Achievement of a table-like magnetocaloric effect in the dual-phase ErZn$_2$/ErZn composite

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**ABSTRACT**

Dual-phase ErZn$_2$/ErZn composite was obtained by induction-melting method. The composite crystallizes in the phases of ErZn$_2$ and ErZn with the weight ratio of 53.8:46.2. The composite undergoes two successive magnetic phase transitions. And accordingly two peaks (partly overlapped) are appeared in the temperature dependence of magnetic part of entropy change ($\Delta S_M(T)$) curves which resulting in a table-like magnetocaloric effect (MCE) and large refrigerant capacity ($RC$). The MCE parameters are comparable or even larger than most of the recently reported potential magnetic refrigerant materials at similar temperature region, making the dual-phase ErZn$_2$/ErZn composite attractive for low-temperature magnetic refrigeration.

**IMPACT STATEMENT**

Table-like magnetocaloric effect (MCE) was realized in dual-phase ErZn$_2$/ErZn composite, the MCE parameters are comparable or even larger than most of the reported materials, making ErZn$_2$/ErZn composite attractive for magnetic refrigeration.

Nowadays, the interest of magnetic materials with giant/large magnetocaloric effect (MCE) has considerably grown because of their potential application for magnetic refrigeration (MR) [1–17]. MCE can be characterized by the magnetic part of entropy change ($\Delta S_M$) in an isothermal process and the temperature change ($\Delta T_{ad}$) in an adiabatic process when the magnetic field is applied or removed which is an intrinsic behaviour for all magnetic solids. The MR technology based on MCE is expected to replace the traditional gas compression/expansion refrigeration technology in near future due to its higher efficiency and more environmental friendly [1–6]. The Ericsson cycle [7,8] which consists of two isothermal and two isomagnetic field processes is proposed to be the best cycle for MR technology.

It is well known that the MR material should possess a constant $\Delta S_M$ in a wide temperature range for an ideal Ericsson cycle. Thus, searching for or producing the MR materials that possess a table-like MCE in a wide temperature range is one of the most important requirements for active applications. This can be indirectly characterized by the parameter of refrigerant capacity ($RC$). For this purpose, series of rare earth (RE)-based alloys and compounds have been systematically studied recently with respect to the MCE properties. And, the table-like MCE have been realized in some of the magnetic materials that undergo multiple successive magnetic transitions or magnetic field-sensitive magnetic transition(s) as well as in some composite materials [9–15].
Among the RE-based alloys and intermetallic compounds, the research related to RE with Zn, Mg, and Cd is not too much [6]. This might be a consequence of the difficulty in sample preparation due to the low boiling point (high vapour pressure) of Zn, Mg, and Cd. Very recently, Li [6] have reviewed the recent progress of MCE in the intermetallic compounds of RE with Zn, Mg, and Cd metals. Some of them process very excellent MCE properties. For examples, a table-like MCE from 20 to 160 K together with very large $RC$ values were observed in Eu$_4$PdMg [13]. A giant low-field reversible MCE around 8 K was reported in TmZn which is related to the field-induced metamagnetic (first ordered) magnetic transition [16], additionally, the MCE and metamagnetic transition in TmZn can be gradually suppressed by hydrostatic pressure [17]. According to the phase diagram of ErZn system, the ErZn compound could co-exist with ErZn$_2$ compound in a wide range [18], thus, the structure, magnetic properties, and MCE in dual-phase ErZn$_2$/ErZn composite were investigated in this letter, and a table-like MCE together with large $RC$ was observed.

The dual-phase ErZn$_2$/ErZn composite was synthesized by induction melting of the high-purity elements of Er and Zn in quartz crucible in a water-cooled sample chamber. Firstly, high-purity Er and Zn with nominal composition of Er$_{40}$Zn$_{60}$ were weighted and sealed in a quartz crucible which was filled with argon pressure of 78 kPa. Then, the quartz crucible was placed in a water-cooled sample chamber of an induction furnace and heated up to 1273 K for 3 min. To ensure the homogeneity, the ingot together with the quartz crucible was turned and melted for 4 times by open the chamber after each melting when the crucible was cooled to room temperature. The phase and composition were characterized by X-ray diffraction (XRD) technology (Rigaku RINT 2200) and the scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) attached (Hitachi SU70). The temperature and magnetic field dependence of magnetization measurements were performed by the vibrating sample magnetometer (VSM) which is an option of the physical property measurement system (Quantum Design PPMS-9).

Figure 1 shows the room temperature XRD pattern and the Rietveld refinement using MAUD program. The refinement reveals that the as-casted ingot mainly crystallizes in two phases, i.e., orthorhombic CeCu$_2$ type ErZn$_2$ phase belonging to the $Imma$ space group and the cubic CsCl type ErZn phase belonging to the $Pm3m$ space with the weight ratio of 53.8:46.2. The small peak around 28 degree which was marked by star in Figure 1 is related to the tiny amount impurity phase of Er$_2$O$_3$. The factors of Rietveld refinement which were calculated by MAUD software are $R_B$ (%) = 12.2 and $R_{\exp}$ (%) = 13.3. The refined lattice parameters $a$, $b$, and $c$ for ErZn$_2$ are 4.446(2), 6.991(4), and 7.591(5) Å, respectively, and the value of $a$ for ErZn is 3.5284(3) Å. These values are well consistent with the values reported in the literature [18]. The Back-scattered scanning electron (BSE) image of the dual-phase ErZn$_2$/ErZn composite is shown in Figure 2. The corresponding secondary electron (SE) image is also displayed in the inset of Figure 2. Both BSD and SE images show similar behaviour, the microstructure obviously consists of two phases under both modes, i.e. dark and white phases (BSE image). By means of the EDS analysis, the dark phase is determined to be ErZn$_2$ with the compositions of 33.1 at. % Er and 66.9 at. % Zn, whereas the white phase is determined to be ErZn with the compositions of 50.3 at. % Er and 49.7 at. % Zn. And, the overall composition of the ingot are 39.4 at.% Er and 60.6 at. % Zn.

Figure 3 shows the temperature dependence of magnetization $\sigma$ (left scale) and $d\sigma_{\text{FC}}/dT$ (right scale) for dual-phase ErZn$_2$/ErZn composite under the magnetic field of $B = 1$ T, the inset shows the temperature dependence of magnetization $\sigma$ under the zero field cooled (ZFC) and field cooled (FC) mode for dual-phase ErZn$_2$/ErZn composite under $B = 0.1$ T. We can note that the dual-phase ErZn$_2$/ErZn composite processes two successive magnetic phase transitions around 9 and 20 K (defined as the inflection point of the $d\sigma/dT$-$T$ curve), which are believed to be corresponding to the transitions of ErZn$_2$ [19] and ErZn [20] compounds, respectively. Additionally, only some small differences between the $\sigma(T)$ curves measured in ZFC and FC mode for dual-phase ErZn$_2$/ErZn composite can be observed at low
Figure 2. Back-scattered scanning electron (BSE) image of the dual-phase ErZn$_2$/ErZn composite. Inset shows the corresponding secondary electron (SE) image of the dual-phase ErZn$_2$/ErZn composite.

Figure 3. Temperature dependence of magnetization $\sigma$ (left scale) and $d\sigma/dT$ (right scale) for dual-phase ErZn$_2$/ErZn composite under the magnetic field of $B = 1$ T. The inset shows temperature dependence of $\sigma$ under the zero field cooled (ZFC) and field cooled (FC) mode for dual-phase ErZn$_2$/ErZn composite under $B = 0.1$ T.

Figure 4. (a) Magnetic field ($B$, increasing only) dependence of the magnetization $\sigma$ for dual-phase ErZn$_2$/ErZn composite. (b) Temperature dependence of magnetic part of entropy change $-\Delta S_M$ for dual-phase ErZn$_2$/ErZn composite.

**Figure 3.** Temperature dependence of magnetization $\sigma$ (left scale) and $d\sigma/dT$ (right scale) for dual-phase ErZn$_2$/ErZn composite under the magnetic field of $B = 1$ T. The inset shows temperature dependence of $\sigma$ under the zero field cooled (ZFC) and field cooled (FC) mode for dual-phase ErZn$_2$/ErZn composite under $B = 0.1$ T.

**temperature. Considering the low $T_C$ and large magnetic anisotropy for ErZn$_2$ and ErZn compounds [19,20], the bifurcate behaviour between ZFC and FC curves for present dual-phase ErZn$_2$/ErZn composite is due to the domain wall pinning effect where the width of domain wall is comparable with that of lattice spacing [21]. A set of magnetic isotherms $\sigma(B)$ for dual-phase ErZn$_2$/ErZn composite up to 7 T with increasing and decreasing magnetic field were measured from 3 to 38 K to understand its MCE properties. Before collecting each $\sigma(H)$ curve, the sample was heated up to 60 K, and then down to the measured temperature using ZFC mode. The temperature interval is 2 K from 4 to 34 K, and the increments of magnetic field are 0.1 T for 0–2 T and 0.25 T for 2–7 T, respectively. No obvious differences between increasing and decreasing magnetic field over the temperature range, i.e. no thermal and magnetic hysteresis can be observed for present dual-phase ErZn$_2$/ErZn composite which is beneficial for active MR application. Several $\sigma(B)$ curves for dual-phase ErZn$_2$/ErZn composite with increasing magnetic field are presented in Figure 4(a) for a clarify. A large reversible MCE for present dual-phase ErZn$_2$/ErZn composite is expected since the magnetization is quite large and it changes rapidly with varying temperature.

According to thermo-dynamical theory, the isothermal magnetic part of entropy changes associated with the magnetic field change is given by

$$\Delta S_M(T, \Delta B) = S_M(T, B) - S_M(T, 0) = \int_0^{B_{\text{max}}} \left( \frac{\partial S(B, T)}{\partial H} \right)_T dB, \quad (1)$$

From the Maxwell’s thermodynamic relation:

$$\left( \frac{\partial S(B, T)}{\partial B} \right)_T = \left( \frac{\partial \sigma(B, T)}{\partial T} \right)_H, \quad (2)$$

we can obtain the following expression:

$$\Delta S_M(T, \Delta B) = \int_0^{B_{\text{max}}} \left( \frac{\partial \sigma(B, T)}{\partial T} \right)_H dB, \quad (3)$$

in which $S_M$, $\sigma$, $B$, and $T$ are the magnetic part of entropy, magnetization of the material, applied magnetic field intensity, and the temperature of the system, respectively. From the $\sigma$ measured at discrete field and temperature intervals, $\Delta S_M$ can be approximately calculated by the
The temperature dependence of isothermal magnetic part of entropy change $-\Delta S_M(T)$ for dual-phase ErZn$_2$/ErZn composite under different magnetic field changes ($\Delta B$) of 0–2, 0–5, and 0–7 T which was calculated from $\sigma(B, T)$ curves by using Equation (4) are given in Figure 4(b). Two pronounced peaks (or shoulder) can be observed in the $-\Delta S_M(T)$ curves around 10 and 20 K which are believed to be corresponded to the ErZn$_2$ and ErZn, respectively. Two peaks overlap with each other and induced a broad table-like behaviour in the $-\Delta S_M(T)$ curves, i.e. table-like MCE in dual-phase ErZn$_2$/ErZn composite, which is beneficial for active MR application. With the magnetic field changes of 0–5 and 0–7 T, the maximum values of the magnetic part of entropy change ($-\Delta S_M^{\text{max}}$) for dual-phase ErZn$_2$/ErZn composite are 19.5 and 25.4 J/kg K, respectively. The value of $-\Delta S_M^{\text{max}}$ for dual-phase ErZn$_2$/ErZn composite is comparable or even obviously larger than those potential magnetic refrigerant materials in the similar temperature region indicate that the dual-phase ErZn$_2$/ErZn composite could be a promising candidate for MR at low temperature.

Another important quality factor of MR materials is the $RC$ which is an indirect measurement of heat transfer in an ideal MR cycle between the cold and hot reservoirs. There are three different methods which are conventionally used to evaluate the values of $RC$ from the $\Delta S_M(T)$ curves: [1,6,13] (1) calculated by integrating of the $\sigma(B, T)$ curves by using Equation (4) are given in Figure 4(b), (2) defined as the product of $\Delta S_M^{\text{max}}$ and $\delta T_{\text{FWHM}}$ (RC-1), and (3) by maximizing the product $\Delta S_M$ and $\delta T$ in the $\Delta S_M(T)$ curve (RC-3) [13]. The values of $\delta T_{\text{FWHM}}$ for dual-phase ErZn$_2$/ErZn composite are 20.2, 22.9, and 25.4 K for the $\Delta B$ of 0–2, 0–5, and 0–7 T, respectively. The values of RC-1, RC-2, and RC-3 are evaluated to be 145, 172, and 96 J/kg for $\Delta H$ of 0–2 T, to be 362, 447, and 232 J/kg for $\Delta H$ of 0–5 T, and to be 503, 645, and 343 J/kg for $\Delta H$ of 0–7 T, respectively. Here, we use the values of RC-1 as the MCE figure-of-merit for comparison with other materials which were calculated in the same way. The magnetic transition temperature(s) $T_M$ together with the MCE parameters ($-\Delta S_M^{\text{max}}$, $\delta T_{\text{FWHM}}$, and RC-1) under the magnetic field change of 0–5 T for dual-phase ErZn$_2$/ErZn composite and some recently reported giant/large MCE materials below 30 K are listed in Table 1 for comparison. We can note that the MCE parameters for present dual-phase ErZn$_2$/ErZn composite are comparable or even obviously larger than these potential magnetic refrigerant materials in the similar temperature region indicate that the dual-phase ErZn$_2$/ErZn composite could be a promising candidate for MR at low temperature.

In summary, dual-phase ErZn$_2$/ErZn composite with a table-like MCE was obtained by induction-melting method. The composite undergoes two successive magnetic phase transitions at 9 and 20 K which are corresponding to the phases of ErZn$_2$ and ErZn, respectively, and resulting two peaks (or shoulder) in the temperature dependence of magnetic part of entropy change curves, $\Delta S_M(T)$. The partly overlapping of these peaks induced a table-like MCE and large $RC$. And accordingly two peaks (partly overlapped) are appeared in the $\Delta S_M(T)$ curves which resulting in a table-like MCE and large value of $\delta T_{\text{FWHM}}$ as well as large $RC$. For the $\Delta B$ of 0–7 T, the value of $-\Delta S_M^{\text{max}}$ reaches 25.4 J/kg K, and the corresponding values of RC-1, RC-2, and RC-3 are 503, 645, and 363 J/kg, respectively. The observed large $RC$ values and reversible table-like MCE make the presently reported dual-phase ErZn$_2$/ErZn composite also attractive as refrigerant, especially for low-temperature MR. Moreover, the present results may also provide a workable way to producing table-like MCE materials with large values of $RC$.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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