

Suppression mechanism of the ferroelectric polarization in multiferroic tetragonal perovskite $\text{Sr}_{1/2}\text{Ba}_{1/2}\text{MnO}_3$

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Ferroelectricity for the ferroelectric perovskite oxides (ABO)₃ have been investigated for decades [1]. In the ferroelectric BaTiO₃, it is well known that the electronic *p-d* hybridization between empty *d* orbitals of titanium and filled *2p* orbitals of oxygen causes a large ferroelectric polarization [2]. In contrast, magnetic-ordering-induced ferroelectric materials (multiferroics) have also been extensively investigated since a large nonlinear magnetoelectric effect was found in the perovskite TbMnO₃ [3]. In tetragonal perovskite BaMnO₃, it is proposed that a large ferroelectricity is induced by the distortion of the Mn and O ions originating from the *p-d* hybridization in the paramagnetic phase. Since the magnetic Mn⁴⁺ ion contributes to the emergence of the ferroelectricity, a large magnetoelectric effect is expected. Sakai *et al.* grew the tetragonal perovskite Sr_{1/2}Ba_{1/2}MnO₃ [4]. A large reduction in the ferroelectric polarization is observed below the magnetic transition temperature. The reduction mechanism of the ferroelectric polarization should be unveiled by dividing the ferroelectric polarization into the respective contributions from the *p-d* hybridization and that from the magnetic interaction.

Here, we report the atomic displacements in the ferroelectric and multiferroic phases of the tetragonal perovskite Sr_{1/2}Ba_{1/2}MnO₃ determined by the crystal-structure analyses [5]. Using a first-principles calculation based on accurate crystal-structure parameters, we quantitatively elucidate the suppression mechanism of the ferroelectric polarization in the multiferroic phase. The synchrotron x-ray diffraction experiments were carried out in the ferroelectric (*T* = 225 K) and multiferroic (*T* = 50 K) phases of the tetragonal perovskite Sr_{1/2}Ba_{1/2}MnO₃. Using the observed diffraction spots, we performed crystal-structure analyses. Comparisons between observed and calculated structure factors are shown in Fig. 1(a, b). Schematic views of the atomic displacements in the ferroelectric and multiferroic phases are shown in Fig. 1(c, d). To understand the effect of the magnetic order on the ferroelectricity in the multiferroic phase, we simulate the ferroelectric polarization in the ground-state G-type antiferromagnetic (G-AFM) structure. In the multiferroic phase, we consider two mechanisms to induce the ferroelectric polarization: hybridization between Mn 3*d* and apical O2 2*p* states (*P*_{hyb}) and in-plane Mn-O1-Mn magnetic exchange striction (*P*_{extr}), as shown in Fig. 1(e). In G-AFM, the magnetic exchange striction prevents the atomic displacement of the side O1 ion, so that total ferroelectric polarization is reduced. We conclude that only positive *P*_{hyb} contributes to the large ferroelectric polarization in the paramagnetic phase. In stark contrast, the magnetic exchange striction induces negative *P*_{extr}, causing the suppression of the ferroelectric polarization in the multiferroic phase.

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Keywords: Multiferroic, Crystal structure analysis, Manganite

Acta Cryst. (2021), A77, C744

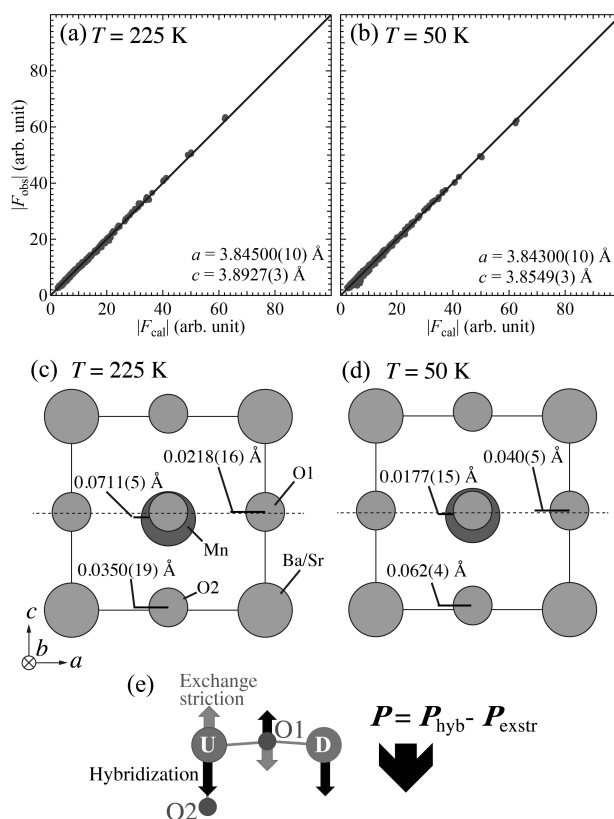


Figure 1. (a, b) Comparison between observed and calculated structure factors at 225 K in the ferroelectric phase and at 50 K in the multiferroic phase of tetragonal perovskite Sr_{1/2}Ba_{1/2}MnO₃. (c, d) The ferroelectric atomic displacements at 225 K and 50 K. (e) Schematic of ionic distortion and ferroelectric polarization for G-AFM. *P*_{hyb} and *P*_{extr} stand for the ferroelectric polarization from the hybridization and the exchange striction, respectively. U and D denote up- and down-spin Mn sites, respectively.