FA2-MS15-P03

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], [a]Dept. Condensed Matter Physics, University of the Basque Country, Bilbao, Spain. [b]Institute of Geosciences, Goethe University, Frankfurt am Main, Germany. [c]HASYLAB at DESY, Hamburg, Germany.
E-mail: josemaria@wm.lc.ehu.es

Piezoelectric ternary flourides with the composition $BaMF_4$ (M = Mn, Zn, Mg, Fe, Ni, or Co) crystallize in polar space group $Cmc2_1$ (Z = 4) at ambient conditions. The M^{2+} 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].

$BaMnF_4$ 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 M^{2+} cations: $BaMgF_4$, $BaZnF_4$, and $BaMnF_4$. The single-crystal diffraction experiments were carried out using the marCCD165 detector at the beamline D3 of the HASYLAB (λ = 0.4 Å). The collected data were indexed and integrated using the XDS program package [4].

Both $BaMgF_4$ and $BaZnF_4$ 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, $B_0 \sim 56$ GPa. At higher pressures, the structure of $BaMgF_4$ 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 $BaZnF_4$ is manifested by the appearance of reflections violating the C centering of the lattice.

In the case of $BaMnF_4$ below 4 GPa, the second-order Birch-Murnaghan equation of state gives a bulk modulus B_0 = 52.1(0.9) GPa. The smaller value of this parameter when compared to those for $BaMgF_4$ and $BaZnF_4$ results from the higher compressibility along the a axis in $BaMnF_4$. 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 $BaMnF_4$ compound, and therefore, to a possible amorphization at higher pressures.

[1] Lapasset J., Bordallo H.N., Almairac R., Nouet J., *Z. Kristallogr. NCS*, 1996, 211, 934. [2] Almairac R., Bordallo H.N., Bulou A., Nouet J., *Phys. Rev.*, 1995 B52, 9379 [3] Posse J.M., Grzechnik A., Friese K., *Acta Cryst.* B, 2009, 65, 576. [4] Kabsch W., *J. Appl. Cryst.*, 1993, 26, 795. [5] DiDomenico M. Jr., Eibschütz M., Guggenheim H.J., Camlibel I., *Solid State Commun.*, 1969, 7, 1119.

Keywords: high pressure, phase transitions, ferroics

FA2-MS15-P04

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. Dubrovinsky[c], C. McCammon[c]. [a]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France.* [b]*Russian Research Center "Kurchatov Institute", 123182 Moscow, Russia.* [c]*Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany.*
E-mail: potapkin@esrf.fr

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 application's 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 $FeBO_3$ grown out of the resonant isotope ^{57}Fe. 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

by vibrating the iron borate crystal [4]. This allows for a complex sample environment, which is especially important for studies under extreme conditions using a diamond anvil cell.Such a source is currently under construction at the ID18 at the ESRF. The source has a beam that is parallel to the initial synchrotron beam, high intensity and allows focusing of the radia-tion down to a spot with the size of several microns. Furthermore, it can work in any mode of stor-age ring operation. Design of the SMS is based on the (333) reflection of iron borate crystal. In combination with the Si (311) reflection, this enables a nearly in-line geometry of the SMS. Use of Kirkpatrick-Baez Mirrors allowed focusing of the beam down to a 10x16 micron spot size for a re-sulting count rate of around 40.000 photons per second. This allowed very fast measurements of Mössbauer spectra, approximately 10 minutes per spectrum, which will be very useful for experiments which simultaneously combine high pressure and high temperature.

[1] G. V. Smirnov *et al.*, *Phys. Rev. B* 55 (1997) 5811. [2] G.V. Smirnov, in *Nuclear Resonant Scattering of Synchrotron Radiation,* edited by E. Gerdau and H. de Waard (Baltzer Science, Busssum, 2000), Hyperfine Interact. 125 (2000) 91[3] T. Mitsui *et al.*, *Jpn. J. Appl. Phys*. 46 (2007) L382 [4] T. Mitsui *et al.*, *Jpn. J. Appl. Phys*. 47 (2008) L7136.

Keywords: Mossbauer spectroscopy, synchrotron radiation applications, geophysics