# Magnetic properties and magnetocaloric effect in $Ho_{6-x}Er_xMnBi_2$ compounds

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Magnetic properties and magnetocaloric effect of compounds $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) are investigated experimentally. All the compounds crystallize in the hexagonal $Zr_6CoAs_2$-type structure and show a sharp drop in the magnetization around their respective magnetic ordering temperature, which is 201 K (x=0), 147 K (x=3), and 98 K (x=6), respectively. Either thermal or magnetic hysteresis around the phase transition is not observed, suggesting a second order phase transition nature. The magnetic entropy change ($\Delta S_m$) calculated from the Maxwell relation using the collected magnetization data is 10.6 (x=6), 7.3 (x=3), and 5.0 J $kg^{-1}$ $K^{-1}$ (x=0), respectively. The shape of the $\Delta S_m$-$T$ curve has a good symmetry below and above the magnetic ordering temperature, and the value of the magnetic entropy change increases monotonously with increasing field change. The calorimetric technique has also been used for $Er_6MnBi_2$ to check the credibility of the magnetic method. © *2010 American Institute of Physics*. [doi:10.1063/1.3359812]

Magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted much attention since it was first discovered by Warburg in the 1920s.[1–5] The magnetic fridge is estimated to consume up to 50% less energy than today's gas fridges that require environmentally toxic gases such as chlorofluorocarbons, high-fructose corn syrup, and hydrochlorofluorocarbons to operate. One key factor to the development of magnetic refrigeration is to search for materials that not only exhibit the giant MCE but also have negligible thermal and field hysteresis. During the past decades, a number of materials have been found to possess giant MCE, such as Gd–Si–Ge,[1,3] La–Fe–Si,[6] Mn–Fe–P–As,[7] Mn–As–Sb,[8] and Ni–Mn–Ga.[9]

Rare earth compounds $R_6TBi_2$ (T=Fe,Mn,Ni) crystallize in the hexagonal $Zr_6CoAs_2$-type structure. Both the types of transition metal and rare earth atoms strongly influence the magnetic structure and hence the magnetic ordering temperature in these compounds. Among the whole series, the Mn-containing compounds show the highest magnetic ordering temperature. Bolotaev *et al.* reported that the magnetization of compound $Er_6MnBi_2$ shows a sharp drop around its magnetic ordering temperature.[10,11] Furthermore, the saturated magnetization in these compounds should be large due to the major contribution of magnetic moment coming from rare earth elements, which probably cause a large MCE. In this paper we study the magnetic properties and MCE of compounds $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6).

Arc melted samples $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) were annealed at 1173 K for 7 days in argon atmosphere, then quenched in liquid nitrogen. X-ray diffraction (XRD) was used to examine the phase purity of the compounds. The dc magnetization and heat capacity were measured using a magnetic property measurement system and a physical property measurement system.

The phase quality of $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) was checked by XRD at room temperature. All the samples crystallize in the almost single phase of hexagonal $Zr_6CoAs_2$-type structure. Figure 1 shows the XRD patterns of $Er_6MnBi_2$ at room temperature. The lattice parameter is a=b=8.142(2) Å and c=4.219(7) Å.

Temperature dependence of magnetization ($M$-$T$) for $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) compounds has been measured under a field of 0.01 T, as shown in Fig. 2. The phase transition temperatures $T_C$, determined as the temperature corresponding to the minimum of $dM/dT$, are 201 K (x=0), 147 K (x=3), and 98 K (x=6), respectively, which are very

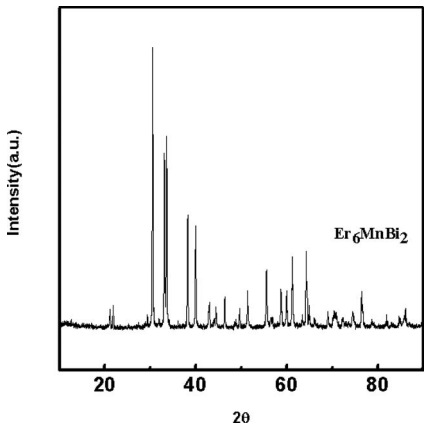


FIG. 1. The XRD patterns of $Er_6MnBi_2$ at room temperature.

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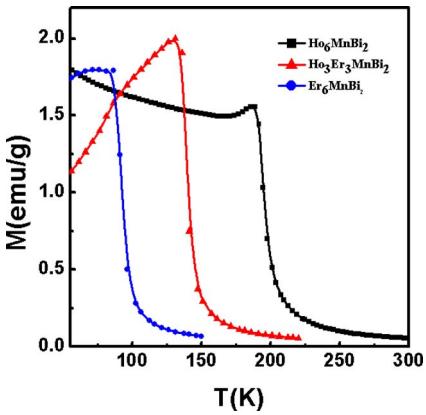


FIG. 2. (Color online) Temperature dependence of magnetization ($M$-$T$) curve at 0.01 T for $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) compounds.

close to the results reported by Morozkin.[11] No thermal hysteresis was detected around the phase transition temperature, suggesting a second order phase transition nature. From point view of Morozkin some noncollinear magnetic structure is present in $Ho_{6-x}Er_xMnBi_2$; therefore the $M$-$T$ curve in the low temperature is a little different from that of the typical ferromagnetic materials.[11] We are attracted by the sharp drop in magnetization around the respective $T_C$, which is related to a large MCE.

We studied the magnetic entropy change of $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) using both magnetic and caloric methods. The isothermal field dependence of magnetization ($M$-$H$) curves were measured around the critical temperatures, as shown in Fig. 3. The sweep rate of the field is slow enough to ensure $M$-$H$ curves to be isothermal. The temperature step is 3 K in the vicinity of $T_C$ and 5 K for the range far away from $T_C$. The magnetic entropy change $|\Delta S|$ is calculated from the Maxwell relation $\Delta S(T,H)=-\int(\partial M/\partial T)_H dH$ using the above collected magnetization data. Figure 4 shows the plots of $|\Delta S|$ versus temperature at the magnetic field change from $H=0$ to $H=2$ and 5 T. The peak value of $|\Delta S|$ is 10.6, 7.3, and 5.0 J $kg^{-1}$ $K^{-1}$ under a magnetic field change from 0 to 5 T for x=6, 3, and 0, respectively, which are roughly comparable with those of $GdAl_2$ ($T_C$=167 K, $|\Delta S|$=7.6 J $kg^{-1}$ $K^{-1}$), a good refrigerant candidate in its relevant temperature range.[12] The shape of $\Delta S_m$-$T$ curve has a good symmetry below and above the magnetic ordering temperature, and the value of the maximal magnetic entropy change increases monotonously with increasing field change, as shown in Fig. 5. In $Ho_{6-x}Er_xMnBi_2$ compounds, the transition metal atoms were not supposed to show local magnetic moment, so the major attribution of magnetization is coming from the rare earth elements with large magnetic moment. The large saturation magnetization and the considerable variation in the magnetization near $T_C$ result in the large magnetic entropy change in $Ho_{6-x}Er_xMnBi_2$ compounds. Either thermal or magnetic hysteresis around the phase transition is not observed, suggesting a second order phase transition nature, which can be the reasons of the good shape symmetry of $\Delta S_m$-$T$ curve below and above the magnetic ordering temperature.

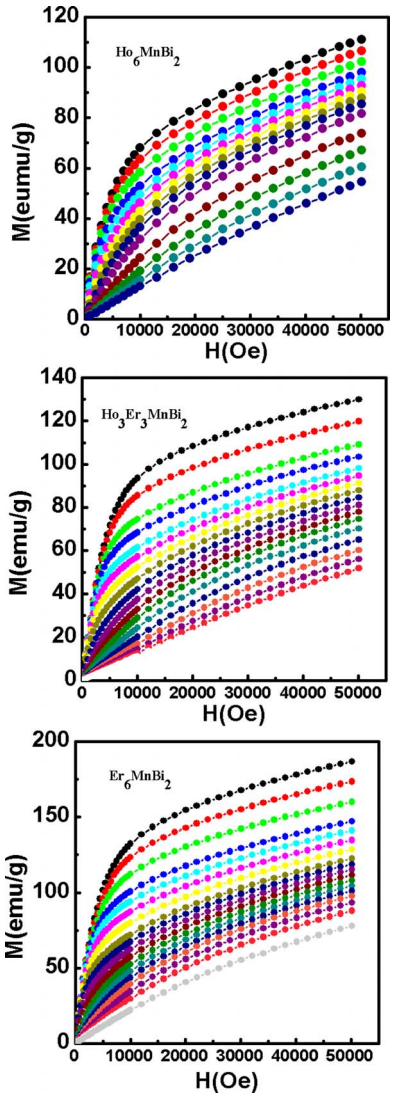


FIG. 3. (Color online) The isothermal field dependence of magnetization ($M$-$H$) curves around the critical temperatures for $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) compounds.

Due to the presence of the noncollinear magnetic structure in the low temperature, the applicability of the Maxwell relation in $Ho_{6-x}Er_xMnBi_2$ compounds needs to be proven. The calorimetric technique is used here. The specific heat of

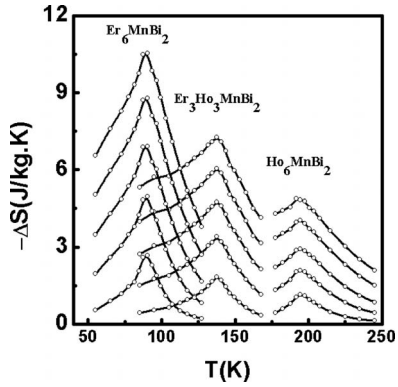


FIG. 4. The magnetic entropy change $|\Delta S|$ vs temperature at the magnetic field change from $H=0$ to $H=2$ and 5 T for $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) compounds.

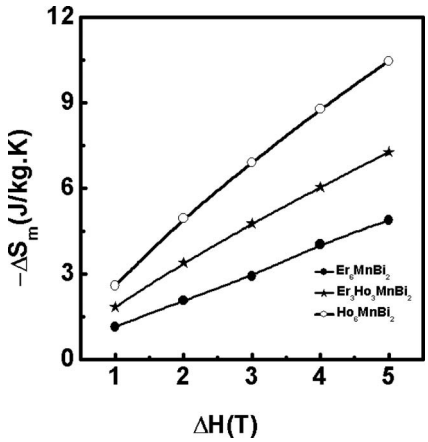


FIG. 5. The applied field change dependence of the magnetic entropy change $|\Delta S|$ for $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6) compounds.

$Er_6MnBi_2$, as shown in Fig. 6, was measured over the temperature range of 2–250 K under the applied field of 0, 2, and 5 T. The λ shape of the *Cp-T* curve near the transition temperature suggests a second order phase transition. The magnetic entropy change $|\Delta S|_M$ can be calculated based on the following equations:

$$S(T) = \int_0^T \frac{C(T)_H}{T} dT + S_{0,H}, \tag{1}$$

$$\Delta S_M = \Delta S = S(H,T) - S(0,T), \tag{2}$$

$$S(T + \Delta T, B = \Delta B + B1) = S(T, B1), \tag{3}$$

Figure 7 displays the temperature dependence of $|\Delta S|$ for various field changes calculated by both magnetic and calorimetric methods. One can find that two techniques yield almost consistent results above the transition temperature, however, the value of $|\Delta S|$ obtained from the magnetic methods is obvious lager than that obtained from the calorimetric method. This may be due to the noncollinear magnetic structure in the low temperature, the magnetic structure will be changed under the applied magnetic field and the Maxwell relation could not get accurate results below the transition temperature.[13]

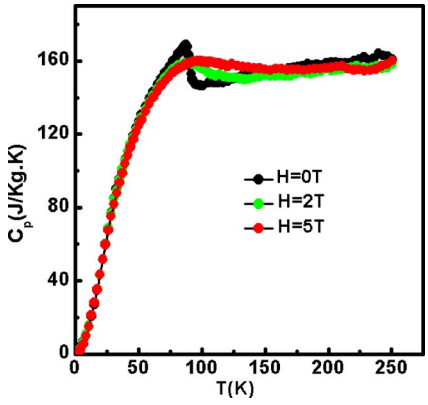


FIG. 6. (Color online) The specific heat of $Er_6MnBi_2$ measured over the temperature range 2–250 K under the applied field of 0, 2, and 5 T.

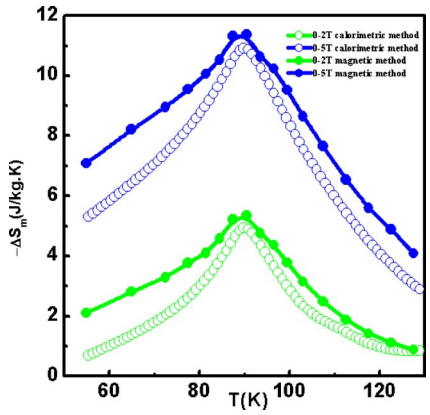


FIG. 7. (Color online) The temperature dependence of $|\Delta S|$ for various field changes calculated by both magnetic and calorimetric methods for $Er_6MnBi_2$.

In conclusion, we have studied the magnetic properties and MCE of compounds $Ho_{6-x}Er_xMnBi_2$ (x=0,3,6). All the compounds show a sharp drop in the magnetization around its respective magnetic ordering temperatures, which are 201 K (x=0), 147 K (x=3), and 98 K (x=6), respectively. The magnetic entropy changes calculated from the Maxwell relation using the collected magnetization data are 10.6 J $kg^{-1}$ $K^{-1}$ (x=6), 7.3 J $kg^{-1}$ $K^{-1}$ (x=3), and 5.0 J $kg^{-1}$ $K^{-1}$ (x=0), respectively. The shape of the $\Delta S$-*T* curve has a good symmetry below and above the magnetic ordering temperature, and the value of the magnetic entropy change increases monotonously with increasing field change. Either thermal or magnetic hysteresis is not observed suggesting a second order phase transition nature.

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