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Magnetocaloric effects of ferromagnetic erbium mononitride

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Abstract

The rare earth mononitride, ErN, has been synthesized by the carbothermic reduction and hot isostatic press methods. The magnetocaloric effect of ErN has been evaluated by calculating the magnetic entropy changes, ΔS, from the magnetization data sets and from the heat capacity measured at various temperatures and applied fields. The two results are in good agreement with each other. The ΔS value of ErN is the highest at 7.5 K and higher than that of $ErNi_2$ reported as the candidate material for the magnetic refrigerant of cryogenic technology. Heat capacity curve against temperature of ErN has a peak at 4.4 K at zero-field. The peak value of the heat capacity of ErN is 507 kJ K^{-1} m^{-3}. This value is larger than those of Er_3Ni used commercially as a magnetic regenerator for the Gifford–McMahon refrigerator. The present results indicate that ErN is a promising material for the magnetic refrigerant and regenerator of cooling systems working above the boiling temperature of helium.

Keywords: Erbium; Nitride; Magnetic entropy; Heat capacity; Magnetic refrigerant; Magnetic regenerator

1. Introduction

The magnetic refrigeration system provides good energy efficiency, especially at cryogenic temperatures [1]. It is, therefore, prospective to apply this system to the helium or hydrogen liquefaction process. To establish this refrigeration technology, it is necessary to obtain the efficient and reliable magnetic refrigerant that possesses a large magnetocaloric effect (MCE) around and above the boiling points of helium and hydrogen (4 and 20 K). The MCE is evaluated by the magnetic entropy change ΔS induced by demagnetization of the refrigerant. The value of ΔS is usually maximized around the magnetic transition temperature, such as the Curie point. We have found that HoN, DyN, TbN and GdN show larger ΔS around their Curie temperatures (18, 21, 44 and 60 K) than those of the intermetallic compounds containing rare earths, $ErAl_2$, $HoNi_2$ or $Dy_xHo_{1-x}Al_2$, which have been proposed as candidates for the magnetic refrigerants for the application [2–5]. For helium liquefaction, we need materials with the larger magnetic entropy change at a temperature slightly higher than the boiling point of helium. ErN is expected to be an effective magnetic refrigerant for helium liquefaction, because rare earth atom concentration in mononitride is larger than that in metal [3] and the magnetic transition temperature of ErN has been reported as 3.4–6 K [6–8].

To realize the helium liquefaction, it is also necessary to get materials with large heat capacity at temperatures below 10 K for the magnetic regenerator, because the heat capacity of helium gas has a peak at 8 K [9]. Since the early 1990s, the development of rare-earth-based magnetic regenerator such as Er_3Ni, having high heat capacity at temperatures below 10 K, has allowed improvement in the cooling power of regenerative-cycle cryocoolers at very low temperatures, permitting the achievement of working

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refrigeration temperatures in the liquid helium [10]. The use of rare earth compounds having a heat capacity peak at a low temperature has made it possible for today's Gifford–McMahon (GM) cryocoolers to achieve cooling powers higher than 1 W at 4.2 K [11]. If materials with larger heat capacity at temperature below 10 K than Er_3Ni are available, the cooling efficiency of GM cryocoolers is improved. Heat capacity of a magnetic material usually shows a peak at its transition temperature. Concentration of Er per volume in ErN is higher than that in Er_3Ni. Therefore, ErN is also expected as one of the candidate materials for the magnetic regenerator working around the boiling temperature of helium, because the concentration of Er per volume in ErN is higher than that in Er_3Ni.

In this paper, we report on magnetic entropy change ΔS and heat capacity C of ErN.

2. Experimental

The sample of ErN was prepared by carbothermic reduction method performed in a nitrogen gas stream. It is quite the same as that employed in our previous works [2,3]. The sample of ErN were also synthesized by hot isostatic press (HIP) methods, because consolidate sample was needed for heat capacity measurement. A rectangular-shaped metal sheet of Er (99.9% purity, 5 mm × 5 mm × 1 mm for magnetization measurement and 1 mm × 1 mm × 0.1 mm for heat capacity measurement) was heated at 1873 K for 2 h under 130 MPa nitrogen atmosphere (99.9999% purity) with HIP equipment (O2-Dr.HIP; Kobelco Co. Ltd.). To examine the phase occurring in the product, the XRD pattern was measured with a diffractometer (RINT Ultima+; Rigaku Corporation) using Cu Kα radiation. The magnetization, M, was measured with a superconducting quantum interference device magnetometer (MPMS system, Quantum Design Inc.) under different applied fields H, up to 5 T, and at different temperatures T, from 100 to 5 K. The specific heat, C, was measured with Heat Capacity System (Oxford Instruments Inc.) under 0 and 5 T, and at different temperatures T, from 25 to 2 K.

The MCE was evaluated by calculating ΔS induced by isothermal demagnetization from H to 0, on the basis of the equation:

$$\Delta S = \int_H^0 \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H. \tag{1}$$

The integrand is replaced by another expression by applying Maxwell's relation, $(\partial S/\partial H)_T = (\partial M/\partial T)_H$, so that ΔS is given by:

$$\Delta S = \int_H^0 \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \tag{2}$$

The MCE is also evaluated from heat capacity $C(T)$. Absolute entropy is expressed by:

$$S_H(T) = \int_0^T \frac{C_H(T)}{T}\,\mathrm{d}T. \tag{3}$$

In this calculation, $C_H(T)$ below 2 K was assumed to be Debye's heat capacity, that is, $C_H(T)$ was in proportion to T^3. Therefore, ΔS is given by:

$$\Delta S(T) = S_0(T) - S_H(T) \tag{4}$$

The present magnetization data sets $M(T, H)$, and specific heat data sets $C(T, H)$ were substituted into these equations, and numerical calculations were carried out to obtain $\Delta S(T, H)$.

3. Results and discussion

The XRD pattern of ErN synthesized by the HIP method is shown in Fig. 1, which indicates that the sample is a single-phase material of the mononitride with a NaCl-type structure. As for the sample prepared by carbothermic reduction, almost the same profile was obtained. The lattice parameters determined by the XRD pattern obtained from the sample prepared by carbothermic reduction is shown in Fig. 2. The lattice parameters of other rare earth mononitrides (GdN, TbN, DyN and HoN) are also plotted against atomic number in Fig. 2 [2,3,6–8,12]. The plots show a fairly good linear relation, which indicates that these mononitrides share a crystal structure with the lattice parameter that varies smoothly with atomic number.

Fig. 3 shows magnetization M versus T curves of ErN synthesized by carbothermic reduction at different field strengths H. For the sample prepared by the HIP method, almost the

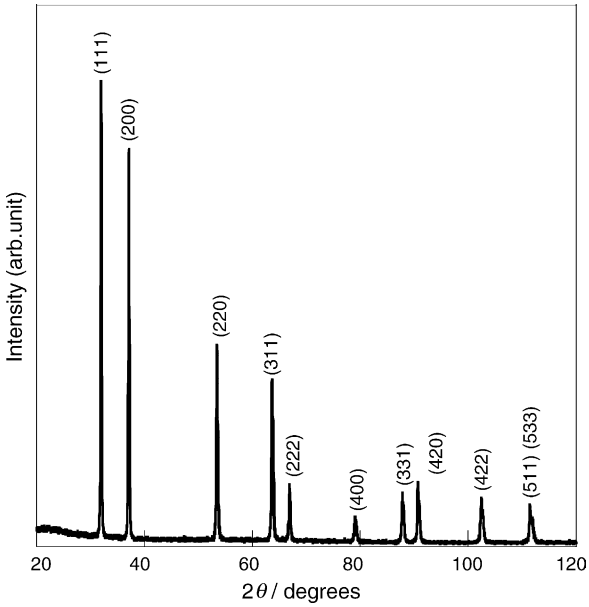

Fig. 1. X-ray diffraction patterns of ErN prepared by HIP method.

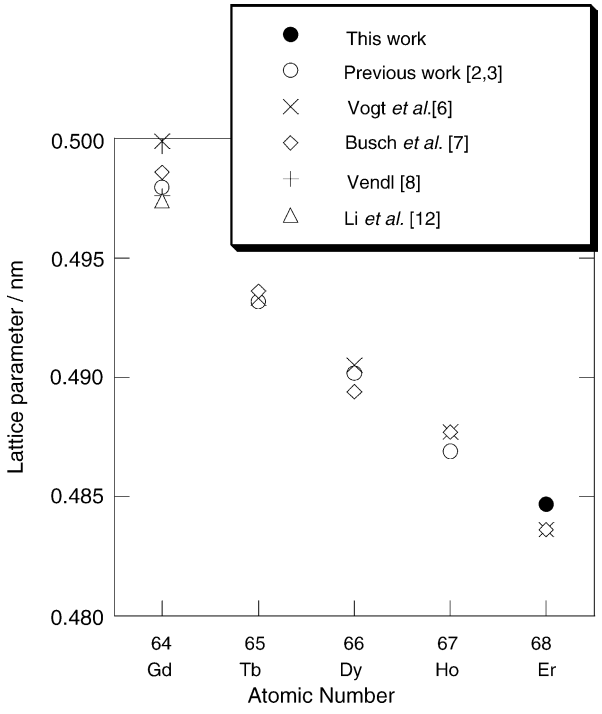

Fig. 2. Lattice parameters of ErN synthesized by the carbothermic reduction method and those of other rare earth nitrides.

same results have been obtained. These plots show clearly order–disorder (ferromagnetic to paramagnetic) transition with increasing temperature. The magnetic entropy change ΔS of ErN synthesized by the HIP method was evaluated by executing numerical calculation on the basis of Eq. (2), and the results are shown in Fig. 4. The ΔS versus temperature curves are noticed to have peaks around 7.5 K, regardless of applied field. This temperature well agrees with Curie temperature T_C of ErN estimated from Arrott plots as shown in Fig. 5. In Fig. 6, the ΔS versus temperature curve of

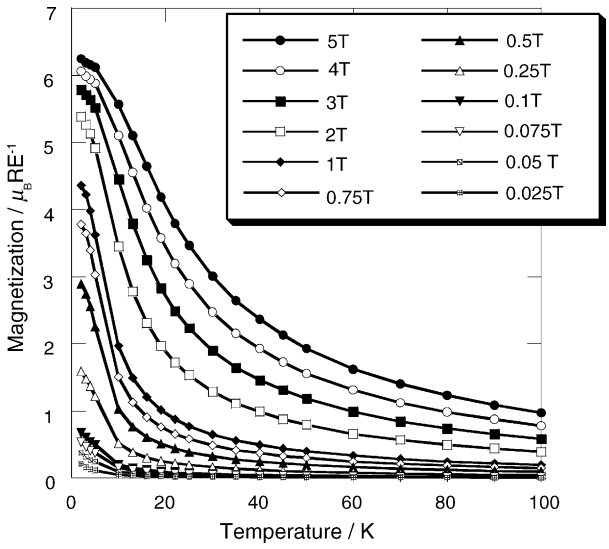

Fig. 3. Magnetization vs. temperature curves at different applied fields for ErN synthesized by the carbothermic reduction.

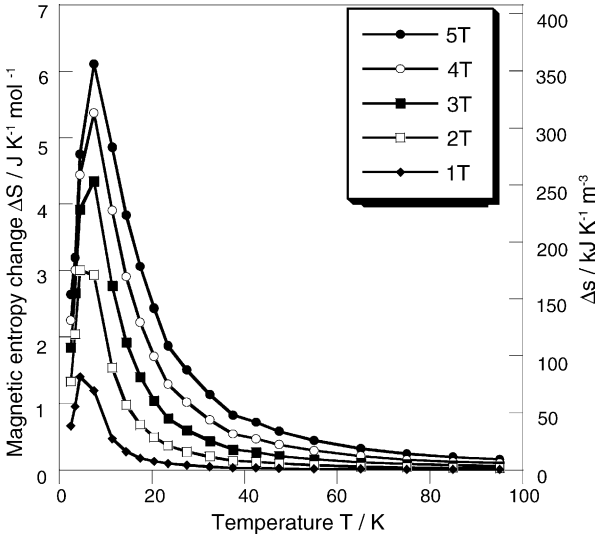

Fig. 4. Magnetic entropy change ΔS vs. temperature curves at different applied fields before demagnetization for ErN synthesized by HIP method.

ErN induced by the demagnetization from 5 to 0 T, together with the plots of GdN, TbN, DyN and HoN [3]. ErN has the largest ΔS values among them. The peak temperature of ΔS of $ErNi_2$, which is a candidate material for the magnetic refrigerant, is 6.6 K and the ΔS value at this temperature has been reported as 253 kJ K^{-1} m^{-3} [13]. The maximum ΔS value of magnetic materials tends to be larger as transition temperature decreases. In spite of this tendency, the maximum ΔS value of ErN is 1.4 times as large as that of $ErNi_2$. This result indicates that ErN is a promising magnetic

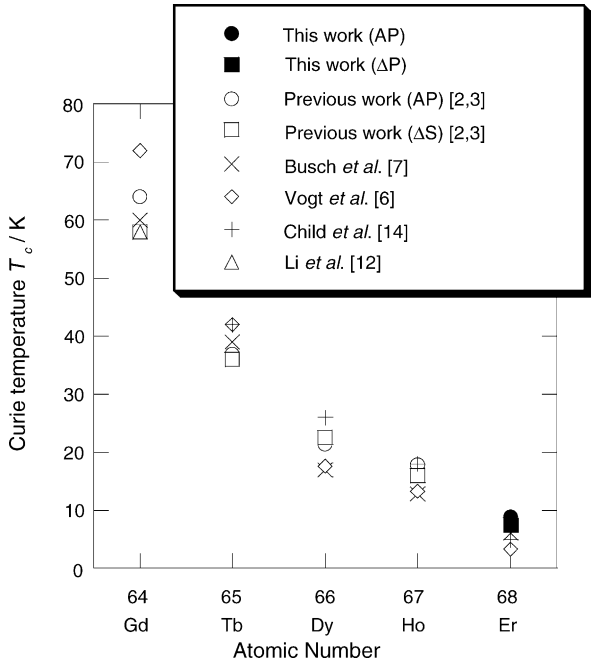

Fig. 5. Curie temperatures determined from the Arrott plots (denoted as AP in the legend), and the temperature of the maximum ΔS (denoted as ΔS in the legend) of ErN synthesized by the carbothermic reduction.

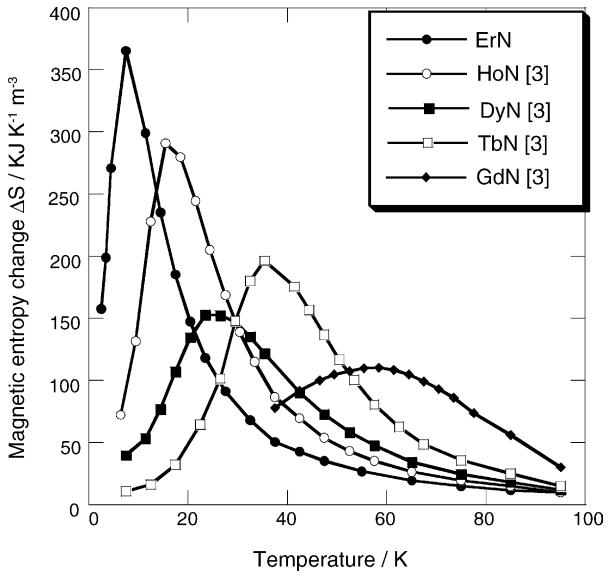

Fig. 6. Magnetic entropy change ΔS induced by demagnetization from 5 to 0 T for ErN synthesized by the carbothermic reduction. For comparison, plots for other rare earth nitrides are shown together.

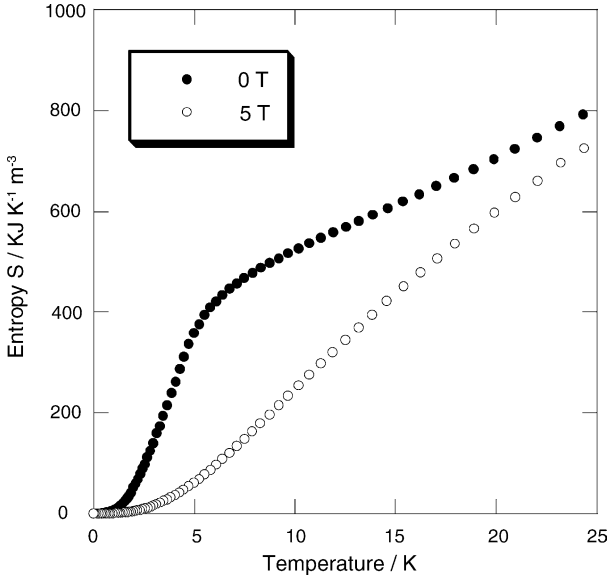

Fig. 8. Entropy S vs. temperature curves calculated from heat capacity of ErN at applied fields of 0 and 5 T.

refrigerant material for the cryogenic system at cryogenic temperatures.

The heat capacity of ErN synthesized by the HIP methods is given in Fig. 7 as a function of temperature at applied fields of 0 and 5 T. For comparison, those of He gas (1 MPa), Pb and intermetallic compounds of Er_3Ni and $Gd_{0.5}Er_{0.5}Rh$ [9], used commercially as magnetic regenerator for GM cryocoolers, are also shown. This plot clearly indicates that the ErN has a potential for a regenerator working near the helium boiling temperature. Fig. 8 shows absolute entropy of ErN at applied fields of 0 and 5 T calculated by the use of Eq. (3). We can also calculate the magnetic entropy change ΔS of ErN from the values of absolute entropy in Fig. 8 by use of Eq. (4). Fig. 9 shows ΔS of ErN as a function of temperature. The two of the three curves show the results estimated from magnetization data sets of ErN synthesized by the carbothermic reduction and the HIP methods, and the other curve shows the results estimated from heat capacity measurements. The two curves estimated from magnetization data well agree with each other. The results calculated from heat capacity measurements are also in moderate agreement with those obtained from magnetization measurements. These consistencies guarantee the accuracy of the results.

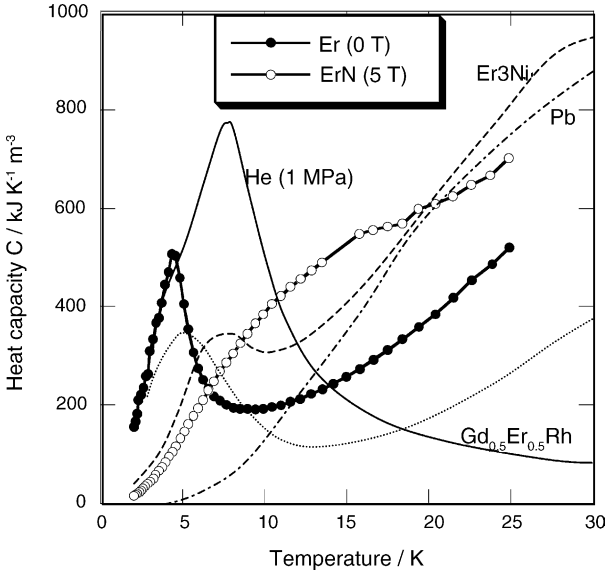

Fig. 7. Heat capacity vs. temperature curves at applied fields of 0 and 5 T for ErN synthesized by the HIP method.

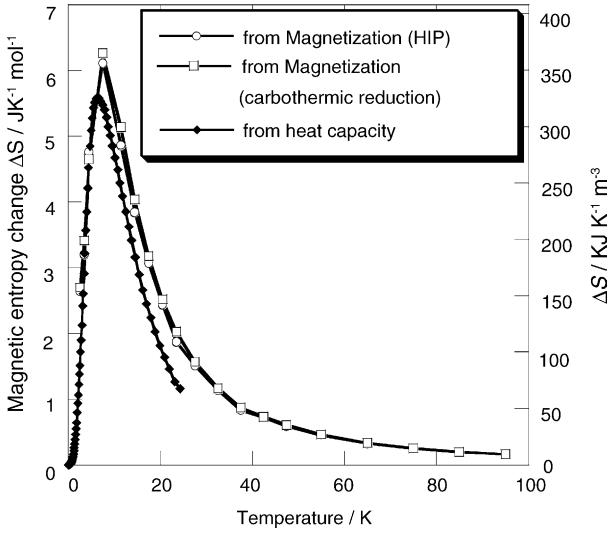

Fig. 9. Magnetic entropy change ΔS vs. temperature curves of ErN calculated from the data sets of magnetization and heat capacity measurements when demagnetized from 5 to 0 T.

4. Summary

Magnetocaloric effect of ErN has been evaluated by calculating the magnetic entropy changes, ΔS, from the magnetization data sets and heat capacity measured at different temperatures and applied fields. The two sets of results have well agreed with each other. The ΔS value of ErN is the highest at 7.5 K and higher than that of $ErNi_2$ reported as one of candidate materials of magnetic refrigerant for cryogenic refrigerant. The heat capacity curve against temperature of ErN has a peak at 4.4 K at zero-field. The peak value of the heat capacity of ErN is $507\,kJ\,K^{-1}\,m^{-3}$. This value is larger than those of Er_3Ni used commercially as a magnetic regenerator for the Gifford–McMahon refrigerator. The present results indicate that ErN is a promising material for a magnetic refrigerant and regenerator for cooling systems working above the boiling temperature of helium.

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