The compounds BaMF₄ (M = Co, Fe, Mn, Ni, Zn, or Mg) crystallize in space group Cmc₂ (Z = 4) at ambient conditions. The cation M is surrounded by six fluorine atoms forming an irregular octahedron. Four of the octahedra are connected via common corners with others, generating puckered layers perpendicular to the b axis. The neighbouring layers are shifted with respect to each other by a translation of a/2. The barium atoms are located in the interlayer spaces [1]. These compounds are interesting due to the fact that some of them (M = Mn, Fe, Co, or Ni) exhibit a multiferroic behaviour [2]. BaMnF₄ has a second-order phase transition to an incommensurate phase at low temperatures (T ~ 250 K) supposedly with superspace group C₂\*(1/2 1/2 γ) with X = (1/2, 1/2, 0, 1/2) as the correct choice. In addition, it exhibits magnetic anomalies at about 50 K and 27 K, the latter being due to a formation of an antiferromagnetic phase [4].

The aim of our study is to examine the structural instabilities [5] in BaMnF₄, BaZnF₄ and BaMgF₄ at low temperatures and high pressures. Powder x-ray diffraction (ID31 beamline, ESRF) and single-crystal x-ray diffraction (SCD beamline, ANKA; our laboratory in Bilbao) experiments were carried out on BaMnF₄, BaZnF₄ and BaMgF₄ from 290 K to 10 K at atmospheric pressure. Both BaZnF₄ and BaMgF₄ do not undergo any phase transitions at low temperatures. On the other hand, our diffraction data on BaMnF₄ indicate that it transforms to an incommensurate monoclinic phase which is affected by twinning. In contrast to the earlier investigations [3], our data indicate the superspace group X₂*(1/2 1/2 γ) with X = (1/2, 1/2, 0, 1/2) as the correct choice. Upon lowering the temperature, the γ component of the modulation wave vector increases and reaches a constant value γ ≈ 0.3948 below 50 K, i.e., in the temperature range in which the magnetic anomalies occur [4].

We also performed high-pressure measurements using single-crystal x-ray diffraction in our laboratory and in HASYLAB/Hamburg (BaZnF₄ and BaMgF₄) as well as Raman spectroscopy (BaZnF₄). The Raman data suggest pressure-induced phase transition in BaZnF₄ at about 5 GPa. Currently, we are analyzing our diffraction data to elucidate the high-pressure structures of BaMgF₄ and BaZnF₄. Our intention is to perform high-pressure single-crystal diffraction experiments to examine the structural behaviour of BaMnF₄.


Keywords: multiferroic; modulated structure; high pressure