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Magnetism, magnetocaloric and magnetodielectric properties of DyVWO6: a new aeschynite-type polar antiferromagnet

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Abstract

We report magnetic, magnetocaloric and magnetodielectric properties of a new polar magnet DyVWO6 crystallizing in the orthorhombic structure (Pna21). It consists of edge-shared dimers of VO6 and WO6 octahedra, which are connected by corner-sharing to form three-dimensional network structure with Dy3+ cations located in the channels. The ordering of V3+ and W6+ cations in the octahedral sites breaks the inversion symmetry of the parent-CaTa2O6 structure (Pnma). Magnetic and heat capacity measurements show that the V3+ and Dy3+ ions undergo antiferromagnetic transitions at \( T_N^V \approx 5 \, \text{K} \) and \( T_N^{Dy} \approx 2.5 \, \text{K} \), respectively. Isothermal magnetization shows a metamagnetic transition at the applied magnetic field of 1 T at 2 K that corresponds to a transition from the antiferromagnetic (AFM) to ferromagnetic (FM) spin structure. Further, this compound exhibits significant magnetocaloric effect (MCE) with a maximum magnetic entropy change (\( -\Delta S_M^{\text{max}} \)) of 8.45 J Kg\(^{-1}\) K\(^{-1}\) at 7 T. In addition to this, we observe a drop in dielectric constant below \( T_N^V \) with a low temperature dielectric relaxation.

1. Introduction

Polar magnets, magnetic materials with polar space group, are the point of interest in condensed matter research because of their interesting physical properties such as magnetism, ferroelectricity, pyroelectricity, piezoelectricity, multiferroicity, and magnetoelectric effects [1–3]. Notably, in search of multiferroics, the polar magnetic oxides become promising candidates because these materials can define a new class of multiferroics for the following reasons: In polar magnets, polar distortion is driven by chemical or charge ordering of cations and thus stabilizes the polar structure right at the formation temperature of these compounds. Consequently, some of these polar materials shown to be pyroelectric at all temperatures and therefore differ from type-I multiferroics [4–7] which undergo ferroelectric (polar) to paraelectric (nonpolar) transition at high temperatures. Further, a change in polarization occurs at the magnetic ordering temperatures which evidence the magnetoelectric coupling. Though this effect is similar to type-II multiferroics [6–8], the inversion symmetry in the later case is broken by magnetic ordering with complex spin structures resulting from magnetic frustration. In contrast, the polar magnets may not necessarily involve complex magnetic structures and therefore one may achieve magnetoelectric effect at high temperatures in these compounds. There are several compounds that can be classified under polar magnets are Fe2Mo3O8, CaBaCo4O7, GaFeO3, Ni3TeO6, Zn2FeTaO6, double perovskites NaYMnWO6 and NaHoCoWO6 [9–16].

In this line, recently Ghara et al. reported ordered aeschynite-type polar magnets, RFeWO6 (\( R = \) Dy, Eu, Tb, and Y) [17]. It has been shown that these compounds crystallize in polar aeschynite-type structure Pna21 due to chemical ordering of Fe3+ and W6+ cations. RFeWO6 (\( R = \) Dy, Eu, Tb, and Y) exhibit interesting magnetic and magnetoelectric multiferroic properties. Neutron diffraction studies on DyFeWO6 revealed that the magnetic structure (MSG: \( C_{6c} \)) is noncollinear and commensurate with the k-vector (0 \( \frac{1}{2} \), \( \frac{1}{2} \)). This polar magnetic structure induces a change in polarization at the magnetic ordering temperature (\( T_N \sim 18 \, \text{K} \)) demonstrating the magnetoelectric coupling. These exciting findings made the aeschynite family an excellent candidate to design...
new polar magnets and opened up a new avenue for further studies. Later, Kim et al reported a new polar magnetic material YCrWO$_6$ which crystallizes in the polar space group $Pna\overline{2}1$, similar to the $R$FeWO$_6$ family [18]. In a recent study, Ghara et al synthesized another aescynite type compound DyCrWO$_6$ with the same structure [19]. Unlike DyFeWO$_6$, where the Dy and Fe-moments show noncollinear ordering, the Cr$^{3+}$ ions exhibit collinear order while the Dy$^{3+}$ moments remain noncollinear. In contrast to the $R$FeWO$_6$ family, the chromium compound does not show magnetoelectric coupling, and therefore it requires further study to understand the role of magnetic structure in inducing change in polarization at $T_N$. However, the compound DyCrWO$_6$ exhibits interesting magnetodielectric and magnetocaloric effects [19].

Here, we report the structure and magnetic properties of a new ordered aescynite-type polar magnet DyVWO$_6$. This compound also crystallizes in the polar orthorhombic structure with the space group $Pna\overline{2}1$ and exhibits second-order antiferromagnetic transition at $T_N^V\sim 5$ K, and $T_N^{Dy} \sim 2.5$ K. Like DyCrWO$_6$, this compound does not show magnetoelectric properties but exhibits a significant magnetodielectric and magnetocaloric effects.
Polycrystalline DyVWO$_6$ sample was prepared by the conventional solid-state method. Stoichiometric amounts of DyVO$_3$ and WO$_3$ were mixed and heat-treated in evacuated and sealed quartz tube at 1000 °C and 1020 °C with intermittent grindings for 24 h. DyVO$_3$ was prepared by reducing DyVO$_4$ under hydrogen at 1200°C.

This crystal structure is isostructural to the known compounds DyFeWO$_6$, DyCrWO$_6$ and YCrWO$_6$([17](#17),[18](#18),[19](#19)).

| Atom | Site | x     | y     | z     | B$_{iso}$(Å$^2$) |
|------|------|-------|-------|-------|-----------------|
| Dy   | 4a   | 0.0417(1) | 0.4556(3) | 0.2500 | 0.430(3) |
| V    | 4a   | 0.1367(4) | 0.9543(8) | 0.9970 | 0.25(2)  |
| W    | 4a   | 0.3521(1) | 0.4478(3) | 0.0032 | 0.25(2)  |
| O1   | 4a   | 0.9851(13) | 0.7680(3) | 0.0430 | 1.0      |
| O2   | 4a   | 0.5366(13) | 0.2530(3) | 0.9600 | 1.0      |
| O3   | 4a   | 0.1988(13) | 0.6410(3) | 0.0750 | 1.0      |
| O4   | 4a   | 0.2765(13) | 0.1090(3) | 0.9460 | 1.0      |
| O5   | 4a   | 0.1496(12) | 0.0640(2) | 0.2380 | 1.0      |
| O6   | 4a   | 0.1273(12) | 0.8370(2) | 0.7660 | 1.0      |

2. Experimental method

Polycrystalline DyVWO$_6$ sample was prepared by the conventional solid-state method. Stoichiometric amounts of DyVO$_3$ and WO$_3$ were mixed and heat-treated in evacuated and sealed quartz tube at 1000 °C and 1020 °C with intermittent grindings for 24 h. DyVO$_3$ was prepared by reducing DyVO$_4$ under hydrogen at 1200 °C (DyVO$_3$ was prepared by heating the stoichiometric amounts of Dy$_2$O$_3$ and V$_2$O$_5$ at 900 °C for 24 h in the air). Powder x-ray diffraction data were collected at room temperature using a PANalytical Empyrean alpha-1 diffractometer with monochromatized Cu Kα radiation. DC magnetization measurements were carried out in the Physical Property Measurement System (PPMS, Quantum Design, USA) in the temperature range of 2–390 K. Agilent E4980A LCR meter was used for temperature-dependent dielectric measurements. The dielectric and specific heat measurements were carried out in the Physical Property Measurement System (PPMS, Quantum Design, USA).

3. Results and discussion

Figure 1 shows the room temperature powder x-ray diffraction pattern of DyVWO$_6$ after Rietveld refinement([20](#20)) that confirmed the polar orthorhombic structure (Pna2$_1$) rather than the disordered structure (Pnma) related to parent compound CaTa$_2$O$_6$([21](#21)). The detailed structural parameters obtained from the refinement are given in table 1 and the corresponding crystal structure is displayed in figure 2(a). We have fixed the thermal parameters of oxygen, considering its poor x-ray scattering factor. From this figure, it is clear that the crystal structure of DyVWO$_6$ consists of edge-sharing dimers of VO$_6$ and WO$_6$ octahedra, which are connected by corner-sharing and form a three-dimensional framework structure where Dy$^{3+}$ cations (DyO$_6$ polyhedra) are located in the cavities. The cationic size and charge differences make the chemical ordering of V$^{3+}$ and W$^{6+}$ ions in the octahedral environment and break the inversion symmetry to form a polar structure. The edge shared VO$_6$ and WO$_6$ octahedra are shown in figure 2(b) where various V–O and W–O bond distances are also given. This crystal structure is isostructural to the known compounds DyFeWO$_6$, DyCrWO$_6$ and YCrWO$_6$([17](#17),[18](#18),[19](#19)).
Figure 3(a) shows the temperature-dependent DC magnetization of DyVWO₆ measured under 100 Oe in both zero-field cooled (ZFC) and field cooled (FC) conditions. It exhibits antiferromagnetic ordering of V³⁺ ions at $T_N^V \sim 5$ K with a weak ferromagnetism. The anomaly at $T_N^{Dy} \sim 2.5$ K corresponds to antiferromagnetic ordering of Dy³⁺ moments. Small irreversibility between ZFC and FC curves below 2 K indicates canting of Dy spins. The susceptibility data in the temperature range 25–390 K were fitted to the Curie-Weiss (CW) law, $\chi = C/(T - \theta_{CW})$, where $C$ is the Curie constant, and $\theta_{CW}$ is Curie-Weiss temperature. The effective paramagnetic moment obtained from the fit is $\mu_{exp} = 11.16 \mu_B/\text{f.u}$, which is in good agreement with the theoretical magnetic moment for free V³⁺ and Dy³⁺ ($\mu_{cal} = 11.02 \mu_B/\text{f.u}$) ions. The Curie-Weiss temperature is found to be $\theta_{CW} = -6$ K. The negative sign of $\theta_{CW}$ indicates that the dominant magnetic interaction is antiferromagnetic, which could arise from super-super exchange interaction of long-term chains, $V^{3+} - O^{2-} - W^{6+} - O^{2-} - V^{3+}$. Isothermal magnetization curves recorded at different temperatures are shown in figure 3(b). The magnetic moment is 5.7 $\mu_B/\text{f.u}$ at 7 T and 2 K which is not saturated within our experimental limit. At 2 K, DyVWO₆ shows the metamagnetic transition from AFM - FM at the critical field of $\sim 1$ T, which is due to the field-induced change in the Dy³⁺ magnetic sublattice resulting from weak exchange interaction of localized 4f electrons. The metamagnetic transition disappears with increasing temperature and follows the global antiferromagnetic nature of V³⁺ ions with the weak ferromagnetic moment.

Further evidence of long-range antiferromagnetic ordering in DyVWO₆ is revealed from our specific heat ($C_p$) measurements. As shown in figure 4, $C_p(T)$ shows a sharp $\lambda$-shaped anomaly at $T_N = 5$ K, indicating that the V³⁺ ion spins undergo long-range antiferromagnetic ordering. The second anomaly at $\sim 2.5$ K confirms the...
antiferromagnetic ordering of Dy$^{3+}$ spins. Both these anomalies were suppressed as we increase the magnetic field and becomes broad, indicating the destabilization of antiferromagnetic ordering.

Considering the strong magnetic field dependence of magnetization at low temperatures, we have investigated the MCE in DyVWO$_6$. In order to calculate the magnetic entropy change, isothermal magnetization has been recorded in one quadrant from 0–7 T and at different temperatures between 2–60 K and the results are shown in figure 5(a). The gradual evolution of these curves to linear behavior characterizes the increasing paramagnetic contribution above $T_N$. Although giant MCEs were reported at first-order magnetic phase transitions, the use of these materials in applications is limited due to their drawbacks such as hysteretic effects, irreversibility of the effect and poor mechanical stability, etc. To avoid such difficulties, materials exhibiting second-order phase transitions are now considered as a good candidate for magnetocaloric materials.

Before we discuss the MCE, we comment on the nature of the magnetic transition using Arrott plots ($M^2$ versus $H/M$ plots), which are shown in figure 5(b). According to Banerjee criterion [22], a magnetic phase transition can be first order when the slope of the Arrott curves is negative whereas it will be second-order when the slope is positive. As can be seen from the figure, the slope of the Arrott plots at all the temperatures is positive, indicating that the DyVWO$_6$ compound undergoes a second-order magnetic phase transition at $T_N^{Dy}$ and $T_N^{V}$. The negative slope of the Arrott plot at 2 K above 1 T, from inset of figure 5(b), may indicate possible first-order transition from AFM—FM phase transition, which is associated with Dy$^{3+}$ spins.

According to thermodynamics, isothermal magnetic entropy changes associated with magnetic field change is given by:

$$\Delta S_M(T, \Delta H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left( \frac{\partial S(T, H)}{\partial H} \right)_T \, dH$$

Figure 6. (a) Temperature-dependent magnetic entropy change ($-\Delta S_M$) under different magnetic fields obtained from $M$ versus $H$ data. (b) Comparison between magnetic entropy change obtained from both $M$ versus $H$ and heat capacity data, respectively.
From Maxwell’s thermodynamic relation,

\[
\left( \frac{\partial S(T, H)}{\partial H} \right)_T = \left( \frac{\partial M(T, H)}{\partial T} \right)_H
\]

we obtain,

\[
\Delta S_M(T, H) = \int_0^H \left( \frac{\partial M(T, H)}{\partial T} \right)_H dH
\]

Using this equation, we have calculated the isothermal magnetic entropy change at different magnetic fields 5, 10, 20, 30, 40, 50, 60, 70 kOe from \( M \) versus \( H \) data recorded at various temperatures which is shown in figure 6(a). The magnetic entropy change \( \Delta S_M \) increases continuously down to the lowest temperature under 5 kOe. For all other fields, \( \Delta S_M \) curves show a maximum around \( T_N \). The maximum value of \( \Delta S_M \) observed is 8.45 J Kg\(^{-1}\) K\(^{-1}\) at 7 T at 9 K, which is close to that reported for DyCrWO\(_6\) \[19\].

Furthermore, we have calculated the magnetic entropy change from the heat capacity data using the following equation,

\[
\Delta S_M = \int_0^T \frac{C_p(T)}{T} dT
\]

The \( \Delta S_M \) obtained from the heat capacity data is almost comparable to that of \( M \) versus \( H \) data as seen in figure 6(b). Overall, these results demonstrate that DyVWO\(_6\) with second-order magnetic phase transition is a good candidate for the magnetocaloric materials.

Figure 7 shows the temperature variation of dielectric constant and corresponding loss measured at different frequencies and magnetic fields. From the frequency dependence of the dielectric constant and corresponding loss under zero field, as shown in figures 7(a), (b), it is clear that there is a dispersion in \( \varepsilon_r \) and \( \tan\delta \) data throughout the temperature range. This kind of dispersion and frequency dependence indicates the dielectric relaxation present in this material. With lowering temperature, we first see a decreasing trend similar to that observed in normal dielectrics, however, with further decreasing temperature a sudden drop in dielectric constant occurs at the magnetic ordering temperature \( \sim 5 \) K under zero magnetic field suggesting the strong magnetodielectric coupling (see figure 7(c)). This anomaly is suppressed with increasing magnetic field and substantially broadened due to change in the spin structure under applied magnetic fields, as evidenced by magnetization and heat capacity data. Correspondingly, loss data also shows a peak around the magnetic ordering temperature and suppressed with the magnetic field, as seen in figure 7(d).
In order to probe the magnetic field effect on the dielectric response of DyVWO₆, we have recorded isothermal magnetocapacitance at several temperatures including 2, 5, 10, and 50 K. The normalized magnetodielectric (Δε) value shown in figure 8, where we see a positive magnetodielectric effect at 2 K with the highest value of 0.8%. We attribute this effect to the step-like behavior, seen in the M versus H data at 2 K. However, the observed magnetodielectric (Δε) values are both positive and negative which can be due to extrinsic effects such as relaxation present at these temperatures [23]. To check whether the dielectric anomaly corresponds to multiferroicity or not, we have carried the pyrocurrent measurements. We did not see any pyrocurrent anomaly at the magnetic ordering temperatures within our experimental limit of 0.1 pA. It is possible that the electric polarization is very weak that could not be detected in our measurement or the magnetic structure is such that there is a weak/no coupling between the spin and lattice similar to that reported for DyCrWO₆ [19].

4. Conclusion

We have investigated magnetic and magnetoelectric properties of a new aeschynite-type polar antiferromagnet DyVWO₆ prepared by the conventional solid-state route. This compound crystallizes in the polar orthorhombic structure with space group Pna₂₁. It exhibits long-range antiferromagnetic ordering of V³⁺ ions at \(T_N = 5\) K and a metamagnetic transition at the critical field of \(\sim 1\) T below the Dy³⁺ ions ordering \(\sim 2.5\) K. DyVWO₆ with second-order magnetic phase transition shows the significant magnetocaloric effect at low temperatures. In addition, we have observed a strong magnetodielectric effect around \(T_N\) and relaxation effects.

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