The Effect of High Pressure on the Crystal Structure of Multiferroic $RbFe(MoO_4)_2$

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The multiferroic materials, demonstrating a coupling between magnetic and electric subsystems, have become a subject of extensive scientific research in recent years [1]. An interesting example of such materials, combining multiferroic phenomena with geometrically frustrated magnetism on two-dimensional triangular lattice, is rubidium molybdate RbFe(MoO4)2 [2]. The crystal structure of $RbFe(MoO_4)_2$ has trigonal P3m1 symmetry at ambient conditions and it is lowered to P3 via temperature-driven structural distortion below T = 180 K. In contrast, the subsequent Raman spectroscopy study revealed two structural phase transitions in $RbFe(MoO_4)_2$ at high pressures, from P3m1 phase to P3 one at P = 0.2 GPa, and to a phase with unknown lower symmetry at P ~ 0.4-0.7 GPa [3]. However, the high pressure behaviour of structural parameters and physical properties of these compounds in the newly formed phases remains unclear. In order to study in detail the high pressure effects on the crystal structure of multiferroic $RbFe(MoO_4)_2$, we have performed a study using X-ray diffraction in 0 – 10 GPa pressure range.

Angle-dispersive X-ray powder diffraction patterns at high pressures up to 10 GPa and ambient temperature were measured at the Extreme Conditions Beamline P02.2 (ECB) at the 3rd generation synchrotron radiation source PETRA III, located at the Deutsches Elektronen Synchrotron (DESY, Hamburg, Germany.) We used the wavelength of λ=0.29118 Å to collect diffraction images on the amorphous silicon flat panel detector bonded to a ScI sincilator (XRD 1621) from Perkin Elmer and located at a distance of 402.33 mm from the sample.

X-ray diffraction patterns (XRD) of $RbFe(MoO_4)_2$ at selected pressures and ambient temperature are shown in figure 1. The obtained values of lattice parameters at ambient conditions for the *P3̄m1* phase, a = 5.671(3) and c = 7.494(5) Å. At higher pressures, new diffraction peaks appear at 2θ = 4.60, 4.95, 5.73 and 5.90°, evidencing the structural phase transition. The successful indexing of diffraction patterns was obtained for the monoclinic unit cell with a C2/c symmetry. Lattice parameters are related to those of the initial trigonal cell as $a_m \sim b_m \sim 2a$, $c_m \sim c$ and $\gamma \sim 115°$.

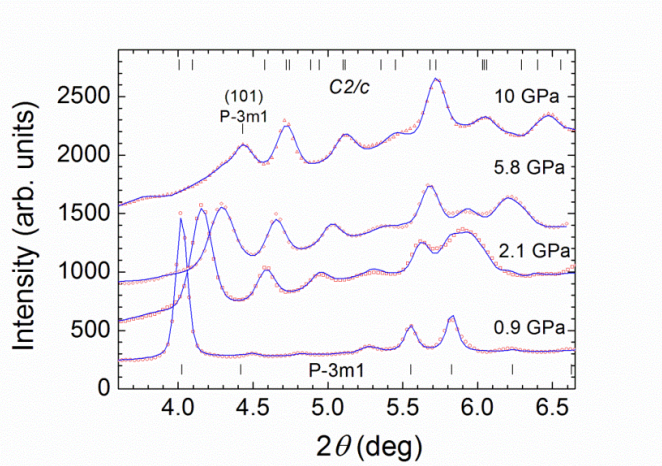

Figure 1: X-ray diffraction patterns of $RbFe(MoO_4)_2$ measured at selected pressures and ambient temperature. Experimental points and calculated profiles are shown. Tickmarks at the bottom and top represent the calculated positions of diffraction peaks for the trigonal phase (at P = 0.9 GPa) and monoclinic phase (at P = 10 GPa), respectively.

At P = 10 GPa, the minor fraction of the trigonal phase was still present in the patterns. The pressure dependencies of lattice parameters and unit cell volume of the trigonal and monoclinic phases of $RbFe(MoO_4)_2$ are shown in Fig. 2. Due to the phase coexistence after the phase transition, their values for the trigonal phase were determined with sufficient accuracy for the pressures up to 2.1 GPa only. At the trigonal-monoclinic phase transition a reduction of the volume per formula unit by about 2.6 % occurs. The lattice compression is anisotropic with the *c*-axis in the trigonal phase and *b*-axis in the monoclinic phase most compressible. The monoclinic angle increases upon compression (Fig. 2).

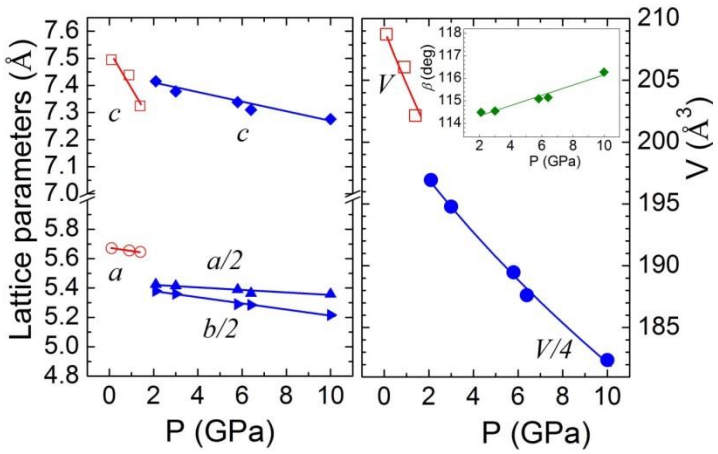

Figure 2: Lattice parameters (left), monoclinic angle (right, inset) and unit cell volume (right) as functions of pressure in the trigonal and monoclinic phases of $RbFe(MoO_4)_2$.

In the trigonal phase of $RbFe(MoO_4)_2$, the Fe atoms form regular triangular (001) planes with intra-planar Fe-Fe distance of 5.67 Å and inter-planar distance of 7.49 Å at ambient pressure. In the monoclinic phase, the pronounced distortion of Fe triangular (-2 2 2) planes occurs, with three inequivalent Fe-Fe intra-planar distances of 5.07, 6.37 and 7.55 Å and inter-planar distance of 7.34 Å, as calculated for P = 5.8 GPa. As a result, the average nearest-neighbor Fe-Fe intra-planar distance is equal to 6.33 Å and it increases by 11 % in comparison with the trigonal phase. This implies a weakening of the magnetic super-exchange interactions for the monoclinic phase.

References

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