Large magnetoelectric coupling in Co₄Nb₂O₉

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Magnetoelectric materials which simultaneously exhibit electric polarization and magnetism have attracted more and more attention due to their novel physical properties and promising applications for next-generation devices. Exploring new materials with outstanding magnetoelectric performance, especially the manipulation of magnetization by electric field, is of great importance. Here, we demonstrate the cross-coupling between magnetic and electric orders in polycrystalline Co₄Nb₂O₉, in which not only magnetic-field-induced electric polarization but also electric field control of magnetism is observed. These results reveal rich physical phenomenon and potential applications in this compound.

Spin-based electronics combining charge and spin degree of freedom is expected to dominate the next-generation technology that overcomes various difficulties in the conventional charge-based electronic device¹–². Acting as an important technique, magnetization manipulated by current has been extensively investigated in metallic and semiconducting materials³–⁵. However, current flow, more or less accompanies energy dissipation, and in this context, insulating materials in which magnetization can be controlled by electric field without major current flow would be fascinating and highly desired. Single-phase magnetoelectric (ME) materials are promising candidates for such an operation by fully exploiting their cross-control of magnetism and polarization⁶–⁷. To attain giant ME coupling in such materials, the electric polarization would be preferably induced by magnetic order⁸. Along this line, type-II multiferroics, in which polarization exists only in a magnetically ordered state and is caused by a particular type of magnetic structure, satisfy the requirement well⁹. Since Tokura et al. published the pioneering work on the large ME effect in TbMnO₃⁹, a great number of type-II multiferroics have been reported these years, such as CuO, hexaferrites, GdFeO₃, CaMnO₁₂, etc¹⁰–¹³. So far as we know, magnetic field control of polarization have been widely exploited in the past decades⁹–¹⁶, however, to the contrary, electric manipulation of magnetism is still quite rarely reported¹²–¹⁷–¹⁹. As mentioned above, electric control of magnetization is expected to play an important role in future technological applications, such as electrical write and magnetic read devices, ME random access memories, and so on²⁰,²¹. Therefore, exploration of materials with large ME coupling, especially the effect of electric control of magnetism is of primary importance. Besides type-II multiferroics, large coupling between magnetization and electric polarization can be realized in another kind of materials with a different form—the linear ME effects. This effect was first investigated in the 1960s and a revival of it is observed recently since large linear ME effects have been obtained in many systems, such as Cr₂O₃, MnTiO₃, Ni₀.₄Mn₀.₆TiO₃, NdCrTiO₅, etc¹⁹,²²–²⁶. Similar to magnetically induced ferroelectricity, this effect occurs in antiferromagnets with broken inversion symmetry as well. At ground state, the electric polarization in these ME materials is zero. However, with increasing magnetic field, the polarization would be developed and increase in intensity, showing a linear ME effect²⁷. Besides these materials, Co₄Nb₂O₉, which is a collinear antiferromagnet and possesses a magnetic point ₃m²⁸, is expected to be a promising candidate as a linear ME material from the viewpoint of magnetic symmetry. According to the earlier report by Kolodiazhnyi et al, a dielectric peak is observed in Co₄Nb₂O₉ near the antiferromagnetic phase transition temperature on the condition that an external magnetic field (>12 kOe) is applied. After excluding some possible origin, the authors contribute the giant magnetodielectric effect in Co₄Nb₂O₉ to magnetically-driven spin-flop phase transition. In general, an anomaly in dielectric constant may indicate a sudden change of electric polarization, such as onset or rotation. Therefore, it is very necessary to study the magnetic-field-induced polarization and ME effect in this compound. In this manuscript, we prepare a polycrystalline Co₄Nb₂O₉ and investigate its magnetic and electric...
into a saturated spin-flip state 30. Fig. 3(b) plots the variation of magnetization as a function of external magnetic field for Co₄Nb₂O₉ at 4 K. A change of slope is observed and no sign of saturation is found until the magnetic field reaches up to 60 kOe. As shown in the inset of Fig. 3(b), a field of about 15.7 kOe can be regarded as the critical field to induce the spin flop transition in Co₄Nb₂O₉, which is evidence by the anomaly in magnetic susceptibilities 31. Recently, the magnetic induced polarization related to spin-flop phase has been reported in some linear ME materials, such as Cr₂O₃, MnTiO₃, etc. 19,32. Therefore, it is necessary to investigate the electric polarization in the spin-flop phase of Co₄Nb₂O₉.

Magnetic field control of electric polarization. In order to confirm the existence of magnetic induced polarization in Co₄Nb₂O₉, we carry out the measurement of pyroelectric current, which is collected under various magnetic fields. Before the measurement, ME cooling from 70 to 10 K with an electric field of 667 kV/m and a magnetic field of 20, 40 and 70 kOe is applied on the sample. Then the pyroelectric current is recorded with increasing temperature at different external magnetic fields. As shown in Fig. 4, no signal of pyroelectric current is observed at zero magnetic fields. However, in the presence of external magnetic field, the pyroelectric current develops in a temperature interval related to the antiferromagnetic phase transition and the peak values of it increase in intensity with increasing magnetic fields. The inset of Fig. 4 shows the change in sign of pyroelectric current at 70 kOe as a function of temperature with positive and negative poling electric field of 667 kV/m, respectively. A rather symmetric temperature dependence of pyroelectric current curve is observed, indicating that the electric polarization can be reversed by electric
field. This result further shows that the electric polarization behavior is dependent on the ME cooling history, which is similar to other linear ME materials.

The temperature dependence of electric polarization, which is obtained by integration of pyroelectric current with respect to time, is shown in Fig. 5. It is obvious that no spontaneous electric polarization was observed in Co$_4$Nb$_2$O$_9$ without the external magnetic field. However, a magnetic-field-induced polarization of 30 $\mu$C/m$^2$ is observed at 10 K with a field of 20 kOe and the induced polarization increases with the increase of applied magnetic field. As shown in the inset of Fig. 5, polarization increases proportionally with increasing magnetic field, showing a linear ME effects. The ME susceptibility $\gamma_{ME} (\gamma_{ME} = P(H) - P(0))$ reaches up to 18.4 ps/m at 70 kOe, which is comparable to the reported linear ME materials, such as MnTiO$_3$ (2.6 ps/m)$^{23}$, NdCrTiO$_5$ (0.51 ps/m)$^{26}$, indicating a large ME coupling in Co$_4$Nb$_2$O$_9$. It is worth noting that the onset temperature of polarization is consistent with the magnetic ordering temperature of 28 K, suggesting the inherent coupling between the magnetic and electric orders in Co$_4$Nb$_2$O$_9$.

**Electric field manipulation of magnetization.** For further characterizing the cross-coupling between magnetism and electric polarization, the thermomagnetic curves of Co$_4$Nb$_2$O$_9$ are measured at 0.1 kOe and selected electric fields (0, 1, 2 MV/m). Before the measurement, a ME cooling is performed under 40 kOe ($H \gg H_C$) and 1 MV/m in order to ensure the same initial magnetization and electric polarization states of the sample. As shown in Fig. 6(a), the thermomagnetic curves show similar behavior under different electric fields while the magnetization increases remarkably with increasing electric field below 28 K, indicating the manipulation of electric field on magnetization. It is worth noting that the magnetization above $T_N$ keeps unchanged with applied electric field, which is ascribed to the disappearance of polarization. The change of magnetization at different electric fields is defined as $\Delta M = M(E) - M(0\, V)$, which is shown in Fig. 6(b). It is obvious that it increases with decreasing temperature and reaches up to the maximum values of 1.7, 3.3 memu/g at 10 K under 1 and 2 MV/m, respectively. Moreover, Fig. 6(c) shows the time dependence of magnetization under a square wave electric field of 2 MV/m. It is obvious that magnetization decreases or increases with removing or applying electric fields, respectively, indicating a stable response to the electric fields, which further demonstrates the modulation of electric field on magnetization in Co$_4$Nb$_2$O$_9$.

**Discussion**

It is known that Co$_4$Nb$_2$O$_9$ has the same spin configuration as that of Cr$_2$O$_3$, which is a time-honored ME material$^{19}$. According to the earlier reports about Cr$_2$O$_3$, it exhibits spin-flop transition and ferroelectricity provided that a high-enough magnetic field is applied$^{19,33,34}$. The neutron scattering result indicates that, below...
polarization can be induced below $T_N$, a staggered magnetization is observed in Cr$_2$O$_3$ in the presence of external magnetic field. Furthermore, the temperature where staggered magnetization occurs is just the onset temperature of ferroelectricity. Based on these results, Kimura et al. argued that the in-field ferroelectricity in Cr$_2$O$_3$ would be attributed to this special magnetic order, staggered magnetization as for Co$_4$Nb$_2$O$_9$, besides the same crystal and magnetic structures as those of Cr$_2$O$_3$, it also shows the spin-flop-induced electric polarization and cross-coupling between polarization and magnetization. Therefore, it is reasonable to ascribe polarization in Co$_4$Nb$_2$O$_9$ to the formation of the magnetic induced spin-flop phase.

Due to the inherent coupling between magnetic and electric orders, changing external magnetic field would modify the spin configuration and the magnitude of polarization, showing the manipulation of magnetic field on polarization. As for the effect of electric field on magnetization, it can be understood as follows: after ME cooling, the polarization can be induced below $T_N$ and an applied electric field would make the net polarization arrange in its direction. Since the magnetism and polarization have the same spin origin, the rearrangement of electric polarization caused by electric field would lead to the rotation of antiferromagnetic regions, and as a consequence, showing the effect of electric field control of magnetization.

In order to understand the linear ME effect in Co$_4$Nb$_2$O$_9$, we can turn to the Ginzburg-Landau expansion of the free energy in terms of electric and magnetic fields ($\mathcal{E}$ and $\mathcal{H}$):

$$F(\mathcal{E}, \mathcal{H}) = F_0 - P_0^i E_i - M_0^i H_i - \frac{1}{2} \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \ldots$$

(1)

Where $\mathcal{E}^S$ and $\mathcal{H}^S$ denote the spontaneous electric polarization and magnetization, whereas, $\epsilon$ and $\mu$ are the electric and magnetic susceptibilities. Differentiation with respect to the electric fields leads to electric polarization:

$$P_i(\mathcal{E}, \mathcal{H}) = -\frac{\partial F}{\partial E_i} = P_0^i + \epsilon_{ij} E_j + \alpha_{ij} H_j + \ldots$$

(2)

The tensor $\alpha$ corresponds to the induction of electric polarization by a magnetic field. In the case of Co$_4$Nb$_2$O$_9$, the spontaneous electric polarization is zero at ground state and a magnetic field can induce a finite electric polarization, which increases with increasing field, indicating a linear ME effect.

In conclusion, we have performed detail measurements on ME properties of polycrystalline Co$_4$Nb$_2$O$_9$. The experimental results reveal that no spontaneous polarization arises below $T_N$ unless a high enough magnetic field is applied. The polarization increases proportionally with the applied magnetic field, showing a linear ME effects. Different from most reported ME materials, an effect of electric control magnetization is observed in this compound. The attractive cross-control between electric polarization and magnetism in Co$_4$Nb$_2$O$_9$ demonstrates an avenue for next generation and low-energy consumption spintronics.

**Methods**

**Sample preparation.** Polycrystalline sample of Co$_4$Nb$_2$O$_9$ was prepared by solid state reaction method. The stoichiometric mixtures of pure Co$_3$O$_4$ and Nb$_2$O$_5$ were well ground and annealed at 1173 K for 10 h in muffle furnace. The resulting powders were then pressed into pellets with a 12 mm diameter under 40 MPa. Finally, the pellets were sintered in air at 1373 K for 5 h followed by cooling down to room temperature. The structure of as-prepared sample was checked using X-ray diffraction (XRD, Bruker Corporation) equipped with Cu Kα radiation at room temperature. The resistivity of Co$_4$Nb$_2$O$_9$ at room temperature exceeds 6 x 10$^9$ Ω cm, which is high enough to support an electric field and ensures the ME measurements.

**Magnetic and electric measurements.** Magnetic properties were measured by superconducting quantum interference device (SQUID, Quantum Design) magnetometer with applied magnetic fields of 0.1, 1, 10, 20, 30 kOe, respectively. As-prepared sample was polished into a thin disk of 0.3 mm in thickness and Au electrodes were sputtered on both sides for electric measurements, which were carried out by Physical Property Measurement System (PPMS, Quantum Design). Pyroelectric current was collected using an electrometer (Keithley 6514A) after poling the sample in an electric field. In detail, the sample was first submitted to the PPMS and cooled down to 70 K. Then a poling electric field of 667 kV/m was applied on the sample with temperature decreasing from 70 to 10 K. In order to release any charges accumulated on the sample surfaces or inside the sample, the sample was short-circuited for long-enough time. During the recording of pyroelectric current, the sample was heated slowly at a warming rate of 3 K/min. Noted that the magnetic field was applied throughout the cooling and warming processes. After ME cooling (1 MV/m, 40 kOe) the sample from 40 to 10 K, the temperature dependence of magnetization was measured under 0.1 kOe with selected electric fields (0, 1, and 2 MV/m). For further investigating the response of magnetization to electric field, the variation of magnetization as a function of a periodic electric field was also measured.

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**Author contributions**

Experiments were designed by Y.F. and D.H.W. and carried out by Y.F., W.P.Z., R.Z., R.J.T., H.Y. and L.Y.L. The date were collected by Y.F. Results were analyzed and interpreted by Y.F., Y.Q.S., S.G.Y., D.H.W., Q.Q.C. and Y.W.D. The manuscript was written by Y.F. and D.H.W. D.H.W. and Y.F. are responsible for project direction, planning and infrastructure.

**Additional information**

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