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Anisotropic magnetic entropy change in $R\text{FeO}_3$ single crystals ($R = \text{Tb}, \text{Tm}, \text{or Y}$)

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Compared with traditional gas-compression/expansion refrigeration, magnetic refrigeration based on magnetocaloric effect (MCE) exhibits the advantages of high energy efficiency and environment friendliness. Here, we created large MCE in $R\text{FeO}_3$ ($R = \text{Tb}$ or Tm) single crystals by the magnetization vector rotation of single crystal with strong magnetocrystalline anisotropy (MCA), rather than merely via the order-disorder magnetic phase transition or magnetic structural transition. Owing to the difference in charge distribution of $4f$ -electrons between Tb^{3+} and Tm^{3+} ions, the rotating field entropy with different signs, $-\Delta S_M^R = 17.42 \text{ J/kg K}$, and $-\Delta S_M^R = -9.01 \text{ J/kg K}$ are achieved at 9 K and 17 K for TbFeO_3 and TmFeO_3 single crystals from b axis to c axis, at 50 kOe, respectively. The finding of the large anisotropic MCE not only advances our understanding of the anisotropy of MCE, but also extends the application for single crystals to magnetic refrigeration.

Magnetocaloric effect (MCE), which describes the temperature change of magnetic materials in an adiabatic process caused by magnetic entropy change ΔS_M under external magnetic field, has been extensively investigated. In comparison with traditional gas-compression/expansion refrigeration, magnetic refrigeration based on MCE exhibits the advantages of high energy efficiency and environment friendliness. The giant or very large magnetic entropy change was obtained in various kinds of magnetic materials, including Gd-based alloys $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})^{1,2}$, Mn-based Ni-Mn-Ga(Sn) alloys^{3,4} and $\text{MnFeP}_{0.45}\text{As}_{0.55}$ ⁵, Fe-based $\text{LaFe}_{13-x}(\text{Si}, \text{Al})_x$ ^{6,7}, as well as rare-earth perovskite-type manganites $(\text{La}_{1-x}\text{M}_x)\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Sr}, \text{and Ba etc.}$)^{8,9}. Although numerous studies on MCE have been concentrated on exploring new materials with giant MCE near room temperature for domestic applications, giant MCE in the low-temperature region from about 30 K down to sub-Kelvin temperatures is also essential for utilization in certain fields, such as liquid hydrogen economy and space application¹⁰.

The magnetic, barocaloric and electrocaloric effects can be tuned or created by element substitution¹¹, pressure^{12–15}, strain^{16,17}, electric field^{18,19}, or elastic force²⁰. The giant magnetic entropy change in the vicinity of magnetic ordering temperature is usually accompanied by a field-induced or temperature-induced magnetic phase transition with the changes in either crystal symmetry or volume²¹. In addition to magnetic entropy change, mechanical properties and chemical stability are key issues for the practical use of magnetic refrigerator²². The material will definitely become very brittle and even break into smaller grains if its crystal symmetry or volume is changed very frequently, and consequently the corrosion resistance and the lifetime of a magnetic refrigerator will be deteriorated. Therefore, it is interesting to explore whether the giant MCE can be created by the magnetization vector rotation of single crystal with strong magnetocrystalline anisotropy (MCA), rather than merely via the order-disorder magnetic phase transition or magnetic structural transition.

Although the anisotropic MCE, which was discovered in Ni single crystal more than 70 years ago²³, is lower than that from the paramagnetic-ferromagnetic phase transition, it should be large for materials with high values of derivatives of the MCA with respect to temperature^{24–35}. Here, we explore the anisotropic magnetic entropy change of $R\text{FeO}_3$ single crystals with $R = \text{Tb}, \text{Tm}$ or Y . The reasons for choosing $R\text{FeO}_3$ ($R = \text{Tb}, \text{Tm}, \text{or Y}$) single crystals are three-fold. Firstly, $R\text{FeO}_3$ show a complex magnetic transformation and spin-reorientation transitions³⁶. The magnetoelectric properties and superfast optomagnetic effect of $R\text{FeO}_3$ single crystal have been extensively investigated^{37,38}. Unfortunately, the effect of the complex magnetic transformation on MCE is not understood yet. Secondly, the magnetic moments of Tb^{3+} ion and Tm^{3+} ion are large, and we can achieve a larger magnetic entropy change in $R\text{FeO}_3$ ($R = \text{Tb}, \text{Tm}$) single crystal according to the relation of $-\Delta S_M^{\text{Max}} = R \ln(2J + 1)$,

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Figure 1. Zero-field-cooled (ZFC) and field-cooled (FC) thermal magnetization curves. (a) of TbFeO_3 along a and c axis; and (b) of TmFeO_3 along a and c axis from 2 K to 300 K under a magnetic field of 100 Oe. Insets: thermal magnetization curves along a and c axis of TbFeO_3 .

where R is the gas constant and J is the total angular momentum of the magnetic ion. Thirdly, the $4f$ shell of Tb^{3+} , Tm^{3+} and Y^{3+} has an oblate, a prolate, and a spherical shape, respectively, a different anisotropy of MCE would be expected between the TbFeO_3 and TmFeO_3 single crystals on the basis of single-ion-anisotropy model³⁹. The rotating field entropy with different signs, $-\Delta S_M^R = 17.42 \text{ J/kg K}$, and $-\Delta S_M^R = -9.01 \text{ J/kg K}$ are achieved at 9 K and 17 K for TbFeO_3 and TmFeO_3 single crystals from b axis to c axis, respectively. The finding not only advances our understanding of the MCE anisotropy in magnetic single crystals, but also opens a new arena for magnetic refrigerator by rotating its magnetization vector.

X-ray diffraction (XRD) patterns and back-reflection Laue XRD patterns demonstrate that RFeO_3 ($R = \text{Tb}$, Tm or Y) single crystals have an orthorhombically distorted perovskite structure with $Pbnm$ symmetry (not shown). Figure 1(a,b) display the zero-field-cooled (ZFC) and field-cooled (FC) thermal magnetization curves along a , c axes from 2 K to 300 K under a magnetic field of 100 Oe for TbFeO_3 and TmFeO_3 single crystals, respectively. The kink point at 3 K indicated by the arrows in inset of Fig. 1(a) corresponds to the ordering temperature of Tb^{3+} moments (T_N^{Tb}). From the inset thermal magnetization curves of a and c axes, two spin-reorientation transitions are observed in the temperature range from 8.5 K to 6 K and 3.5 K to 2.5 K, corresponding to the spin-reorientation of Fe^{3+} moments from $\Gamma_4(G_x, A_y, F_z)$ configuration to $\Gamma_2(F_x, C_y, G_z)$ configuration, and then back to the high temperature configuration $\Gamma_4(G_x, A_y, F_z)$ ^{36,37,40}. From the thermal magnetization curves of a and c axes of TmFeO_3 single crystal shown in Fig. 1(b), a spin-reorientation transitions is observed in the temperature range from 85 K to 95 K, corresponding to the spin-reorientation of Fe^{3+} moments rotate from $\Gamma_4(G_x, A_y, F_z)$ configuration to $\Gamma_2(F_x, C_y, G_z)$ configuration³⁶.

Figure 2(a–c) illustrate the isothermal magnetization curves along a , b and c axes of TbFeO_3 single crystal in the temperature range of 2–40 K with an interval of 2 K, respectively. The magnetization curves for these three directions are different either in shape or in magnetization values. Data for increasing and decreasing the magnetic field at 2 K to 10 K along all the three directions are given, for better viewing we enlarged the data along b axis in the inset, which demonstrates a little hysteresis loss in the cycling process. A spin-flip phenomenon can be observe along a , b and c axis of the TbFeO_3 single crystal at 2 K due to the antiferromagnetic interaction of Tb - Tb ions^{40,41}. Form the data we can see that the easy magnetization direction (EMD) lies in ab plane for TbFeO_3 single crystal. The significant difference in the isothermal magnetization curves along a , b and c axis of TbFeO_3 single crystal implies that an anisotropic MCE can be expected.

At temperature T , the magnetic entropy change due to applied field H can be calculated from the isothermal curves by the Maxwell relation

$$\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH = \sum_0^H \left(\frac{M|_{T+\Delta T} - M|_{T-\Delta T}}{(T + \Delta T) - (T - \Delta T)} \right) \Delta H \quad (1)$$

where the slope of two adjacent data points is approximatively used for the numerical calculation of the gradient of $(\partial M / \partial T)_H$.

By selecting $\Delta T = 1 \text{ K}$ and $\Delta H = 2 \text{ kOe}$, the calculated $-\Delta S_M$ vs temperature is shown in Fig. 2(d–f) for fields along a , b and c axis, respectively. A large anisotropy of MCE is observed in TbFeO_3 single crystal along ab plane and c axis. The maximum values of $-\Delta S_M$ are achieved of 24.05 J/kg K and 20.18 J/kg K in a field of 70 kOe at 11 K along a axis and 9 K along b axis, respectively. The values of $-\Delta S_M$ along c axis are smaller than those along a and b axis above the ordering temperature of Tb^{3+} moments ($T_N^{\text{Tb}} \sim 3 \text{ K}$). Around $T_N^{\text{Tb}} \sim 3 \text{ K}$, a field-induced transition from antiferromagnetic configuration of Tb^{3+} moments to ferromagnetic one results in $-\Delta S_M = 10.55 \text{ J/kg K}$.

Figure 3(a–c) illustrate the isothermal magnetization curves along a , b and c axis of TmFeO_3 single crystal in the temperature range of 2–40 K with an interval of 2 K, respectively. In contrast to TbFeO_3 single crystal, TmFeO_3 single crystal exhibits a uniaxial magnetic anisotropy with EMD along c -axis. The magnetic entropy

Figure 2. Isothermal magnetization curves and magnetic entropy change of TbFeO_3 single crystal. (a) magnetization curves along a axis, (b) magnetization curves along b axis, (c) magnetization curves along c axis; (d) magnetic entropy change along a axis, (e) magnetic entropy change along b axis, and (f) magnetic entropy change along c axis.

Figure 3. Isothermal magnetization curves and magnetic entropy change of TmFeO_3 single crystal. (a) magnetization curves along a axis, (b) magnetization curves along b axis, (c) magnetization curves along c axis, (d) magnetic entropy change along a axis, (e) magnetic entropy changes along b axis, and (f) magnetic entropy change along c axis.

Figure 4. Isothermal magnetization curves and magnetic entropy change of YFeO₃ single crystal.

(a) magnetization curves along *a* axis, (b) magnetization curves along *b* axis, (c) magnetization curves along *c* axis, (d) magnetic entropy change along *a* axis, (e) magnetic entropy change along *b* axis, and (f) magnetic entropy change along *c* axis.

change $-\Delta S_M$ calculated from the isothermal curves using the equation (1) is shown in Fig. 3(d–f) for fields along the *a*, *b* and *c* axis, respectively. The maximum values of $-\Delta S_M$ are achieved of 11.93 J/kg K in a field of 70 kOe at 17 K along *c* axis, whereas $-\Delta S_M$ for *a* and *b* axes are about one order of magnitude smaller than those along *c* axis in the whole temperature range.

The anisotropy of magnetic entropy change results from the MCA. In general, the overall MCA of RFeO₃ single crystal is the sum of R³⁺ sublattice anisotropy and Fe³⁺ sublattice one, as similar with RMnO₃ series²⁹. In order to separate the individual contribution from R³⁺ ion sublattice, we measured the magnetization curves and magnetic entropy change of YFeO₃ single crystal for comparison. Since Y ion has non-magnetic moments, and consequently makes no contribution to the overall MCA. Therefore, it affords a separate investigation of the Fe³⁺ sublattice anisotropy. Isothermal magnetization curves along *a*, *b* and *c* axis of YFeO₃ single crystal are shown in Fig. 4(a–c), respectively. The magnetization curves indicate that the magnetic anisotropy among *a*, *b* and *c* axis is not significant. Furthermore, the magnetic entropy change of YFeO₃ are nearly zero (Fig. 4(d–f)), suggesting that the anisotropy of magnetic entropy change in TbFeO₃ and TmFeO₃ single crystals is arisen mainly from the contribution of Tb³⁺ and Tm³⁺ ions sublattice anisotropy.

In the first approximation, the MCA constant $K_{1,R}$ can be described as⁴².

$$K_{1,R} = -\frac{3}{2}\alpha_J A_2^0 < r_{4f}^2 > (3J_{R,Z}^2 - J_R(J_R + 1)) > \quad (2)$$

where α_J is the second-order Stevens coefficient, and A_2^0 is the second-order crystalline electrical field (CEF) coefficient. $< r_{4f}^2 >$ is the squared 4*f* shell radius. J_R is the Hund's rules angular moment of R ion.

Since the sign of A_2^0 for orthorhombically distorted perovskite structure RFeO₃ (R = Tb, Tm or Y) single crystals is the same and negative⁴³, the easy magnetization directions of these single crystals are governed by the sign of the second-order Stevens factor α_J of rare earth ions. The signs of α_J for Tb³⁺ and Tm³⁺ are negative and positive, respectively. Therefore, the MCA constants $K_{1,Tb} < 0$, and $K_{1,Tm} > 0$, suggesting that the easy magnetization direction of TbFeO₃ and TmFeO₃ single crystals aligns in *ab* plane and *c* axis, respectively. Similar results were also observed in DyFeO₃ and ErFeO₃ single crystals^{33,34}.

The connection between anisotropic magnetic entropy change and magnetic anisotropy is evident from the field-dependence of $-\Delta S_M$ for TbFeO₃ single crystal at 9 K and TmFeO₃ single crystal at 17 K along different axis (Fig. 5(a,c)). For magnetic refrigeration application, not only a large entropy change value, but also a large refrigeration capacity (RC) is required. RC is defined as

$$RC = \int_{T_1}^{T_2} \Delta S_M dT \quad (3)$$

Figure 5. Calculated $-\Delta S_M$ and refrigeration capacity (RC). (a) field dependence of magnetic entropy changes of TbFeO₃ along *a*, *b* and *c* axis at 9 K, and (b) refrigeration capacity; (c) field dependence of magnetic entropy change of TmFeO₃ along *a*, *b* and *c* axis at 17 K, and (d) refrigeration capacity.

where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M$ peak. The RC is the measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigerator as a function of field. The field-dependent refrigeration capacity of TbFeO₃ and TmFeO₃ single crystals is shown in Fig. 5(b) and Fig. 5(d). The three directions manifest obvious anisotropy with values of RC in a field of 70 kOe are 504.8 J/kg, 319.9 J/kg and 11.4 J/kg for *a*, *b* and *c* axes for TbFeO₃ single crystal, respectively. For TmFeO₃ single crystal, we also see obvious anisotropy with values of RC in a field of 70 kOe are 34.8 J/kg, 47.8 J/kg and 279.2 J/kg for *a*, *b* and *c* axis. It is interesting that both TmFeO₃ single crystal and TbFeO₃ single crystal exhibit a strong magnetocrystalline anisotropy between *ab* plane and *c* axis, and almost magnetic isotropy in *ab* plane.

The rotating magnetic entropy change $-\Delta S_M^R$ can be obtained by rotating the crystal from *b* to *c* axis and measuring the corresponding isothermal magnetization curves. Figure 6(a,b) indicate the representative isothermal magnetization curves at different angles for temperatures of 8 K and 10 K for TbFeO₃ single crystal and of 16 K and 18 K for TmFeO₃ single crystal, respectively. Taking *b* axis as the starting angle, we can get the rotating magnetic entropy change $-\Delta S_M^R$ as a function of angle by using Eq. (1). As is shown in Fig. 7(a,b), the largest values of $-\Delta S_M^R = 17.42$ J/kg K can be achieved at temperature of 9 K for TbFeO₃ and $-\Delta S_M^R = -9.01$ J/kg K can be achieved at temperature of 17 K for TmFeO₃ both under a magnetic field of 50 kOe from *b* to *c* axis. Since RFeO₃ (*R* = Tb, Tm) single crystals exhibit almost magnetic isotropy in *ab* plane and a strong magnetocrystalline anisotropy between *ab* plane and *c* axis, Fig. 7(c–d) display the “expected” magnetic entropy change $-\Delta S_M^R$. As proposed by Kuz'min and Tishin²⁴, the large and reversible anisotropic magnetic entropy change with broad temperature span suggests that a promising candidate for new type magnetic refrigeration can be achieved by simply rotating the RFeO₃ (*R* = Tb, or Tm) single crystals or magnet.

In conclusion, we investigated the MCE of RFeO₃ single crystals along *a*, *b* and *c* axis. The large MCE with broad temperature span and little hysteresis loss is ideal for the application of magnetic refrigeration operated in a wide temperature window. The detailed analysis of magnetization data shows that both TbFeO₃ single crystal and TmFeO₃ single crystal exhibit a strong magnetocrystalline anisotropy between *ab* plane and *c* axis and almost magnetic isotropy in *ab* plane. Owing to the difference in charge distribution of 4*f*-electrons between Tb³⁺ and Tm³⁺ ions, the rotating field entropy with different signs, $-\Delta S_M^R = 17.42$ J/kg K, and $-\Delta S_M^R = -9.01$ J/kg K are achieved at 9 K and 17 K for TbFeO₃ and TmFeO₃ single crystals from *b* axis to *c* axis, respectively. This discovery not only gives us a deeper insight into the understanding of the MCE anisotropy in spin canting anti-ferromagnetic single crystal, but also opens a new arena for rotary magnetic refrigerator by rotating its magnetization vector.

Methods

TbFeO₃, TmFeO₃ and YFeO₃ ceramic were prepared with the starting material Tb₄O₇ (>99.9%), Tm₂O₃ (>99.9%), Y₂O₃ (>99.9%) and Fe₂O₃ (>99.9%) with the ratio of stoichiometric. Then, they were pressed into pellets and sintered in air atmosphere for 48 hours using the solid state reaction method at 1250 °C, 1300 °C and 1300 °C.

Figure 6. Representative isothermal magnetization curves at different angles in bc plane. (a) of TbFeO_3 single crystal at 8 K and 10 K; (b) of TmFeO_3 single crystal at 16 K and 18 K. 0 and 90 correspond to the b and c directions, respectively.

Figure 7. Rotating field entropy changes $-\Delta S^R(\alpha)$ from b axis to c axis vs magnetic field. (a) of TbFeO_3 single crystal at 9 K; (b) of TmFeO_3 single crystal at 17 K; (c) “expected” anisotropy of magnetic entropy change of TbFeO_3 single crystal; and (d) “expected” anisotropy of magnetic entropy change of TmFeO_3 single crystal.

X-ray diffraction (XRD) patterns showed the prepared samples were single-phase with $P6_{3mm}$ crystallographic symmetry. The ceramics were compressed into rods under the hydrostatic pressure and sintered at 1400°C for 48 hours. TbFeO_3 , TmFeO_3 and YFeO_3 single crystals were grown with four ellipsoidal mirrors (Crystal Systems Inc,

FZ-T-10000-H-VI-VP) by the floating zone method. X-ray diffraction (XRD) patterns were collected by Rigaku D/MAX 2400 x-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406\text{\AA}$). Back-reflection Laue x-ray diffraction measurements were carried out to determine the crystallographic direction. Magnetization measurements were performed on commercial superconducting quantum interference device (SQUID) magnetometer (Quantum design MPMS-XL).

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Author Contributions

Z.H.C. designed the experiments. Y.J.K., X.Q.Z. and Y.M. grew the single crystal. Y.J.K. carried out the magnetic entropy changes experiments and calculation. All the co-authors contributed to the analysis and discussion for the results. Z.H.C. wrote the paper with the input from all the co-authors.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

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