Magnetism of the Single Crystal Mg-V-O Spinel

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Abstract. In MgV\textsubscript{2}O\textsubscript{4} with normal spinel structure (AB\textsubscript{2}O\textsubscript{4}), there is magnetic frustration of V\textsuperscript{3+} (3d\textsuperscript{2+}) ions located on B-sites, if an antiferromagnetic interaction among B-site spins is essential for its magnetism. The excess Mg substituted materials such as Mg\textsubscript{1+x}V\textsubscript{2−x}O\textsubscript{4}, may construct isolated magnetic triangular lattices, because some of B-sites forming magnetic tetrahedral lattice are substituted by non-magnetic Mg ions, while the normal spinel MgV\textsubscript{2}O\textsubscript{4} contains tetrahedral magnetic ion networks. Here, we have succeeded in growing single crystals of Mg–V–O system spinel oxide by conventional floating-zone method. The valence numbers and abundance ratio of V ions in the single crystal were estimated by wavelength-dispersive X-ray fluorescence analysis and X-ray photoelectron spectroscopy analysis. Although the composition ratio was Mg:V = 1:2, a small amount of Mg and V ion partly replace each other between A- and B-sites in this crystal. The composition formula is described as (Mg\textsubscript{1−x}V\textsubscript{x})(V\textsubscript{2−x}Mg\textsubscript{x})O\textsubscript{4}. The single crystal shows magnetic transition at around 12 K and large negative antiferromagnetic Weiss temperature about −840 K, and the frustration parameter \( f = 70 \) estimated by those temperatures. This result suggests the existence of strong magnetic frustration in our material.

1. Introduction

Geometrically frustrated spin systems have been merited attention to study those ground states and properties. The spinel compounds have one of the typical crystal structure for geometric frustrated systems, because magnetic ions on B-sites tetrahedral network (pyrochlore lattice) form the three-dimensional geometric frustration spin system, in the case that an antiferromagnetic interaction among B-site spins is essential for its magnetism.

There are reported about varieties of spinel oxide compounds such as MgV\textsubscript{2}O\textsubscript{4}, Mg\textsubscript{1.3}V\textsubscript{1.7}O\textsubscript{4}, and Mg\textsubscript{2}VO\textsubscript{4}, in the Mg–V–O system [1,2]. Especially in MgV\textsubscript{2}O\textsubscript{4} with normal spinel structure, it is known that there is a strong magnetic frustration at V\textsuperscript{3+} (3d\textsuperscript{2+}) ions located on B-sites. This compound shows large negative Weiss temperature around -750 K, and successive phase transitions in a low field. Although the one is a magnetic transition at 65 K accompanied with the cubic-tetragonal structural phase transition, the other is just a magnetic transition at 42 K without any structural modification [3-5]. Moreover, the effect of substitution on A or B sites
such as Li$_x$Mg$_{1-x}$V$_2$O$_4$ ($x = 0$–1) and Mg(V$_{1-x}$Al$_x$)$_2$O$_4$ ($x = 0$–0.25), had been studied. These materials also have normal spinel type structure. According to the previous reports [6], the effect of substitution of Mg$^{2+}$ by Li$^+$ on the A-sites produces a change of the valence number on some of V ions from 3+ to 4+. As a result of variation in Li$_x$Mg$_{1-x}$V$_2$O$_4$, while the successive phase transitions are observed on the magnetic susceptibilities for $0 \leq x < 0.07$, only a broad peak is observed for $0.07 \leq x \leq 0.7$. In $x = 0.8$ and 0.9, there is no sign of phase transition. In this case, the magnetic ions V$^{3+}$ and V$^{4+}$ are located on the whole B-sites.

On the other hand, when some of magnetic V$^{3+}$ ions are substituted by non-magnetic Al$^{3+}$ ions on B-sites [3,4], there is no change for the valence number. The substitution influences exchange interactions between magnetic ions located on the B-sites. In fact, on the magnetic susceptibility of Mg(V$_{1-x}$Al$_x$)$_2$O$_4$ in $x = 0.05$ and 0.15, spin glass behavior is observed instead of successive phase transitions. In addition, it seems that the magnetic frustration remains in these substituted compounds considering the relation between magnetic transition temperature and negative Weiss temperature.

Meanwhile, a Mg substituted Mg–V–O normal spinel oxide is also one of the examples with a different valence number and exchange interactions on the B-sites. Especially, Mg$_{1.3}$V$_{1.7}$O$_4$ with normal spinel type structure, its detail of crystal structure is already reported, contains not only magnetic tetrahedral but some of isolated triangular lattices [2], because some of B-sites forming magnetic tetrahedral lattice are substituted by non-magnetic Mg ions. In this material, V ions take valence number 3+ and 4+. Therefore, the different magnitude exchange interactions are produced between V ions. However, there is no report on magnetic properties for this Mg–V–O system normal spinel oxide. In order to understand the influence of compositive substitution, we have prepared high-quality single crystal grown by a floating zone (FZ) method. In this paper, we report the results of magnetic susceptibility measurements using the FZ single crystals of the frustrated magnet of Mg–V–O spinel.

2. Experiments

Polycrystalline Mg–V–O was synthesized by standard solid-state reaction techniques. The starting materials were MgO (99.9%) and V$_2$O$_3$ (99.9%) powders. We prepared several polycrystalline mixtures with molar ratio of MgO : V$_2$O$_3 = x : 1$ ($x = 1.0$–1.8). The mixed ingredients were formed into a rod with a diameter of 5 mm and pressed by a cold-isostatic press. Then, the rod was sintered at 1000°C for 6 h in a gas flow of Ar (99%) and H$_2$ (1%) at the rates 50 cc/min. The polycrystalline product was revealed to be black. For growing single crystals of Mg–V–O system spinel oxide, we employed a self-flux FZ method using image furnace with two-elliptical mirrors and two 1.5 kW halogen lamps (Model SC2-MDH-11020, NEC Machinery).

This furnace can form smaller molten zones. The length of molten zone was about 4 mm or less. The best condition was mixed Ar (99%) and H$_2$ (1%) 0.5 MPa, and scan speed 35 mm/h. We tried to grow the single crystal on several conditions, thereby we have succeeded in growing of single crystals. Typical dimensions of shaped crystals were $40 \times 3 \times 3$ mm$^3$. Single crystallizing was confirmed by the Laue method. Figure 1 shows a piece of single crystal Mg$_2$V$_4$O$_7$ spinel, and the Laue photograph of a (lil) surface, as shown in Fig 2. The characterization of phases at room temperature was performed by powder X-ray diffraction (XRD) analysis diffractometer using CuKα radiation (MiniFlex2, Rigaku Co.). In order to obtain the composition ratio of Mg and V element, we employed wavelength-dispersive X-ray fluorescence (XRF) analyses (SEA5120A, SHI NanoTechnology Inc.). The valence number of V ion was confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Quantum2000, ALVAC-PHI Inc.). Figure 3 shows a example of the diffraction pattern. The XRD pattern using crushed single crystals shows no impurity peaks. Furthermore, we investigated the structural phase transition between room temperature to 18 K (Ultrace18, Rigaku Co. and Model HC-2, APD CRYOGENICS Inc.). As a result, there is no
change of the crystal structure down to 18 K.
Magnetic susceptibility, AC magnetic susceptibility and DC magnetization measurements were performed on the usual zero-field-cooled (ZFC) and field-cooled (FC) procedures with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL) in the temperature range between 2 and 300 K in a DC magnetic field from 0 to 50 kOe and an AC field amplitude 3.8 Oe, the frequency range from 1 to 1.5 kHz.

3. Results and discussion
From the results of spectral energy distribution in XRF analyses, we made sure the composition ratio of Mg:V = 1.0:2.0. The XPS analyses indicate that the valence number of V ion is 3+ [7]. Moreover, we tried to apply Rietveld analysis for the XRD pattern, and the XRD pattern showed that the crystal structure was the normal spinel structure. From XRD result, we confirmed that single-phase sample was obtained. These XRF, XPS, and XRD results proved the composition formula as Mg$_2$V$_{3+2}$O$_4$. However, the XRD pattern was not completely consistent with the MgV$_2$O$_4$, but almost similar to the pattern of Mg$_{1.3}$V$_{1.7}$O$_4$ [2]. In addition, the intensity ratio of this pattern has no accordance with the Mg$_2$VO$_4$ inverse-spinel type structures. So, it seems
that a part of Mg and V ions replace each other in this material. Therefore, we presumed the improved composition formula as $(\text{Mg}_{1-x}\text{V}_x)(\text{V}_2-x\text{Mg}_x)\text{O}_4$. Rietveld analysis was applied for the XRD pattern in order to refine this composition formula. The best-fitted value of analysis result is $x = 0.08$, namely, $(\text{Mg}_{0.92}\text{V}_{0.08})(\text{V}_{1.92}\text{Mg}_{0.08})\text{O}_4$. There are sixteen equivalent B-sites per a unit-cell at the spinel structure. In the case of $x = 0.08$, it indicates that only one V ion should be substituted. In this partial inverse spinel case, almost all B-sites form magnetic tetrahedral lattices. Thus, the ratio also makes this material induce the magnetic frustration like MgV$_2$O$_4$. In this regard, however, there is a possibility to have effect upon the exchange interaction between A- and B-sites.

The temperature dependence DC magnetic susceptibilities under various fields show in Fig. 4.
The direction of the applied magnetic fields was $\langle 110 \rangle$ in this measurement. The spin-glass like behavior is observed at about $T_g = 12.5$ K. This behavior is similar to the Mg(V$_{0.85}$Al$_{0.15}$)$_2$O$_4$. Figure 5 shows the AC magnetic susceptibility under various frequencies. The real part of AC magnetic susceptibilities show magnetic anomalies at around 12.5 K for all frequency. On the other hand, these anomalies at the imaginary part of one disappear above 233 Hz. However, because the range of error bars is large, we can not come to a decision whether this peak hides in the noise or vanishes at this stage. According to these results, these peaks on ZFC in $\chi_{DC}$ become broad in the higher field and those temperatures in $\chi_{AC}$ depend on the frequency, these anomalies ascribe spin glass transition.

Figure 6 shows the magnetic field dependence of the magnetizations for several temperatures. At 2.0 K, we observed a slight hysteresis in magnetization curve, although the loop did not appear above $T_g$. It seems that this remnant magnetization is caused by freezing spins in spin glass phase. The reason, why this partial inverse spinel shows spin glass behavior, may be explained by its characteristic alignment of V ions. In the case of our partial inverse spinel, some of Mg and V ions are exchanged each other, the normal spinel MgV$_2$O$_4$ reveals Mg(V) ions at A-(B-)sites. According to these results, the exchange interaction between A- and B-sites is produced and probably involves the ferromagnetic interaction. It seems that this complicated interaction brings on spin glass behavior.

Above $T_g$, the magnetic susceptibility seems to obey the Curie-Weiss law with a temperature-independent paramagnetic contribution. We fitted the observed susceptibility at temperatures between 100 and 300 K with the formula, $\chi(T) = \chi_0 + C / (T - \Theta_W)$, where $\chi_0$, $C$, and $\Theta_W$ are the temperature-independent term, the Curie constant and the Weiss temperature, respectively. The best-fitted values of $\chi_0$, $C$, and $\Theta_W$ are $1.8 \times 10^{-5}$ emu/mol V, 0.63 emu-K/mol V, and 820 K, respectively. The frustration parameter $f = 70$ estimated by Weiss temperature suggests the existence of strong magnetic frustration. Assuming $g = 2.0$ and $L = 0$, the Curie constant
reminds of the quantum spin number $S = 0.73$. Thus, this value reminds that the V ions take the valence number 3+ and 4+. However, as a result of XPS, V ions in this material take only 3+. The effective Bohr - magneton $p_{\text{eff}} = 2.25 \mu_B$ is deduced from the Curie constant. This value is smaller than normal spinel MgV$_2$O$_4$ of its. This result suggests that the $g$-value is not 2. It is speculation that the spins on V ions are observed smaller than $S = 1$ by strong magnetic frustration. With increasing magnetic field, at around 60 K, a magnetic anomaly appears in susceptibility. This anomaly can not be observed in low field and the result of X-ray powder diffraction pattern establishes no structural phase transition at around 60 K. However, at this time, we do not have clear description of this transition.

4. Conclusions
Using FZ method, we have succeeded in growing single crystals of ($\text{Mg}_{0.92}\text{V}_{0.08}$)($\text{V}_{1.92}\text{Mg}_{0.08}$)$\text{O}_4$ with normal spinel type structure oxide. The composition ratio was estimated by Rietveld analysis. We found the existence of strong magnetic frustration and observed spin glass behavior. There is no evidence for structural phase transition at $T_g$. To research this question is issue in the future.

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6. References
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