（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI **Experimental Report** J-PARC

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Neutron Diffraction Study of Mn1-xFe2+xO4 under high-pressure
and high-temperature

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装置名 Name of Instrument/（BL No.）
Planet ATSUHIME (BL11)

実施日 Date of Experiment
2017 /1 /23 to 2017 /1 /30

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.

Mixed manganese ferrites having high Curie temperatures and magnetization depending on the composition form an important class of magnetic materials used in many technological application.

Solid solution between Fe_3O_4 to Mn_3O_4 has been paid a large attention in geoscience and material science because of their magnetic and electronic properties. They are the most fundamental ferrite in the industrial materials. Present experiment aims to elucidate magnetic structures and properties of Mn3O4, Mn2FeO4, and MnFe2O4.

sample	Structure	ideal site occupancy	hypothetical magnetism
Mn_3O_4	fct spinel	$(Mn^{2+})[Mn^{3+}Mn^{3+}]O_4$	paramagnetic
Mn_2FeO_4	fct spinel	$(Mn^{2+}_{1-d},Fe^{3+}_{d})[Mn^{3+}_{1+d}Fe^{3+}_{1-d}]O_4$	ferrimagnetic
$MnFe_2O_4$	fcc spinel	$(Mn^{2+}_{1-d},Fe^{3+}_{d})[Mn^{3+}_{d}Fe^{2+}_{d}Fe^{3+}_{2-2d}]O_4$	ferrimagnetic

where d is a composition and acts as the inversion parameter with δ = 0 (1) standing for the inverse (normal) case.Under extreme conditions, high-pressures and/or low temperatures, these properties or structure transformation are extreme significant subject to understand magnetic oxide materials.

Tetragonal spinel structure is characterized by Jahn-Teller (J-T) effect of $Mn^{3+}(3d^4)$ resulting in the distorted structure from cubic spinel structure.

Three powder samples of Mn_3O_4, Mn_2FeO_4 and $MnFe_2O_4$ were prepared at 1300℃ for 48 hours in consideration of the partial pressure of oxygen $PO_2=10^{-3}$ with CO_2 gas flowing apparatus.

All samples listed above can be removed from J-PARC to our institution.

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。）

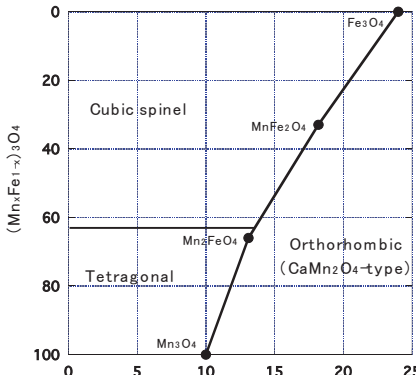
The lattice parameters of the ferrites are a function of Mn-concentration. The unit cell parameter increases with increasing Mn content due to the difference in the ionic radii.

The lattice parameter is also changed with cation ordering in A an B site, which may be attributed to shifting on some Fe^{3+} ions under extreme conditions in spite of same bulk composition.

However, X-ray scattering powers (scattering factor) of these two atoms Fe (atom No 26) and Mn (atomic No. 25) are very similar. Neutron diffraction has an effective investigation for precise diffraction study of these solid solutions because of big difference in the scattering lengths. Mn has a negative coherent scattering length of **-3.73*fm***, which is an extremely rare case in the all elements. On the other hand Fe has **9.54f*m***. By making use of this great advantage, we aim the following two TOF precise powder diffraction studies under high-pressures and high temperatures:

Structure change with pressure

It was clarified by our synchrotron radiation that Mn_2FeO_4 was transformed to orthorhombic $CaMn_2O_4$ type structure at 13 GPa and changed to paramagnetic. The transition pressures of other compounds in the solid solution of Fe_3O_4 – Mn_3O_4 system are Fe_3O_4 (24 GPa), $MnFe_2O_4$ (18.36GPa) and Mn_3O_4 (10GPa).



These solid solutions of $Mn_{3-x}Fe_xO_4$ have a ferrimagnetic property. The Currie temperatures of many of them have been known under ambient pressure: Fe_3O_4 (858K), $MnFe_2O_4$ (563K) and Mn_2FeO_4 (413K) Mn_3O_4 (41.8K). Our present proposal aims the experiments of Mn_2FeO_4.

1. Currie temperature change as a function of pressure by powder diffraction.
2. Magnetic structure under high-pressure condition by diffraction pattern change.
3. Cation ordering or intra crystalline cation exchange by site occupancy test.

Using PLANET at BL-11, neutron powder diffraction experiment of Mn2FeO4 was conducted with increasing temperature up to 1200℃ under high-pressure of 2 GPa and 4 GPa.

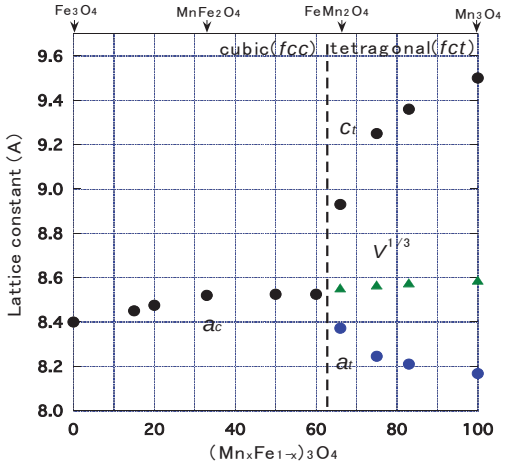
1atm	20℃	tetragonal	ferrimagnetic
2GPa	20℃	tetragonal	ferrimagnetic
	300℃	cubic	paramagnetic
	800℃	cubic	paramagnetic
	1200℃	cubic	paramagnetic
4GPa	20℃	tetragonal	ferrimagnetic
	800℃	cubic	paramagnetic
	1200℃	cubic	paramagnetic

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

II. Pressure dependence Jahn-Teller effect (J-T)

Mn rich phases bearing Mn^{3+}($3d^4$ with $3t_{2g}$ $1e_g$) in the octahedral site produce the lattice distortion by the J-T effect. These phases have a tetragonal structure ($I4_1/amd$ z=4) and have the elongated structure in the direction of the *c* axis with *c/a*>1. We intended the following experiments of Mn_2FeO_4. (At ambient pressure Mn_3O_4 transforms from tetragonal to cubic structure at 1473K with dissolution of the J-T effect.)

Lattice constant of $(MnxFe_{1-x})_3O_4$



Observed lattice constant change of $(MnxFe_{1-x})_3O_4$ due to the Jahn-Teller effect with the content of Mn component is presented at ambient conditions in the left figure. Mn_2FeO_4 in the solid solution is a boundary between cubic (fcc) and tetragonal (fct). The tetragonal phase (fct) transforms to cubic spinel structure at high temperature. The transition temperature of Mn3O4 is known to be 1200℃.

Pressure dependence of Jahn-Teller transition temperature of Mn_2FeO_4.was clarified using PLANET with increasing temperature andchanging pressure.

At 4 GPa

Hysteresis of J-T transition of Mn_2FeO_4（33% Fe3O4）at 4 GPa was detected: With the first heating, tetragonal phase transformed to the cubic structure over 800℃. However, with increasing temperature, it presents a structure transition from tetragonal to cubic structure at120-140℃ and with cooling it recovered to the low-temperature form of the tetragonal phase from the cubic phase at about 120-100℃. The observed structure change indicates a first-order transition having a hysteresis, which implies the local-domain ordering transition rather than electronic spin ordering transition. The high-temperature form of the cubic phase was observed at 1200℃ without decomposition, and after the cooling to room temperature the tetragonal phase was recovered, which indicates the observed transition is a reversible transition.

At 2 GPa

With elevating temperature Mn_2FeO_4 transformed from tetragonal to cubic structure at 160-180℃ and with lowering temperature the latter phase changes back to the former phase at 160-140℃. A small hysteresis was detected. Decomposition of Mn_2FeO_4 to Mn(Fe)O was confirmed over 1200℃. The decomposed phase was gradually grown during cooling. Recrystallization to the original Mn_2FeO_4 phase was not observed at ambient conditions.

Two data sets at 2 GPa and 4 GPa proved the J-T transition du to Mn^{3+} is the first-order transition in Mn bearing oxides. . Ordering probability of the local distorted domains with tetragonal lattice induces the tetragonal –to- cubic transition at high temperature.

At further heating at high temperature Mn-ferrite is decomposed to Mn(Fe)O oxides.

Magnetic structure analyses of ferrimagnetic Mn2FeO4 as a function of pressure and temperature are conducted using program FulProf.