

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.

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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.

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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

distribution maps obtained from the maximum entropy method (MEM) describe that 13.4 % of protons exist at inter-layer space. Proton diffusion constants were estimated as $1.9(1) \times 10^{-10}$ m²/s at 393 K and $2.1(3) \times 10^{-10}$ m²/s at 413 K respectively. The structural change corresponds to a rotational mode of SeO₄ tetrahedra, which is led from the group theoretical analysis from *R3m* to *C2/c*. A diffusive spectrum was observed around 0 meV at the L-point (0.5 2 0) above *T_C* as an over dumped phonon mode. The rotational mode of SeO₄ tetrahedra drives the improper ferroelastic phase transition, and assists the disconnection and reconstruction of hydrogen bonds in the high temperature phase.

Keywords: neutron diffraction elastic and inelastic, proton conductivity, phase transitions

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X-ray diffuse scattering and a local structure of (CH₃)₄NCdCl₃ (TMCC) and related compounds

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A local structure of TMCC has been determined by configurational-bias reverse Monte Carlo method basing on X-ray diffuse scattering data. Two phases have been analysed and refined: phase I at 293 K, *P6₃/m* space group, *a* = 0.9139(1) nm, *c* = 0.6723(1) nm, and phase Γ at 410 K, *P6₃/mmc* space group, *a* = 0.9235(1) nm, *c* = 0.6742(1) nm. A model dividing CdCl₆ octahedra chains into elementary bricks has been implemented in order to take into account coupling between orientation of TMA molecules and local deformations of the octahedra chains. The resulting structures contain the subchains of CdCl₆ octahedra shifted longitudinally away from their average positions. Their lengths show the Poisson-like distribution with an average value of about 6 unit cells. X-ray diffuse scattering effects observed on the *hk0* plane require the existence of the transverse subchain displacements. Additional transversal correlation between longitudinal shifts of the subchains is needed to explain weak modulation effects and diffuse streaks observed on the planes perpendicular to *c**.

Keywords: disordered systems, diffuse scattering, reverse Monte Carlo

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Magnetoelastic effects in BiMn₂O₅: A high-resolution synchrotron x-ray diffraction study

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Multiferroic materials with coexisting (anti)ferromagnetism and ferroelectricity have attracted renewed attention, due to the

interesting physics involved as well as relevant potential applications in spintronics. A fairly strong coupling amongst ferroelectric and magnetic order parameters may occur as a result of exchange striction effects in magnetic structures lacking an inversion center. Below the magnetic ordering temperature, slight atomic displacements take place and strengthen (weaken) the satisfied (frustrated) interactions, breaking the inversion symmetry of the structure and leading to ferroelectricity. In this work, synchrotron x-ray diffraction measurements were performed on single crystalline and powder samples of BiMn₂O₅. A linear temperature dependence of the unit cell volume was found between TN=38 K and 100 K, suggesting that a low-energy lattice excitation may be responsible for the lattice expansion in this temperature range. Between T* ~65 K and TN, all lattice parameters showed incipient magnetoelastic effects, due to short-range spin correlations. An anisotropic strain along the *a*-direction was also observed below T*. Below TN, a relatively large contraction of the *a*-parameter following the square of the average sublattice magnetization of Mn was found, indicating that a second-order spin Hamiltonian accounts for the magnetic interactions along this direction. Polycrystalline samples grown by distinct routes and with nearly homogeneous crystal structure above TN presented structural phase coexistence below TN, indicating a close competition amongst distinct magnetostructural states in this compound.

Keywords: BiMn₂O₅, multiferroics, high-resolution x-ray powder diffraction

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A strategy to prepare multiferroic materials

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Manganese doped bismuth titanate is a potential multiferroic material, displaying both ferroelectricity and ferromagnetism. This is because of the layered nature of the Aurivillius structure which involves the stacking of octahedral perovskite blocks in between layers of bismuth oxide. An *n*=3 Aurivillius structure, with 3 layers of octahedral units in the perovskite block, are of special interest to solid state chemists. This is because the *n*=3 arrangement, provides simultaneously, a locally symmetric environment for the B-cations in the middle octahedral layer of the perovskite block and also a structurally distorted environment for the B-cations in the top and bottom octahedral layers of the perovskite block. The stability in maintaining this structural distortion is due to the 6s² lone pair of electrons from the bismuth in the bismuth oxide layer. This unique structure can accommodate the usually conflicting requirements of ferroelectric and ferromagnetic properties to coexist. The objective would be to incorporate a layer of magnetic manganese cations within the middle octahedral layer, which benefits from the symmetrical environment, and integrate titanium into the top and bottom octahedral layers. This would introduce ferromagnetic properties to bismuth titanate, which is already a well-known ferroelectric material. Synchrotron X-ray diffraction has already been used to determine the structure of some of these compounds and together with magnetic property measurements, it is a step forward in uncovering the relationship between the observed ferroelectric and ferromagnetic properties of these compounds and their atomic structure.

Keywords: materials structure and characterisation, X-ray