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Local and average structure of Mn- and La-substituted $BiFeO_3$

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ABSTRACT

The local and average structure of solid solutions of the multiferroic perovskite $BiFeO_3$ is investigated by synchrotron X-ray diffraction (XRD) and electron density functional theory (DFT) calculations. The average experimental structure is determined by Rietveld refinement and the local structure by total scattering data analyzed in real space with the pair distribution function (PDF) method. With equal concentrations of La on the Bi site or Mn on the Fe site, La causes larger structural distortions than Mn. Structural models based on DFT relaxed geometry give an improved fit to experimental PDFs compared to models constrained by the space group symmetry. Berry phase calculations predict a higher ferroelectric polarization than the experimental literature values, reflecting that structural disorder is not captured in either average structure space group models or DFT calculations with artificial long range order imposed by periodic boundary conditions. Only by including point defects in a supercell, here Bi vacancies, can DFT calculations reproduce the literature results on the structure and ferroelectric polarization of Mn-substituted $BiFeO_3$. The combination of local and average structure sensitive experimental methods with DFT calculations is useful for illuminating the structure-property-composition relationships in complex functional oxides with local structural distortions.

1. Introduction

Lead-free piezoelectrics are environmentally friendly alternatives to the state-of-the-art lead-containing $Pb(Zr,Ti)O_3$ (PZT) based materials [1]. $BiFeO_3$ is the most studied multiferroic material and crystallizes in a rhombohedral polar *R3c* structure [2–5], displays high Néel (T_N) and Curie (T_C) temperatures of 370 °C and 830 °C, respectively, and a large spontaneous polarization (*Ps*) of ~90 μC/cm^2 [6–10]. Solid solutions based on $BiFeO_3$ have shown promising piezoelectric properties around morphotropic phase boundaries (MPB), and substitution on the *A* and *B* site of $BiFeO_3$ has been the topic of numerous studies [11–14]. Substituting Fe with Mn [15–19], and Bi with La [20–24], are the most common isovalent B-site and A-site modifications of $BiFeO_3$, respectively. The majority of doping studies have focused on thin films or the macroscopic properties and average structure of ceramics. However, the effect of local symmetry breaking around dopant atoms, and the structural coherence, has received little attention. As local structural distortions affect the chemical bonding, such distortions are imperative to the structure-property relationships.

La doping of $BiFeO_3$ ceramics has been reported to enhance the macroscopic ferroelectric properties [25], although this implies a dilution of the Bi sublattice. This is surprising as the Bi $6s^2$ lone pair is primarily responsible for ferroelectricity. Improved ferroelectric properties of La-substituted $BiFeO_3$ ceramics may thus stem from suppression of the secondary phases mullite, $Bi_2Fe_4O_9$, and sillenite, $Bi_{25}FeO_{39}$, which are difficult to avoid [26]. $Bi_{1-x}La_xFeO_3$ shows complete solid solubility for all values of x, but the phase diagram is complex, with experimental findings of compositional regions with more than two coexisting phases, which in principle violates Gibbs phase rule [22]. $BiFe_{1-x}Mn_xO_3$ does not show full solid solubility at ambient pressure, and decomposes to mullite and sillenite phases for $x > 0.3$ [17]. High pressure synthesis, on the other hand, allows complete solid solubility of $BiMnO_3$ and $BiFeO_3$ [27,28]. Manganese substituted $BiFeO_3$ is prone to oxygen hyperstoichiometry ($3+\delta$), which strongly affect the crystal lattice, electrical conductivity, and phase-transition temperatures [16,17]. The *R3c* phase field for $BiFe_{1-x}Mn_xO_{3+\delta}$ extends up to $x_{Mn} \leq 0.3$ and up to $x_{La}=0.1$ for $Bi_{1-x}La_xFeO_3$, implying that the ferroelectric *R3c* structure is more sensitive to dilution of the Bi sublattice than the Fe sublattice. A summary of literature data on Mn and La substitution of $BiFeO_3$ is provided in Table 1.

In this work we use pair distribution functions (PDF) obtained from high energy synchrotron X-ray diffraction to investigate the local and average structure of La and Mn-substituted $BiFeO_3$. Due to the difference in X-ray scattering lengths between light oxygen and the heavier cations in $BiFeO_3$, oxygen positions can only be extracted with limited accuracy, while the method is highly sensitive to structural disorder in the cation sublattices. We find that the same dopant concentration causes greater local distortions when introduced to the

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Table 1
Selected properties of Mn and La substitution of $BiFeO_3$.

	$BiFeO_3$	$Bi_{1-x}La_xFeO_3$	$Bi_{1-x}Mn_xFeO_3$
Magnetic moment Fe/Mn (μ_B)	3.7 ± 0.03 [15]	3.79 ± 0.03, x=0.07 [15]	3.35, x=0.1 [24] 2.98, x=0.2 [24]
Spontaneous polarization ($\mu C/cm^2$)	90–100, DFT [7] 50–60, film [5]	42, x=0.2 [29] 22, x=0.3 [30]	10, x=0.3 [15]
Curie temperature (°C)	830 [9,10]	754, x=0.05 [20] 677, x=0.1 [20,23]	773, x=0.1 [17] 715, x=0.2 [17] 660, x=0.3 [17]

Bi sublattice than the Fe sublattice. Our Density functional theory (DFT) calculations show that the average structure models from conventional reciprocal space diffraction give higher calculated spontaneous polarizations than the experimentally reported values. Attention to local structural distortions, and including point defects, in the DFT model is required to reproduce the experimental structure and spontaneous polarization of Mn-substituted $BiFeO_3$.

2. Experimental and computational details

Samples of $BiFeO_3$ (BFO), $BiFe_{0.875}Mn_{0.125}O_3$ (BFMO125), $BiFe_{0.75}Mn_{0.25}O_3$ (BFMO25) and $Bi_{0.9}La_{0.1}FeO_3$ (BLFO10) were prepared by a conventional solid-state synthesis route described previously [16,17,23], where the samples are fired in air for 5 min at 900 °C and furnace cooled at a rate of ~200 °C/h. X-ray total scattering data were collected at beamline 11-ID-B (90 keV with λ=0.13702 Å) at Argonne National Lab. The pair distribution function (PDF) was obtained with the PDFgetX3 software [31] using a Q_{max} of 23.0 $Å^{-1}$. Structural modeling with full range fitting of the G(r) function was carried out using the PDFgui software [32] with the parameters obtained from the XRD Rietveld refinements as starting structural models. The crystal structure was analyzed by Rietveld refinement using the General Structure Analysis System (GSAS) program [33].

Density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) [34,35] using the PBEsol functional [36]. The standard PBE PAW potentials Bi_d ($5d^{10}6s^26p^3$), La ($5s^25p^65d^16s^2$), Fe_pv ($3p^63d^74s^1$), Mn_sv($3s^23p^64s^23d^5$) and O ($2s^2p^4$) supplied with VASP were used and plane waves were expanded up to a cutoff energy of 550 eV. Brillouin zone integration was done on a 4×4×2 gamma centred k-point grid for the hexagonal $Bi_6Fe_6O_{18}$ cell with 30 atoms, with corresponding k-point densities for larger cell sizes. The Hellman-Feynman forces on the atoms were relaxed until they were below 10^{-3} eV/Å. The magnetic order of the Fe sublattice was initialized as the G-type collinear antiferromagnetic ordering in concordance with the magnetic order of bulk BFO [19]. Hubbard U values of 4, 3 and 10 eV were applied to Fe 3d, Mn 3d and La 4f, respectively. Bader charges were calculated as described in Ref. [37], and ferroelectric polarization was calculated by the Berry phase approach [38].

3. Results and discussion

Phase pure $BiFeO_3$ (BFO) $BiFe_{0.875}Mn_{0.125}O_3$ (BFMO125), $BiFe_{0.75}Mn_{0.25}O_3$ (BFMO25) and $Bi_{0.9}La_{0.1}FeO_3$ (BLFO10) bulk powders were successfully prepared by solid state synthesis and the synchrotron XRD patterns shown in Fig. 1a. All patterns could be indexed with the *R3c* trigonal space group in agreement with previous work [17,23], and the refined average structural parameters are summarized in Table 2. The *R3c* structure with hexagonal axis is shown in Fig. 1b. We adopted the atomic positions setting used by Sosnowska et al. [19] with the Bi fixed at the origin, Fe in (0,0,z) and O in (x,y,z).

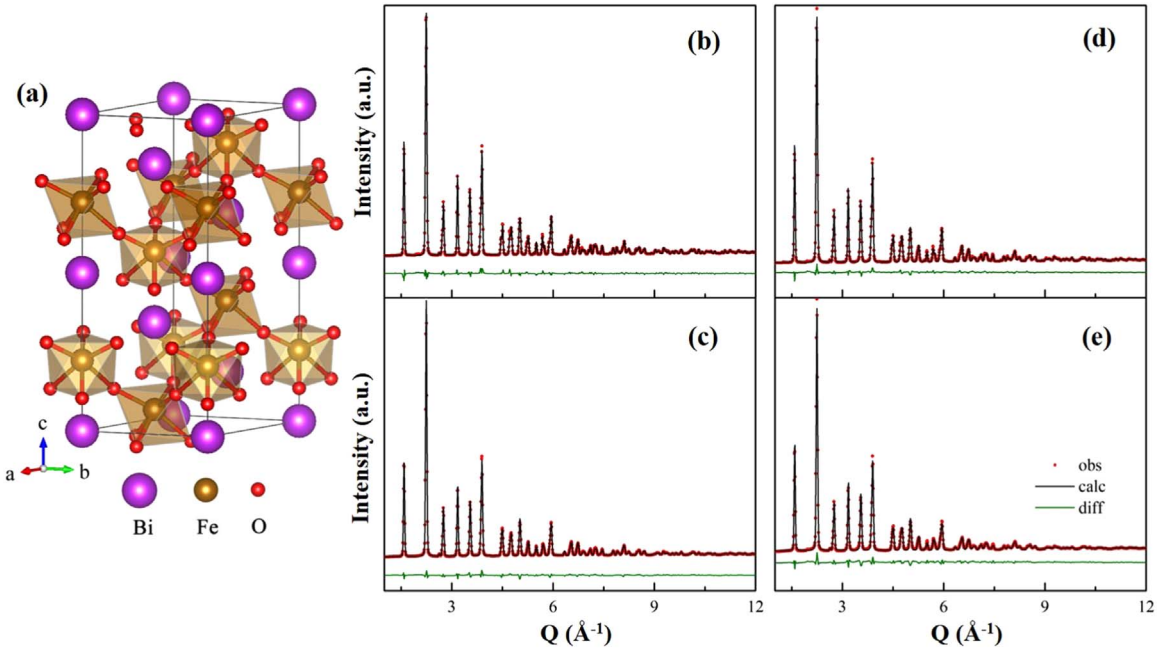

Fig. 1. (a) The hexagonal *R3c* $BiFeO_3$ unit cell with 30 atoms. (b)-(e) Rietveld pattern for *R3c* $BiFeO_3$ (BFO), $BiFe_{0.875}Mn_{0.125}O_3$ (BFMO125), $BiFe_{0.75}Mn_{0.25}O_3$ (BFMO25) and $Bi_{0.9}La_{0.1}FeO_3$ (BLFO10) showing the experimental (red crosses), calculated (black line) and difference (green line) powder XRD profiles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).