Single crystal growth of Mn₄Nb₂O₉ and its structure-magnetic coupling

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A single crystal of Mn₄Nb₂O₉ of about 8 mm in diameter and 30 mm in length was successfully grown by a newly designed one-step method based on the optical floating zone technique. Clear Laue spots and sharp XRD Bragg reflections attest the good crystal quality. The antiferromagnetic phase transition at $T_N = 108.4$ K of the Mn₄Nb₂O₉ single crystal was observed along the $c$ axis, which contrasts with Co₄Nb₂O₉ belonging to the same structural family. Structural changes with $a$-axis shrinkage and $c$-axis expansion at $T_N$ demonstrate a significant and anisotropic magnetostriction effect.

Introduction

Recently, $A_4B_2O_9$ ($A =$ Co, Mn, $B =$ Nb, Ta) have attracted more attention due to their spin flop phase transition, magnetodielectric effect, and magnetoelectric effect. Mn₄Nb₂O₉ was first prepared and studied by Bertaut et al. X-ray diffraction (XRD) studies showed that Mn₄Nb₂O₉ possesses a trigonal crystal structure (space group $P3c1$) with two formula units per cell. The magnetic structure of Mn₄Nb₂O₉ has also been reported by Bertaut et al. and further confirmed by Schwarz et al. According to the results of neutron diffraction, below Néel temperature (about 125 K), Mn spins order along the $c$ axis and form chains along the lines $1 \frac{1}{3} z$ (spins) and $1 \frac{2}{3} z$ (−spins) with antiparallel inter-chain coupling.

Experimental details

Polycrystalline Mn₄Nb₂O₉ decomposes easily, so that it is difficult to synthesize by conventional solid-state reaction technique. Here, a one-step method based on the optical floating zone technique was designed to grow the single crystal of Mn₄Nb₂O₉. The stoichiometric mixtures of Nb₂O₅ (99.99% @ Alfa Aesar) and MnCO₃ (99.9% @ Alfa Aesar) powders were well grounded and calcined at a temperature of 900 °C for 6 h under the protection of Ar gas flow. The milled pre-sintered material (that is a mixture of MnNb₂O₆ and MnO₄ confirmed by XRD) was isostatically pressed into a cylindrical shape of 70 mm length and 8 mm diameter at 70 MPa and sintered at 1100 °C at a rate of 2 °C min⁻¹ for 12 h. Single crystal of Mn₄Nb₂O₉ was then successfully grown in an optical floating zone furnace (FZ-T-10000-H-VI-P-SH, Crystal Systems Corp.) with 4 × 1000 W halogen lamps installed as infrared radiation sources by using the rod of the above prepared mixture. The temperature of the molten zone focused by mirrors was...
precisely controlled by adjusting the power of the lamps. During the growth, the molten zone was moved upwards at a rate of 5 mm h\(^{-1}\), with the seed rod (lower shaft) and the feed rod (upper shaft) counter rotating at 30 rpm in Ar gas flow by 4 L min\(^{-1}\). A single crystal of Mn\(_4\)Nb\(_2\)O\(_9\) of about 8 mm in diameter and 30 mm in length with black shining surface was obtained, as shown in Fig. 1a. The room temperature crystal structure was characterized by XRD (XRD, D/max2200) using Cu K\(_\alpha\) radiation. Low temperature XRD data were collected with a high accuracy home-made Bragg–Brentano diffractometer equipped with a copper source monochromatic radiation \(\lambda = 1.54056\) Å issued from a 18 kW Rigaku rotating anode, from 90 K to 900 K under air atmosphere by using a cryofurnace and a furnace with an accuracy better than 0.1 K and 2 K, respectively. Variation of temperature steps is 5 K from 90 K to 150 K. The step is 0.02\(^{\circ}\) and integration time is 4 s, respectively. Crystallographic orientation was determined by using back-reflection Laue X-ray photography with tungsten target (with the X-ray beam of 0.5 mm in diameter) and additionally confirmed by standard XRD. Measurements of the magnetization were conducted using a Physical Property Measurement System (PPMS-9, Quantum Design Inc.) with Vibrating Sample Magnetometer (VSM) option. The temperature and magnetic field increasing/decreasing rates are 1.5 K min\(^{-1}\) and 0.01 T s\(^{-1}\), respectively. The temperature and magnetic field ranges are 2–400 K and –9 to 9 T, respectively. The sensitivity of the VSM is 10\(^{-9}\) A m\(^2\).

**Results and discussion**

Rietveld method\(^a\) as implemented in the FullProf program\(^b\) was used for the refinement of the structure parameters, based on the powder (ground single crystal by agate mortar) XRD data of Mn\(_4\)Nb\(_2\)O\(_9\) as shown in Fig. 1b. The powder diffraction patterns can be assigned to a single-phase corundum trigonal crystal structure\(^1\) with P\(_3\)\(_3\)c1 space group which is similar to that of Co\(_4\)Nb\(_2\)O\(_9\).\(^5,7\)\(^\text{a}\) The lattice parameters obtained are \(a = b = 5.32449\pm 0.00016\) Å and \(c = 14.32222\pm 0.00043\) Å. The unit cell of Mn\(_4\)Nb\(_2\)O\(_9\) is thus larger than that of Co\(_4\)Nb\(_2\)O\(_9\) and this is due to the slightly larger ionic radius of Mn\(^{2+}\) with respect to that of Co\(^{2+}\).
Mn$_4$Nb$_2$O$_9$ given by Bertaut et al.$^3$ where Mn spins align to the $c$ axis and form chains along the lines $\frac{1}{3} z$ (+spins) and $\frac{2}{3} z$ (−spins) with antiparallel inter-chain coupling can be thus used to explain the magnetic measurements of Mn$_4$Nb$_2$O$_9$.

To reveal the occurrence of the spin flop in Mn$_4$Nb$_2$O$_9$ single crystal, we further measured magnetization curves under a strong external field ($H = 7$ T) along $c$ axis. As shown in Fig. 3b, the behavior is different from Co$_4$Nb$_2$O$_9$ as $M_c(T)$ here shows no change with comparison to $M_c(T)$ measurement under a field of $H = 0.01$ T. This demonstrates that the spin flop does not occur along $c$ axis even though the applied magnetic field is up to 7 T.

Furthermore, the magnetic field dependences of the magnetization along $a$ and $c$ axes at 5 K were measured (Fig. 4). A linear $M_a(H)$ curve with no slope abnormality is shown in Fig. 4a indicating that there is no antiferromagnetic ordering component along the $a$ axis. In Fig. 4b, although there is a deviation from the linear behavior in $M_c(H)$ curve at around 4 T, the induced magnetization is not reached up to 7 T which confirms that the critical magnetic field to induce the spin flop transition in single crystal Mn$_4$Nb$_2$O$_9$ is larger than 7 T. There is no doubt that the critical magnetic field of single crystal Mn$_4$Nb$_2$O$_9$ is much larger than 0.75 T found in single crystal Co$_4$Nb$_2$O$_9$. The Zeeman energy which induces the spin flop can be expressed as:$$E_{\text{Zeeman}} = -\mu_0 M_{\text{Net}} H_{\text{Ext}} \cos \theta$$ (1)

where $\mu_0$, $M_{\text{Net}}$, $H_{\text{Ext}}$ and $\theta$ represent respectively the vacuum permeability, the magnetic moments of Mn$^{2+}$, the external magnetic field, and the angle between $M_{\text{Net}}$ and $H_{\text{Ext}}$. The magnetic moment of Mn$^{2+}$ is known to be larger than that of Co$^{2+}$. The $\theta$ angle for both Co$_4$Nb$_2$O$_9$ and Mn$_4$Nb$_2$O$_9$ is $\pi$ as the magnetic moments of Co$^{2+}$ and Mn$^{2+}$ in Co$_4$Nb$_2$O$_9$ and Mn$_4$Nb$_2$O$_9$ align in antiferromagnetic configurations along $a$ and $c$ axis, respectively. The Zeeman energy of Mn$_4$Nb$_2$O$_9$ is thus larger than that of Co$_4$Nb$_2$O$_9$ under the same external magnetic field. The antiferromagnetic coupling between the magnetic moments of Mn$^{2+}$ is larger than the difference of Zeeman energy between both systems. Therefore, Mn$_4$Nb$_2$O$_9$ requires a larger critical magnetic field to induce the spin flop metamagnetic transition.

In order to check if the antiferromagnetic phase transition is accompanied with structural changes, the (300) and (006) Bragg reflections along $a$ and $c$ axis, respectively were measured by...
varying the temperature. As shown in Fig. 5a, the (300) Bragg reflections shift towards higher 2θ degrees by decreasing the temperature. In contrast to (300) Bragg reflections, the (006) Bragg reflections first shift to higher 2θ angles on cooling and then shift to lower 2θ degrees as shown in Fig. 5b. The peak positions of the Bragg reflections can then be obtained by fitting the corresponding (300) and (006) Bragg reflections using Gaussian function fitting. The a and c lattice parameters as a function of temperature between 90 K and 150 K are plotted in Fig. 5c and d, respectively. As the temperature decreases, there is a structural change of a shrinkage along a direction and expansion along c direction below around 110 K which is exactly the $T_N$ of Mn$_4$Nb$_2$O$_9$ evidenced above using magnetic measurements. There is therefore an obvious magnetostriction effect occurring at the AFM phase transition. This result is appealing to further investigations for instance by studying the magnetic behavior under pressure/stress and/or the resulting strain under magnetic field. Furthermore, if the structure-magnetic coupling is strong enough, it opens the door towards strain-engineering of the magnetism in Mn$_4$Nb$_2$O$_9$. Finally, we also applied an electric field across the magnetic transition showing that no magnetoelectric coupling exists. Further work is needed to study the interaction between structure and magnetism in Mn$_4$Nb$_2$O$_9$ single crystal.

**Conclusion**

In summary, we have successfully synthesized Mn$_4$Nb$_2$O$_9$ single crystal with a single phase of corundum-type structure by a one-step method based on the optical floating zone technique. Characterizations of the crystal by X-ray diffraction and Laue photographs analysis show the good quality of the crystal. An antiferromagnetic phase transition is found at Néel temperature $T_N = 108.4$ K. In contrast to Co$_4$Nb$_2$O$_9$, such AFM ordering is along c axis and the spin flop transition cannot be achieved with magnetic field up to 7 T. A structural modification with shrinking of the a direction and expansion of c direction takes place at $T_N$ and indicates a magnetostriction effect. We also applied an electric field across the magnetic transition showing that no magnetoelectric coupling exists. Further work is needed to study the interaction between structure and magnetism in Mn$_4$Nb$_2$O$_9$ single crystal.

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