Structural stability of the BaMF$_4$ compounds at high pressures (M = Zn, Mg, Mn)

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Ternary fluorides with the general formula BaMF$_4$ (M = Mn, Zn, Mg, Fe, Ni, or Co) crystallize in space group Cmc$_2$1 with lattice parameters $a \sim 4.2$ Å, $b \sim 14.7$ Å and $c \sim 5.9$ Å. Their unit cell volumes depend linearly on the $M^{+2}$ cationic radii. In addition, the $M^{+2}$ radius has a critical influence on the stability of the compounds as the compound with the largest $M^{+2}$ cation, BaMnF$_4$, shows an incommensurate phase transition at $T \sim 245$ K [1-2]. Other members of the family do not provide any evidence of phase transitions down to 10 K [1].

At ambient conditions, the $M^{+2}$ cations are surrounded by six fluorine atoms forming an irregular octahedron that share four anions with the others and generate layers perpendicular to [010] (Figure 1). Between these layers, the barium atom is allocated with the coordination number 9 [3-4].

The strong relation between the cationic radii, the unit-cell volumes and the stability of the compounds, suggests that the crystal structures might also be significantly influenced by the application of hydrostatic pressure. For our in situ high pressure experiments in diamond anvil cells we chose three members 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 at the wavelength of 0.4 Å. The collected data were integrated using the XDS program package [5].

Both in BaMgF$_4$ and BaZnF$_4$, the lattice parameters decrease smoothly on compression up to 5 GPa. The pressure dependence of the unit cell volumes can be fitted using the second order Birch-Murnaghan equation of state, obtaining similar bulk moduli for BaMgF$_4$ and BaZnF$_4$, $B_0 = 55.9(1.2)$ GPa and $B_0 = 55.7(0.5)$ GPa, respectively (fixed values obtained from previous powder x-ray diffraction measurements [1] were assumed as $V_0$).

In the pressure range from 4.79 GPa to 6 GPa, the drastic change of the unit-cell volume indicates a first-order phase transition in BaZnF$_4$. In addition, the deviation of the $\gamma$ angle from 90 degrees indicates that the space group symmetry of the high pressure phase is monoclinic (Figure 2).

For BaMgF$_4$ between 4.81 GPa and 6.13 GPa, we also observed a discontinuous behavior of the lattice parameters. However, they do not show the same behavior as in BaZnF$_4$ and it seems that
there is no monoclinic distortion of the lattice. Currently, we are working on the structure determination of the high pressure polymorphs of BaZnF\textsubscript{4} and BaMgF\textsubscript{4}.

In the case of BaMnF\textsubscript{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\textsubscript{4} and BaZnF\textsubscript{4} results from the higher compressibility of the a parameter in BaMnF\textsubscript{4}. Above 4 GPa, we observe a broadening of the Bragg reflections (which gets stronger at higher pressures) that makes their indexing impossible. This fact can be related to the loss of crystallinity of the BaMnF\textsubscript{4} compound, and therefore, a possible amorphization of the crystal at higher pressures.

Figure 2: Normalized lattice parameters and unit cell volume of BaZnF\textsubscript{4} as a function of pressure. The red line represents the second order Birch-Murnaghan equation of state: \(B_0 = 55.7(0.5)\) GPa, \(V_0 = 349.324(5)\) Å\(^3\), \(a_0 = 4.203679(23)\) Å, \(b_0 = 14.57271(10)\) Å and \(c_0 = 5.848186(50)\) Å.

References