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XAFS Study on Local Structure of Bi-Layered Oxide Ferroelectrics

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Introduction

Bi-layered perovskite-type oxides, such as $(Bi,La)_4Ti_3O_{12}$, are promising candidates for non-volatile Ferroelectric Random Access Memory (FeRAM) because of their high remanent polarization, low coercive field and good fatigue characteristics [1]. As for the $(Bi,La)_4Ti_3O_{12}$, it was reported recently that Bi_2SiO_5-addition in the preparation processes of thin films was effective for an improvement of fatigue characteristics [2]. In addition, it was also demonstrated that a partial substitution of Mo^{6+} for Ti^{4+} enhanced the remanent polarization of bulk samples. At this moment, however, it is still ambiguous how the addition of the bismuth silicates and the Mo^{6+} substitution affect the crystal structures.

From such background, this study investigated $(Bi,RE)_4(Ti,Mo)_3O_{12}$ (RE=La, Nd) and $Bi_4Si_3O_{12}$-added ones from the viewpoint of the ferroelectric properties and the crystal structures.

Experimental

$(Bi,RE)_4(Ti,Mo)_3O_{12}$ was prepared by means of a conventional solid-state reaction. In this process, a final sintering was carried out in air at 1000 °C for 1 h. A $Bi_4Si_3O_{12}$ addition was performed by firing a mixture of the prepared $(Bi,RE)_4(Ti,Mo)_3O_{12}$ and $Bi_4Si_3O_{12}$ in air at 1000 °C for 1 h. These products were identified by powder X-ray diffraction measurements. As ferroelectric-property investigations, *P-E* hysteresis loops of the samples were measured at a frequency of 1~10 Hz, and then remanent polarization, P_r, and coercive field, E_c, were evaluated. Temperature dependencies of dielectric constants, ε_s, and dielectric losses, $\tan\delta$, were also investigated with LCR meter. In order to clarify an effect of the $Bi_4Si_3O_{12}$-addition on the crystal and electronic structures, we measured X-ray absorption fine structure (XAFS) spectra with a transmission mode at BL7C and BL9C installed at Photon Factory. By analyze the data with REX2000 program, effects of the Mo substitution and $Bi_4Si_3O_{12}$ addition on the structures were discussed.

Results and Discussion

X-ray diffraction patterns demonstrated that the main phase was a monoclinic layered perovskite structure (S. G.: *B1a1*), even after $Bi_4Si_3O_{12}$ addition. From lattice constants calculated from the patterns, it was also indicated that Ti^{4+} site was partially occupied by Mo^{6+}. As for these samples, we measured *P-E* hysteresis loops and temperature-dependencies of ε_s and $\tan\delta$. As a result, it was found that the remanent polarization and the Curie temperature became larger and lower, respectively, by the $Bi_4Si_3O_{12}$ addition and the Mo substitution.

Generally, such changes in the ferroelectric properties are considered to be related with structural distortions in the crystals. In order to estimate the distortion in $Bi_4Si_3O_{12}$-added $(Bi,RE)_4(Ti,Mo)_3O_{12}$, we measured Ti *K*-edge XAFS spectra for the samples. Fig. 1 shows Fourier transforms of the EXAFS. The first coordination peaks given in this figure can be attributed to the Ti-O shells. If we assume the the oxygen content is independent of the metal composition, the smaller peaks of the $Bi_4Si_3O_{12}$-added $(Bi,RE)_4(Ti,Mo)_3O_{12}$ compared with the samples without the addition indicate that the Ti-O_6 distortion was increased by the $Bi_4Si_3O_{12}$ addition. This may be one of the reasons why the addition was effective for the ferroelectric-property improvement.

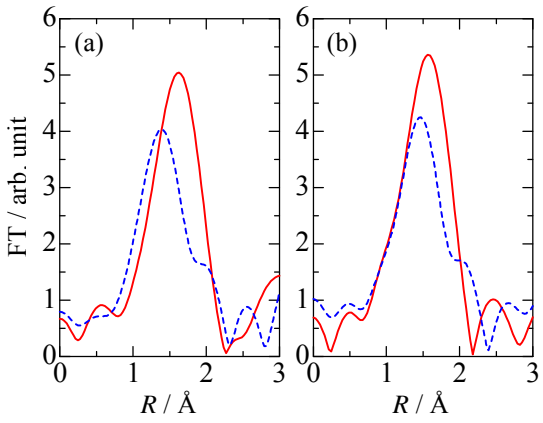

Fig. 1 Fourier transforms of Ti *K*-edge EXAFS spectra for $Bi_{4-x}RE_xTi_{3-y}Mo_yO_{12}$ (solid line) and 5 mol% $Bi_4Si_3O_{12}$-added one (broken line).
(a) RE=La, x=0.75, y=0.12, (b) RE=Nd, x=0.85, y=0.12

References

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