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Phase transitions in the BaMF₄ compounds at high pressures (M = Zn, Mg, Mn). Jose M. Posse^a, Karen Friese^a, Wolfgang Morgenroth^b, Martin Tolkiehn^c, Andrzej Grzechnik^a, ^aDept. Condensed Matter Physics, University of the Basque Country, Bilbao, Spain.

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Piezoelectric ternary fluorides with the composition BaMF₄ (M = Mn, Zn, Mg, Fe, Ni, or Co) crystallize in polar space group Cmc2₁ (Z = 4) at ambient conditions. The M₂₊ cations are surrounded by six fluorine atoms forming irregular octahedra that share four anions with others to generate layers perpendicular to [010]. Between these layers, the Ba atoms are located with the coordination number 9 [1],[2].

BaMnF₄ undergoes a phase transition to an incommensurate phase at T = 245 K and atmospheric pressure [3]. Other members of the family do not provide any evidence of phase transitions down to 10 K. The strong relation between the cationic radii, the unit-cell volumes, and the stability of these compounds at low temperatures suggests that their crystal structures could also be significantly influenced by the application of hydrostatic pressure. For our *in situ* high pressure experiments in diamond anvil cells we chose three materials with very different ionic radii of the M₂₊ cations:

BaMgF₄, BaZnF₄, and BaMnF₄. The single-crystal diffraction experiments were carried out using the marCCD165 detector at the beamline D3 of the HASYLAB ($\lambda = 0.4 \text{ \AA}$). The collected data were indexed and integrated using the XDS program package [4].

Both BaMgF₄ and BaZnF₄ undergo phase transitions at about 5 GPa. The fits of the second-order Birch-Murnaghan equation of state to the compressibility data of their low-pressure phases give similar bulk moduli, B₀ ~ 56 GPa. At higher pressures, the structure of BaMgF₄ is no longer polar (Cmcm, Z = 4) and is isostructural with the hypothetical paraelectric phase that was previously postulated [5] to occur at high temperatures and atmospheric pressure. On the other hand, the phase transition in BaZnF₄ is manifested by the appearance of reflections violating the C centering of the lattice.

In the case of BaMnF₄ below 4 GPa, the second-order Birch-Murnaghan equation of state gives a bulk modulus B₀ = 52.1(0.9) GPa. The smaller value of this parameter when compared to those for BaMgF₄ and BaZnF₄ results from the higher compressibility along the a axis in BaMnF₄. Above 4 GPa, we observe broadening of Bragg reflections that makes their indexing and integration impossible. This fact can be related to the loss of crystallinity of the BaMnF₄ compound, and therefore, to a possible amorphization at higher pressures.

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Synchrotron Mössbauer source for geophysical studies at the ESRF. V. Potapkin^{1,b}, A.I. Chumakov^{a,b}, R. Rüffer^a, G.V. Smirnov^b, S.L. Popov^b, L.

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Nuclear resonant scattering of synchrotron radiation brought to life a time-differential analogue of conventional energy-resolved Mössbauer spectroscopy. This allowed for significant progress in many fields of research, especially in surface science, material science, biophysics and geophysics. Progress in geophysical applications however, is somewhat moderated by "inconvenient" magnetic and electronic properties of many geophysical relevant materials for studying in time-domain. Indeed, the advantages of time-resolved Mössbauer spectroscopy are most evident for systems with well-resolved hyperfine structures. However, many relevant in geophysical studies materials either do not have large hyperfine interactions, or the splitting collapses at high pressure. In these cases, conventional energy-resolved Mössbauer spectroscopy would be more suitable. However, energy-resolved Mössbauer spectroscopy utilizes radioactive sources whose brilliance is several orders of magnitude lower than that of synchrotron radiation. Therefore, high-pressure studies with Mössbauer spectroscopy require very long measuring time and are limited to moderate pressures. Moreover, the collimating of radiation from radioactive sources is difficult. This reduces the quality of the results due to pressure gradients. Earth's lower mantle minerals contains only 5 to 20 wt% of iron, which makes the measurements even more time consuming. Therefore, there are only a few reported works on *in situ* Mössbauer spectroscopy of samples relevant to the Earth's mantle, and nearly none of them were conducted under high pressure and high temperature conditions simultaneously. The problem can be solved combining the outstanding properties of synchrotron radiation with the energy-resolved approach. In brief, what is needed is a synchrotron source of Mössbauer radiation. The possibility to develop such a source was demonstrated at the Nuclear Resonance Beamline ID18 at the European Synchrotron Radiation Facility (ESRF) in 1997 [1]. The key element of the source is a perfect single crystal of iron borate FeBO₃ grown out of the resonant isotope ⁵⁷Fe. Iron borate is a canted antiferromagnet with Néel temperature 75.35°C. The period of the magnetic structure is two times larger than that of the crystallographic structure. Therefore, all (NNN) reflections with odd N are forbidden for electronic scattering but allowed for nuclear scattering. These reflections select from a white spectrum of synchrotron radiation only x-ray photons in the energy range around the nuclear resonance. Such a beam is not yet suitable for Mössbauer spectroscopy, because it consists of four energy components of the magnetically split nuclear levels. In order to achieve a single line source, one needs to heat the crystal close to its Néel temperature, where the collapse of the magnetic structure provides a single line spectrum with the energy width of ~15 neV [2]. Recently, the same approach has been implemented at the SPring-8 [3], where an intensity of the SMS of ~20 000 photons per second was reached. In addition, the experimental scheme was successfully developed where the Doppler shift was achieved