MLF Experimental Report	提出日 Date of Report Aug. 15, 2017
課題番号 Project No. 2017A0256 実験課題名 Title of experiment Investigation into the nanoscale fluctuation of the atomic-displacement-type ice state by the PDF analysis 実験責任者名 Name of principal investigator Noriaki Hanasaki 所属 Affiliation Osaka University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） NOVA(BL-21) 実施日 Date of Experiment May 25-29, 2017

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.

*Spinel-type Titanate Oxides $Mg_{1+x}Ti_{2-x}O_4$ (x=0, 0.01, 0.06, 0.125, 0.25, 0.32, and 0.4)

*Powder sample

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 sample ($Mg_{1+x}Ti_{2-x}O_4$) was put in V-Ni cell (6mmϕ-13cm). The neutron powder diffraction was measured in BL21 (NOVA) . In each sample of the composition x, we measured the neutron diffraction at 150K. In x=0.01 and 0.06, we also measured the neutron diffraction at the bottom temperature (BT, 20K) and the room temperature (RT). In these measurements, we used the machine changing the sample automatically. We succeeded in obtaining the diffraction data in all the samples. On the basis of the measured diffraction pattern, we calculated the atomic Pair Distribution Function (PDF). In order to analyze the PDF, we performed the simulation of the PDF by use of the software PDFgui, and obtained the local positions of the Ti, Mg, and O atoms.

Experimental results

According to the previous reports, the $MgTi_2O_4$ undergoes the structural transition from the cubic phase to the tetragonal phase at 260K, which is associated with the Ti-Ti dimerization [1,2]. Figure 1 shows the experimental

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

results of the PDF at 150K and 300K in $Mg_{1.01}Ti_{1.99}O_4$. The dip at the distance r = 2.1A is ascribed to the atomic correlation of the Ti-O pair. The peak at r = 3.0A corresponds to the correlation of the Ti-Ti and O-O pairs. The x-ray diffraction measurement suggests that the structural transition occurs at 220K - 230K in $Mg_{1.01}Ti_{1.99}O_4$. One kind of the distance in the Ti-O pair, Ti-Ti pair, and O-O pair exist in the cubic phase, while there are several kinds of the distances in the these pairs in the tetragonal phase. In the low-temperature tetragonal phase, the peak at r = 3.0A becomes more sharp than the high-temperature cubic phase. This is attributed to the smaller U values of the Debye Waller factors in the Ti and O ions, which accompanies the Ti-Ti dimerization, as compared to the cubic phase. Though there are several kinds of the Ti-O pairs around r = 2.1A, the depth of the dip at r = 2.1A hardly changes owing to the smaller U value of the Ti and O ions.

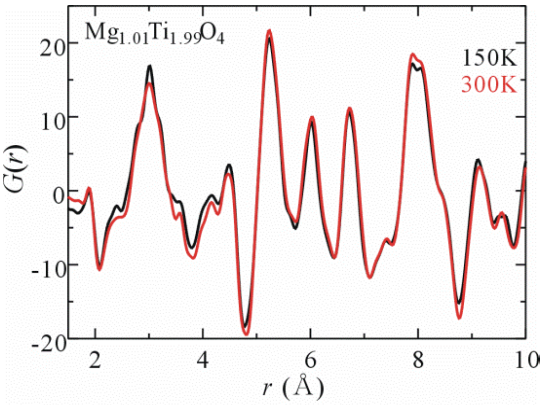

Figure 1 atomic Pair Distribution Function in $Mg_{1.01}Ti_{1.99}O_4$

Figure 2 shows the experimental results of the PDF in $Mg_{1+x}Ti_{2-x}O_4$ (x = 0, 0.01, 0.06, 0.125, 0.25, 0.32, and 0.4) at 150K. Around x = 0.02, the x-ray diffraction suggests the phase transition between the tetragonal phase and the cubic phase. In x=0-0.06, however, the dip at r = 2.1A and the peak at r = 3.0A still remain sharp. No clear change was observed in the PDF in this x range. This suggests the tetragonal short range order exists in x>0.02 in the cubic phase. In x>0.125, the depth of the dip decreases clearly. The height of peak at r = 3.0A also is reduced. The neutron scattering lengths of the Mg and O atoms have a positive sign, while that of the Ti atom has a negative one. Thus, the substitution of the Ti ion with the Mg ion reduces the depth of the dip at r = 2.1A and the height of the peak at r = 3.0A. The detailed PDF analysis reveals the tetragonal local order, which is associated with the ice-type Ti displacement, still exists in x<0.32.

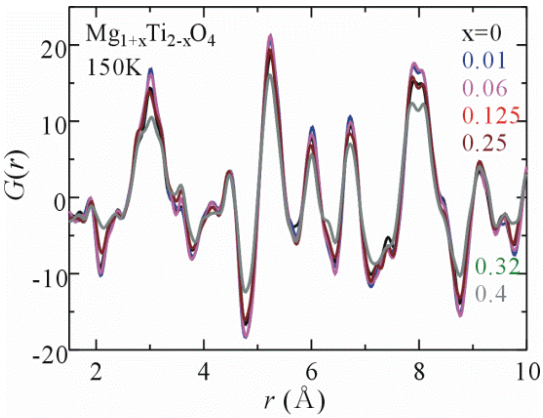

Figure 2 atomic Pair Distribution Function in $Mg_{1+x}Ti_{2-x}O_4$

Reference

[1] M.Isobe *et al.*, *J.Phys.Soc.Jpn.* **71**, 1848 (2002).

[2] M.Schmidt *et al.*, *Phys.Rev.Lett.* **92**, 056402 (2004).