MLF Experimental Report	提出日 Date of Report 2017/5/29
課題番号 Project No. 2016B0005 実験課題名 Title of experiment Magnetic structure of 12L-perovskites $Ba_4LnMn_3O_{12}$ 実験責任者名 Name of principal investigator Yoshihiro Doi 所属 Affiliation Hokkaido University	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD (BL-08) 実施日 Date of Experiment 3/20-3/26

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.

12L-perovskites $Ba_4LnMn_3O_{12}$ (four powdered samples with Ln = Ce, Pr, Tb, and Ho)

B-site-defect 12L-perovskite $Ba_2La_2ZnW_2O_{12}$ (powdered sample)

Layered oxides $BaSrFe_4O_x$ (two powdered samples with different chemical treatments)

Layered oxides $BaCaFe_4O_x$ (two powdered samples with different chemical treatments)

Melilite-related oxides $Sr_2MnGe_2O_7$ (powdered sample)

Complex oxides with a low-dimensional structure $BaCa_2Mn_6Sb_3O_{18}$ (powdered 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.

(1) 12L-perovskite $Ba_4CeMn_3O_{12}$

In order to determine the crystal structure and magnetic structure of 12L-perovskite $Ba_4CeMn_3O_{12}$, three measurements were carried out at 5 K, 20 K, and room temperature by using the cryostat (5K refrigerator). **Fig. 1** shows the neutron diffraction profile at room temperature. From this data, it is found that $Ba_4CeMn_3O_{12}$ has the 12L-perovskite structure (**Fig. 2**) in which the B site cations Ce and Mn occupy different octahedral sites (CeO_6 octahedron and Mn_3O_{12} trimer) with no structural disordering and oxygen defect. At 8.2 K this compound shows an antiferromagnetic transition due to the long-range magnetic ordering of Mn_3O_{12} trimer having an S = 3/2 spin at low temperatures. However, the profiles collected at 5 and 20 K are almost the same, and any magnetic Bragg peaks were not detected in the 5 K data below T_N. This discrepancy may be due to that the ordered

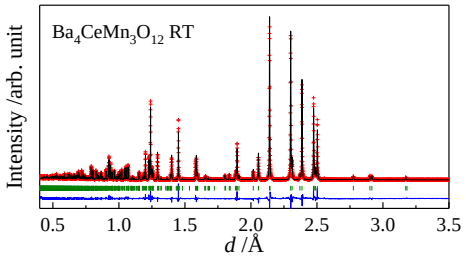

Fig. 1 Neutron diffraction profile of 12L-perovskite $Ba_4CeMn_3O_{12}$.

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

magnetic moment of Mn^{4+} ion is too small. Among three Mn ions in Mn_3O_{12} trimer, there exists a strong antiferromagnetic interaction between adjacent Mn ion, and this cluster behaves as a magnetic cluster with ground state of up-down-up spin state (a net spin is S = 3/2 per cluster). The result of neutron diffraction may indicate that the Mn ions lost its localized spin at low temperatures. In addition, it is considered that the magnetic frustration due to the triangular arrangement of clusters also reduces the ordered moments.

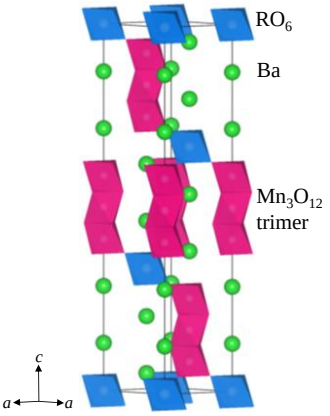

Fig. 2 Crystal structure of 12L-perovskite $Ba_4LnMn_3O_{12}$ (Ln = Ce, Pr, Tb, and Ho).

(2) 12L-perovskite $Ba_4TbMn_3O_{12}$

We have measured the neutron diffraction profiles for the new compound 12L-perovskite $Ba_4TbMn_3O_{12}$ at 5, 20, and 50 K. Form the data at 50 K, it is clarified that this compounds adopts the same 12L-perovskite structure. The $Ba_4TbMn_3O_{12}$ shows a ferrimagnetic transition at 40 K arising from the magnetic interaction between Tb^{4+} ion and Mn_3O_{12} cluster. From the data at lower temperatures, we found the magnetic reflections with k = (0, 0, 0) and analyzed the magnetic structure. The ordered magnetic moments of Tb^{4+} ions are parallel to c-axis with a ferromagnetic arrangement (5.5 μ_B per Tb at 5 K). On the other hand, the magnetic moments of Mn^{4+} ions are not detected in these data, which may be derived from the same reason as $Ba_4CeMn_3O_{12}$.

(3) 12L-perovskites $Ba_4PrMn_3O_{12}$ and $Ba_4HoMn_3O_{12}$

In view of the difficulty in the detection of Mn magnetic reflection in this series of compounds and the low T_N of these two compounds, we have carried out the measurements only at room temperature. From these measurements, we have determined their crystal structures in detail. The Pr compound adopts the same structure as Ce and Tb analogues; however, it is found that the Ho compound has a significant oxygen defect, i.e., the exact chemical formula is $Ba_4HoMn_3O_{12-\delta}$. In this 12L-perovskite structure, there are two crystallographic sites for oxygen ions (O1: edge oxygen in the Mn_3O_{12} trimer; O2: inner oxygen in the trimer). From the Rietveld analysis, it is determined that this defect is equally observed in both sites and total amount δ is ~0.4. This fact may mean that the oxidation state of Mn ions is tetravalent despite the difference in the oxidation state of Ln ions.

(4) B-site-defect 12L-perovskite $Ba_2La_2ZnW_2O_{12}$

In order to determine the detailed crystal structure, we have performed the measurements for seven samples at room temperature. As one of them, we show the result of $Ba_2La_2ZnW_2O_{12}$. This compound also has a 12L-perovskite-related structure and the B-site defect with an ordered arrangement among the vacancy, Zn, and W ions. From the Rietveld analysis of the data, we found new information about this type of compounds: the correct structural model (R–3) against the established model (R–3m) for a long time (1960s ~) and the layered ordering of A site cations (Ba and La). This series of compounds $Ba_2La_2MW_2O_{12}$ (M = transition metals) is attracting attention as new candidates of two-dimensional triangular magnets; thus, we obtained important results to understand their physical properties.