

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)

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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