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The phenomenon of conversion polymorphism in Bi-containing metastable perovskites†

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A post-synthesis thermal treatment of metastable phases in the high-pressure stabilised perovskite $BiFe_{1-y}Sc_yO_3$ system results in the irreversible formation of polymorphs which represent novel polar and antipolar structures with interesting magnetic properties. Such annealing-stimulated polymorphism is believed to be a general phenomenon which can be found in other systems.

Many solid phases, which are at equilibrium under high pressure and high temperature, can be quenched to ambient conditions, where they remain kinetically stable (usually referred to as the metastable phases). Very often, these phases represent new structural polymorphs with useful and unique properties.[1,2] This method, known as high-pressure synthesis, therefore, is widely used to obtain novel materials with improved functionalities. It is particularly effective to stabilize the compact structures like the perovskite one. Indeed, with the application of high-pressure synthesis, the class of perovskite materials has been substantially extended.[3–5] Organic and inorganic compounds with the perovskite structure are known to host many fascinating physical phenomena, such as high-temperature superconductivity, metal–insulator transition, ferroelectricity, multiferroic and photovoltaic properties.[6–10] The flexibility of the perovskite structure to accommodate many different cations and anions provides an excellent playground to design materials with controlled properties. This is particularly important to develop new multiferroics –materials that combine both ferroelectric and magnetic degrees of freedom with a prototype example of $BiFeO_3$. In this perovskite compound, ferroelectricity is promoted by the lone electron pair of the Bi^{3+}, while magnetic ordering with a very high transition temperature is imposed by extremely strong superexchange interactions between the Fe^{3+} cations.[11] Using different doping/substitution strategies many multiferroics with promising characteristics have been derived from $BiFeO_3$.[12–14] Regarding the Fe-site substitutions, the relative amounts of dopant necessary to change the $R3c$ structure of the parent compound can only be incorporated into the lattice under high-pressure condition. In such a way, metastable perovskites in the systems $Bi(Fe,B^{3+})O_3$ where B^{3+} = Mn,[15] Co,[17] Cr,[17] Ga[18] and Sc[19] have been obtained.

Our previous studies of the high-pressure stabilized $BiFe_{0.5}Sc_{0.5}O_3$ composition under post-synthesis heating/cooling thermal cycling revealed the formation of a novel polar perovskite phase, where a large electric polarization coexists with a spontaneous ferromagnetic component.[20] It was not possible, however, to anticipate the general character of the observed irreversible behaviour based on this single composition. In the present work, we systematically studied the transformation of perovskite phases and their magnetic properties in the whole $BiFe_{1-y}Sc_yO_3$ series. For the compositions with $y \geq 0.2$, the perovskite phases can only be stabilized under high-pressure conditions[19] and the metastable phases were subject to post-synthesis thermal treatment. As a result, we observed a set of annealing-stimulated irreversible phase transformations between the different metastable perovskite phases. This remarkable behaviour allowed us to obtain these perovskites at ambient conditions in different polymorphs, which represent novel structures with interesting magnetic properties. Irreversible phase transformations upon thermal treatment were also reported for individual compositions of other high-pressure stabilized systems such as $BiFe_{0.8}Mn_{0.2}O_3$ and $BiFe_{0.8}Co_{0.2}O_3$.[15,16] The $BiFe_{1-y}Sc_yO_3$ series is, however, the first example where this behaviour is observed for practically the whole series of the metastable compositions, except for a few very narrow ranges. We refer to the annealing-stimulated

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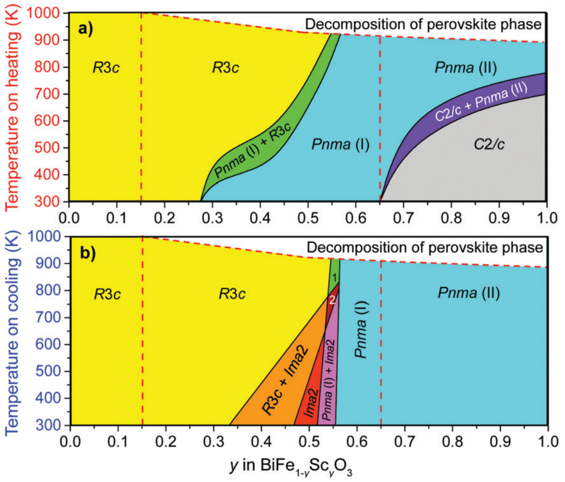

Fig. 1 State diagram of the perovskite phases of the $BiFe_{1-y}Sc_yO_3$ series upon heating to their temperature stability limit (top panel, a) and upon subsequent cooling (bottom panel, b). The areas marked as 1 and 2 correspond to the *Pnma* (I) + *R3c* phase mixture and the *Pnma* (I) + *R3c* + *Ima*2 phase mixture, respectively (see the ESI,† Sections 1–3 for details).

irreversible transformations as "conversion polymorphism" and demonstrate that this is a rather general phenomenon, which has been likely overlooked in many other metastable phases.

Based on the *in situ* temperature XRD study, detailed in Sections 1–3 of the ESI,† the phase diagrams of the as-prepared compositions of the $BiFe_{1-y}Sc_yO_3$ series on heating (Fig. 1a) and cooling (Fig. 1b) were plotted. Except for the two narrow regions ($y \leq 0.25$) and ($0.55 < y < 0.65$), the temperature–composition phase fields are essentially different, demonstrating the phenomenon of conversion polymorphism. The top part of the diagram (Fig. 1a) indicates the irreversible transitions (both complete and incomplete), while the transitions shown in the bottom part (Fig. 1b) are all reversible. A remarkable feature is that the pattern of the phase diagram depends on the maximum annealing temperature. This implies that by means of controlled annealing, materials with different combinations of the perovskite phases are obtained. This feature can be used, *e.g.*, to design new materials with a morphotropic phase boundary. The compositions which do not demonstrate the irreversible transformations are those where either the as-prepared phase is stable ($0 \leq y \leq 0.15$) or the as-prepared phases undergo no phase transformation until decomposition (the rhombohedral *R3c* phase with y between 0.15 and 0.25 and orthorhombic phase with a $PbZrO_3$-related structure, indicated as *Pnma* (I), when $0.55 < y < 0.65$).

The phase diagrams shown in Fig. 1 reveal three compositional ranges in the $BiFe_{1-y}Sc_yO_3$ system, $0.25 < y < 0.35$, $0.35 < y < 0.55$ and $0.65 < y \leq 1$, which convert into three distinct polymorphs, *R3c*, *Ima*2 and *Pnma* (II), respectively. In the previous observations of the irreversible behaviour upon annealing,[15,16] the transformations occurred between the known phases, which were neighbours in the corresponding composition–temperature phase diagrams. The remarkable feature of this conversion phase diagram is that it contains two new phases, namely *Ima*2 and *Pnma* (II), which have no stability ranges at ambient conditions in the as-prepared compounds with any Fe-to-Sc ratio. The only way to obtain these phases is a conversion from the high-pressure stabilized ones. This indicates that the conversion polymorphism is a powerful tool to produce novel materials. In addition, the presence of three ranges of compositions, converting to distinct polymorphs, strongly suggests that this behaviour is not a specific property of a particular phase but is a rather general phenomenon. Indeed, there is nothing really peculiar in this system, from a chemical or crystallographic point of view, which should make it unique and prevent this phenomenon from occurring in other systems. As possible candidates, which might demonstrate a conversion polymorphism, we can suggest recently reported metastable perovskites (and their solid solutions) with small A-site cations such as the Sc^{3+} and In^{3+}.[21]

The conversion stabilized perovskites exhibit remarkable properties that are demonstrated below by the most representative examples. The as-prepared $BiFe_{0.7}Sc_{0.3}O_3$ phase – *Pnma* (I) irreversibly transforms to the polar modification *R3c* isostructural to that in the undoped $BiFeO_3$ (Fig. 1, see also Section 4 of the ESI†). The magnetic ground states of these perovskites are, however, drastically different. The latter exhibits incommensurate cycloidal magnetic structure stable in the whole temperature range below $T_N \sim 640$ K.[11] The structure is stabilized by anti-symmetric exchange activated by the polar structural distortions.[22] The magnetic ground state of the converted $BiFe_{0.7}Sc_{0.3}O_3$ has been found to be collinear G-type with the spins polarized along the threefold axis (Fig. 2d). This magnetic structure is very unusual and allows no spin-canting. To the best of our knowledge, it is the first example of a $BiFeO_3$-derived composition, when the collinear magnetic structure does not activate the anti-symmetric exchange and therefore is selected by a single ion-anisotropy term of the nominally isotropic Fe^{3+} cations. This unusual magnetic structure of $BiFe_{0.7}Sc_{0.3}O_3$ is stable only below $T_m \sim 230$ K (Fig. 2a). Above this temperature, it turns into the incommensurate cycloid similar to that of the ground state of $BiFeO_3$ (Fig. 2b and c). This behaviour highlights the role of the single ion anisotropy, which is very close to the antisymmetric term in the energy scale and competes with it.

The $BiFe_{1-y}Sc_yO_3$ compositions close to the 1:1 ratio between Fe and Sc are converted to a new polar perovskite structure with the *Ima*2 symmetry (Fig. 1).[20] The structure combines polar displacements of Bi and O along the pseudocubic [110] direction and anti-phase octahedral tilting about the polar axis. The polar distortion is very big, indicating a large polarization value. In addition, these compositions exhibit a weak ferromagnetic ground state with a high transition temperature, making them attractive as multiferroic materials.

The as-prepared monoclinic[23] $BiFe_{1-y}Sc_yO_3$ compositions with $y \geq 0.7$ (see Section 5 of the ESI† for details) irreversibly transform to a new antiferroelectric-like structure with the orthorhombic *Pnma* symmetry and a complex superstructure (denoted as *Pnma* (II) in Fig. 1). This polymorph is different from the well-known $PbZrO_3$-like structure observed in many $BiFeO_3$-derived systems.[13–15] The latter shares the same space group and the same superstructure type, but the unit cell

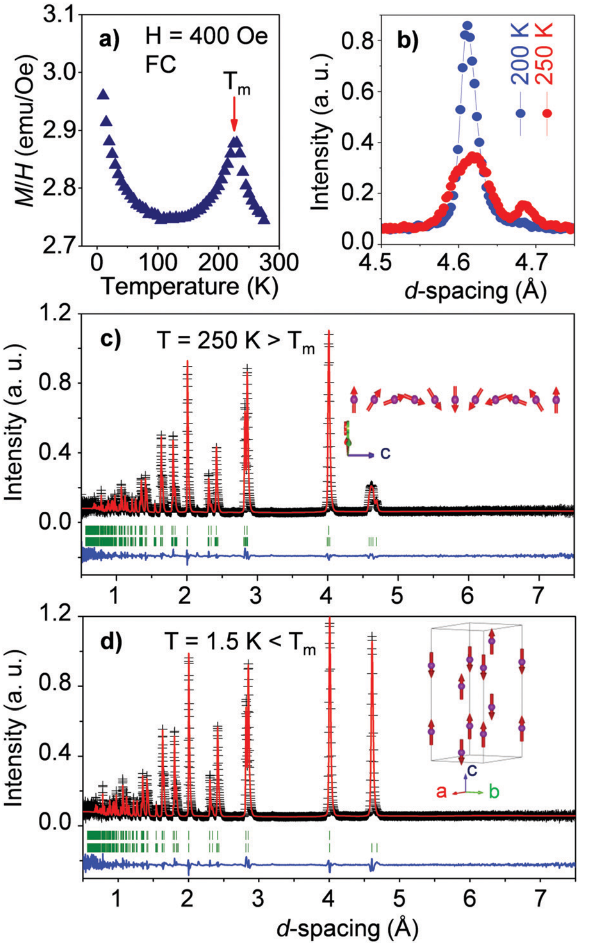

Fig. 2 The magnetic susceptibility as a function of temperature for the conversion-stabilized polar *R*3*c* modification of $BiFe_{0.7}Sc_{0.3}O_3$ (a). A portion of the neutron diffraction patterns in the vicinity of the strongest magnetic reflection (1/2,1/2,1/2), referring to the pseudocubic unit cell, measured below and above the magnetic transition at $T_m \sim 230$ K (b). Rietveld refinement of the neutron diffraction patterns collected at different temperatures for the polar *R*3*c* polymorph of $BiFe_{0.7}Sc_{0.3}O_3$ (c) and (d). Insets show the corresponding magnetic structures, cycloidal at *T* = 250 K and collinear G-type at *T* = 1.5 K.

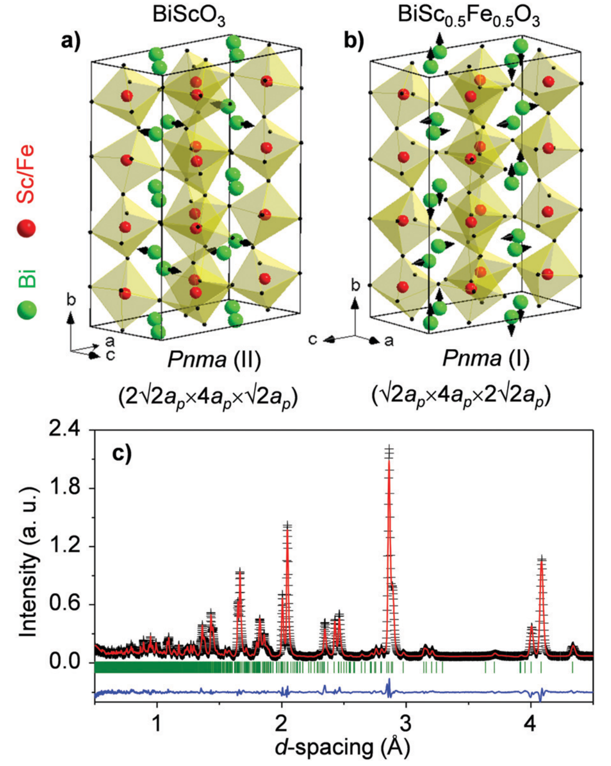

Fig. 3 The schematic representation of the two different *Pnma* structures with the ($2\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$) superstructure, *Pnma* (II) (a) and ($\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$) superstructure, *Pnma* (I) (b). Black arrows show Bi-displacements in the Λ_3 mode with the k = 1/4, 1/4, 1/4 propagation vector. Rietveld refinement of the room temperature neutron diffraction pattern of the new orthorhombic polymorph of $BiScO_3$ (c).

choice is different. The *Pnma* (II) structure found in the present study is characterized by the ($2\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$) supercell, whereas the superstructure in the *Pnma* (I) lattice reported before is ($\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$). Using the same cell ($\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$) for both structures, the symmetry of the former is *Pcmn*. The different unit cell choice implies essentially different distortions involved. As a representative example, let us discuss the conversion-stabilized orthorhombic polymorph for the end member of the series, namely $BiScO_3$. The atomic coordinates for this perovskite determined using a joint refinement of the X-ray and neutron diffraction patterns (Fig. 3c see also Fig. S12, ESI†) are summarized in Table S7 of the ESI.† The model was also confirmed by numerous density functional theory (DFT) calculations using possible space groups and both experimental and relaxed structural parameters (see Section 5 of the ESI† for details). We have also performed a decomposition of the structural distortions of the novel orthorhombic phase with respect to the symmetry-adapted displacement modes of the undistorted cubic perovskite lattice with the $Pm\bar{3}m$ space group (see Table S8 of the ESI†).[24] The mode decomposition procedure revealed that the largest structural distortions are the anti-phase octahedral tilting (R_4^+ oxygen displacement mode) and antiferroelectric-like displacements of Bi and O (Λ_3 displacement mode) quadrupling the pseudocubic unit cell in all three directions (propagation vector star k = (1/4, 1/4, 1/4)). The latter is shown in Fig. 3a along with the similar displacive mode characteristic of the ($\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$) *Pnma* (I) structure for comparison (Fig. 3b). The *Pnma* (I) structure is often discussed as a combination of the $PbZrO_3$-type of the structural distortions with an unusual tilting pattern combining both in-phase and out-of-phase octahedral rotations.[12,25] No such representation is possible for the *Pnma* (II) structure. Although this structure is also related to the $PbZrO_3$ structural type, rotation of rigid octahedra along the *b*-axis is not possible here. This indicates that the unusual octahedral tilting is not the crucial ingredient for the formation of the ($\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$) superstructure and in fact the latter is mainly driven by the antiferroelectric-like cation displacements.

Let us discuss the high-pressure stabilized perovskite compositions and their transformations in general. The most compact phases (which are definitely more favourable under high pressure) are antipolar. In other words, the displacements of the neighbouring cations in their oxygen polyhedra are antiparallel. As a result, the spontaneous polarisation either does not appear or is negligibly small. At the same time, the intermediate metastable phases obtained by the conversion of the high-pressure prepared metastable phases are less compact and can allow parallel displacements of the cations. Hence, one can expect a large spontaneous polarisation specifically in the converted metastable perovskites.

The metastable phases obtained by quenching from high-pressure and high temperature are under huge mechanical stress. Provided that annealing is done with a relatively slow increasing temperature, the mechanical stress will be released gradually and one can reach conditions, where the perovskite system is in a state that corresponds to a lower pressure and, thereby to another crystal phase. The $BiFe_{1-y}Sc_yO_3$ system is an excellent example of this concept and this is probably related to the fact that the energy landscape of the Bi-based perovskites consists of many almost degenerate phases,[26] which can be switched by some perturbations such as pressure.

In conclusion, our systematic structural study of the high-pressure stabilized perovskites of the $BiFe_{1-y}Sc_yO_3$ series revealed a set of annealing-stimulated irreversible transformations between the different metastable phases. This behaviour, referred to as ''conversion polymorphism'', allowed us to obtain these perovskites in different polymorphs at ambient conditions. These polymorphs represent the novel ferroelectric and antiferroelectric perovskite structures with interesting magnetic properties. In particular, a new orthorhombic modification of $BiScO_3$ has been obtained and a novel magnetic phase transition from an unusual collinear magnetic ground state to a cycloidal structure has been found in the converted polar *R*3*c* modification of the $BiFe_{0.7}Sc_{0.3}O_3$ composition. The conversion polymorphism is suggested as an extension of high-pressure synthesis and can be applied to other systems to obtain new materials with interesting properties and improved functionality. The method can be generalized and the post-synthesis thermal treatment can be performed at various pressures (different from the pressure of the initial synthesis). This provides distinct thermodynamic paths and opens a way to stabilize and explore a variety of metastable phases which are close in energy.

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Conflicts of interest

There are no conflicts to declare.

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