# Magnetocaloric effect in Gd-based bulk metallic glasses

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Magnetocaloric effect and refrigerant capacity of Gd-based $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ bulk metallic glasses are investigated. It is found that the magnetic entropy changes compare favorably with that of Gd and are slightly larger than that of the known crystalline magnetic refrigerant compound $Gd_5Si_2Ge_{1.9}Fe_{0.1}$. Their good refrigerant efficiency combining with high electrical resistivity, high thermal stability, outstanding mechanical properties, tunable nature, and sufficiently soft magnetic property make them an attractive candidate for magnetic refrigerants in the temperature range of 10–100 K. © *2006 American Institute of Physics*.
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Magnetic materials exhibiting large magnetocaloric effect (MCE) attract tremendous attention due to their potential application as magnetic refrigerants.[1–5] Compared with conventional gas refrigerants, the magnetic refrigerants have advantages of both high efficiency and environmentally friendliness demonstrating their promising future. Magnetic refrigeration is based on the magnetocaloric effect that is an intrinsic property of the magnetic material. For a magnetic material exhibiting MCE, the alignment of randomly oriented magnetic moments by an external magnetic field results in the reduction of the magnetic entropy of the material. When the magnetic field is subsequently turned off, the magnetic moments randomize again, which conversely leads to cooling effect. Advancing this technology requires enhancing the MCE at a wide temperature range and exploring the efficient magnetic materials used as refrigerants.

To gain large MCE, in addition to choose proper thermodynamic cycle, the magnetic properties of the material are of great importance.[6] Intensive works have been done mostly on various crystalline materials. It has been suggested that glassy materials can be also attractive for application for magnetic refrigerants,[7–10] because they display many unique properties associated with their intrinsic nature, such as the tailorable nature of the ordering temperature, the high electrical resistivity and thus small eddy current heating, and high corrosion resistance. However, little work has been done about the MCE of glassy materials. There is only one report about the MCE of bulk metallic glass[11] (BMG) and other few about glassy ribbons.[7–10]

Last decade, BMGs regained considerable interest as excellent engineering materials, because they can be obtained readily at comparatively low cooling rate owing to their good glass-forming ability.[12] Very recently a series of heavy rare earth (Ho, Gd, Tb, Dy, and Er) based BMGs with large magnetic moments and profuse magnetic structure has been developed.[13–17] Combining with their high electrical resistivity and tailorable nature associated with disorder structure, outstanding mechanical properties, and high thermally stability, these BMGs may be considered as suitable candidates for magnetic refrigerants.

In this letter, the MCE of Gd-based BMGs under a modest magnetic field has been reported. Large magnetic entropy changes comparable with Gd metal have been obtained. Our work shows that this kind of material appears to be an ideal candidate for the active magnetic refrigerants working in the temperature range of 10–100 K.

The Gd-based BMGs with nominal compositions $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ were prepared by arc melting pure Co, Al, Zr, Er, and Gd in a Ti-gettered argon atmosphere. The ingot was remelted and suck cast into a Cu mold to get a cylindrical rod of 3 mm in diameter. Their amorphous nature was ascertained by x-ray diffraction (XRD) using a MAC Mo3 XHF diffractometer with Cu $K\alpha$ radiation and transmission electron microscope. Thermal analysis was carried out in a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). The temperature and field dependences of magnetization were measured in physical properties measurement system 6000 of Quantum Design Company.

Figure 1 shows the XRD patterns of the as-cast Gd-based BMGs. The broad diffraction peaks and no appreciable peaks indicate that full glassy rods can be obtained for the alloys at least 3 mm in diameter. Their glassy nature was

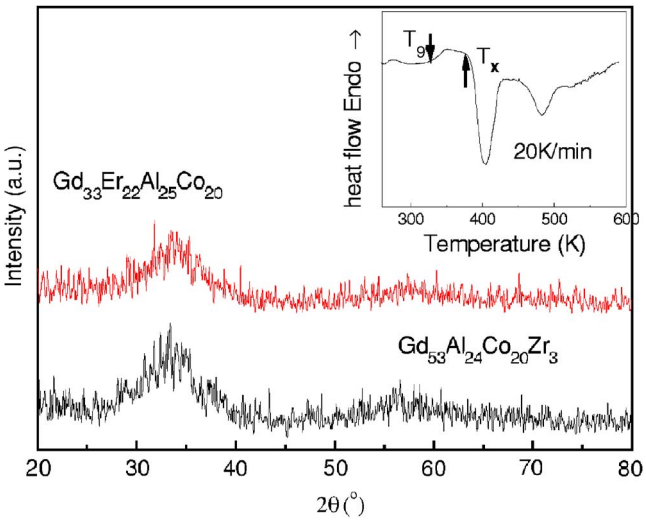


FIG. 1. (Color online) XRD patterns taken from the cross-sectional slice of the as-quenched Gd-based BMGs rods (diameter is 3 mm). The inset shows the DSC curve of $Gd_{53}Al_{24}Co_{20}Zr_3$.

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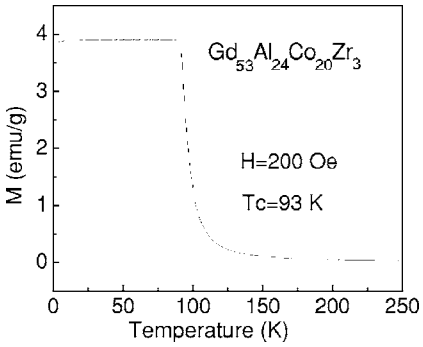


FIG. 2. Temperature dependence of the magnetization under a magnetic field of 200 Oe for $Gd_{53}Al_{24}Co_{20}Zr_3$ BMG.

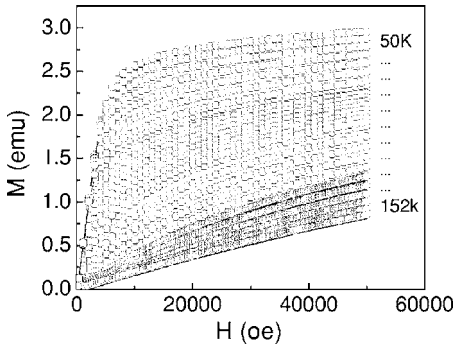


FIG. 4. Isothermal magnetization as a function of magnetic field at various temperatures.

also confirmed by DSC as shown in the inset of Fig. 1. The remarkable feature of the DSC trace of $Gd_{53}Al_{24}Co_{20}Zr_3$ is that the alloy exhibits an endothermic reaction due to glass transition and two exothermic peaks due to crystallization. Figure 2 shows the temperature dependence of the magnetization determined in an applied field of 200 Oe for the $Gd_{53}Al_{24}Co_{20}Zr_3$ alloy. The Curie temperature ($T_C$) is about 93 K. Even though the strong disorder effect exists in the sample, one can see that the magnetization varies sharply at the ordering temperature as that in the known crystalline magnetic refrigerant material of MnFePSb.[5] According to the Maxwell relation, the large magnetic entropy may be expected. We note that nearly all the heavy rare earth elements can be made in bulk glassy form in a wide concentration range.[13] Thus, the transition temperature can be tuned easily in large temperature range of 10–100 K not only by choosing different heavy earth element bases in the BMGs but also by alloying several rare earth elements in proper proportion in a single phase. The advantage of wide choice of alloy compositions available in the rare earth based BMGs makes them an attractive choice for refrigerants in multistage magnetic refrigerators. Figure 3 shows that the magnetic hysteresis of $Gd_{53}Al_{24}Co_{20}Zr_3$ is small even at 2 K (the coercivity is ~60 Oe), which is considered to be a very favorable characteristic of magnetic refrigerant application. This is expected because Gd has no orbit momentum unlike other rare earth metals, which makes the magnetocrystalline anisotropy relatively small. It is therefore relatively easy to magnetize and demagnetize the material due to its small coercivity.

Isothermal magnetization curves of *M-H* with increasing filed in a wild temperature range are displayed in Fig. 4. In the vicinity of $T_C$ the temperature step of 3 K was chosen, and a step of 5 K for the regions far away from $T_C$. The sweeping rate of field is slow enough to ensure the data are recorded in an isothermal process. In an isothermal process of magnetization, the total magnetic entropy change of the system due to the application of a magnetic field can be derived from Maxwell relation by integrating over the magnetic field,

$$\Delta S_m = \int_{H_{\min}}^{H_{\max}} \left(\frac{\partial M}{\partial T}\right) dH, \tag{1}$$

where $H_{\min}$ ($H_{\min}$ is usually fixed to zero) and $H_{\max}$ represent the initial and final values of magnetic field, respectively. Maximal value of 5 T of the magnetic field was used in our experiments. To derive the temperature dependence of magnetic entropy change, the numerical approximation of the integral is usually applied,

$$\Delta S_m = \sum_i \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta H, \tag{2}$$

where $M_i$ and $M_{i+1}$ are the experimental values of the magnetization at $T_i$ and $T_{i+1}$ under an applied magnetic field $H_i$, respectively.

By measuring the isothermal *M-H* curves at various temperatures, we evaluate the magnetic entropy change associated with the *H* variation according to Eq. (2). Figure 5

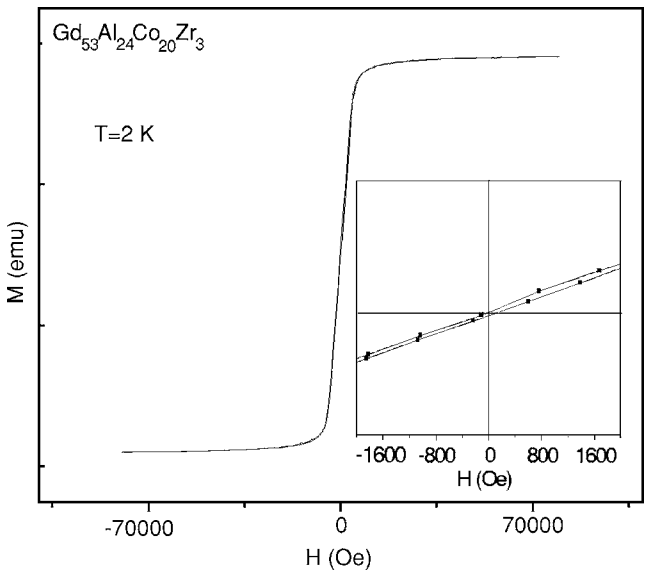


FIG. 3. Magnetic hysteresis of $Gd_{53}Al_{24}Co_{20}Zr_3$ BMG at 2 K. The inset shows the enlarged part.

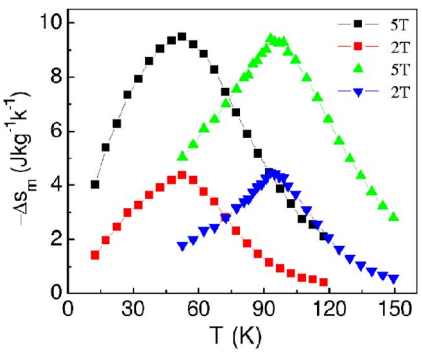


FIG. 5. (Color online) Magnetic entropy changes as a function of temperature for $Gd_{53}Al_{24}Co_{20}Zr_3$ (triangle) and $Gd_{33}Er_{22}Al_{25}Co_{20}$ (square) BMGs under 2 and 5 T.

TABLE I. Magnetic entropy changes upon allying a field $H$ to various materials and related parameters. The $a$ and $c$ stand for the amorphous and crystalline states, respectively.

| Material | Structure | Applied field (T) | $\Delta S_m$ (J kg$^{-1}$ K$^{-1}$) | Transition temperature (K) | Refrigerant capacity (J kg$^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| $Gd_{53}Al_{24}Co_{20}Zr_3$ | $a$ | 5 | 9.4 | 93 | 590 | Presentwok |
| $Gd_{33}Er_{22}Al_{25}Co_{20}$ | $a$ | 5 | 9.47 | 52 | 574 | Presentwok |
| Gd | $c$ | 5 | 9.8 | 293 | ··· | 6 |
| $Gd_5Si_2Ge_2$ | $c$ | 5 | 18.6 | 276 | 306 | 1 |
| $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ | $c$ | 5 | 7 | 276 | 360 | 18 |
| $Fe_{70}B_5C_5Si_3Al_5Ga_2P_{10}$ | $a$ | 1.5 | 1.65 | ~588 | 74 | 22 |
| $Fe_{60}Cr_{14}Cu_1Nb_3Si_{13}B_9$ | $a$ | 3 | 0.9 | 226 | ··· | 8 |
| $Pd_{40}Ni_{22.5}Fe_{17.5}P_{20}$ | $a$ | 5 | 0.58 | 94 | ··· | 11 |

shows the $-\Delta S_m$ as a function of temperature under 2 and 5 T. The peak values of $-\Delta S_m$ are 9.40 J kg$^{-1}$ K$^{-1}$ at 93 K and 9.47 J kg$^{-1}$ K$^{-1}$ at 52 K for $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$, respectively. As seen in Fig. 5, the peak and width of $-\Delta S_m$ are dependent on the change of $H$, and both the height and width increase obviously with increasing filed. The reduction of $T_C$ by replacing some percents of Gd by Er can be attributed to the lower magnetic interaction and transition temperature of Er. The peaks values of $-\Delta S_m$ are comparable with that of Gd which is considered as good magnetic refrigerant. These values are also much larger than that of Pd-based BMGs (0.58 J kg$^{-1}$ K$^{-1}$) (Ref. 11) and Fe- and Co-based glassy ribbons (~0.6–0.9 J kg$^{-1}$ K$^{-1}$).[8] Partially substitution of Gd and replacement of Si and Ge (Si and Ge are widely used in the crystalline magnetic refrigerant Gd-based compounds[1,18]) using transitional metals can reduce the cost of the Gd-based refrigerant alloys.

The larger MCE in Gd-based BMGs is due to the larger magnetic moment of Gd. Our study also show that the structural disorder reduces $T_C$ and leads to a broader peak in the magnetic entropy change due to fluctuation of the exchange integral, but the refrigerant efficiency of Gd remains. Another relevant parameter characterizing the refrigerant efficiency of the material is the refrigerant capacity (RC), which is measured in literature by different methods.[19,20] We estimate the RC by the product of the peak entropy change and the full width at half maximum of the peak. The RC values for $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ are determined to be 780 and 714 J kg$^{-1}$, respectively. The RC can also be determined by numerically integrating the area under the $\Delta S_m - T$ curve using the temperatures at half maximum of the peak as the integration limits. The RC values for $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ computed by this method are 590 and 574 J kg$^{-1}$, respectively. These values are much larger than those of $Gd_5Si_2Ge_2$ (305 J kg$^{-1}$) and $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ (360 J kg$^{-1}$ K$^{-1}$),[18] indicating the better refrigerant efficiency of the Gd-based BMGs. The high RC is due to the glassy structure which extends the large MCE into larger temperature range. Usually, the crystalline materials exhibit large MCE concentrated in a narrow temperature range. For example, in $Gd_5Si_2Ge_2$ and $MnFeP_{0.45}As_{0.55}$ (Ref. 5) in which large MCE are observed, the temperature range of the half maximum of the entropy change peak is less than 30 K, and in $Ni_2Mn_{1-x}Cu_xGa$ (Ref. 21) less than 5 K. While, in $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ BMGs the temperature ranges extend to 83 and 75 K, respectively. For comparison, magnetocaloric properties of some typical materials including our materials are listed in Table I.

In summary, large MCE have been observed in $Gd_{53}Al_{24}Co_{20}Zr_3$ and $Gd_{33}Er_{22}Al_{25}Co_{20}$ BMGs. Their maximum value of the magnetic entropy change compares favorably with that of Gd and slightly larger than that of the magnetic refrigerant $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ compound. Furthermore, the BMGs have much wide temperature range of the large MCE, which leads to the increased RC. In manufacturing, the glassy alloys are much easily to be fabricated compared to that of the magnetic refrigerant compounds.

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