

Crystal structure, phase transitions and magnetic behaviour of the BiFeO₃-based perovskite solid solutions

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Bismuth ferrite is one of few materials in which the coexisting (anti)ferroelectric order and the (anti)ferromagnetic order are caused by independent mechanisms. Ferroelectricity in BiFeO₃ is induced by the electronic instability of the lone-pair Bi³⁺ cations, while the antiferromagnetism in this material results from the superexchange interactions between Fe³⁺ cations. Besides, the distorted crystal structure of this perovskite, involving large polar atomic displacements and octahedral tilting, gives rise to competing antisymmetric Dzyaloshinskii-Moriya interactions. The part of antisymmetric exchange associated with the polar distortions favours a spatially modulated ground state in the form of a long-period incommensurate cycloid. On the contrary, the antisymmetric exchange imposed by the octahedral tilting requires a non-modulated canted weak ferromagnetic state. In the undoped BiFeO₃, the former contribution wins, promoting the long-period modulated spin ordering that averages the net magnetization to zero. This modulation, however, can be suppressed via chemical modification. Chemical modifications in the iron site of BiFeO₃ represent the direct approach to tune the magnetic behaviour of this material. However, using the conventional synthesis routes, it is possible to achieve the substitution rates of a few atomic percent only. Most of the reported single-phase BiFe_{1-y}B³⁺_yO₃ perovskite compositions with y>0.10 were prepared via high-pressure synthesis.

In high-pressure stabilized perovskite solid solutions of the BiFe_{1-y}Sc_yO₃ system, a series of structural transitions with increasing y was found. Moreover, it was revealed that annealing of the as-prepared perovskite phases results in irreversible transformations into new structural phases with interesting combinations of ferroic orders [1]. In the 0.1 ≤ y < 0.3 range, some peculiarities of the temperature-dependent magnetic moment below T_N were observed and associated with possible transitions between different antiferromagnetic structures corresponding to collinear, canted, and cycloidal spin arrangements. Similar temperature anomalies of the magnetic behaviour below T_N were then revealed in the Fe-rich compositional range of the BiFe_{1-y}[Zn_{0.5}Ti_{0.5}]_yO₃ perovskites [2].

In this work, we considered the compositional behaviours of the crystal structure and the magnetic properties of the BiFe_{1-y}B³⁺_yO₃ perovskites (where B³⁺ = Ga, Co, Mn, Cr, [Zn_{0.5}Ti_{0.5}] and Sc) in the vicinity of parent bismuth ferrite. Among these, Cr³⁺, Mn³⁺, and Co³⁺ are magnetic cations of transition metals from the same 3d series to which iron belongs, while Ga³⁺, Sc³⁺ and [Zn_{0.5}Ti_{0.5}]³⁺ are non-magnetic. Besides, as compared with iron, gallium is smaller, scandium is considerably bigger, and [Zn_{0.5}Ti_{0.5}]³⁺ is slightly bigger than Fe³⁺ in octahedral coordination. The crystal structure sequences, phase diagrams and the T_N(y) dependences are compared and discussed.

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