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Role of Fe Doping on Local Structure and Electrical and Magnetic Properties of $PbTiO_3$

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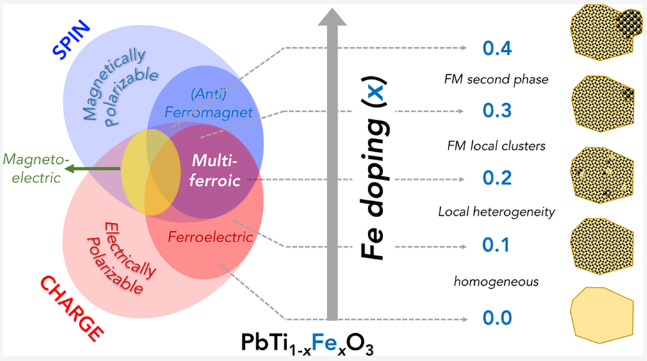
ABSTRACT: The local structure and multiferroic properties of iron-doped lead titanate ($PbTi_{1-x}Fe_xO_{3-\delta}$) samples was investigated over the entire composition range ($x = 0-1$). Inherent polarization in $PbTiO_3$ decreases due to Fe^{3+} incorporation up to the solubility limit ($x \sim 0.3$), although homogeneous doping persists only up to $x = 0.1$. Ti prefers highly distorted oxygen octahedra for any x value, while Fe prefers more symmetric O-deficient polyhedra ($Fe-O_n$). The charge compensating oxygen vacancies induce local tilting of the $Fe-O_n$ polyhedra beyond a critical x value ($x \geq 0.2$), promoting magnetic interaction between two adjacent Fe atoms. The strain induced by local heterogeneity could act as a coupling force between magnetic and ferroelectric properties. Fe-rich clusters evolve into ferromagnetic $PbFe_{12}O_{19}$ with increased Fe doping. $PbTi_{1-x}Fe_xO_{3-\delta}$ ($x \geq 0.3$) samples therefore have separate origins for the ferroelectric ($PbTi_{1-x}Fe_xO_{3-\delta}$) and magnetic ($PbFe_{12}O_{19}$) phases.



■ INTRODUCTION

Multiferroics are single-phase materials that simultaneously exhibit more than one of ferromagnetic, ferroelectric, or ferroelastic order parameters.[1] Such coupling provides an additional degree of freedom over conventional ferroelectric or ferromagnetic materials in terms of device fabrication, since polarization of the material can be switched by using either the magnetic or electric fields.[2−4] This explains the popularity of multiferroics for potential applications[5] in the fields of spintronics, data storage, read heads, multistate memory devices, electro-optic devices, and so on. However, room temperature multiferroics exhibiting both ferroelectric and antiferromagnetic ordering are quite rare due to the mutually exclusive prerequisite criteria fundamental to ferroelectricity (empty d orbital) and ferromagnetism (partially occupied d orbital).[6,7] Fulfilling both criteria simultaneously to achieve magnetoelectric cross-coupling therefore constitutes the essence of finding new multiferroics.

The search for multiferroics has a major focus on perovskite oxides (chemical formula ABO_3) due to their robust structural integrity which can support wide tunability of the type and quantity of dopants. Natural single-phase multiferroic perovskites like $BiFeO_3$,[8,9] $BiMnO_3$,[10] and $TbMnO_3$[2] are antiferromagnetic. While $BiFeO_3$ suffers from Bi volatilization leading to high leakage current,[11] $BiMnO_3$ is antiferromagnetic below room temperature,[10] and $TbMnO_3$ has a very low ordering temperature.[2] Such factors severely limit the possibility of potential applications. A novel approach to achieve multiferroicity in a perovskite is to dope magnetic ions (d^n system) in a ferroelectric perovskite. Examples include perovskites with B-site constituted by d^0 metal ions (e.g., Ti^{4+}, Nb^{5+}, and Zr^{4+}) where large spontaneous polarization originates due to off-centered displacement of the d^0 ion within the O_6 octahedra. Replacing d^0 ions by d^n would naturally decrease the inherent polarization, so the challenge lies in generating the magnetic response while retaining the electric polarization as much.

This concept has led to extensive studies on doping 3d magnetic transition elements in ferroelectric perovskites,[12−18] for example, titanates. The Ti^{4+} ion is formally in a d^0 state so that the lowest unoccupied energy levels are Ti 3d states that tend to hybridize with O 2p which stabilizes the ferroelectric distortion in titanates.[19] Efforts to dope prototype ferroelectric

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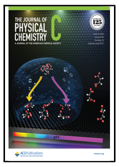

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