MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2014B0063 実験課題名 Title of experiment Crystal structure of dielectric oxynitride perovskite: anionic distribution effect & its industrial application 実験責任者名 Name of principal investigator Yuji Masubuchi 所属 Affiliation Hokkaido University	装置責任者 Name of responsible person Shuki Torii 装置名 Name of Instrument/（BL No.） SuperHRPD / BL-08 実施日 Date of Experiment 2014/12/15-2014/12/16

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Name of sample: oxynitride perovskite

Chemical formulae: 1. $LaTiO_2N$ (powder), 2. $La_{0.8}Sr_{0.2}TiO_{2.2}N_{0.8}$ (powder), 3. $SrTaO_2N$ (powder), 4. $SrTaO_2N_{0.9}$ (powder), 5. $Ga_{0.75}Zn_{0.25}N_{0.75}O_{0.25}$ (powder)

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Experimental method:

The oxynitride samples were prepared by nitridation of the oxide precursors under ammonia flow at 950 °C for 20 – 100 h. In order to investigate an effect of the nitrogen release on the crystal structure, $SrTaO_2N$ was heat-treated at 1500 °C under 0.2 MPa of N_2 flow for 3 h. Crystalline phases were confirmed by powder XRD. Chemical compositions of the oxynitrides were analyzed by using both XRF and oxygen/nitrogen analyzer.

Neutron diffraction patterns for the oxynitride samples were measured at room temperature by SuperHRPD. In the measurements, the powders were loaded in a vanadium can and then mounted in the apparatus. The computer program Z-Rietveld was used for the structural refinement.

Results:

Crystal structure of the $LaTiO_2N$ perovskite has been reported in both space groups of orthorhombic Imma and triclinic I-1 (P-1) [1,2]. In the present study, diffraction line splitting observed by using the high resolution powder diffractometer is fitted well by the triclinic cell with space group of I-1.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Figure 1 shows a Rietveld refinement profile for $LaTiO_2N$ by using the structural model with I-1. The refined structural parameters are listed in Table 1. There are three kinds of anionic cites and much amount of nitrogen was observed in O/N2 site. The other two sites were predominantly occupied by oxide ions. Preferred distribution of oxide and nitride ions may be related to the dielectric property of $LaTiO_2N$ as suggested in similar oxynitride perovskite, $SrTaO_2N$ [3]. We also analyzed the crystal structure of $La_{0.8}Sr_{0.2}TiO_{2.2}N_{0.8}$ to investigate the relationship between the O/N ratio and the anionic distribution. The preferred anionic distribution of the oxynitride perovskite resulting from the non-stoichiometric composition has been investigated.

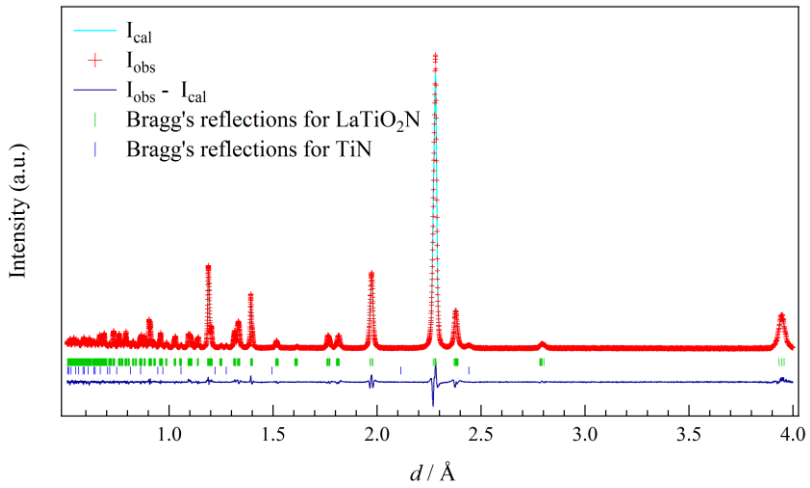

Fig. 1 Rietveld refinement profile for the high resolution neutron powder diffraction data of $LaTiO_2N$ (S.G.; I-1).

Table 1 Structural parameters of the $LaTiO_2N$ refined from the high resolution neutron powder diffraction data. Space group: I-1, (a = 0.56055(1) nm, b = 0.78685(1) nm, c = 0.55742(1) nm, α = 90.205(2) °, β = 90.164(2) °, γ = 89.971(4) °, R_{wp} = 5.88 %, R_e = 2.83 %, S^2 = 4.32).

Atom	site	x	y	z	B / $\times 10^{-2}$ nm^2	Site occupancy
La	4*i*	0.5031(5)	0.2486(5)	0.9993(5)	0.054(6)	1
Ti1	2*a*	0	0	0	0.22(1)	1
Ti2	2*f*	0	0.5	0	0.22(1)	1
O/N1	4*i*	0.4405(6)	0.7482(6)	0.5097(6)	0.41(1)	0.776(4)/0.224
O/N2	4*i*	0.2631(7)	0.0325(7)	0.2460(7)	1.05(3)	0.411(5)/0.589
O/N3	4*i*	0.2619(8)	0.4681(8)	0.7598(8)	0.36(3)	0.814(5)/0.186

References

[1] M. Yashima, M. Saito, H. Nakano, T. Takata, K. Ogisu, K. Domen, *Chem. Comm.*, **46** (2010) 4704-4706.

[2] D. Logvinovich, L. Bocher, D. Sheptyakov, R. Figi, S. G. Ebbinghaus, R. Aguiar, M. H. Aguirre, A. Reller, A. Weidenkaff, *Solid State Sci.*, **11** (2009) 1513-1519.

[3] Y.-R. Zhang, T. Motohashi, Y. Masubuchi, S. Kikkawa, *J. Ceram. Soc. Jpn.*, **119** (2011) 581-586.