

Effects of Mn Addition and Compensating Oxygen Vacancies on the Ferroelectric Properties of BaTiO₃

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The Mn dopant has been intensively used to improve the electromechanical properties of perovskite oxides. It increases coercive fields, quality factors and dielectric constants [1,2], reduces dielectric losses and hysteretic fatigues[3], stabilizes domain structures[4] among other effects. Since Mn is magnetic and multivalent, its behavior in polar materials is quite complex [5,6] and has been poorly understood from the electronic point of view. It has been discovered in recent experiments on spin-electric couplings in Mn defects in ZnO that the Mn²⁺ spin Hamiltonian is extremely sensitive to an external electric field [7]. In the presence of an electric field, ions are displaced and, as a result, the dimension of the crystal change. This change in the strain is known as piezoelectricity and has a vast range of applications. It has been proposed, however, that this effect can be increased in aged BaTiO₃ (BTO) [8]. Although this could extend the frame of conventional multiferroicity and give new perspective for studies of the phenomenon and potential applications, there has been limited first-principles theoretical study of defects on ferroelectrics and piezoelectricity.

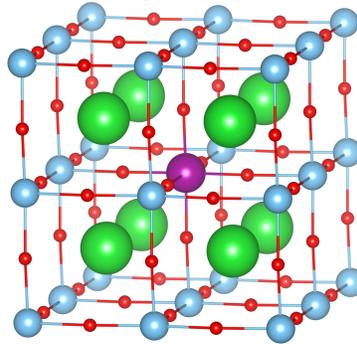


Fig 1. 2x2x2 Mn-doped BaTiO₃ supercell. Red, blue, green and purple balls correspond to Oxygen, Titanium, Barium and Manganese atoms, respectively.

Using density functional theory, we have investigated the equilibrium geometry and electronic properties of Mn ion on *A* or *B* sites of BTO perovskite structure, and with compensating oxygen vacancies, V_O. We have used a 40- and 39-atom supercell with a single Mn and Mn-V_O complex, respectively (See Fig. 1). In our studies, we have used both GGA (Wu-Cohen) and GGA+U with U=8 and J=0.8 eV. Our calculations have been carried out with ABINIT code using PAWs. We have studied the change in the oxidation state of Mn occupying *B* site in response to local environment changes, such as the presence of oxygen vacancies. We also have investigated the role of the oxygen vacancies around Mn impurity in order to engineer reversible domain switching in aged samples. Mn ions go in the *B* site (Ti⁴⁺) rather than *A* site (Pb²⁺ or Ba²⁺) in that the radius of Mn is closer to that of *B* atom [9]. This phenomena causes oxygen vacancies in the lattice, which would boost the electric conductance. Thus, understanding the role of defects in the O vacancy formation and transducer ageing would be a key to design reversible switching devices.

We have found that the Mn ion, in the presence of an oxygen vacancy, in the BTO is in a more centered position than the original Ti⁴⁺ (see Fig. 2). This shift modifies the ferroelectric properties of BTO. We have used the modern theory of polarization implemented in Quantum espresso code to calculate the polarization of Mn-doped BTO. Table 1 shows the change in the polarization for different structures considered in this work. We find that the polarization of BTO:Mn in a 40 atom supercell with a single

Mn, with Mn on the B site, is 0.077 C/m^2 , is lower than un-doped BTO. It can, however, be increased to 0.092 C/m^2 when considering Mn- V_{O} defects. Although this value is smaller than that found in un-doped BTO, 0.33 C/m^2 , it is still larger than most multiferroics.

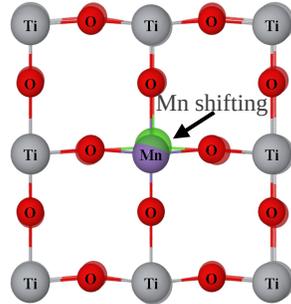


Fig. 2. After fully relaxation, Mn ion is shifted to a more centered position when an oxygen vacancy is present.

We also compare our findings with previous work in V-doped BTO and co-substitution of N and F for oxygen in $\text{BTO}_{2.8}\text{N}_{0.1}\text{F}_{0.1}$, where the polarization has also been found to decrease because the doping [10,11]. In order to analyze the consequences of the changes in the electronic and ferroelectric properties of the Mn-doped, V_{O} vacancy and BTO perovskite, we also calculate the effective charges and dielectric constants for our structures. As a final remark, we also investigate the effect of an external electric field on the polarization. This effect is a key point in the achievement of recoverable electro-strain without using external force. Understanding the effect of a perpendicular external electric field on the polarization of BTO:Mn- V_{O} is a necessary key to exploit the idea of reversible domain switching.

Structure	$P(\text{C/m}^2)$
BTO	0.335
BTO:Mn	0.077
BTO:Mn- V_{O}	0.092

Table 1. Polarizations in C/m^2 .

Acknowledgements

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