

Analysis of rare-earth substitution for BaTiO₃ by XAFS

Takanori ISHIKAWA¹, Kenji OHNUMA¹, Ken-ichi KAKIMOTO¹, Hitoshi OHSATO^{1*} and Youichi MIZUNO²

¹Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

²Taiyo Yuden co., Ltd., 5607-2 Nakamuroda, Haruna-Machi, Gunma-Gun, Gunma 370-3347, Japan

Introduction

The thickness of a layer of multi layer ceramic capacitor becomes thinner to obtain and higher capacity. It is, therefore, important to enhance the reliability for the microstructure of the thin dielectric layer sandwiched by electrode layers. The microstructure and electric properties of BaTiO₃ have been improved by addition of rare-earth oxides. To discuss the mechanism, it is important to examine the solid solution structure of rare-earth doped BaTiO₃ (ABO₃).

In previous studies, preferential soluble sites of rare-earth in BaTiO₃ have been presumed by Rietveld refinement analysis. As a result, the preferential soluble site has been clarified by their ionic radii.

In this study, rare-earth doped BaTiO₃ solid solutions were analyzed by XAFS to reveal the information of the fine structure of BaTiO₃.

Experimental

Model samples of (Ba_{1-x}R_x)(Ti_{1-x}R_x)O₃ (R=Eu or Sm, x=0.03, 0.05 and 0.10) were prepared by a conventional solid reaction method. The L₃-edge XAFS spectra of Eu (6.98keV) and Sm (6.72keV) were measured at BL-7C in the Photon Factory, KEK, Tsukuba, Japan. The X-rays were monochromatized with Si (111) crystal at the station, and the absorption spectra were observed in a transmission mode.

The EXAFS data were refined by REX2000 program (ver.2.3). The k³-weighted EXAFS functions were used for the calculation of the radial structure functions, in the k-region of 3.0-9.2 Å⁻¹ for Eu L₃-edge EXAFS spectra and 3.0-9.1 Å⁻¹ for Sm L₃-edge EXAFS spectra. The backscattering amplitudes and phase shifts were calculated. Furthermore, the spectra of [Ba(Ti,R)O₃] were simulated for comparison by FEFF7 software.

Results and Discussion

Figure 1 shows the Fourier transformed k³-weighted EXAFS spectra for (Ba_{1-x}Eu_x)(Ti_{1-x}Eu_x)O₃ (x=0.03, 0.05 and 0.10) and (Ba_{1-x}Sm_x)(Ti_{1-x}Sm_x)O₃ (x=0.03, 0.05 and 0.10). The measured samples exhibited separated peaks, indicating the existence of different R-O distances. The peak located at around 1.8Å represents the nearest neighbor shell around R in B site that is composed of 6 oxygen atoms. The peak located at around 2.5 Å represents the nearest neighbor shell around R in A site that is composed of 12 oxygen atoms. The simulated EXAFS spectra show a strong peak which locates at

smaller R than 2.0Å. On the other hand, the observed peak at 2.5Å was assigned to the peak of R-O(12CN). This result indicates that R is soluble in both A and B sites of BaTiO₃.

Table 1 shows the structural parameters derived from EXAFS analysis of the R-L₃ edge of (Ba_{1-x}R_x)(Ti_{1-x}R_x)O₃. The interatomic distances between R and oxygen for B-site (6CN) were about 2.34Å (R=Eu) and 2.36Å (R=Sm) in all compositions. These values are almost equal to the sum of the ionic radii [1] of R³⁺ and O²⁻: 0.947Å (Eu³⁺ 6CN), 0.958Å (Sm³⁺ 6CN) and 1.4Å (O²⁻ 6CN). The interatomic distance between Ti⁴⁺ (0.605Å, 6CN) and O²⁻ was about 2.0Å. It means that B-site expands by the substitution of R³⁺ to the B-site of BaTiO₃, because ionic radii are in the order of Sm³⁺ (0.958 Å) > Eu³⁺ (0.947 Å) > Ti⁴⁺ (0.605Å). On the other hand, the interatomic distances between R and oxygen for A-site (12CN) were about 2.66-2.77Å in all compositions. A-site of BaTiO₃ contracts by R³⁺ incorporation, because the interatomic distance (2.84Å) between Ba²⁺ and O²⁻ are larger than that (2.66-2.77 Å) between R³⁺ and O²⁻.

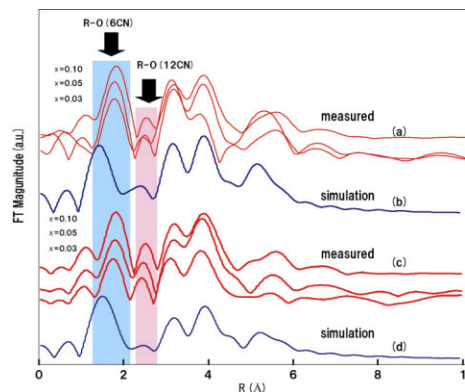


Figure 1. Fourier transformed k³-weighted EXAFS spectra for (a) (Ba_{1-x}Eu_x)(Ti_{1-x}Eu_x)O₃ (x=0.03, 0.05 and 0.10), (b) Spectrum simulation of Eu for [Ba(Ti,Eu)O₃], (c) (Ba_{1-x}Sm_x)(Ti_{1-x}Sm_x)O₃ (x=0.03, 0.05 and 0.10) and (d) Spectrum simulation of [Ba(Ti,Sm)O₃].

Table 1. Structural parameters derived from EXAFS analysis of R-L₃ edge of (Ba_{1-x}R_x)(Ti_{1-x}R_x)O₃; interatomic distance R and Debye-Waller factor σ².

Composition x	A-site (12CN)		B-site (6CN)	
	R _{Ba-O} (Å)	σ ² (Å ²)	R _{Ba-O} (Å)	σ ² (Å ²)
0.030	2.662	0.017	2.345	0.008
0.050	2.723	0.017	2.347	0.016
0.100	2.759	0.003	2.346	0.019
	R _{Sm-O} (Å)		R _{Sm-O} (Å)	
0.030	2.671	0.031	2.360	0.020
0.050	2.727	0.031	2.363	0.012
0.100	2.763	0.031	2.362	0.018

References

[1] R.D.Shannon, Acta Cryst. A32, 751(1976)

*ohsato.hitoshi@nitech.ac.jp