Property Control by Defect Engineering on Bismuth Layer-structured Ferroelectrics

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Abstract

Bismuth layer-structured ferroelectrics (BLSFs) have attracted interest as the candidate material for non-volatile and fatigue-free ferroelectric memories. Their ferroelectricity originates from perovskite layers interleaved with bismuth oxide layers. The polarization properties are much affected by defects as A-site-cation vacancies and oxide-ion vacancies, as well as component cations and number of BO6 octahedra in the perovskite layers. In the present paper, the defect-related modification of polarization properties, defined as defect engineering, is presented on typical BLSFs, SrBi2Ta2O9 and Bi4Ti3O12. In SrBi2Ta2O9 (SBT), modification by trivalent Bi, La, Pr ions at the A(Sr)-site gives A(Sr)-site vacancies for charge compensation and atomic shifts in the perovskite units. The experiments using single crystals of Bi-modified SBT revealed a large remanent polarization (Pr) reaching 25 microC/cm2 with a low coercive field (Ec) of 22 kV/cm. The modification by La and Pr in SBT ceramics led to a lower Ec than that of Bi-SBT ceramics keeping the same remanent polarization. While, SBT ceramics modified with a large content of Nd showed a higher Ec, due to the formation of oxide-ion vacancies as well as Sr vacancies. These results indicate that polarization properties of SBT can be managed by the defect control for low-voltage-operating memories or FET-type ferroelectric memories. In Bi4Ti3O12 (BIT), the control of oxide-ion vacancies plays an important role in its polarization properties. While undoped BIT ceramics are hard to show a sufficient polarization hysteresis loop, the doping of small amount of V and W with higher valences than Ti improves the polarization properties. The doping of higher-valent cations decreases oxide-ion vacancies, resulting in a large remanent polarization. The decease in oxide-ion vacancies was confirmed by conductivity measurements and also suggested by calculation of defect formation energies in the perovskite layers.