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Multiferroic materials and heterostructures / Matériaux et hétérostructures multiferroïques

Bismuth-based perovskites as multiferroics

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ABSTRACT

This review devoted to multiferroic properties of bismuth-based perovskites is divided into two parts. The first one focuses on BiFeO₃ and summarizes the recent progress made in the studies of its pressure–temperature phase diagram and magnetoelectric coupling phenomena. The second part discusses in a more general way the issue of polar– and multiferroic–phases in BiBO₃ perovskites and the competition between ferroelectricity and other structural instabilities, from an inventory of recently synthesized compounds.

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R É S U M É

Cette revue consacrée aux pérovskites multiferroïques à base de bismuth BiBO₃ est scindée en deux parties. La première est consacrée au cas de BiFeO₃ et résume les progrès récents réalisés dans l'étude de son diagramme de phases pression–température et de ses phénomènes de couplage magnéto-électrique. La seconde partie aborde de manière plus générale, à partir d'un inventaire des composés récemment synthétisés, la question de la stabilité des phases polaires – et multiferroïques – dans les pérovskites BiBO₃ et la compétition entre la ferroélectricité et les autres instabilités structurales.

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1. Introduction

Multiferroics are materials that possess simultaneously magnetic and ferroelectric order. Although found separately in a large number of ABO₃ perovskites (along with virtually the full scope of possible functional properties, including superconductivity, piezoelectricity, insulating/metal/semiconducting behavior etc.), the simultaneous combination of ferroelectricity and magnetism in a single-phase ABO₃ perovskite is rather scarce. The reason for this was rationalized in a seminal paper by N. Hill, who pointed out that in most classical ferroelectrics, typically the titanates PbTiO₃ and BaTiO₃, the polar cation shifts are caused by a second-order Jahn–Teller effect, or hybridization, involving B-site ions with d⁰ electrons, whereas in contrast, the presence of unsaturated d electrons is required for the transition elements to acquire a magnetic moment. In

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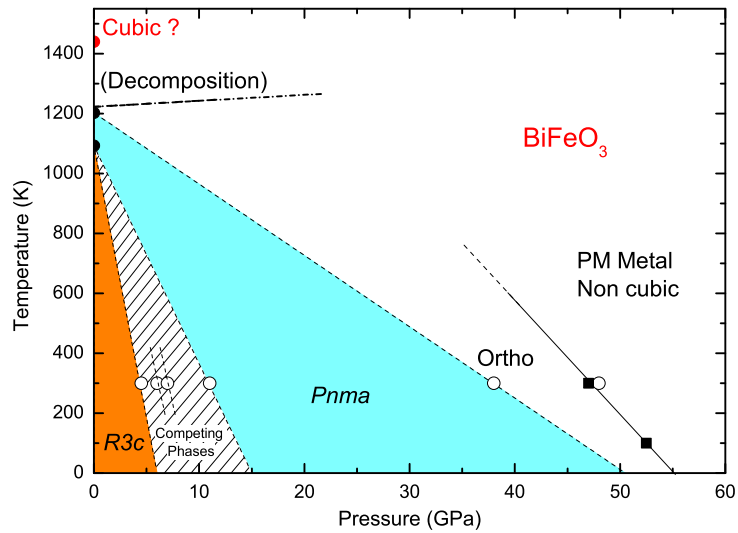


Fig. 1. (Color online.) Pressure–temperature diagram for bulk BFO, reproduced from Ref. [9]. The transition temperature to a cubic phase at ambient pressure lies beyond the decomposition temperature and is a theoretical prediction [10].

order to waive this contradiction and reconcile ferroelectricity and magnetism, one therefore has to induce ferroelectricity by other mechanisms. One such alternative is found in rare-earth manganites at low temperatures, where ferroelectricity is induced by the cycloidal spin order; this has defined the so-called “type-II multiferroics” [1]. Another track that has been followed in the recent years is to induce ferroelectricity and magnetism on two different crystallographic sites of the perovskite, namely bismuth on the *A*-site and a magnetic transition metal (Fe, Mn, etc.) on the *B*-site. The ferroelectric off-centering of the Bi^{3+} cation is favored by the $6s^2$ electron “lone pair”. This type of multiferroic is best exemplified in BiFeO_3 (BFO), which has become a model system for so-called ‘type-I’ multiferroics and has stimulated a significant international research effort over the past years.

In our short review, we will in a first part discuss recent advances on BFO. For this, we will take a review published in 2009 as a starting point [2] and focus on the progress made since then on the pressure–temperature phase diagram, the magnetoelectric coupling, and exchange bias. In the second part, we shall move away from the special case of BFO and address the issue of ferroelectricity in Bi-based perovskites in general, in the light of the recent progress in synthesizing these compounds, especially with magnetic cations on the *B*-site, and subsequent studies.

2. BiFeO_3 updated

2.1. Structural and ferroelectric properties

The room-temperature structure of BFO, also called α phase, is a distorted perovskite structure with a slight rhombohedral distortion [3]. It exhibits both large octahedra tilts along the [111] pseudo-cubic direction and a strong ferroelectric polarization, both treated as pseudo-proper order parameters. This is a major originality of the BFO structure as compared to classical ferroelectrics. It notably contrasts with the typical compounds CaTiO_3 and PbTiO_3 , where in both cases, the cubic cell is calculated to be unstable upon both tilt and ferroelectric instabilities, but in practice, the crystal lowers its energy by developing one instability only (tilts for CaTiO_3 , polar displacements for PbTiO_3) while the second one is inhibited. A consequence of these two interacting instabilities in BFO is a rather complex temperature–pressure phase diagram that is characterized by multiple phase transitions as illustrated in Fig. 1. On the theory side, this richness is perhaps best illustrated by the first-principles calculations by Diéguez et al. [4], who have found an unusually large number of (meta)stable structures for BFO with different ferroelastic, ferroelectric and magnetic properties, with the perspective of multiferroic properties and strong magnetoelectric coupling at room temperature. Recent reports of a structural phase transition close to room temperature in highly compressively strained BFO thin films add further support to this [5–7]. The recent advances in thin-film structures, also of considerable interest, are out of scope here, but can be found in another chapter of this review by Yang et al. and in Ref. [8].

Experimentally, the phase sequence with temperature has been a long-standing controversy. Two phase transitions from the α to the so-called β and γ phases have been identified some time ago at 825 °C (1098 K) and 931 °C (1204 K) before decomposition occurs just about 10 °C above. The determination of the crystal structure of the β and γ phases has been very difficult and controversial, due to the proximity of the decomposition temperature. The most recent neutron studies [11,12] indicate that both the β and γ phases are paraelectric orthorhombic phases with *Pnma* structure, the $\alpha \rightarrow \beta$ then corresponding to the Curie temperature T_C and the $\beta \rightarrow \gamma$ transition being an isostructural transition, also associated with an insulator-to-metal (IM) transition.

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