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 \( \text{RFeO}_3 \) (\( R = \text{Tb} \) or \( \text{Tm} \)) 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 \( \text{Tb}^{3+} \) and \( \text{Tm}^{3+} \) ions, the rotating field entropy with different signs, \(-\Delta S_M^b = 17.42 \text{ J/kg K}, \) and \(-\Delta S_M^c = 9.01 \text{ J/kg K} \) are achieved at 9 K and 17 K for \( \text{TbFeO}_3 \) and \( \text{TmFeO}_3 \) 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 \( \Delta S_M \) 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 \( \text{Gd}_x(\text{Si}, \text{Ge})_{1-x} \), Mn-based Ni-Mn-Ga(Sn) alloys \( \text{MnFeP}_{0.45}\text{As}_{0.55} \), \( \text{Fe}\)-based \( \text{LaFe}_{13-x}(\text{Si}, \text{Al})_x \), as well as rare-earth perovskite-type manganites \( \text{(La}_{1-x}\text{M})\text{MnO}_3 \) \( \text{(M = Ca, Sr, and Ba etc.)} \). 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 application.

The magnetic, barocaloric and electrocaloric effects can be tuned or created by element substitution, pressure, strain, electric field, or elastic force. 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 volume. In addition to magnetic entropy change, mechanical properties and chemical stability are key issues for the practical use of magnetic refrigeration. 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 ago, 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. Here, we explore the anisotropic magnetic entropy change of \( \text{RFeO}_3 \) single crystals with \( R = \text{Tb}, \text{Tm} \) or \( Y \). The reasons for choosing \( \text{RFeO}_3(R = \text{Tb}, \text{Tm}, \text{or Y}) \) single crystals are three-fold. Firstly, \( \text{RFeO}_3 \) show a complex magnetic transformation and spin-reorientation transitions. The magnetoelastic properties and superfast optomagnetic effect of \( \text{RFeO}_3 \) single crystal have been extensively investigated. Unfortunately, the effect of the complex magnetic transformation on MCE is not understood yet. Secondly, the magnetic moments of \( \text{Tb}^{3+} \) and \( \text{Tm}^{3+} \) ions are large, and we can achieve a larger magnetic entropy change in \( \text{RFeO}_3(R = \text{Tb}, \text{Tm}) \) single crystal according to the relation of \( -\Delta S_M^{\text{Max}} = \text{Rln}(2J + 1) \),
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 model$^{39}$. The rotating field entropy with different signs, $-\Delta S_M^b = 17.42$ J/kg K, and $-\Delta S_M^c = -9.01$ 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 = Tb, Tm or Y) single crystals have an orthorhombically distorted pervoskite structure with Pbnm symmetry (not shown). Figure 1(a,b) display the zero-field-cooled (ZFC) and field-cooled (FC) thermal magnetization curves along $a$ and $c$ axis from 2 K to 300 K under a magnetic field of 100 Oe, respectively. Insets: thermal magnetization curves along $a$ and $c$ axis of TbFeO$_3$.

![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$_3$.](image)

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 ($T_N^{3+}$). 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 $\Gamma_1(G_xA_yF_z)$ configuration to $\Gamma_1(F_xC_yG_z)$ configuration, and then back to the high temperature configuration $\Gamma_1(G_xA_yF_z)$. From the thermal magnetization curves of $a$ and $c$ axes of TbFeO$_3$ single crystal shown in Fig. 1(b), a spin-reorientation transition is observed in the temperature range from 85 K to 95 K, corresponding to the spin-reorientation of Fe$^{3+}$ moments rotate from $\Gamma_1(F_xC_yG_z)$ configuration to $\Gamma_1(F_yC_yG_z)$ configuration$^{40}$. 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. A spin-flip phenomenon can be observed 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 $a$ axis and $9$ K along $c$ axis, respectively. The values of $\Delta M$ along $a$ and $b$ axes from 2 K to 300 K under a magnetic field of 100 Oe for TbFeO$_3$ and TmFeO$_3$ single crystals, respectively.

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

$$\Delta S_M(T, H) = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH = \sum_{0}^{H} \left( \frac{M_{T+\Delta T} - M_{T-\Delta T}}{(T+\Delta T) - (T-\Delta T)} \right) \Delta H$$

(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 $\Delta T = 1$ K and $H = 2$ 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 $a$ and $b$ plane and $c$ axis. The maximum values of $-\Delta S_M$ are achieved at 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 ($T_N^{3+} \sim 3$K). Around $T_N^{3+} - 3$K, a field-induced transition from antiferromagnetic configuration of Tb$^{3+}$ moments to ferromagnetic one results in $-\Delta S_M = 10.55$ 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 TbFeO₃ 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 TmFeO₃ 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.
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 $R$FeO$_3$ single crystal is the sum of $R^{3+}$ sublattice anisotropy and $Fe^{3+}$ sublattice one, as similar with $RMnO_3$ series$^{29}$. In order to separate the individual contribution from $R^{3+}$ ion sublattice, we measured the magnetization curves and magnetic entropy change of $Y$FeO$_3$ 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 $Fe^{3+}$ sublattice anisotropy. Isothermal magnetization curves along $a$, $b$ and $c$ axis of $Y$FeO$_3$ 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 $Y$FeO$_3$ are nearly zero (Fig. 4(d–f)), suggesting that the anisotropy of magnetic entropy change in TbFeO$_3$ and TmFeO$_3$ single crystals is arisen mainly from the contribution of $Tb^{3+}$ and $Tm^{3+}$ ions sublattice anisotropy.

In the first approximation, the MCA constant $K_{1,R}$ can be described as$^{42}$.

$$K_{1,R} = -\frac{1}{2} \alpha_J A_J^0 < r_{JZ}^2 > (3 f_{R,Z}^2 - f_R (f_R + 1))$$

(2)

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

Since the sign of $A_J^0$ for orthorhombically distorted pervoskite structure $R$FeO$_3$($R = Tb, Tm$ or $Y$) single crystals is the same and negative$^{43}$, the easy magnetization directions of these single crystals are governed by the sign of the second-order Stevens factor $\alpha_J$ of rare earth ions. The signs of $\alpha_J$ for $Tb^{3+}$ and $Tm^{3+}$ 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 $Tb$FeO$_3$ and $Tm$FeO$_3$ single crystals aligns in $ab$ plane and $c$ axis, respectively. Similar results were also observed in DyFeO$_3$ and ErFeO$_3$ 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 $Tb$FeO$_3$ single crystal at $9$ K and $Tm$FeO$_3$ 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

$$RC = \int_{T_1}^{T_2} \Delta S_M dT$$

(3)
where $T_1$ and $T_2$ are the temperatures corresponding to both sides of the half-maximum value of $-\Delta S_M^{\text{peak}}$. 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 TbFeO$_3$ and TmFeO$_3$ 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 TbFeO$_3$ single crystal, respectively. For TmFeO$_3$ 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 $c$ axes. It is interesting that both TmFeO$_3$ single crystal and TbFeO$_3$ 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 TbFeO$_3$ single crystal and of 16 K and 18 K for TmFeO$_3$ 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 TbFeO$_3$ and $-\Delta S_M^{R} = -9.01$ J/kg K can be achieved at temperature of 17 K for TbFeO$_3$ both under a magnetic field of 50 kOe from $b$ to $c$ axis. Since RFeO$_3$ ($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 Tishin, 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 RFeO$_3$ ($R = $ Tb, or Tm) single crystals or magnet.

In conclusion, we investigated the MCE of RFeO$_3$ single crystals among $a$, $b$ 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 TbFeO$_3$ single crystal and TmFeO$_3$ 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 Tb$^{3+}$ and Tm$^{3+}$ ions, the rotating field entropy with different signs, $-\Delta S_M^{ab} = 17.42$ J/kg K, and $-\Delta S_M^{c} = -9.01$ 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. 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**

TbFeO$_3$, TmFeO$_3$ and YFeO$_3$ ceramic were prepared with the starting material Tb$_2$O$_3$ (>99.9%), Tm$_2$O$_3$ (>99.9%), Y$_2$O$_3$ (>99.9%) and Fe$_2$O$_3$ (>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.
X-ray diffraction (XRD) patterns showed the prepared samples were single-phase with $Pbnm$ 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, 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.

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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.

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