MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2016A0282 実験課題名 Title of experiment Investigation into 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 Dept. of Physics, 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 23 - 26, 2016

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 titanates $Mg_{1+x}Ti_{2-x}O_4$ (x=0, 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 ($Mg_{1+x}Ti_{2-x}O_4$) is put in the V-Ni cell (6mmϕ×13cm). The neutron powder diffraction was measured in BL21 (NOVA). In each sample of the composition x, we measured the diffraction at bottom temperature (BT, ~20K) and room temperature (RT). In x=0, we measured the diffraction at high temperature (450K), as well. 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).

Experimental Results

Figure 1 shows the PDF in x=0 ($MgTi_2O_4$) at BT, RT, and 450K. The dip at the distance r = 2.1A and the peak at r = 3.0A are ascribed to the atomic correlation of the Ti-O atoms, and Ti-Ti and O-O atoms, respectively. The shoulder structure at r = 3.6A comes from the Mg-O atoms. The peaks at r = 4.1-4.5A originates from the O-O atoms. The temperature dependence of the PDF was clearly observed at r = 4.1-4.5A.

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

According to the previous report, the $MgTi_2O_4$ undergoes the structural transition at 260K, which is associated with the Ti-Ti dimerization [1,2]. As a possible origin of the temperature dependence at r = 4.1-4.5A, the Ti-Ti dimerization can change the O position and the O-O correlation.

We performed the PDF analysis in the range r < 10A. When one assumes the cubic phase, we obtained the R_w = 21.8%, 17.3%, and 13.1% at BT, RT, and 450K. In this calculation, the Debye Waller factors are variable. The R_w value at BT is higher than those at RT and 450K. This result is consistent with the fact that the $MgTi_2O_4$ undergoes the structural transition from the cubic phase into the tetragonal phase near 260K. The R_w value at RT is also higher than that at 450K, though the RT is higher than transition temperature (260K). This high R_w value at RT indicates that the short-range fluctuation of the Ti-Ti dimerization exists at the higher temperature than the transition temperature.

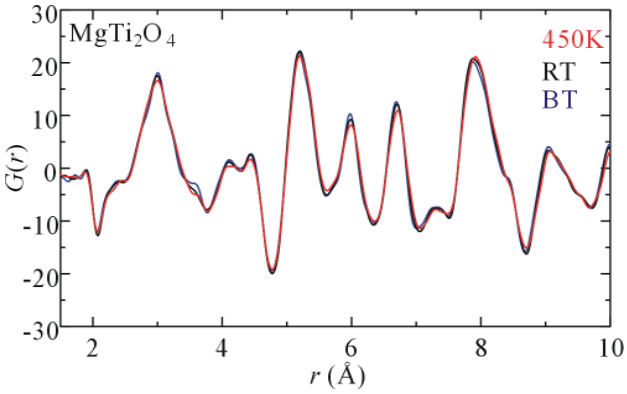

Figure 1 atomic Pair Distribution Function in $MgTi_2O_4$

Figure 2 displayed the PDF at BT in $Mg_{1+x}Ti_{2-x}O_4$ (x=0, 0.125, 0.25, 0.32, and 0.4). In $Mg_{1+x}Ti_{2-x}O_4$, the Ti ions (B sites) are partly substituted with the Mg ions. The absolute value of the signal of Ti-O and Ti-Ti near r = 2.1A and 3.0A is reduced, respectively, since the sign of the neutron scattering length in Mg is different from that in Ti. We also found that the signal of O-O changes with the Mg composition x. The signal feature of O-O in the high Mg-doped sample is similar to that measured at high temperatures in $MgTi_2O_4$. Probably, the Mg doping suppresses the short-range fluctuation of the Ti-Ti dimerization. The detailed analysis is in progress.

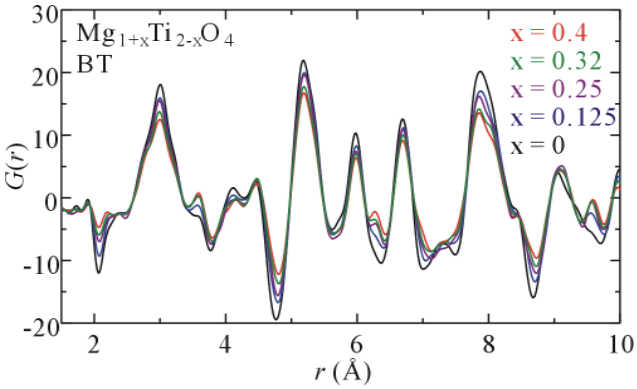

Figure 2 atomic Pair Distribution Function in $Mg_{1+x}Ti_{2-x}O_4$ (x=0, 0.125, 0.25, 0.32, and 0.4)

Reference

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

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