Finite-temperature Properties of Rare-Earth-Substituted $BiFeO_3$ Multiferroic Solid Solutions and Superlattices

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Multiferroics form an important class of materials that possess coupled long-range-ordered electric and magnetic degrees of freedom.[1] Such magneto-electric coupling is promising for designing new devices taking advantage of the control of magnetic properties by the application of an electric field; or vise versa. The most studied multiferroic to date is bismuth ferrite ($BiFeO_3$ or BFO) because it exhibits ferroelectricity at a high Curie temperature ($T_C \approx 1100$ K) as well as possesses a magnetic ordering (which consists of a G-type based cycloid in the bulk) with a Néel temperature $T_N \approx 640$ K, therefore rendering it a room-temperature multiferroic having a large spontaneous polarization (~90 μC/cm^2).

However, BFO has several drawbacks, such as large coercive fields and high leakage currents,[2] which can be detrimental for some applications. Such drawbacks can be resolved by alloying BFO with $RFeO_3$ materials for which *R* is a rare-earth element.[2–5] Recent investigations on the $(Bi_{1-x}R_x)FeO_3$ solid solutions revealed striking behaviors. Examples include modulated phases observed in the compositional range bridging the well-known ferroelectric *R3c* state (for low *R* concentrations) and the well-determined antipolar *Pnma* phase (for higher *R* compositions). Interestingly, the precise structure and atomic characteristics of these bridging phases are not fully resolved.[2-8] In particular, the nature and role of oxygen octahedral tiltings and antipolar motions in these phases are subject to debate. These bridging phases are further believed to be associated with an enhancement of the piezoelectric responses,[3] whose precise origin remains to be confirmed. Another example of striking behaviors in $(Bi_{1-x}R_x)FeO_3$ is the strong decrease of the ferroelectric Curie temperature, T_C, at which the *R3c* state disappears versus the weak dependency of the magnetic Néel temperature, T_N, when increasing the *R* composition, which can therefore lead to the interesting possibility of T_C being equal to T_N (and thus to the optimization of magneto-electricity) for some concentration. Moreover, applying an electric field in the *Pnma* state of *R*-doped BFO systems can lead to an antiferroelectric-to-ferroelectric phase transition (since *Pnma* is antipolar in nature and is close in energy to the

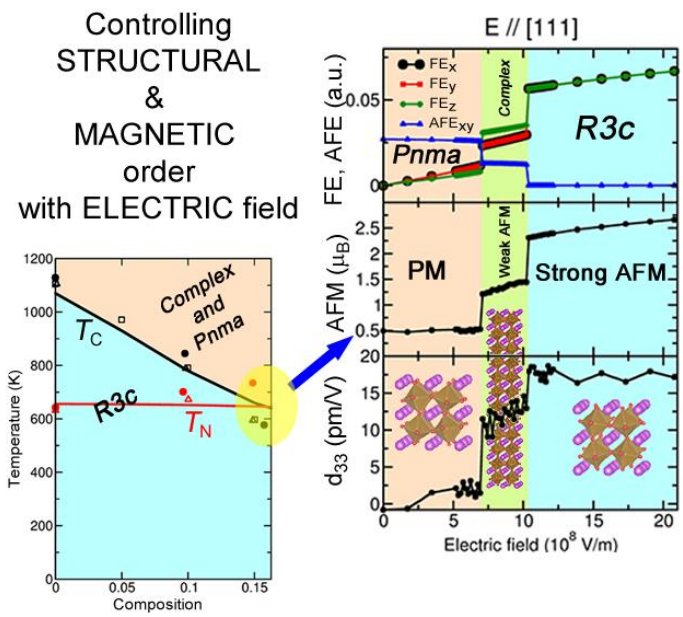

Figure 1 At the composition that $T_C \approx T_N$ and the temperature slightly above T_C, the application of an electric field can induce simultaneously structural and magnetic transitions.

ferroelectric *R3c* state in these compounds) that has the potential to be utilized in antiferroelectric capacitors and thus holds promise for energy storage devices.[9]

An atomistic scheme that accurately mimics $(Bi_{1-x}R_x)FeO_3$ solid solutions at finite temperature is therefore highly desirable in order to understand their unusual properties at a microscopic level as well as to guide the design of efficient devices. We are not aware that such scheme exists, likely due to the formidable challenge in treating well the finite-temperature and alloying effects on the subtle magnetic and structural properties of large supercells made of doped BFO compounds. Here we demonstrate that it is possible to develop such scheme, and apply it to study finite-temperature properties of disordered $Bi_{1-x}Nd_xFeO_3$ (BNFO) as representative of rare-earth-doped BFO systems (note that the choice of *R*=Nd is also motivated by the fact that numerous measurements have been conducted on this particular system,[3,4,10–12] which will therefore allow us to ground our predictions). Remarkably, this scheme can 1) reproduce very well observed properties, 2) resolve aforementioned issues, and 3) even predict novel and useful features in this important material [13].

This original numerical scheme can also be applied to ordered BNFO systems, e.g., 1/1 BFO/NFO layered superlattice for which each (001) layer has a *Pnma* structure. This latter system can therefore exhibit the so-called hybrid-improper-type ferroelectricity (HIF) [14]. The use of our developed atomistic technique allows to determine the effect of temperature and applied electric field on the polarization and its switching [15] as well as on the dielectric response associated with HIF. These numerical results can be further analyzed and understood within a Landau-type model.

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