Giant low-field cryogenic magnetocaloric effect in polycrystalline $LiErF_4$ compound

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Antiferromagnetic $LiErF_4$ has attracted extensive attention due to its dipolar interaction domination and quantum fluctuations action. In the present work, the crystal structure, cryogenic magnetic properties, and magnetocaloric effect (MCE) of polycrystalline $LiErF_4$ compound are investigated. Crystallographic study shows that the compound crystallizes in the tetragonal scheelite structure with $I4_1/a$ space group. It exhibits an antiferromagnetic (AFM) phase transition around 0.4 K, accompanied by a giant cryogenic MCE. At 1.3 K, the maximum values of magnetic entropy changes are 24.3 J/kg·K, 33.1 J/kg·K, and 49.0 J/kg·K under the low magnetic field change of 0–0.6 T, 0–1 T, and 0–2 T, respectively. The giant MCE observed above Néel temperature T_N is probably due to the strong quantum fluctuations, which cause a large ratio of the unreleased magnetic entropy existing above the phase transition temperature. The outstanding low-field MCE below 2 K makes the $LiErF_4$ compound an attractive candidate for the magnetic refrigeration at the ultra-low temperature.

Keywords: $LiErF_4$, magnetocaloric effect, ultra-low temperature

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1. Introduction

Ultra-low temperature plays an essential role in a variety of fields, providing crucial support to frontier scientific, such as space exploration, quantum communication, and low temperature physics.[1–5] The currently dominant refrigeration technology for ultra-low temperatures is ^{3}He dilution refrigeration. ^{3}He is very scarce, expensive, and unstably supplied, which appeals for great interests in alternative refrigeration technology. Magnetic refrigeration technology, based on the magnetocaloric effect (MCE) of magnetic materials, is another viable method to achieve ultra-low temperature.[6–9] Compared with ^{3}He dilution refrigeration, its main advantages are the simple construction of device and without the usage of expensive ^{3}He. Magnetic entropy change ($-\Delta S_M$) is a vital parameter for evaluating the MCE. In the past few decades, a great deal of compounds with large $-\Delta S_M$ below 2 K have been reported, such as $Gd_3Ga_5O_{12}$,[10,11] GdF_3,[12] $GdPO_4$,[13] $Gd(OH)_3$,[14] $Gd(OH)CO_3$,[15] and $Gd(HCOO)_3$.[16] The recently reported magnetic materials $Gd_{20}Ho_{20}Tm_{20}Cu_{20}Ni_{20}$,[17] $Er_{20}Ho_{20}Gd_{20}Ni_{20}Co_{20}$,[18] Gd_2MgTiO_6,[19] and $GdFe_2Si_2$[20] all exhibit excellent magnetocaloric performance. However, for most of them, a large $-\Delta S_M$ is usually induced by relatively high magnetic field changes ($\Delta\mu_0 H \geq$ 0–2 T), which require expensive superconducting magnets. Low magnetic fields ($\Delta\mu_0 H \leq$ 0–2 T) provided by conventional permanent magnets can remarkably reduce the cost and save the space of magnetic refrigerator. Therefore, there is a growing demand for materials that pursue a large $-\Delta S_M$ under a low magnetic field change at ultra-low temperatures.

Lithium rare earth tetrafluorides ($LiREF_4$) with the tetragonal scheelite structure were widely studied because their tightly bound 4f electrons are far enough apart that the dipolar interactions dominate exchange interactions. And excellent MCE of $LiGdF_4$[21] and $LiHoF_4$[22] have been confirmed. The maximum $-\Delta S_M$ values for $LiGdF_4$ and $LiHoF_4$ are 44.9 J/kg·K and 25.9 J/kg·K under $\Delta\mu_0 H = 2$ T, respectively. Moreover, dipolar antiferromagnetic material $LiErF_4$ receives considerable attention due to its peculiar physical properties.[23–28] In 2012, Kraemer *et al.* reported that $LiErF_4$ is a bilayer antiferromagnet (AFM) with a Néel temperature (T_N) around 0.38 K and any of its nearest neighbor exchange interaction cancels, thus the spin can be easily flipped to ferromagnetic state by applying a low magnetic field. In addition, Kramers doublet ground state isolated by a gap 2.25 meV is also observed from neutron spectroscopy experiment in this compound, which indicates the system can be regarded as a pseudo spin 1/2 system at ultra-low temperature, with the existence of dimensional reduction phenomenon, implying the strong quantum fluctuations in $LiErF_4$. The quantum fluctuations may have significant influence on MCE at ultra-low temperature. What is more, a large number of unreleased mag-

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netic entropy is also observed from the heat capacity measurements. Therefore, $LiErF_4$ probably has a large MCE above T_N induced by low magnetic fields.

In this work, the crystal structure, cryogenic magnetic properties, and MCE of polycrystalline $LiErF_4$ are investigated. It is shown that $LiErF_4$ exhibits an AFM phase transition around 0.4 K. A giant MCE induced by a low magnetic field is discovered in $LiErF_4$ around 1.3 K, which makes $LiErF_4$ an attractive candidate of magnetic refrigerant materials at ultra-low temperature.

2. Experimental details

Polycrystalline $LiErF_4$ compound was obtained through solid-state reaction of ErF_3 and LiF. Firstly, analytically pure ErF_3 and LiF were thoroughly ground and uniformly mixed according to appropriate proportions, and 40% extra LiF were added to compensate for volatilization during the heating process. Then, the mixture was put in a graphite crucible and this graphite crucible was reversely sealed by another larger graphite one. In order to reduce the oxidation and volatilization, the graphite crucible was put into another corundum crucible, the interspace was full of graphite powder and then sealed with a lid. Finally, the corundum crucible was transferred to a muffle furnace and sintered at 1000 °C for 1 hour. The sample was characterized by x-ray powder diffraction (XRD) measurement in Bruker D8A A25 x-ray powder diffractometer by using Cu $K\alpha$ radiation. Magnetization measurements were performed on a MPMS with a SQUID (Quantum Design) magnetometer in the temperature ranging from 2 K to 300 K, and the ultra-low temperature magnetic properties were measured on a MPMS-3 with ^{3}He insert in the temperature ranging from 0.4 K to 2 K.

3. Results and discussion

Room temperature XRD pattern of $LiErF_4$ and the Rietveld refinement curves analyzed by the Rietica software are shown in Fig. 1.

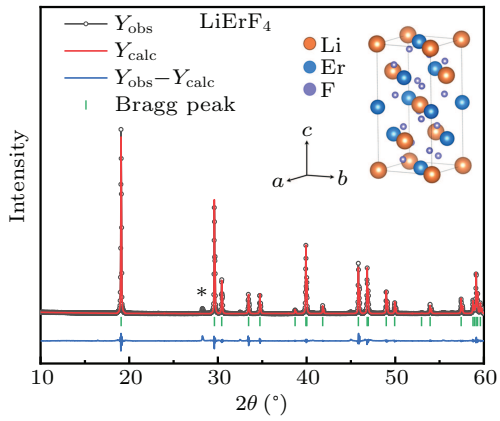


Fig. 1. Room temperature XRD pattern and Rietveld refinement curve of the $LiErF_4$ compound. The inset presents the crystal structure of $LiErF_4$.

The value of Rp (%) determined from the refinement is 7.01 for $LiErF_4$. Results confirm that the sample is crystallized in the tetragonal scheelite phase (space group $I4_1/a$). The refined lattice parameters a, b, and c were determined to be 5.162 Å, 5.162 Å, and 10.708 Å, respectively. These values are very close to those in previous reports.[29–31] A feeblish extra diffraction peak marked by an asterisk can be observed around $2\theta = 28°$, which was inferred to be the diffraction peak of ErOF produced by the reaction of ErF_3 with the tiny amount of air remaining inside the crucible.

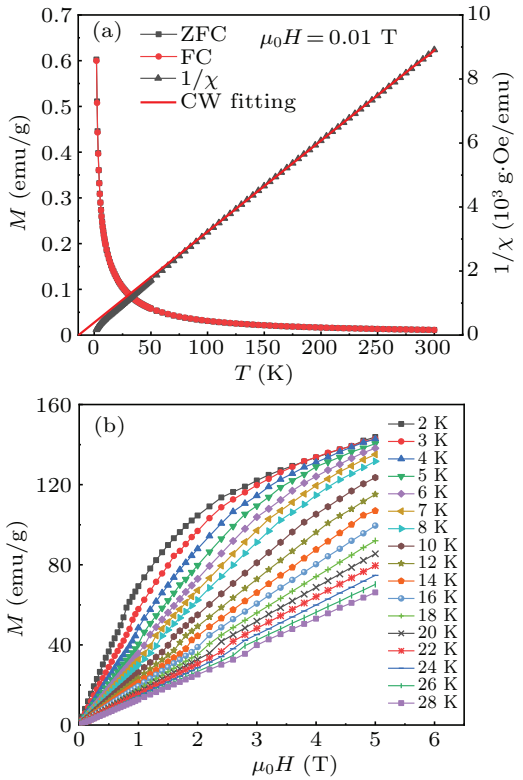


Fig. 2. (a) The temperature ranging from 2 K to 300 K, temperature dependence of ZFC and FC magnetization (left scale) and inverse susceptibility $1/\chi$ (right scale) for $LiErF_4$ compound under a magnetic field of 0.01 T. (b) Magnetization isotherms of $LiErF_4$ in the temperature ranging from 2 K to 28 K under magnetic fields up to 5 T.

From Fig. 2(a), no obvious difference is identified from the zero field cooling (ZFC) and field cooling (FC) curves, which indicates that the compound has good thermomagnetic reversibility. The inverse susceptibility ($1/\chi$) obeys the Curie–Weiss law $\chi^{-1} = 3K_B(T-\theta_P)/N(\mu_B\mu_{eff})^2$ in the temperature ranging from 100 K to 300 K, where θ_P and C are the paramagnetic (PM) Curie temperature and the Curie–Weiss constant, respectively. The effective magnetic moment (μ_{eff}) and θ_P values acquired by the Curie–Weiss fitting are 8.38 μ_B and −14.12 K, respectively. The value of μ_{eff} is less than the theoretical effective moment ($g\sqrt{J(J+1)} = 9.59\ \mu_B$) of Er^{3+} free ion, which may be caused by the crystal field effect. A negative θ_P value also indicates the antiferromagnetic interaction domination in $LiErF_4$. Figure 2(b) shows the isothermal magnetization curve (M–H) measured under magnetic fields up to

5 T in the temperature range from 2 K to 28 K. Each isothermal M–H curve shows a linear relationship under the magnetic fields lower than a critical magnetic field, while the linear relationship changes as the magnetic fields increase. The critical magnetic field of each isothermal M–H curve is different and gradually increases corresponding to the temperature from 2 K to 28 K. This phenomenon will be studied in our future work.

The magnetic entropy change ($\Delta S_{\rm M}$) can be calculated by the Maxwell equation

$$\Delta S_{\rm M}(T, \Delta H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H {\rm d}H.$$

The temperature dependence of $-\Delta S_{\rm M}$ under different magnetic fields from 2 K to 28 K is shown in Fig. 3. The maximum values of $-\Delta S_{\rm M}$ under the magnetic field change of 1 T, 2 T, and 5 T are 7.6 J/kg·K, 17.5 J/kg·K, and 26.6 J/kg·K for $LiErF_4$, respectively.

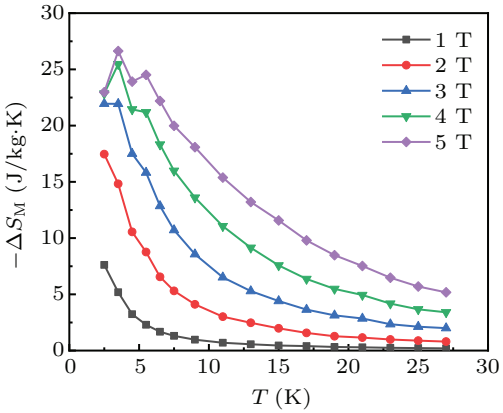


Fig. 3. Magnetic entropy change of $LiErF_4$ in the temperature ranging from 2 K to 28 K under $\Delta\mu_0 H$ from 0–1 T to 0–5 T.

In order to investigate the MCE of $LiErF_4$ below 2 K, magnetization measurements were performed in the temperature ranging from 0.4 K to 2 K. The temperature dependences of ZFC and FC magnetizations (M) of $LiErF_4$ under 0.01 T are displayed in Fig. 4(a). The magnetization values of ZFC in Figs. 2(a) and 4(a) have a discrepancy at 2 K, which is probably caused by the different magnetic measurement equipment. Both the ZFC and FC curves increase monotonically as the temperature decreases and the inflection points appear around 0.4 K. A cusp is observed around 0.4 K both in ZFC and FC curves, indicating the occurrence of an antiferromagnetic transition at this temperature, which is consistent with $T_{\rm N} = 0.38$ K reported in previous papers.[23,27,32]

Figure 4(b) shows the isothermal magnetization curve (M–H) measured under magnetic fields of up to 5 T in the temperature ranging from 0.4 K to 1.6 K. The magnetization at ultra-low temperature increases more rapidly with the increase of magnetic field. In addition, all isothermal magnetization curves tend to overlap completely at $\Delta\mu_0 H \geq$ 0–3 T, and does not reach saturation under a magnetic field of 5 T. The magnetization at 5 T is 6.79 $\mu_{\rm B}/{\rm Er}^{3+}$, which is significantly smaller than the free Er^{3+} ion saturation moment $g_J J = 9.0\ \mu_{\rm B}$. This is attributed to the potential anisotropy of polycrystalline $LiErF_4$, which makes it difficult to saturate the magnetization in the hard axis direction. Kraemer *et al.* reported that *ab* plane is the easy magnetization plane and *c* axis is the hard magnetization axis for single crystalline $LiErF_4$.[27] Therefore, a larger $-\Delta S_{\rm M}$ is expected by applying magnetic field in *ab* plane of single crystalline $LiErF_4$.

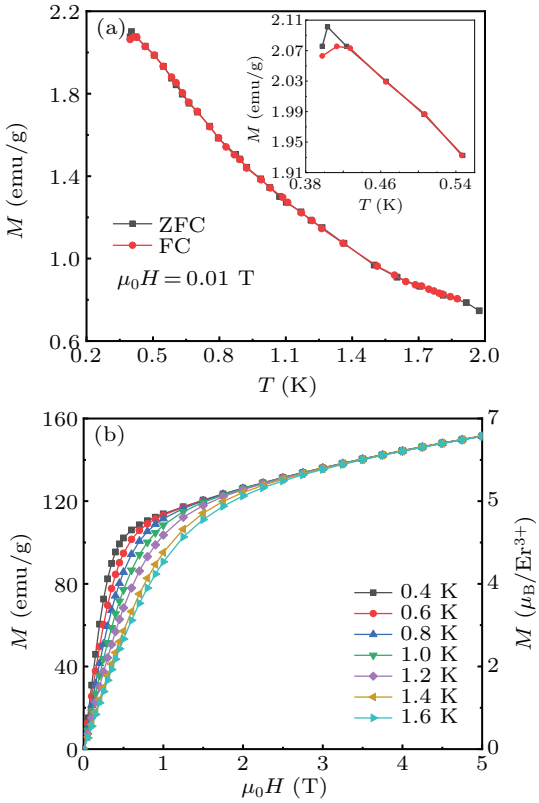


Fig. 4. (a) Temperature dependence of ZFC and FC magnetization for $LiErF_4$ in the temperature ranging from 0.4 K to 2 K under a magnetic field of 0.01 T. The inset presents an enlarged view of the temperature from 0.4 K to 0.6 K. (b) Magnetization isotherms of $LiErF_4$ in the temperature ranging from 0.4 K to 1.6 K under magnetic fields up to 5 T.

Figure 5(a) presents that an extremely large $-\Delta S_{\rm M}$ in $LiErF_4$ is observed above $T_{\rm N}$. The values of $-\Delta S_{\rm M}$ are 24.3 J/kg·K, 33.1 J/kg·K, and 49.0 J/kg·K under $\Delta\mu_0 H$ = 0–0.6 T, 0–1 T and 0–2 T, respectively. For $\Delta\mu_0 H \leq$ 0–0.6 T, the value of $-\Delta S_{\rm M}$ decreases with increasing temperature. The $-\Delta S_{\rm M}$ curve shows a platform-like shape between 0.4 K and 1.3 K, which is favorable to achieve high cooling efficiency, at which $\Delta\mu_0 H$ is between 0–0.8 T and 0–1 T. However, at $\Delta\mu_0 H \geq$ 0–1.5 T, the value of $-\Delta S_{\rm M}$ increases with increasing temperature and reaches a maximum around 1.3 K.

The giant MCE observed above $T_{\rm N}$ may be due to strong quantum fluctuations which cause a large ratio of the unreleased magnetic entropy existing above the phase transition temperature.[26,27,29,33] Figure 5(b) shows the magnetic field

change ($\Delta\mu_0 H$) dependences of $-\Delta S_M$ at selected temperatures. The $-\Delta S_M$ curves climb up rapidly under low magnetic field changes ($\Delta\mu_0 H < 0$–2 T). Especially, at 0.5 K, a giant MCE can be obtained by induced magnetic field below 1 T. While for $\Delta\mu_0 H > 2$ T, the $-\Delta S_M$ values increase quite slowly, reaching the maximum values of 51.2 J/kg·K, 51.7 J/kg·K, and 52.0 J/kg·K for $\Delta\mu_0 H = 0$–3 T, 0–4 T and 0–5 T, respectively. Results show that $LiErF_4$ possess a giant MCE induced by a low magnetic field ($\Delta\mu_0 H \leq 0$–2 T). It is indicated that applied field of 2 T is large enough to motivate the potential MCE of $LiErF_4$ compound, which makes it a suitable magnetocaloric material serving in permanent magnets.

For comparison, the magnetocaloric parameters of $LiErF_4$ and certain excellent cryogenic magnetic coolants are listed in Table 1. The $-\Delta S_M$ of $LiErF_4$ compound under $\Delta\mu_0 H \leq 0$–2 T is much larger than those of other refrigerant materials, and the T^{max} (temperature of the corresponding $-\Delta S_M^{max}$) is extremely low. Notably, the $-\Delta S_M$ of $LiErF_4$ at $\Delta\mu_0 H = 0$–1 T is much larger than its value at $\Delta\mu_0 H = 0$–2 T compared to $Gd_3Ga_5O_{12}$ (GGG), a typical cryogenic magnetocaloric material in the low-temperature region. Therefore, the excellent low-field MCE makes $LiErF_4$ an attractive candidate for magnetic refrigerant materials at ultra-low temperature.

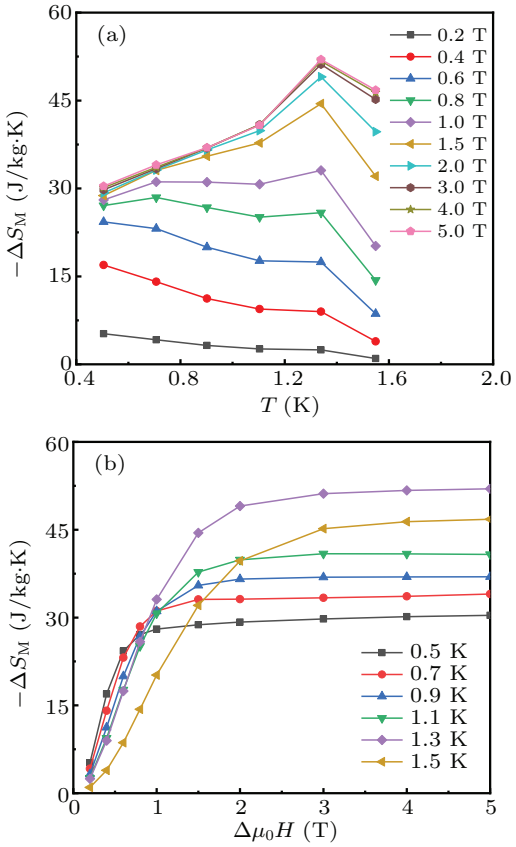


Fig. 5. Magnetic entropy changes of $LiErF_4$ in the temperature ranging from 0.4 K to 1.6 K under $\Delta\mu_0 H$ from 0–0.2 T to 0–5 T (a) as a function of temperature and (b) as a function of the magnetic field change.

Table 1. Experimental values of T_N or T_C, T^{max} and magnetocaloric parameters of $LiErF_4$ compared with certain cryogenic magnetocaloric materials under $\Delta\mu_0 H \leq$0–2T.

Compound	T_N/T_C (K)	T^{max} (K)	$\Delta\mu_0 H$ (T)	$\lvert -\Delta S_M^{max} \rvert$ (J/kg·K)	References
$Gd_3Ga_5O_{12}$(GGG)	0.8	1.2	2	20.48	[11]
$GdPO_4$	2.0	3.0	2	27.2	[13]
$Gd(OH)_3$	–	2.0	2	26.9	[14]
$Gd_2O(OH)_4(H_2O)_2$	–	2.0	2	17	[14]
$Gd(HCOO)_3$	0.4,0.8	1.1	2	43.7	[16]
$Gd(OH)CO_3$	0.7	1.8	2	32.4	[15]
$LiGdF_4$	< 0.5	1.0	2	∼ 44.9	[21]
GdF_3	1.25	2.0	1	∼ 25.6	[12]
		2.0	2	45.5	
$LiErF_4$	0.4	1.3	1	33.1	this work
		1.3	2	49.0	

4. Conclusions

In brief, polycrystalline $LiErF_4$ compound with the tetragonal scheelite structure was synthesized, and the cryogenic magnetic properties and MCE were investigated. The compound is identified as an antiferromagnet with T_N around 0.4 K, and a giant MCE is observed above T_N under low magnetic fields providable by relatively cheap permanent magnets. The maximum values of $-\Delta S_M$ are 33.1 J/kg·K and 49.0 J/kg·K around 1.3 K under the magnetic field change of 0–1 T and 0–2 T, respectively. More remarkably, it exhibits a significant magnetic entropy change (24.3 J/kg·K) at magnetic field changes down to 0–0.6 T. The significant low-temperature magnetocaloric performance at low magnetic field proves that the $LiErF_4$ compound is a competitive magnetic refrigerant candidate for ultra-low temperature refrigeration.

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