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Antiferromagnetic phase transition in garnet-type $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$

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ABSTRACT

Ferrimagnetism has been extensively studied in garnets, whereas it is rare to find the antiferromagnet. Present work will demonstrate antiferromagnetism in the two Mn–V-garnets. Antiferromagnetic phase transition in $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$ has been found, where the magnetic Mn^{2+} ions locate only on octahedral *A* site. The heat capacity shows sharp peak due to antiferromagnetic order with the Néel temperature $T_N=23.8$ K for $AgCa_2Mn_2V_3O_{12}$ and $T_N=14.2$ K for $NaPb_2Mn_2V_3O_{12}$. The magnetic entropy change over a temperature range 0–50 K is 13.9 J K^{-1} mol-Mn^{2+}-ions^{-1} for $AgCa_2Mn_2V_3O_{12}$ and 13.6 J K^{-1} mol-Mn^{2+}-ions^{-1} for $NaPb_2Mn_2V_3O_{12}$, which are in good agreement with calculated value of Mn^{2+} ion with spin $S=5/2$. The magnetic susceptibility shows the Curie–Weiss behavior over the range 29–350 K. The effective magnetic moment μ_{eff} and the Weiss constant θ are $\mu_{eff}=6.20\ \mu_B$ Mn^{2+}-ion^{-1} and $\theta=-34.1$ K (antiferromagnetic sign) for $AgCa_2Mn_2V_3O_{12}$ and $\mu_{eff}=6.02\ \mu_B$ Mn^{2+}-ion^{-1} and $\theta=-20.8$ K for $NaPb_2Mn_2V_3O_{12}$.

1. Introduction

The garnet-type oxides have been considerable attraction in the field of materials science, for example, $Y_3Fe_5O_{12}$ and its family as magnetic materials, rare-earth-doped $Y_3Al_5O_{12}$ crystals as optical materials, and $R_3Ga_5O_{12}$ (*R*: rare earth) as adiabatic demagnetization refrigeration materials [1–3]. More recently, $Li_6BaLa_2Ta_2O_{12}$, and $Li_7La_3Zr_2O_{12}$ having garnet-related type structure have gained attention as solid-state electrolyte of all solid-state rechargeable batteries because of their good lithium conduction properties [4–8]. On the other hand, garnet-type oxides have been investigated in the field of solid-state physics. In particular, their magnetic properties have been studied in wide aspects both theoretically and experimentally [1,9–15].

Vanadate garnets [16–22] can provide the diluted magnetic system where magnetic ions locate only on *A* site, or non-magnetic system. Recently, we have reported that the V-garnets of $AgCa_2Co_2V_3O_{12}$ and $AgCa_2Ni_2V_3O_{12}$ exhibit the antiferromagnetic phase transition with the Néel temperature $T_N=6.39$ K and $T_N=7.21$ K, respectively [19]. The crystal and magnetic structure have been identified with X-ray [20,21] and neutron powder diffraction studies [22], in our previous reports for $AgCa_2Co_2V_3O_{12}$, $AgCa_2Ni_2V_3O_{12}$, $AgCa_2Mn_2V_3O_{12}$, and $NaPb_2Mn_2V_3O_{12}$. The detailed magnetic and thermal properties have been carried out for $AgCa_2Co_2V_3O_{12}$, and $AgCa_2Ni_2V_3O_{12}$.

In this work, we focus on a systematic experimental study of thermal and magnetic properties of two Mn–V-garnets $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$, which is an extension of our previous works of V-garnets. A lot of studies concerned with ferrimagnetism have been published for many garnets. The antiferromagnetism has not been studied in detailed for the garnets so far, except our previous study [19]. Present work demonstrates an antiferromagnetism in the Mn–V-garnets.

The garnet-type structure has cubic symmetry of the space-group *Ia*-3*d* (no. 230). The general structural formula can be represented as $\{C_3\}[A_2](D_3)O_{12}$, where *C* (the multiplicity and the Wyckoff letter: 24*c*), *A*(16*a*), and *D*(24*d*) sites are the cation sites. The *C*, *A*, and *D* cation sites are surrounded by O^{2-} ions at the dodecahedron, octahedron, and tetrahedron, respectively. Fig. 1 shows crystal structure of $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$ [21]. The structure images were drawn using a computer program VESTA [23]. Ag^+ and Ca^{2+} (or Na^+ and Pb^{2+}), only magnetic Mn^{2+}, and V^{5+} ions occupy the *C*, *A*, and *D* sites, respectively. The structural formula is described as $\{AgCa_2\}[Mn_2](V_3)O_{12}$ and $\{NaPb_2\}[Mn_2](V_3)O_{12}$. The lattice constant $a=12.596(2)$ Å for $AgCa_2Mn_2V_3O_{12}$ is smaller than $a=12.876(2)$ Å for $NaPb_2Mn_2V_3O_{12}$, because the average ionic radius at *C* site is 1.17 Å for $AgCa_2Mn_2V_3O_{12}$ and 1.25 Å for $NaPb_2Mn_2V_3O_{12}$ [24].

2. Experimental methods

Preparation conditions of polycrystalline $AgCa_2M_2V_3O_{12}$ (M=Mn, Zn) and $NaPb_2Mn_2V_3O_{12}$ are reported in Ref. [16,17,21]. Polycrystalline $NaPb_2Zn_2V_3O_{12}$, as an isotypic non-magnetic V-garnet, was also

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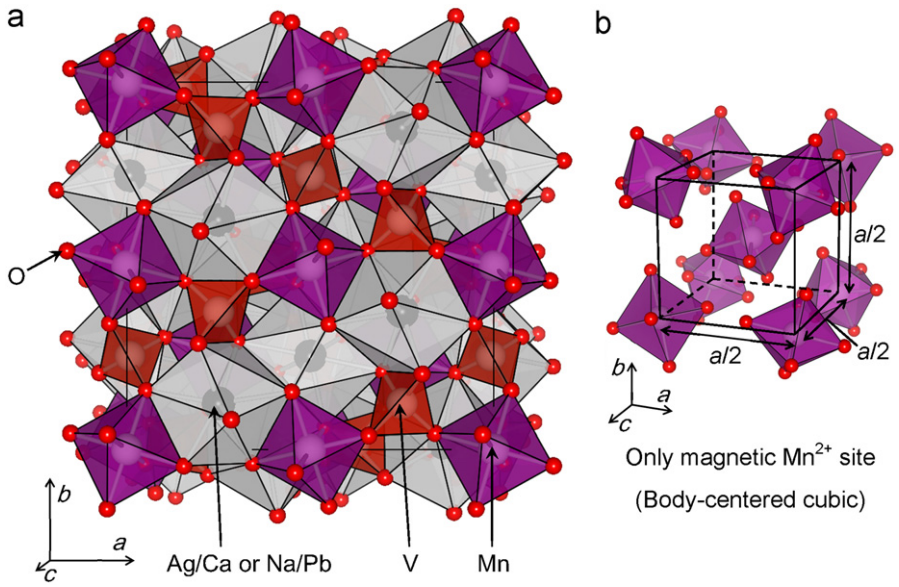

Fig. 1. (a) Crystal structure and (b) only magnetic Mn^{2+} site with body-centered cubic for $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$.

synthesized by solid-state reaction. The starting materials (purity $>99.9\%$) of Na_2CO_3, PbO, ZnO, and V_2O_5 were mixed in the calculated ratio. Mixed powder materials were heated to 1023 K for 24 h. The synthesis results of $NaPb_2Zn_2V_3O_{12}$ are summarized in the supplementary file (Appendix A).

The heat capacity C_P was measured over the range 0.6–60 K in zero-field by a relaxation method using a commercial calorimeter (Quantum Design, PPMS equipped with a heat capacity option). The dc magnetic susceptibility χ was measured over the range 2.0–350 K under zero-field-cooled (ZFC) and field-cooled (FC) conditions using an *rf*-SQUID magnetometer (Quantum Design, MPMS) in an applied field of $H=0.1$ kOe, 5.0 kOe, and 10 kOe.

3. Results and discussion

3.1. Heat capacity

3.1.1. Measured heat capacity

Fig. 2 shows measured heat capacity C_{total} per molar formula-unit as a function of temperature for (a) $AgCa_2M_2V_3O_{12}$ (M=Mn, Zn [19]), and (b) $NaPb_2M_2V_3O_{12}$ (M=Mn, Zn). Mn–V-garnets $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$ exhibit a sharp peak due to the antiferromagnetic phase transition at the Néel temperature of $T_N=23.8$ K and $T_N=14.2$ K, respectively. On the other hand, Zn–V-garnets $AgCa_2Zn_2V_3O_{12}$ and $NaPb_2Zn_2V_3O_{12}$ are non-magnetic.

The measured heat capacity of $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$ exhibits the slight increase with decreasing temperature below about 1.0 K, while the increase is not found in $AgCa_2Zn_2V_3O_{12}$ and $NaPb_2Zn_2V_3O_{12}$. We presumed the increase indicates the tail of the nuclear–spin heat capacity due to the nuclear Zeeman effect of Mn nucleus, discussed below.

The magnetic heat capacity $C_{magnetic}$ of $AgCa_2Mn_2V_3O_{12}$ and $NaPb_2Mn_2V_3O_{12}$ is obtained by means of the subtraction of lattice heat capacity $C_{lattice}$ and nuclear–spin heat capacity $C_{nuclear}$ from the measured heat capacity ($C_{magnetic}=C_{total}-C_{lattice}-C_{nuclear}$).

3.1.2. Lattice heat capacity

The heat capacities of $AgCa_2Zn_2V_3O_{12}$ [19] and $NaPb_2Zn_2V_3O_{12}$ do not exhibit any magnetic anomaly, and then the lattice heat capacity is only observed that ($C_{total}=C_{lattice}$).

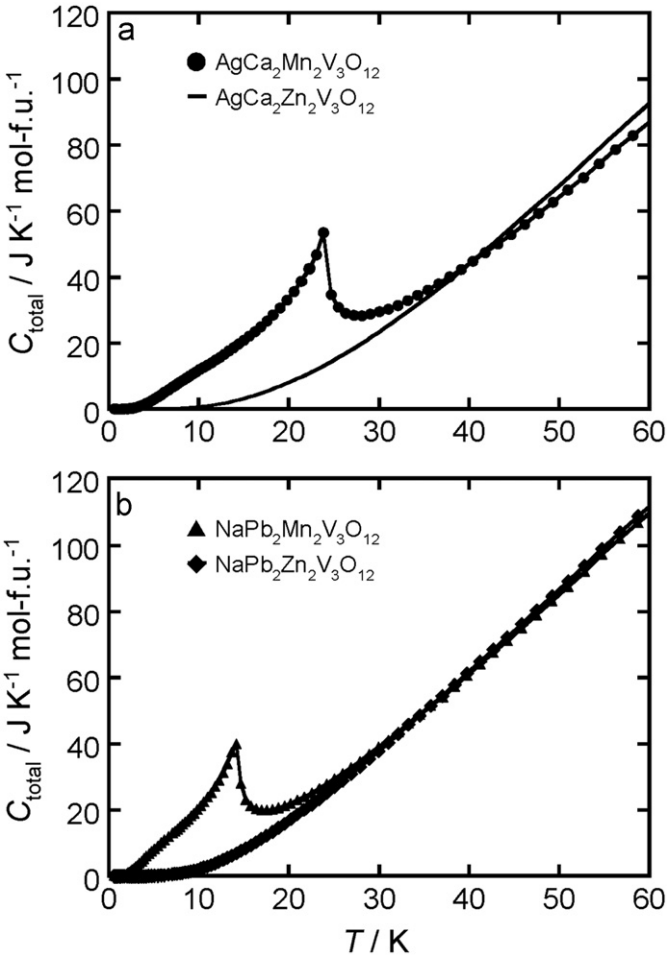

Fig. 2. Heat capacity C_{total} as a function of temperature for (a) $AgCa_2M_2V_3O_{12}$ (M=Mn, Zn [19]) and (b) $NaPb_2M_2V_3O_{12}$ (M=Mn, Zn).

The curve of $NaPb_2Zn_2V_3O_{12}$ in Fig. 2(b) shows only lattice heat capacity, following the Debye T^3 approximation, below 4.2 K.

$$C_{lattice}=\left(\frac{12}{5}\right)\pi^4 N_A k_B r\left(\frac{T}{\Theta_D}\right)^3=1943.8r\left(\frac{T}{\Theta_D}\right)^3, \quad (1)$$