mo-K α_1 radiation and by neutron diffraction at the E6 instrument at the Hahn-Meitner facility (Berlin). Rietveld refinements of diffraction patterns revealed that the synthesis path indeed has an influence on the spinels formed. Due to the different precursor materials spinels with different chemical compositions and varying amounts of by-phases are obtained. Neutron diffraction experiments performed on selected samples calcined between 1050°C and 1300°C show only minor changes of the Co and Ni distribution on the octahedral and the tetrahedral position with temperature. This indicates that already at lower temperatures the spinels formed are in equilibrium. Structure refinement strategies as well as the selection of instrument geometry and radiation source shows a strong influence on the refined structure data.

Keywords: spinel, crystallization of materials, data precision

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Phase transition studies in multiferroic Pb(Fe_{1/2}Nb_{1/2})O₃ and its solid solution with PbTiO₃

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Recent years have witnessed enormous interest in the multiferroic materials because of the presence of more than one ferroic/ anti-ferroic orders: such as ferroelectric, ferroelastic and ferromagnetic/ antiferromagnetic. Pb(Fe_{1/2}Nb_{1/2})O₃ (PFN), is a multiferroic exhibiting a diffuse ferroelectric phase transition at 385K and two antiferromagnetic transitions at 143K and 9K, respectively. It is an attractive material for use in multilayer ceramic capacitors and other electronic devices due to its high dielectric constant, diffuse phase transition behaviour and low sintering temperature. The phase diagram of its solid solution with PbTiO₃ (i.e. (1-x)Pb(Fe_{1/2}Nb_{1/2})O₃-xPbTiO₃ or PFN-xPT) shows a morphotropic phase boundary (MPB) similar to that in the well known Pb(Zr_xTi_{1-x})O₃ (PZT), (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-xPT) and (1-x)Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PZN-xPT) ceramics. We present here the results of synchrotron powder x-ray diffraction, dielectric and magnetization studies on 'phase-pure' PFN and PFN-xPT. It was found for the

first time that PFN shows negative thermal expansion behaviour in the magnetically ordered phase indicating spin-lattice coupling [1]. PFN-xPT undergoes a monoclinic to tetragonal morphotropic phase transition at $x \sim 0.08$ [2] leading to a peak in the composition dependence of the high frequency dielectric constant similar to that in the well known MPB ceramics (like PZT, PMN-xPT and PZN-xPT etc.). It was also found that addition of PT in PFN dilutes the magnetic interaction as a result of which the Neel temperature (T_{N1}) first decreases and finally disappears for the PbTiO_3 reach end of the MPB.

References:

- [1] S. P. Singh et al, Appl. Phys. Lett. **90**, 242915 (2007).
[2] S. P. Singh et al, J. Phys.: Condens. Matter **19**, 036217 (2007).

Keywords: multiferroic, Negative Thermal Expansion, morphotropic phase boundary

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Twinned crystal structures and equations of state of b- Na_2ThF_6 and NaTh_2F_9

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Actinide fluorides are considered for nuclear applications. It is thus important to know their structural and physical properties. This includes the conditions at which they are stable and their equations of state. We studied b- Na_2ThF_6 and NaTh_2F_9 using powder and single-crystal x-ray diffraction in diamond anvil cells at HASYLAB and at our high-pressure laboratory in Bilbao. The twinned structure of b- Na_2ThF_6 ($P321$, $Z = 1$) is built of chains of face-sharing capped trigonal prisms ThF_9 along the c axis. Capped trigonal prisms around the Na atoms share their basal and equatorial faces with each other. The twin operation is a 2-fold rotation around the c axis. b- Na_2ThF_6 is stable at least to 6.4 GPa. The evidence for the ferroelastoelectric and ferrobilastic $P321 - P-62m$ phase transition could be the existence of the twin domains. This transformation would convert the twinning operation into a true symmetry element of $P-62m$, when the z coordinate of the Na atom in $P321$ assumes the ideal value of $1/2$. The pressure-induced tendency of the z coordinate of the Na atom to converge to $1/2$ indicates that the transition could occur at high pressures. NaTh_2F_9 is stable at least to 5.0 GPa. Its twinned structure ($I-42m$, $Z = 4$) is composed of corner-sharing ThF_9 tricapped trigonal prisms and distorted NaF_6 octahedra. The twinning element is a three-fold axis from cubic symmetry. The ThF_9 polyhedra are rigid and it is the volume changes of the octahedra around the Na atoms that have the major contribution to the bulk compressibility. The compressibility data for b- Na_2ThF_6 and NaTh_2F_9 could be fitted with the Murnaghan equations of state. The larger bulk modulus of NaTh_2F_9 could be explained by its larger molar ratio of the ThF_4 and NaF components than that in b- Na_2ThF_6 .

Keywords: materials inorganic, high-pressure phase transformations, nuclear technology

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Mössbauer spectroscopy study of the structural transition in the new multiferroic $\text{GdFe}_3(\text{BO}_3)_4$

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The new multiferroic gadolinium iron borate $\text{GdFe}_3(\text{BO}_3)_4$ has been studied by the Mössbauer spectroscopy at ^{57}Fe nuclear in the temperature range 80-295 K. Recently, the cascade of the structural and magnetic phase transitions were discovered in $\text{GdFe}_3(\text{BO}_3)_4$ [1-4]. A single-crystal X-ray structure study [3] shows that $\text{GdFe}_3(\text{BO}_3)_4$ exhibits the $R32$ structure at room temperature and it has the $P3_121$ space group at 90 K. This effect can be related to the presence of two nonequivalent sites for Fe atoms, giving rise to two different iron helicoidal chains at 90 K, which become identical at temperatures above the first-order structural phase transition (155 K) as it was discovered from Raman spectroscopy and heat capacity measurements [1,4]. For the Mössbauer measurements, a high-quality single crystals of $\text{GdFe}_3(\text{BO}_3)_4$ enriched with ^{57}Fe isotope up to 96% were grown using a $\text{K}_2\text{Mo}_3\text{O}_{10}$ -based flux. We found that Mössbauer spectra of $\text{GdFe}_3(\text{BO}_3)_4$ could not be fitted by one quadruple doublet even at room temperature. The best fit can be obtained using two asymmetric doublets with close quadruple splitting and isomer shift values. This result points to presence of two close but nonequivalent sites for the Fe ions and confirms the single-crystal X-ray data. Asymmetry of the quadruple doublets is an extra argument to presence iron helicoidal chains. However, temperature dependence of the quadruple splitting points to complex character of the structure rearrangement of $\text{GdFe}_3(\text{BO}_3)_4$ in the temperature range 80-180 K.
[1]. R.Z. Levitin et al. Pis'ma v ZHETF. V. 79, iss. 9, pp. 531-534, (2004).
[2]. A.K. Zvezdin et al. JETP Lett., 81 #6, 335, (2005).
[3]. S.A. Klimin et al. Acta Cryst. B, 61, 481-485, (2005).
[4]. D. Fausti et al. Physical Rev. B, 74, 024403, (2006)

Keywords: Mossbauer spectroscopy, multiferroic materials, structural phase transitions

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Structural and dynamical studies on protonic conductor $\text{K}_3\text{H}(\text{SeO}_4)_2$

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Neutron powder diffraction, quasi elastic neutron scattering and inelastic neutron scattering measurements were performed to examine the mechanism of phase transition and protonic conduction of $\text{K}_3\text{H}(\text{SeO}_4)_2$. The SeO_4 tetrahedra in the high temperature phase were rotationally displaced with the occupancy $1/3$ and the crystal structure in the room temperature phase was remain locally. Proton