強誘電体における酸素空孔分布制御—遷移金属イオンとの相互作用を利用した欠陥設計

Controlled oxygen-vacancy distribution in Ferroelectrics— Materials Design exploiting the interaction with transition metal ions—

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Spontaneous polarization (P_s) in ferroelectrics offers opportunities to develop sensors, actuators, medical transducers, and non-volatile memories. Recently, ferroelectric tunnel junctions have attracted much attention owing to their potential applications in non-destructive readout memories[1]. In all these applications, the control of domain structures and polarization states by applying external fields are crucial to achieving desirable properties. Even though ferroelectric bulk has the insulating nature, charged domain walls act as an electrically conductive interface, which leads to possibilities for domain-wall memories[2]. Moreover, utilizing a high mobility of defects enables to create a p–n junction that can be erased and inverted by electric fields[3]. Here, we report a practical route to designing oxygen-vacancy distributions by utilizing the interaction with transition-metal dopants. Our thin-film experiments combined with *ab-initio* theoretical calculations for $BiFeO_3$ demonstrate that isovalent dopants such as Mn^{3+} with a partly or fully electron-occupied e_g state can trap oxygen vacancies, leading to a complete polarization switching.

For TM = Ti, V, and Cr, $V_O^{\bullet\bullet}$ does not find an energetically favourable site inside the lattice; the vacancies in the vicinity of the bottom electrode are pulled toward its interface owing to a strong depolarization field arising from the discontinuity of P_s, suggesting a formation of an $V_O^{\bullet\bullet}$-rich layer. This defective layer has been reported for non-doped $BiFeO_3$ films. By contrast, the cells with TM = Mn, Co, Ni, and Cu provide a stable position of $V_O^{\bullet\bullet}$, i.e., the 1st NN site adjacent to the TMs. Provided that the concentration of TMs is higher than that of $V_O^{\bullet\bullet}$ and also that the attractive interaction between $V_O^{\bullet\bullet}$ and TMs is sufficiently strong, $V_O^{\bullet\bullet}$ is trapped by TMs in an equilibrium state.

For a robust switching of P_s by applying electric fields, in addition to the attractive interaction of $V_O^{\bullet\bullet}$-TM, the doped lattice should meet the following requirements: the first is a high solubility limit of TM, the second is the stable valence state of TM^{3+}, and the third is the electronic character of TM that does not lead to a significant increase in leakage current. Here, we choose Mn as a TM because of the following reasons: Mn can be introduced into the lattice in a wide composition range and the valence state is controllable to Mn^{3+}. Moreover, the empty d_{x2-y2} state of the Mn cell with $V_{O1}^{\bullet\bullet}$ is far above the VBM, and thereby a leakage current is expected to be relatively low.

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2. Seidel, J. *et al.* Conduction at domain walls in oxide multiferroics. *Nat. Mater.* **8**, 229–234 (2009).
3. Yang, C.-H. *et al.* Electric modulation of conduction in multiferroic Ca-doped $BiFeO_3$ films. *Nat. Mater.* **8**, 485–493 (2009).