# MLF Experimental Report	提出日 Date of Report 2017/01/25
課題番号 Project No. NO2015A0208 実験課題名 Title of experiment Structural and magnetic studies of the mixed valence alkali sesquioxide Rb_4O_6 実験責任者名 Name of principal investigator Prassides Kosmas 所属 Affiliation WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University	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 2016/06/03 – 2016/06/06

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.

Rubidium sesquioxide, Rb_4O_6

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.

Neutron time-of-flight (TOF) powder diffraction experiments were carried out with the NOVA TOF diffractometer at J-PARC. The structural and magnetic investigations of the mixed valence rubidium sesquioxide, Rb_4O_6, with varying temperature were the prime target of the experiments. The main strategy was to study this material after different cooling protocols and investigate its valence transition, which strongly depends on the cooling protocol employed. Temperature control in the temperature range of 10 – 340 K was attained with a helium cryostat. At first, ultra-slow cooling from room temperature to a base temperature of 10 K with a very slow decreasing rate of 2 K/hour was performed. A high-statistics long scan at 10 K and temperature ramp from 10 to 320 K together with a long scan at 320 K were carried out. The continuously collected datasets were saved in 10-min intervals, which corresponded to a temperature change, $\Delta T = 3$ K. Subsequently, rapid cooling of the sample after warming at 320 K was achieved via direct deep-quenching into a bath of liquid nitrogen (77 K) and subsequent cooling to 10 K inside the cryostat. The same temperature scan from 10 up to 260 K was carried out after rapid cooling. Another temperature scan on cooling with $\Delta T = 4$ K from 340 to 100 K was finally executed. Once the datasets were processed and summed into the desired blocks, Rietveld analysis of the processed neutron diffraction profiles using the FullProf suite was undertaken.

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

The experimental results show that in both cases of ultra-slow cooling and quenching protocols to base temperature (10 K), cubic (space group $I\bar{4}3d$) and tetragonal (space group $I\bar{4}2d$) are present (Fig. 1). The phase fractions of the tetragonal phase were 36% and 31% for ultra-slow cooling and quenching protocols, respectively. The tetragonal phase fraction on heating to 320 K increased to 38%.

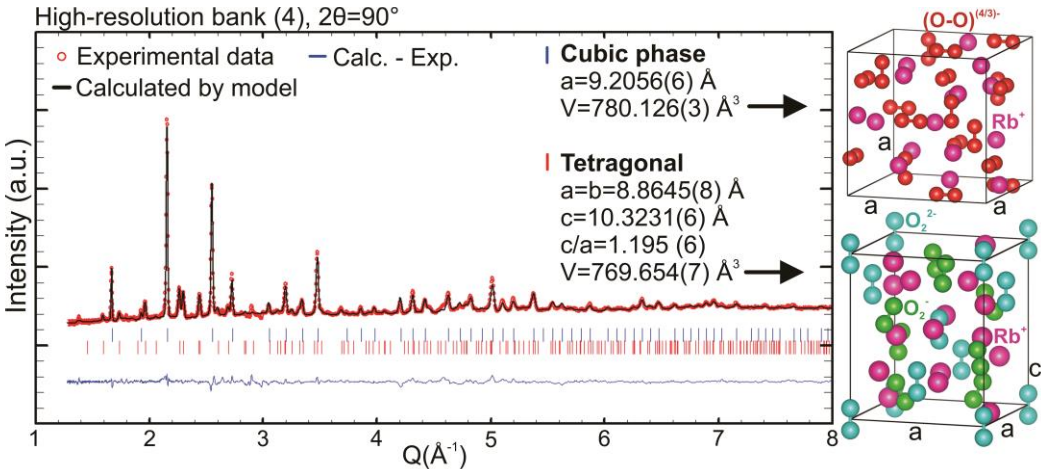

Fig. 1 Representative TOF neutron diffraction pattern obtained at 10 K after either ultra-slow cooling or quenching protocol (left). The crystal structure of the cubic (top) and tetragonal (bottom) Rb_4O_6 phases (right).

Temperature scans on heating in both cases show no new diffraction peaks appearing or disappearing with shifts due to thermal expansion of the crystal lattice. The same stands for the data obtained on cooling. On the other hand, the cooling protocol influences clearly the extent of the transformation. This is connected with cubic-to-tetragonal phase transformation of the sample, and thus to its valence transition, which is seen mainly after ultra-slow cooling (cubic phase: 64%). In the case of the quenching, the analysis showed that the cubic phase is more pronounced (69%). The observation of higher ratio of the cubic phase points out that more sample undertook either valence-delocalization of valence-localization.

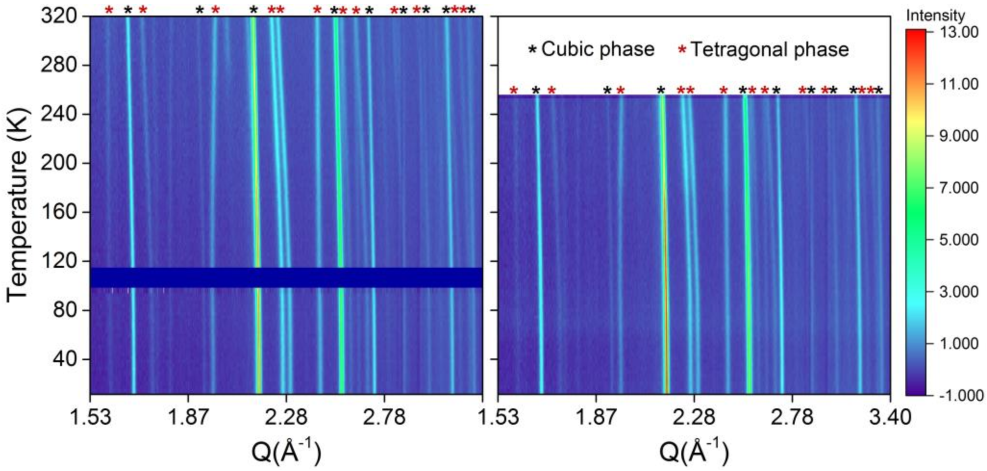

Fig. 2 Temperature response of the diffraction pattern of Rb_4O_6 on warming to 320 K after ultra-slow cooling (left) and quenching protocol up to 260 K (right).

To conclude, we observed clear differences in the evolution of the phase fractions of the two co-existing valence-localised (tetragonal) and valence-delocalised (cubic) phases depending on the cooling protocol type. In addition, no evidence for the existence of magnetic Bragg scattering at low temperatures is present. Detailed analysis of the structural results is in progress.