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Local structure of perovskite type lanthanum titanium oxynitrides

Yuji Masubuchi[1,*] Daiki Habu[1], Shinichi Kikkawa[1],
Takashi Takeda[2], Kei-ichiro Murai[3], and Akira Yoshiasa[4]
[1]Hokkaido Univ., Sapporo 060-8628, Japan
[2]NIMS, Tsukuba 305-0044, Japan
[3]Tokushima Univ., Tokushima 770-8506, Japan
[4]Kumamoto Univ., Kumamoto 860-8555, Japan

1 Introduction

Perovskite type oxynitrides, $SrTaO_2N$ and $BaTaO_2N$ have attracted much attention because of a report of their superior dielectric properties [1]. We have prepared highly densified $SrTaO_2N$ ceramics by sintering with sintering additive and post-annealing in ammonia [2]. A local ordering of nitride anions in the *cis*-configuration was reported for TaO_4N_2 octahedra in $SrTaO_2N$ [3]. This ordering may affect the dielectric properties of the perovskite oxynitrides.

$LaTiO_2N$ was reported to crystallize in triclinic perovskite having a space group of I-1 [4]. Another report suggested an orthorhombic lattice with Imma [5]. Partial anion ordering has been assumed on $LaTiO_2N$ in the former crystal structure. Solid solution between $LaTiO_2N$ and $SrTiO_3$ changing the O/N ratio will affect the local anion ordering. Dielectric constants estimated from powder mixtures between the oxynitrides and low melting paraffin increased from $LaTiO_2N$ to $La_{0.8}Sr_{0.2}TiO_{2.2}N_{0.8}$.

In this study, the local structure around the Ti cation and oxidation state of Ti in the oxynitride solid solution were investigated by using the X-ray absorption measurement.

2 Experiment

$La_{1-x}Sr_xTiO_{3.5-d}$ (x = 0 or 0.2) oxide precursors obtained by firing mixtures of La_2O_3, $SrCO_3$ and TiO_2 were nitrided under NH_3 flow of 100 mL/min at 980~1100 °C. Crystalline phase was characterized using powder X-ray diffraction for the nitrided products. X-ray absorption spectra of Ti K-edge were measured in transmittance mode at the beam line 9C in Photon Factory, in KEK. The spectra were analyzed using the program REX2000 [6]. Neutron diffraction was performed in Super-HRPD in J-PARC and analyzed by using the software Z-Rietveld.

3 Results and Discussion

The nitrided products were single phase of perovskite. Their chemical composition was measured by using an O/N analysis to be $LaTiO_{2.011(18)}N_{1.017(3)}$ for x=0 and $La_{0.8}Sr_{0.2}TiO_{2.19(1)}N_{0.85(1)}$ for x=0.2, which agreed with the nominal compositions. The lattice parameters of the $LaTiO_2N$ were almost comparable with the reported values in Ref. [4] and which shrunk in the solid solution $La_{0.8}Sr_{0.2}TiO_{2.2}N_{0.8}$. Structural analysis for the $LaTiO_2N$ using the neutron diffraction data suggested the oxynitride crystallized in triclinic perovskite structure having a space group of I-1. The absorption edge position and pre-edge peaks of the Ti K-edge in the oxynitrides did not change significantly by increasing the nitridation temperature or by formation of the solid solution as shown in Fig. 1. Partial anion ordering of the $LaTiO_2N$ may be maintained in the oxynitride solid solution. Further studies on structural refinement and local structure in the oxynitrides will lead to a better understanding of the intrinsic crystal structure of the oxynitrides and their dielectric properties.

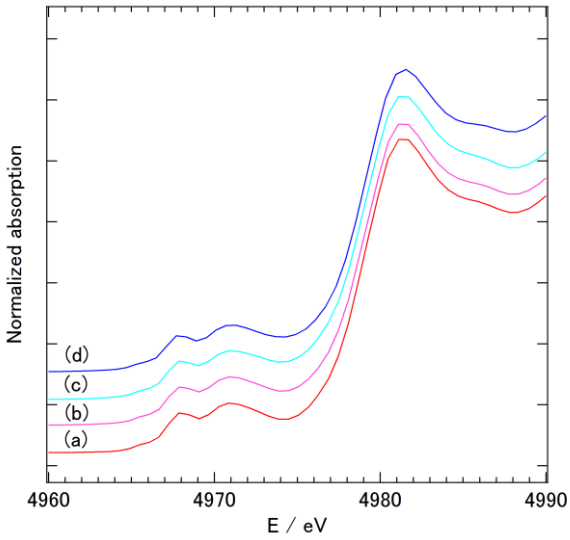

Fig. 1 XANES spectra of the Ti K-edge of the nitrided products $LaTiO_2N$ at 980 °C (a), 1050 °C (b), 1100 °C (c) and $La_{0.8}Sr_{0.2}TiO_{2.2}N_{0.8}$ nitrided at 980 °C (d).

References

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* yuji-mas@eng.hokudai.ac.jp