MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2013B0109 実験課題名 Title of experiment Observation of temperature development of "charge glass state" in perovskite oxides by using PDF analysis 実験責任者名 Name of principal investigator Katsuaki Kodama 所属 Affiliation Japan Atomic Energy Agency	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） NOVA (BL21) 実施日 Date of Experiment 2014/3/12-14 2014/4/27-28

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.

Powder sample of $YBaCo_2O_5$ (about 2.6g) and $Pr_{0.55}Ca_{0.45}MnO_3$ (about 3.3g)

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.

$YBaCo_2O_5$ and $Pr_{0.55}Ca_{0.45}MnO_3$ exhibit the structural phase transition at about 220 K and 230 K, respectively. Below their transition temperatures, their compounds are in the charge ordered phases because the unit cell of the former compound includes inequivalent Co sites with the valences of +2 and +3, and the unit cell of the latter includes inequivalent Mn sites with the valences of +3 and +4. However, they exhibit non-metallic electrical conductivity even above their transition temperatures although all Co and Mn sites are equivalent, respectively. These results suggest that the valence electrons of Co and Mn sites are localized with short-range periodicity like a glass in their high temperature phases.

In order to reveal the local lattice distortion caused by short-range charge ordering, we have performed PDF (atomic pair distribution function) analysis on powder neutron diffraction data of $YBaCo_2O_5$ and $Pr_{0.55}Ca_{0.45}MnO_3$ obtained by using NOVA. The diffraction data were collected at 150, 250, 320, 370, and 450 K for $YBaCo_2O_5$, and at 200 and 300 K for $Pr_{0.55}Ca_{0.45}MnO_3$, respectively. Figure 1 shows the diffraction pattern of $YBaCo_2O_5$ at 450 K and the fitting result by using z-Rietveld. In the analysis, the reported

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

tetragonal structure with a space group P4/mmm which includes a single Co site is used. The calculated line almost reproduces the observed diffraction pattern, confirming that the averaged structure at 450 K is the tetragonal with P4/mmm. In Fig. 2, the atomic pair distribution function G(r) obtained at 450 K is shown by open circles. The blue line shows the fitting result using the tetragonal structure with P4/mmm corresponding with the averaged structure. The line almost reproduces the observed data. However, large discrepancy between observed and calculated G(r) is observed in the region below about 3.5 Å as shown in Fig. 3. Red line in the figure shows the fitting result using the orthorhombic structure model with space group Pmma corresponding with the charge ordered phase below 220 K. The fitting is improved and the red line reproduces G(r) below 3.5 Å, suggesting that the local lattice distortion similar to the charge ordered phase with the correlation length of about 3.5 Å exist at 450 K. The atomic distances between Co and O atoms averaged in the two kinds of CoO_5 pyramids are estimated from the above PDF analysis. The averaged distances of Co(1)-O and Co(2)-O are 2.020(4) and 1.936(4) Å, respectively, almost corresponding with the values reported for the charge ordered phase. These results suggest that the valence electrons of Co site are localized with short-range periodicity. Analyses on the data at other temperatures to reveal the temperature development of the local lattice distortion and on the data of $Pr_{0.55}Ca_{0.45}MnO_3$ are in process.