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Table-like magnetocaloric effect and enhanced refrigerant capacity in $Eu_8Ga_{16}Ge_{30}$-EuO composite materials

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A large reversible magnetocaloric effect (MCE) and enhanced refrigerant capacity (*RC*) were observed in multiphase composite materials composed of type-I clathrate $Eu_8Ga_{16}Ge_{30}$ and EuO. $Eu_8Ga_{16}Ge_{30}$ undergoes two successive ferromagnetic transitions at 10 K and 35 K, and EuO exhibits a ferromagnetic transition at 75 K. A large *RC* of 794 J/kg for a field change of 5 T over a temperature interval of 70 K was achieved in the $Eu_8Ga_{16}Ge_{30}$–EuO composite with a 40%-60% weight ratio. This is the largest value ever achieved among existing magnetocaloric materials for magnetic refrigeration in the temperature range 10 K-100 K. Adjusting the $Eu_8Ga_{16}Ge_{30}$ to EuO ratio is shown to produce composites with table-like MCE, desirable for ideal Ericsson-cycle magnetic refrigeration. The excellent magnetocaloric properties of these $Eu_8Ga_{16}Ge_{30}$–EuO composites make them attractive for active magnetic refrigeration in the liquid nitrogen temperature range. © *2011 American Institute of Physics*. [doi:10.1063/1.3654157]

Magnetic refrigeration is an environmentally friendly technology that uses a magnetic field to change the magnetic entropy of a material (i.e., the magnetocaloric effect, MCE), thus allowing the material to serve as a refrigerant.[1] This technology yields a much higher cooling efficiency (about 20%-30%) than conventional gas compression techniques.[2] Producing a magnetocaloric material that possesses a large magnetic entropy change (ΔS_M) over a wide temperature range, i.e., a large refrigerant capacity (*RC*),[3–5] is of interest for magnetic refrigeration applications. For ideal Ericsson-cycle based magnetic refrigeration, a magnetocaloric material should possess a constant ΔS_M in the refrigeration temperature range (known as "table-like" MCE).[6,7] In this context, magnetocaloric materials that undergo multiple successive magnetic phase transitions seem to meet these criteria as the presence of magnetic multiphases broadens the $\Delta S_M(T)$ curves and consequently enhances the *RC*.[5–7] However, the multiphase magnetocaloric materials reported in the literature are found to exhibit either a relatively small ΔS_M (Refs. 3 and 8) or non-uniform $\Delta S_M(T)$ curves.[3,9,10] For instance, the broadening of ΔS_M over the temperature range 20 K–300 K has been observed in multiphase $LuFe_2O_4$; however, the magnitude of ΔS_M of this material is $\sim$1 J/kg K for a field change of 6 T.[8] This underscores the need for developing magnetocaloric materials that fulfill the above criteria.

$Eu_8Ga_{16}Ge_{30}$ semiconductors with the clathrate hydrate crystal structure are widely known for their interesting physical properties,[11] including thermoelectric properties.[12] Our recent work on large and reversible MCE in these materials indicates they may also be of interest for thermomagnetic cooling applications.[13–15] In particular, a giant magnetic entropy change at $T_C \sim 13$ K was observed in the $Eu_8Ga_{16}Ge_{30}$ type-VIII clathrate ($-\Delta S_M = 11.4$ J/kg K for $\mu_o\Delta H = 3$ T),[13] in addition to a relatively large *RC* for the $Eu_8Ga_{16}Ge_{30}$ type-I clathrate.[14,15] The $Eu_8Ga_{16}Ge_{30}$ type-I clathrate undergoes two successive magnetic transitions, one at 10 K and the other at 35 K. These clathrates also exhibit negligible thermal and field hysteresis losses, as they belong to the class of materials with a second-order magnetic transition (SOMT). These results allow for the possibility of using $Eu_8Ga_{16}Ge_{30}$ clathrates as host matrices to fabricate composite materials with desirable magnetocaloric properties for active magnetic refrigeration (AMR).

We report on the large table-like MCE and enhanced *RC* in $Eu_8Ga_{16}Ge_{30}$ type I clathrate–EuO composites that undergo multiple successive magnetic transitions at 10 K, 35 K, and 75 K. It is shown that the presence of magnetic multiphases and the combination of $Eu_8Ga_{16}Ge_{30}$ and EuO in the right proportion are important for producing composite materials with enhanced RC and table-like MCE.

High-quality polycrystalline type-I $Eu_8Ga_{16}Ge_{30}$ was synthesized by melting a stoichiometric mixture of the high purity elements inside a BN crucible by an induction furnace, in a nitrogen atmosphere, at 1000 °C for 10 min followed by water quenching.[13] EuO (Ames Laboratories, 99.9%) was used as received. Powdered specimens of the $Eu_8Ga_{16}Ge_{30}$-EuO composites were made by repetitive grinding and mixing of the two compositions in the desired ratios by weight. Approximately 50 mg of the composites with clathrate-to-EuO ratios of 20%-80%, 40%-60%, 50%-50%, 60%-40%, 65%-35%, 70%-30%, and 80%-20% were placed in plastic ampoules for magnetic measurements. The magnetic measurements were performed using a commercial Physical Property Measurement System from Quantum Design in the temperature range of 5 to 300 K for applied fields up to 7 T. The ΔS_M of the specimens was calculated from the family of *M-H* isotherms using the Maxwell relation $\Delta S_M = \mu_0\int(\partial M/\partial T)_H dH$, where *M* is the magnetization, *H* is the magnetic field, and *T* is the temperature.[13] The *RC* was calculated as $RC = [-\Delta S_M]_{max} \times \delta T_{FWHM}$, where

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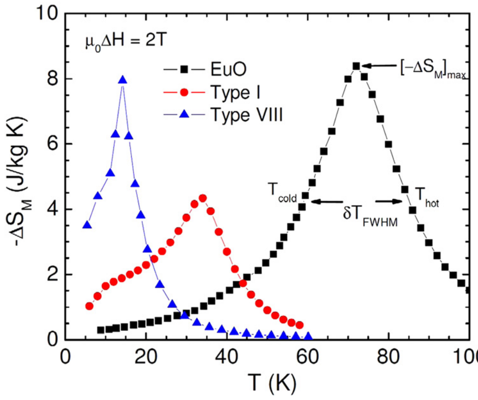

FIG. 1. (Color online) Temperature dependence of $-\Delta S_M$ at 2 T for the $Eu_8Ga_{16}Ge_{30}$ type-VIII clathrate, the $Eu_8Ga_{16}Ge_{30}$ type-I clathrate, and EuO.

δT_{FWHM} is the full width at half maximum (FWHM) of the $\Delta S_M(T)$ curve.[1]

Figure 1 shows the temperature dependence of $-\Delta S_M$ for $\mu_o\Delta H = 2$ T for type-VIII $Eu_8Ga_{16}Ge_{30}$ and type-I $Eu_8Ga_{16}Ge_{30}$ clathrates, and EuO. As shown in the figure, the three compounds exhibit peaks at their Curie temperatures. The $-\Delta S_M$ and *RC* values are 8 J/kg K and 60 J/kg for the type-VIII clathrate, 4.5 J/kg K and 80 J/kg for the type-I clathrate, and 8.5 J/kg K and 120 J/kg for EuO. The $-\Delta S_M$ and *RC* values for the EuO reported here are similar to those reported previously by Ahn *et al.*,[16] who showed that EuO is one of the best candidate materials for magnetic refrigeration around 70 K. The type-I clathrate undergoes a secondary magnetic transition at 10 K in addition to the ferromagnetic transition at 35 K, resulting in a broadened $\Delta S_M(T)$ curve at low temperatures and consequently an enhanced *RC*.[14] This explains why the type-I clathrate possesses a larger *RC* as compared with the type-VIII clathrate, even though the magnitude of ΔS_M of the former is about half smaller than that of the latter. The focus in this paper is therefore on exploring the MCE and *RC* in the type-I clathrate–EuO composites.

Figure 2(a) shows the temperature dependence of $-\Delta S_M$ for different applied field changes up to 6 T for the 40%-60% type-I-EuO composite. Figure 2(b) shows the temperature dependence of $-\Delta S_M$ for the field change of $\mu_o\Delta H = 6$ T for the 40%-60% and 70%-30% composites. As shown in Figure 2, a proper combination of $Eu_8Ga_{16}Ge_{30}$ and EuO not only broadens the $\Delta S_M(T)$ curves but also retains the large values of $-\Delta S_M$ in the composite specimens (for example, $-\Delta S_M \sim 13$ J/kg K for $\mu_o\Delta H = 6$ T for the 40%-60% composite). For active magnetic refrigeration, it is necessary to have a uniform distribution of $\Delta S_M(T)$. This has been achieved in the present composite specimens at sufficiently high magnetic fields. In addition, tuning the $Eu_8Ga_{16}Ge_{30}$ to EuO ratio can produce composites that possess table-like $\Delta S_M(T)$ curves (Figure 2(b)) desirable for an ideal Ericsson-cycle magnetic refrigeration.

Figure 3(a) shows the variation in the *RC* and the δT_{FWHM} curves as a function of weight percent of $Eu_8Ga_{16}Ge_{30}$ and EuO for $\mu_o\Delta H = 5$ T. The *RC* values of the composite specimens are greater than that of $Eu_8Ga_{16}Ge_{30}$. The larger *RC* values of the composites result from the increase of both ΔS_M and δT_{FWHM}. This arises from the

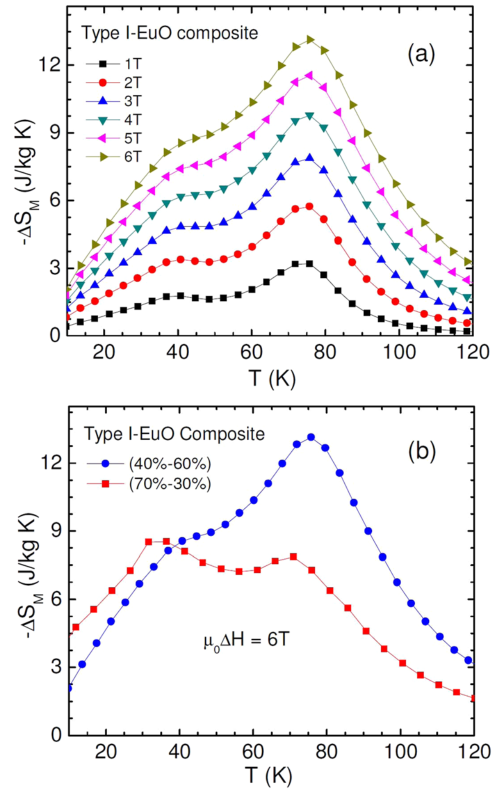

FIG. 2. (Color online) Temperature dependence of $-\Delta S_M$ at different fields up to 6 T (a) for the 40%-60% $Eu_8Ga_{16}Ge_{30}$ type-I clathrate-EuO composite and (b) for the 40%-60% and 70%-30% composites.

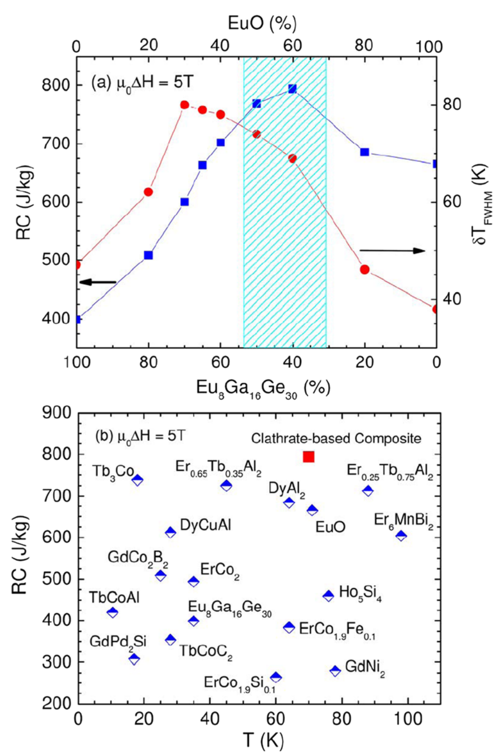

FIG. 3. (Color online) (a) *RC* and δT_{FWHM} for $Eu_8Ga_{16}Ge_{30}$-EuO composites as a function of the weight percent of the constituents; (b) *RC* values of the 40%-60% $Eu_8Ga_{16}Ge_{30}$-EuO composite and other magnetocaloric candidate materials, including Tb_3Co and TbCoAl (Ref. 17), $GdCo_2B_2$ (Ref. 18), $GdPd_2Si$ (Ref. 19), $TbCoC_2$ (Ref. 20), $ErCo_2$ and $ErCo_{1.9}Si_{0.1}$ (Ref. 21), DyCuAl (Ref. 22), $DyAl_2$ (Ref. 23), $Er_{0.65}Tb_{0.35}Al_2$ and $Er_{0.25}Tb_{0.75}Al_2$ (Ref. 24), $ErCo_{1.9}Fe_{0.1}$ (Ref. 25), $GaNi_2$ (Ref. 26), Ho_5Si_4 (Ref. 27), and Er_6MnBi_2 (Ref. 28).

relative contributions to the *RC* from ΔS_M and δT_{FWHM}, as the *RC* is the product of both. It should be noted that while δT_{FWHM} increases, ΔS_M decreases in the composites relative to EuO. For the clathrate-based composites containing less than 35 wt.% EuO, the increase in δT_{FWHM} is less than the decrease in ΔS_M. As a result, *RC* is smaller in these composites as compared with that of EuO. For the clathrate-based composites containing large amounts of EuO (above 35 wt.%), the increase in δT_{FWHM} is greater than the decrease in ΔS_M thus resulting in a larger *RC* in the composites relative to that of EuO. Among the five composite specimens we investigated, the 40%-60% composite shows the largest *RC* (~794 J/kg for $\mu_o \Delta H = 5$ T). This *RC* value is greater than that of EuO (~665 J/kg) for the same field change of 5 T. It is also worth noting that while the *RC* of the 65%-35% composite is almost equal to that of EuO, the table-like MCE (i.e., the relatively constant ΔS_M with temperature) observed for this composite over a wide temperature range (20 K–80 K) makes it a better choice for Ericsson-cycle based magnetic refrigeration.

Figure 3(b) shows a detailed comparison of the *RC* between the 40%-60% composite with other magnetocaloric candidate materials for active magnetic refrigeration in the temperature range of 10 K–100 K. The type-I clathrate–EuO composite shows the largest *RC* in this group of magnetocaloric materials while possessing nearly zero thermal and field hysteresis losses due to the fact that it is SOMT. These magnetocaloric properties make it one of the best candidate materials for active magnetic refrigeration around 70 K.

In summary, a large reversible MCE and enhanced RC in type-I $Eu_8Ga_{16}Ge_{30}$ clathrate–EuO composites were observed. The presence of multiple successive magnetic phase transitions and the appropriate ratio of $Eu_8Ga_{16}Ge_{30}$ to EuO are important factors in producing composite materials with enhanced RC and/or table-like MCE. These magnetocaloric properties demonstrate that these composites have potential for active magnetic refrigeration applications in the liquid nitrogen temperature range.

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