



First principles study of the effect of lanthanide substitutions on ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

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Abstract – Using first principles density functional theory and atomic scale thermodynamics the energetics of incorporating two lanthanide metals (La and Pr) into ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is evaluated. It is found that substitution on Bi sites within the pseudo-perovskite block is preferred and that this inhibits oxygen vacancy formation. This is beneficial since oxygen vacancies are known to cause ferroelectric fatigue. The energy landscape for lanthanide substitution and vacancy formation depends on the relative abundance of Bi, La and Pr and the oxygen partial pressure. The results provide fundamental support for the observation that lanthanide incorporation improves the ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a promising ferroelectric material with a layered perovskite structure (Fig 1). Below the Curie temperature (675°C) it has orthorhombic symmetry and exhibits a large spontaneous polarization (0.5 Cm^{-2} along the a -axis), a low dielectric constant (107 at 20°C) and high piezoelectric constants ($d_{33} = 25 \times 10^{-12} \text{ CN}^{-1}$). It is thus a good candidate for FRAM applications and high temperature piezoelectric devices. However its properties are not ideal since it suffers from ferroelectric fatigue, low remanent polarization and low electrical resistivity. To reduce these undesirable effects BIT has been modified by the incorporation of various lanthanide metals to form solid solutions. The addition of La and Pr is found to be especially beneficial because they are thought to be linked to an increase in the stability of the structure and a reduction in the concentration of oxygen vacancies. Oxygen vacancies are known to cause ferroelectric fatigue by pinning domain boundaries and can also be a source of hole carriers which increases the conductivity. It is thought that the lanthanide metals substitute on Bi sites in the central pseudo-perovskite block, stabilizing the TiO_6 octahedra and making oxygen vacancy formation less likely.

In this paper we examine in detail the energetics of La and Pr incorporation in BIT using first principles density functional theory and atomic scale thermodynamics. Previous calculations have only considered defect-free BIT. Different Bi substitution sites within the structure are chosen and the influence of this on the oxygen and bismuth vacancy formation energies is determined. The effects of the substitutions on the atomic and electronic structure of BIT are described using a density of states and Mulliken population analysis. It is found that La and Pr both prefer to incorporate within the pseudo-perovskite block (rather than the Bi_2O_2 layers) as previously believed but the detailed energetics depends on the relative abundance of Bi, La and Pr and the oxygen partial pressure (Fig 2). Finally it is confirmed that lanthanide incorporation in BIT does inhibit oxygen vacancy formation, thus providing fundamental support for the experimental observations.

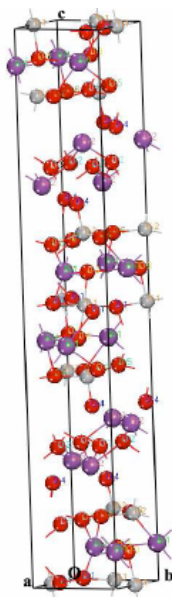


Figure 1: Atomic structure of orthorhombic BIT

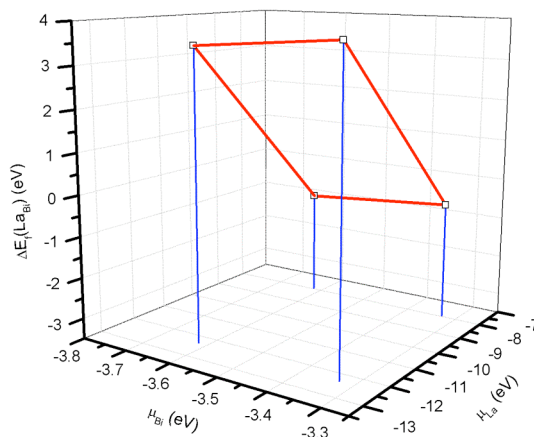


Figure 2: Limiting range of La substitution energies in the pseudo-perovskite block of BIT