



High-pressure stability relations, crystal structures, and physical properties of perovskite and post-perovskite of NaNiF_3

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ABSTRACT

NaNiF_3 perovskite was found to transform to post-perovskite at 16–18 GPa and 1273–1473 K. The equilibrium transition boundary is expressed as P (GPa) = $-2.0 + 0.014 \times T$ (K). Structure refinements indicated that NaNiF_3 perovskite and post-perovskite have almost regular NiF_6 octahedra consistent with absence of the first-order Jahn–Teller active ions. Both NaNiF_3 perovskite and post-perovskite are insulators. The perovskite underwent a canted antiferromagnetic transition at 156 K, and the post-perovskite antiferromagnetic transition at 22 K. Magnetic exchange interaction of NaNiF_3 post-perovskite is smaller than that of perovskite, reflecting larger distortion of Ni–F–Ni network and lower dimension of octahedral arrangement in post-perovskite than those in perovskite.

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1. Introduction

Recent studies in geoscience indicated that MgSiO_3 perovskite (Pv) transforms to a polymorph with layered structure called “post-perovskite” (pPv) phase at about 125 GPa and 2500 K [1,2]. It is generally accepted that the MgSiO_3 -rich pPv is a dominant phase of the D” layer of the Earth’s lowermost mantle. Because MgSiO_3 pPv is stable at extremely high pressure and unquenchable to ambient condition, several analog materials which are isostructural to the MgSiO_3 pPv and quenchable to ambient conditions have been investigated to obtain insights to the properties of MgSiO_3 pPv [e.g., 3, 4]. The analog materials were, for example, investigated to study lattice preferred orientation of pPv at high pressure [5,6].

The pPv-type structure in ABX_3 has orthorhombic symmetry, and is formed by alternatively stacking up A ion layer and BX_3 cluster layer along the **b**-axis. This BX_3 cluster layer is constructed by BX_6 octahedra which link to neighbor octahedra by edge- and corner-sharing along the **a**- and **c**-axes, respectively.

In material science and condensed matter physics, the pPv-type ABX_3 compounds have interesting physical properties due to quasi-low dimensional lattice. In general, electronic interactions such as electron correlation effects and quantum fluctuation, which are enhanced in lower-dimensional electronic systems

than three-dimensional one, often play a dominant role to cause unique phenomena such as high- T_C superconductivity, Peierls and Mott metal-insulator transitions, and quantum spin system. Recently, the authors reported one-dimensional integer spin magnetic chain for t_{2g} system of pPv-type CaRuO_3 [7]. CaRuO_3 pPv may give important information about Haldane’s conjecture which suggests that ground state of one-dimensional magnetic chain with integer spin is different from that with half-integer spin [8], like Y_2BaNiO_5 with linear corner-shared NiO_6 octahedral chains [9]. Metal-insulator transition has also been observed in the pPv-type $\text{Ca}_{1-x}\text{Na}_x\text{IrO}_3$ [10]. Variable range hopping conduction has been observed in CaRhO_3 pPv [11].

Although further studies on various pPv compounds are needed in both geoscience and materials science, there are only eleven known pPv compounds of oxides and fluorides, among which eight compounds are quenchable, as shown below. In addition, lattice distortion due to the first-order Jahn–Teller active ions may affect anisotropic crystal growth, lattice preferred orientation, and plastic deformation and slip in the pPv compounds. Therefore, it is desirable to find more new pPv compounds. Among fluorides, only two compounds have been known as pPv, NaMgF_3 [12] and NaZnF_3 [13]. The two fluorides are good analog materials for MgSiO_3 , because they exhibit the Pv–pPv transition and have no ions with first-order Jahn–Teller electronic configurations.

This paper reports results of high pressure synthesis of NaNiF_3 pPv, phase relations, crystal structures, and magnetic, dielectric and thermal properties for NaNiF_3 Pv and pPv. To our knowledge,

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NaNiF₃ pPv is the first synthesis of pPv compound with unpaired electrons in only e_g orbitals and no first-order Jahn–Teller electronic configurations.

2. Experimental methods

2.1. High-pressure high-temperature experiments

Starting materials were an equimolar mixture of NaF and NiF₂, and synthesized phases of NaNiF₃ Pv and pPv. Synthesis method of NaNiF₃ Pv is described below. NaF (Wako Pure Chemical Industries, 99.0%) and NiF₂ (Alfa Aesar, 99%) were mixed in 1:1 M ratio in an agate mortar, and the mixture was molded into a pellet. This sample handling was done in an Ar-filled glove box. The pellet was heated at 500 °C for 12 h in Ar gas flow. The product was identified as NaNiF₃ Pv with very small amounts of NiO and NaF by powder X-ray diffraction (XRD) experiments using CrK α radiation (Rigaku, RINT2500V). High pressure–high temperature phase equilibrium experiments were made using a Kawai-type multi-anvil high-pressure apparatus at Gakushuin University. Tungsten carbide anvils with truncated edge length of 2.5 mm were used as second-stage anvils. The starting materials were packed into an Au capsule. The Au capsule was put in the central part of a cylindrical Pt heater which was placed in a pressure-medium of semi-sintered MgO octahedron of 7 mm edge length. A BN sleeve was inserted between the Au capsule and the Pt heater for electrical insulation. A LaCrO₃ sleeve was placed between the Pt heater and the MgO octahedron for thermal insulation. Pressure calibration at room temperature was made by transitions of ZnS (15.6 GPa) [14], GaAs (18.3 GPa) [14] and GaP (23 GPa) [15]. Pressure was further calibrated at 1273 K using phase boundaries of Mg₂SiO₄ olivine – modified spinel transition [16], Mg₂SiO₄ modified spinel – spinel transition [17], and MgSiO₃ ilmenite – Pv transition [18]. Temperature was measured by a Pt–Pt/13%Rh thermocouple, the hot junction of which was positioned in the central part of the Pt heater. Experimental errors for P and T were estimated to be ± 0.3 GPa and ± 30 K, respectively. The sample was held at 12–21.3 GPa and 1273–1523 K for 10–30 min, quenched to room temperature under the pressure, and pressure was slowly reduced to ambient pressure. The recovered samples were examined by using the powder and micro-focus XRD apparatus and a scanning electron microscope (SEM, JEOL JSM-6360) with an energy dispersive X-ray spectrometer (EDX, Oxford Instruments INCA Energy 300).

The sintered samples used for physical property measurements and synchrotron X-ray powder diffraction measurements were synthesized by the multi-anvil high-pressure apparatus. Tungsten carbide anvils with truncated edge length of 5 mm were used. Starting material and the synthesis method were the same as those for the phase equilibrium experiments describe above. The synthesis was made at 15 GPa and 1373 K for NaNiF₃ Pv and at 17 GPa and 1273 K for NaNiF₃ pPv for heating duration of 30 min. It was confirmed that the recovered samples of sintered polycrystalline Pv and pPv were the single-phase materials by the micro-focus XRD measurements.

2.2. Synchrotron X-ray powder diffraction experiments and crystal structure refinements

Synchrotron powder XRD experiments were carried out at SPring-8 BL02-B2 beam line. The XRD data were collected at room temperature (300 K), using a Debye–Scherrer camera in a 2θ range from 3° to 74° with angle resolution of 0.01°. The wavelength of the X-ray was determined as 0.51973 Å by XRD pattern of fluorite-type CeO₂. The polycrystalline NaNiF₃ Pv and

pPv were finely ground in an agate mortar, and each powder was packed in a glass capillary. The X-ray diffraction pattern was taken with rotating the sample along the capillary axis. The obtained XRD patterns were analyzed by Rietveld refinements for NaNiF₃ Pv and by maximum entropy method (MEM)/ Rietveld refinements for NaNiF₃ pPv using RIETAN-FP/VENUS package [19]. The initial crystal structure models of NaNiF₃ Pv and pPv were those of CaRuO₃ Pv and pPv [3], respectively. The site occupancies for all the sites in both NaNiF₃ Pv and pPv were fixed to unity. NaF was included as the second phase in the Rietveld analysis of both the synthesized samples of NaNiF₃ Pv and pPv.

2.3. Measurements of physical properties

The static magnetization measurements were performed by applying external magnetic fields of 0.1 and 50 kOe using a commercial superconducting quantum interference device (SQUID) (MPMS, Quantum Design). The magnetic data were collected with slow warming in a magnetic field after cooling without applying the field (zero-field cooling process, ZFC), and then slow cooling with applying the field (field cooling process, FC). Isothermal magnetization was measured at 2, 150 and 300 K for NaNiF₃ Pv and at 2, 22, 100 and 300 K for NaNiF₃ pPv. The heat capacity measurements were performed using a commercial setup (PPMS, Quantum Design) by a quasi-adiabatic thermal relaxation method without applying the external magnetic field for NaNiF₃ Pv, and with 0 and 70 kOe for NaNiF₃ pPv. The sample pellets of NaNiF₃ Pv (6.07 mg) and pPv (7.02 mg) were used for the magnetic and heat capacity measurements. The size of both the cylindrical samples was about 1.6 mm in diameter and 3.2 mm in height. The dielectric permittivity of the polycrystalline NaNiF₃ pPv (0.84 mm in thickness) was measured by the frequency-response analysis (4284 precision LCR meter, Agilent) at frequencies of 1, 10, 100, 500 and 1000 kHz. Au electrodes were sputtered on both opposite surfaces of the sintered sample pellet, and silver wires were fixed on the electrodes with silver paste.

3. Results and discussion

3.1. Synthesis of pPv-type NaNiF₃ and structural refinements of NaNiF₃ Pv and pPv

The powder XRD pattern of the sample recovered from 17 GPa and 1273 K was different from that of NaNiF₃ Pv and any other known compounds in the system Na–Ni–F, though NaF was observed as the small amount of impurity. On the other hand, the powder XRD pattern of the sample kept at 15 GPa and 1373 K showed that of Pv. This means that structural phase transition occurred between the two pressure (P) temperature (T) conditions. The SEM–EDX analysis indicated that the compound recovered from 17 GPa and 1273 K had Na:Ni atomic ratio of 1.06(5):0.97(3), suggesting the single phase material of NaNiF₃ composition. Fig. 1 indicates a back-scattered electron image of the run product synthesized at 17 GPa and 1273 K. The major grains of the run product have needle-like shape with up to about 0.1 mm length. The color of NaNiF₃ the new phase was green, while that of NaNiF₃ Pv was yellowish green. Most of the peaks of synchrotron XRD pattern of the run product from 17 GPa and 1273 K could be indexed on the basis of the pPv structure. However, 10 weak diffraction peaks (at most 4% in relative intensity) in the synchrotron XRD pattern could not be indexed with any known compounds in the Na–Ni–F system (details are shown in Supporting information). These weak peaks were also observed in the synchrotron XRD pattern of NaNiF₃ Pv. Furthermore, intensities of these weak peaks were changed in

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