5–3 Doping Effect of Ferroelectrics

— Improvement of Ferromagnetic Mechanism of Bismuth Ferrite —

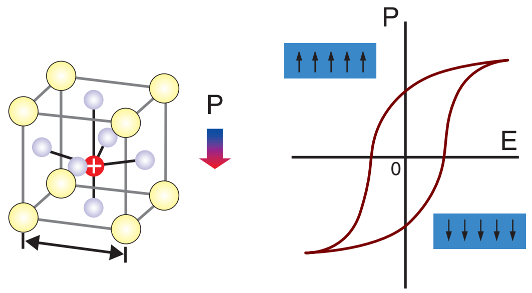

Fig.5-11 Hysteresis loop of ferroelectric material
An electric field applied to a ferroelectric material redistributes the electric charge in the material. This phenomenon is called polarization. The direction of polarization in a crystal is visualized by the D-E hysteresis loop.

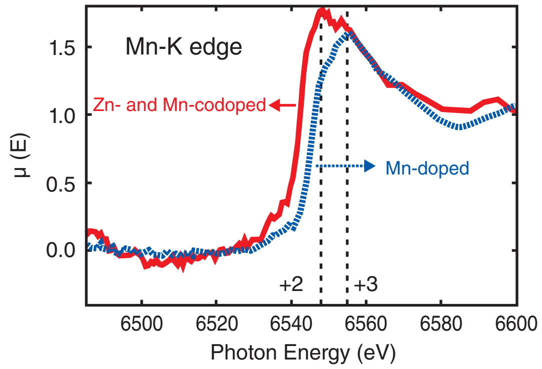

Fig.5-13 XAFS spectra of doped Mn
The valence of Mn differs between samples doped with both Zn and Mn, and those doped with Mn only.

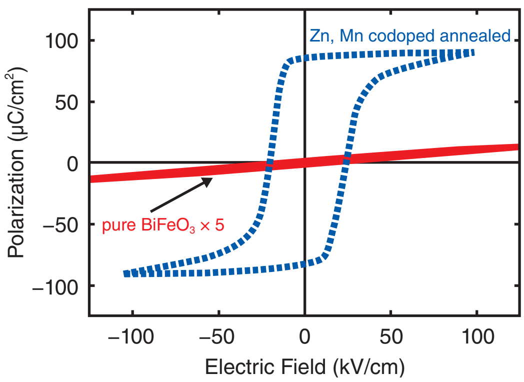

Fig.5-12 D-E hysteresis loop of bismuth ferrite
Although bismuth ferrite is slightly affected by an external electric field, its ferroelectric properties are dramatically improved by doping with small amounts of Zn and Mn, and a hysteresis loop develops.

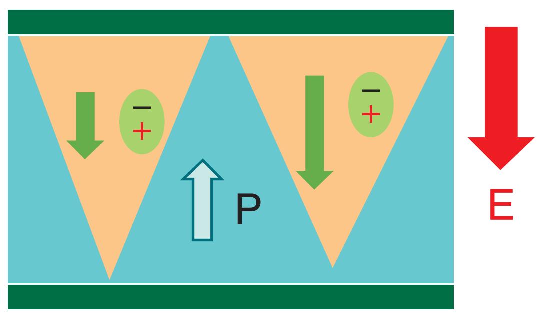

Fig.5-14 Defect-induced polarization reversal
Since the valence and local structure of the host phase differs from that of the dopants, the doped Zn and Mn generate defect-induced polarization, which nucleates domain reversal. Consequently, the ferroelectricity of bismuth ferrite improves and the hysteresis loop opens.

When a ferroelectric thin film is implanted with a small number of ions from the ion beam irradiation equipment, its ferroelectric property is often improved. However, as few ions can become embedded in a thin film, a detailed structural analysis is precluded, and the mechanism by which the ions improve the ferromagnetic properties cannot be clarified. However, ion implantation into bulk medium induces the same effect, allowing investigation of the doping effect.

Although bismuth ferrite ($BiFeO_3$) exhibits small polarization, its ferroelectric property is dramatically improved by codoping with small quantities of zinc (Zn) and manganese (Mn). Figs.5-11 and 5-12 illustrate the polarization principle and the D-E hysteresis loop of $BiFeO_3$, respectively. The coercive electric field of $BiFeO_3$ is very large and spontaneous polarization is rare. However, spontaneous polarization is incited by codoping with Zn and Mn.

Here we investigated ferromagnetic improvement in $BiFeO_3$ codoped with small quantities of Mn and Zn codoping. As the valence of Zn is stable, the investigation relies on the fluctuating valence of Mn. Moreover, local structure analysis is more suitable than conventional crystal structure analysis because the surrounding doped ions break the translational symmetry of the $BiFeO_3$ structure. The X-ray absorption fine structure (XAFS) was then measured using beamline BL14B1 in SPring-8, which is dedicated to JAEA.

Fig.5-13 shows the results of the XAFS measurements. The Mn valence state in codoped $BiFeO_3$ (+2) differs from that in Mn-doped $BiFeO_3$. Because hetero-valence ion doping alters the structure of the bismuth sites, it induces polarization defects. These defects initiate domain reversal in the presence of an electric field. The polarization reversal induced by the defect, which improves the ferroelectric property of the codoped $BiFeO_3$, is shown in Fig.5-14.

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Reference

Yoneda, Y. et al., Electronic and Local Structures of Mn-Doped $BiFeO_3$ Crystals, Physical Review B, vol.86, no.18, 2012, p.184112-1-184112-11.