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Stability of the BaMF₄ (M = Mg, Zn, Mn) materials

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Ternary fluorides $BaMF_4$ (M = Mn, Zn, Mg, Fe, Ni, Cu, or Co) are piezoelectric at ambient conditions. Their multiferroic properties have been discussed in [1], [2]. Due to their high transparency, they can be used for optical applications [3]. Recently, BaMgF₄ has been suggested as a material for scintillators [4].

We studied the crystal structures of three BaMF₄ representatives (M = Mg, Zn, or Mn) as a function of temperature and pressure [5], [6]. Their crystal structure ($Cmc2_1$, Z = 4) is built of slabs of corner-sharing MF₄ octahedra which are stacked perpendicular to the crystallographic b axis. The Ba²⁺ ions, which are eleven-fold coordinated by fluorine in BaMnF₄ and BaZnF₄ and thirteen-fold coordinated in BaMgF₄, are incorporated between these layers. The hypothetical paraelectric polymorphs are not observed at ambient pressure since the estimated temperatures of the corresponding phase transitions to the centrosymmetric structures lie above the melting points of the compounds [7]. The unit-cell volumes of the BaMF₄ fluorides are linearly correlated with the ionic radius of the M2+ ion.

Our low-temperature x-ray diffraction investigations show that BaMnF₄, which is the compound with the largest M^{2+} ion, undergoes a phase transition to a twinned incommensurate phase at T = 245 Kand atmospheric pressure [5]. The formation of the modulated phase in BaMnF₄ arises from the incorporation of the large Mn²⁺ cation in the octahedral sheets and the resulting increase of the cavity occupied by the Ba^{2+} ion. The other two compounds (M = Mg, Zn) do not provide any evidence for phase transitions down to 10 K [5].

Single-crystal high-pressure diffraction studies at room temperature show that BaMgF₄ undergoes a reversible second-order phase transition to the paraelectric phase (space group Cmcm, Z = 4) at about 6 GPa [6]. BaZnF₄ undergoes a reversible first-order phase transition to a monoclinic structure (space group P11n, Z = 4). Both high- and lowpressure polymorphs coexist in the pressure range 5-7 GPa [6]. Ba MnF_4 maintains the Cmc2₁ structure up to pressures of 4 GPa. Above this pressure the diffraction intensities are rapidly decreasing and at 6 GPa no single-crystal diffraction could be detected in our experiment any more.

The results of our investigations indicate that considerations of geometrical parameters and of ionic radii of the M2+ cations are not sufficient to predict the behaviour of the BaMF₄ compounds at high pressures. The incorporation of a smaller M2+ cation is not equivalent to compressing the BaMF4 materials meaning that the application of hydrostatic pressure is not exactly comparable to the exertion of chemical pressure in these fluorides.

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Keywords: fressure, fluorides, phase transitions

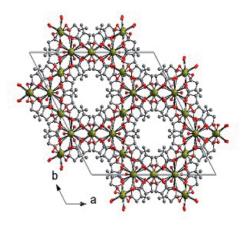
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Novel organic-inorganic hybrid materials prepared at elevated temperatures and pressures

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Hydro(solvo)thermal methods of synthesis constitute a convenient, clean route to novel metal carboxylates with open structures. In contrast, their synthesis in solution at room temperature, usually lead to layered structures. Depending on the nature of the carboxylic acid used as starting material, different reactions such as rearrangement, isomerization, addition, decomposition, decarboxylation, etc., may occur under hydrothermal conditions and could produce interesting derivatives, not attainable by direct synthesis. For example, the reaction of itaconic acid (methylene succinic acid) with either CaCO₃ or BaCO₃ in aqueous solution at room temperature, results in layered structures [1]. However, when the reaction is carried out with CaCO₃ by hydrothermal methods, a structure where the itaconate ligands undergo addition to form citramalate is obtained by slow evaporation of the filtrate. From the precipitate, a Ca-itaconate with a honeycomb-type arrangement is obtained (see figure). With BaCO₃, the hydrothermal reaction produces a compound where two itaconate ligands suffered an isomerization to citraconates and one ligand undergoes addition and isomerization to dimethylfumarate. In the reaction BaCO₃-mesaconic acid, the hydrothermal conditions lead to partial decomposition of the mesaconate moieties to produce bridging fumarate groups, in contrast with the structure obtained at room temperature [2]. These and other interesting compounds (La-aconitic acid, for example) will be presented and discussed in detail.



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