

Magnetocaloric effect of rare earth mono-nitrides, TbN and HoN

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Abstract

Rare earth (RE) mono-nitrides, TbN and HoN, were synthesized by the carbothermic reduction method. Their magnetocaloric effect (MCE) was evaluated by calculating the magnetic entropy changes, ΔS , from the magnetization data sets measured at various temperatures and applied fields. The ΔS value of HoN was highest at 18 K and larger than that of DyNi₂ reported as the candidate material of magnetic refrigerant for hydrogen liquefaction. The ΔS value of TbN was highest at 44 K and comparable with that of (DyHo)Al₂ with the transition temperature of 46 K.

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1. Introduction

The magnetic refrigeration involves an intrinsically small irreversibility and may provide refrigeration systems of good energy efficiencies especially at cryogenic temperatures [1,2]. It is, therefore, encouraged to apply the magnetic refrigeration system to the hydrogen liquefaction process, which would be an essential part of infrastructure of the near future society driven by the hydrogen energy. To establish this refrigeration technology, it is necessary to fabricate an efficient and reliable magnetic refrigerant material that involves a large magnetocaloric effect (MCE) around and above the boiling temperature of hydrogen, 20 K. The performance of MCE is evaluated by the magnetic entropy change ΔS induced by demagnetization of the refrigerant. The MCE is usually maximized around the magnetic transition temperature, reflecting the spontaneous transition between order and disorder states of the spin alignment. So far, some materials have been proposed as the candidate refrigerant [3–12]: some of intermetallic compounds

composed of rare earth (RE) and transition metals or Si/Ge elements involving a first-order magnetic transition.

We have proposed another class of material, RE mono-nitrides [13]. Mono-nitrides of Dy and Gd, and the solid solution of them, Gd_xDy_{1-x}N, have been synthesized by the carbothermic reduction method. They have the NaCl type crystal structure with higher RE packing densities than those of the metallic phase in the hexagonal closed pack structure. Their magnetic transition temperature varies with x in Gd_xDy_{1-x}N in a range between boiling temperatures of hydrogen and nitrogen. The involved magnetic entropy changes ΔS showed MCE comparable with those of the candidate materials so far reported. We pointed out that this material class is worth considering as a candidate for the magnetic refrigerant for liquefying hydrogen on the basis of these experimental findings and the following three additional advantages. (1) The RE nitride does not react with hydrogen, because it is thermodynamically more stable than the hydride, whilst the intermetallic compounds containing rare earth element are likely to react with hydrogen. When the intermetallic compounds are hydrides, magnetic properties of them change [14–17]. (2) The RE nitride generally has a high thermal conductivity. (3) The RE mono-nitride does not undergo a first-order magnetic transition but the usual second-order magnetic transition, so that this material

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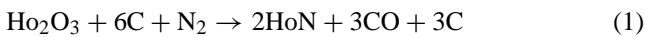
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has no concern with material degradation due to crystal structure change.

In this paper, we report on our finding of other RE mono-nitrides, HoN and TbN, which exhibit ΔS much larger than those of the materials we reported previously.

2. Experimental

Mono-nitride samples of HoN and TbN were synthesized by the carbothermic reduction method performed in nitrogen gas stream. It is quite the same method as that employed in our previous work [13]. Powders of Ho_2O_3 or Tb_4O_7 of 99.99% purity and amorphous carbon were thoroughly mixed with a mortar and pestle. The amorphous carbon was charged as twice as the required stoichiometric amount. The mixed powder was shaped into pellets and heated at 1773 K in a reaction tube through which 99.9995% purity nitrogen gas flowed during the reaction for 15 h. The reaction occurring when Ho is nitrided is expressed as follows:



To compare the present experiment with our previous results, we also synthesized monolithic GdN and DyN again in the same nitriding batch together with HoN and TbN. To examine the phase occurring in the product, the powder XRD pattern was measured with a diffractometer (RINT Ultima+; Rigaku Corporation) using Cu K α radiation. The magnetization, M , was measured with a superconducting quantum interference device magnetometer (MPMS system, QUANTUM DESIGN, Inc.) under various applied fields H , up to 5 T, and at various temperatures T , from 100 to 5 K. The measurements were carried out in a sequence; the applied field was swept downward at a constant temperature, and then the sample was cooled down to the next temperature at zero-field. To avoid oxidation of the product, the specimen for the measurement was shielded from air and prepared in an argon-filled glove box connected to the reaction system.

No special treatment was performed to remove the excess carbon noticed in Eq. (1), so that an amount of free carbon should have remained in the product. Carbonitride did not seem to form in our samples because the present magnetic data sets and lattice parameters reasonably agreed with those of the mono-nitrides so far reported [18–21]. The amorphous free carbon is magnetically invisible so that it contributes only to the weight of each product. However, we took the weight of carbon into account according to Eq. (1) in calculating the specific magnetization. The weight of free carbon was not more than a few weight percent.

The MCE was evaluated by calculating the magnetic entropy change ΔS induced by isothermal demagnetization from H to 0, which is expressed by

$$\Delta S = \int_H^0 \left(\frac{\partial S}{\partial H} \right)_T dH \quad (2)$$

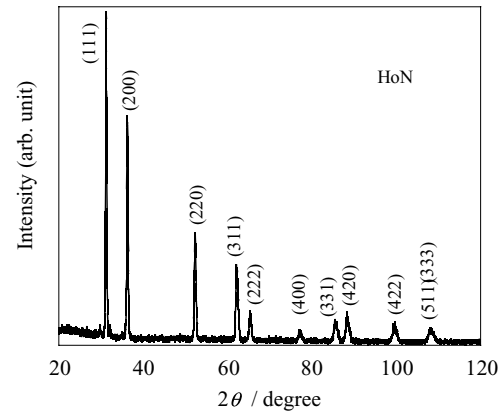


Fig. 1. Lattice parameters of rare earth mono-nitrides.

The integrand is replaced by another expression by applying Maxwell's relation, $(\partial S/\partial H)_T = (\partial S/\partial H)_H$, so that ΔS is given by the following equation:

$$\Delta S = \int_H^0 \left(\frac{\partial M}{\partial T} \right)_T dH \quad (3)$$

The present magnetization data sets $M(T, H)$ were substituted into this equation and numerical calculations were carried out to obtain $\Delta S(T, H)$.

3. Results and discussion

The XRD pattern of HoN is shown in Fig. 1, which indicates that the sample is a single-phase material of the mono-nitride in the NaCl type structure. The pattern of TbN was of the same quality. The lattice parameters determined for the RE mono-nitrides are plotted against the atomic number of the involved RE element in Fig. 2, in which plots for the $\text{Gd}_x\text{Dy}_{1-x}\text{N}$ are shown together [13]. The plots show a fairly good linear relation, which indicates

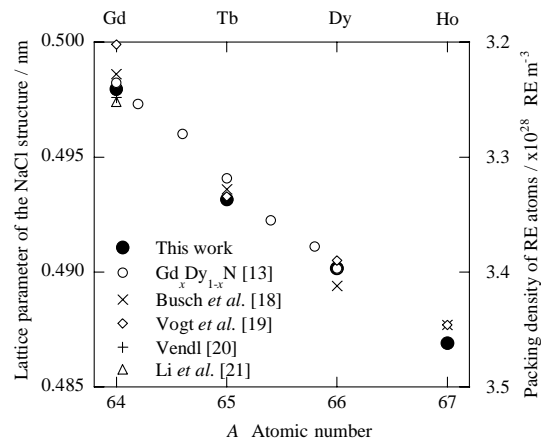


Fig. 2. Powder XRD patterns of HoN and TbN synthesized by the carbothermic reduction method. Data for the solid solutions of GdN and DyN are also given against the average atomic number (open circles (○) except for those at $A = 64$ and 66).

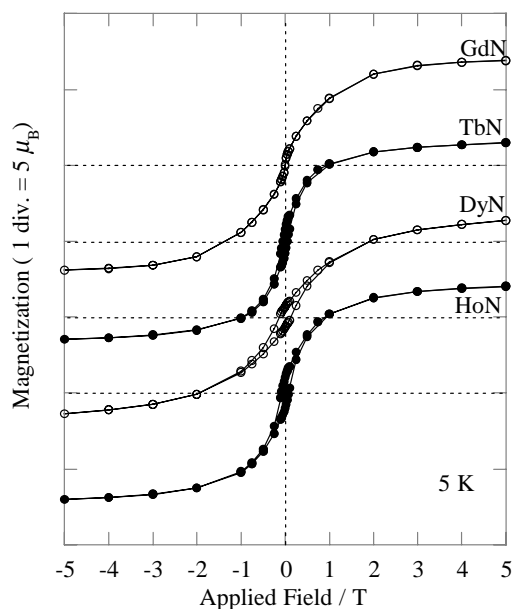


Fig. 3. Magnetization hysteresis loops of GdN, TbN, DyN, and HoN measured at 5 K.

that these mono-nitrides share a crystal structure with the lattice parameter continuously varying. The second ordinate gives the packing densities of the RE atoms corresponding to these lattice parameters. These densities are 7–8% higher than those of metallic Tb and Ho, $3.11 \times 10^{28} \text{ RE m}^{-3}$, and $3.21 \times 10^{28} \text{ RE m}^{-3}$, respectively. The high RE packing density is an advantageous property from the viewpoint of application as magnetic refrigerant.

Fig. 3 shows full magnetization loops of GdN, TbN, DyN, and HoN measured at 5 K. The curves of TbN and HoN exhibit small but significant remanences and coercivities, and almost full saturations at 5 T. The magnetization values at 5 T normalized to the RE metal are around $7 \mu_B$, reflecting that all the moments align almost along the external field. These facts clearly indicate the occurrence of the ferromagnetism. The loop widths of TbN and HoN are narrower than that of DyN and wider than that of GdN, and both the mono-nitrides seem magnetically softer than DyN but harder than GdN.

The present loops of GdN and DyN agree fairly well with those measured in our previous work, indicating good reproducibility in our material syntheses and measurements. Therefore, comparison amongst these four mono-nitrides in terms of the MCE would be of significance. The Curie temperature, T_C , of each sample was estimated by making an Arrott plot. The obtained T_C values are plotted against RE atomic number in Fig. 4 together with literature values and those obtained in our previous work [18,19,21,22]. The present values agree reasonably well with the literature values, and show good reproducibility for GdN and DyN.

Fig. 5a shows M versus T curves of TbN at various values of H , which were obtained by reconstructing the M versus H curves measured at various T . The magnetic entropy change ΔS was evaluated by executing numerical calcula-

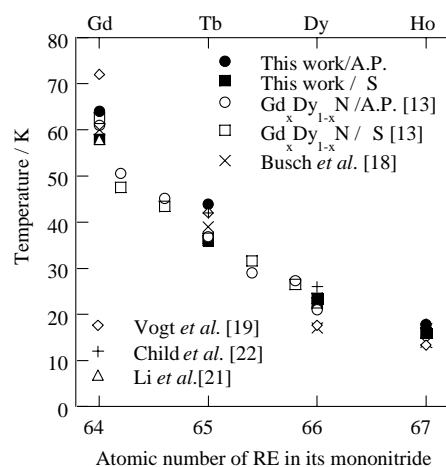


Fig. 4. Magnetic transition temperatures determined from the Arrott's plot (denoted as A.P. in the legend), and the temperature of the maximum ΔS (denoted as ΔS in the legend) observed in rare earth mono-nitrides. Data for the solid solutions of GdN and DyN are also given against the average atomic number.

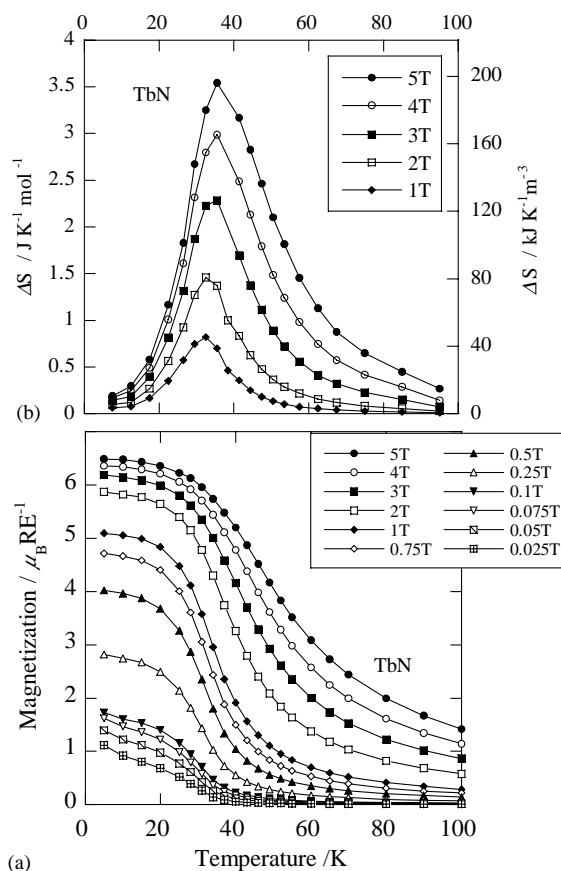


Fig. 5. (a) Magnetization vs. temperature curves at various applied fields. (b) Magnetic entropy change ΔS vs. temperature curve at various fields applied before the demagnetization. Both are for TbN.

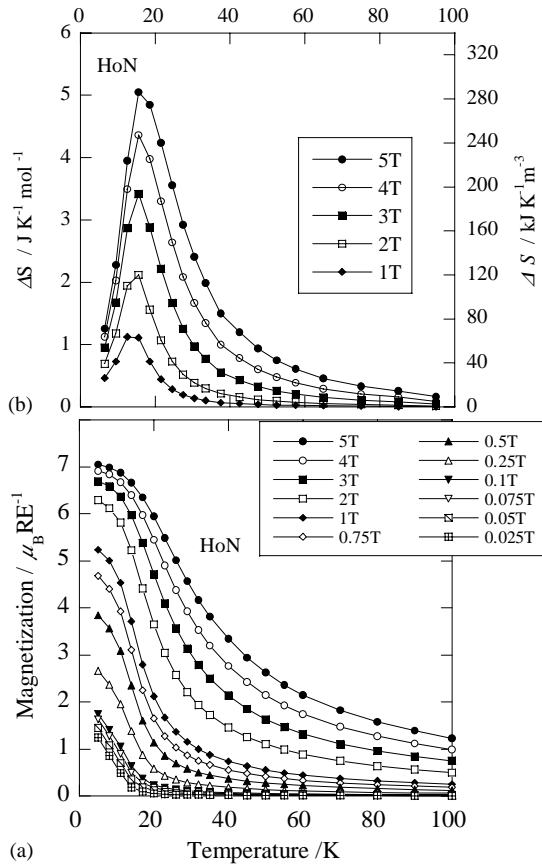


Fig. 6. (a) Magnetization vs. temperature curves at various applied fields. (b) Magnetic entropy change ΔS vs. temperature curve at various fields applied before the demagnetization. Both are for HoN.

tion on the basis of Eq. (3), and the results are shown in Fig. 5b. The ΔS versus T curves are noticed to have peaks around 35 K regardless of the applied field. The remanence and the coercive force were negligible down to a temperature a few degrees below the peak temperature of each ΔS - T curve. Since zero-remnance supports the validity of Maxwell's equation, the ΔS values around the peak and at higher temperatures are reliable. The results obtained with the same procedure for HoN and GdN, are shown in Figs. 6 and 7, respectively. The data for DyN is not shown here, because it has been already reported and a fair reproducibility was confirmed. Features similar to those in Fig. 5 are noticed again in Figs. 6 and 7, while the peak temperatures are quite different. In Fig. 4, these peak temperatures are plotted. A linear relation with temperature is noticed all over the plots, including those for the solid solutions of the $Gd_{1-x}Dy_xN$. Figs. 2 and 4 not only support the reliability of the present experiments and analyses, but also reconfirm that mono-nitrides of Gd, Tb, Dy, and Ho may be regarded as a class of materials with continuously changing crystallographic and magnetic properties.

It is pointed out that the M versus T curves of GdN exhibit particular behavior in that the curves at relatively lower field, <1 T, show a very broad cusp around 30–40 K fol-

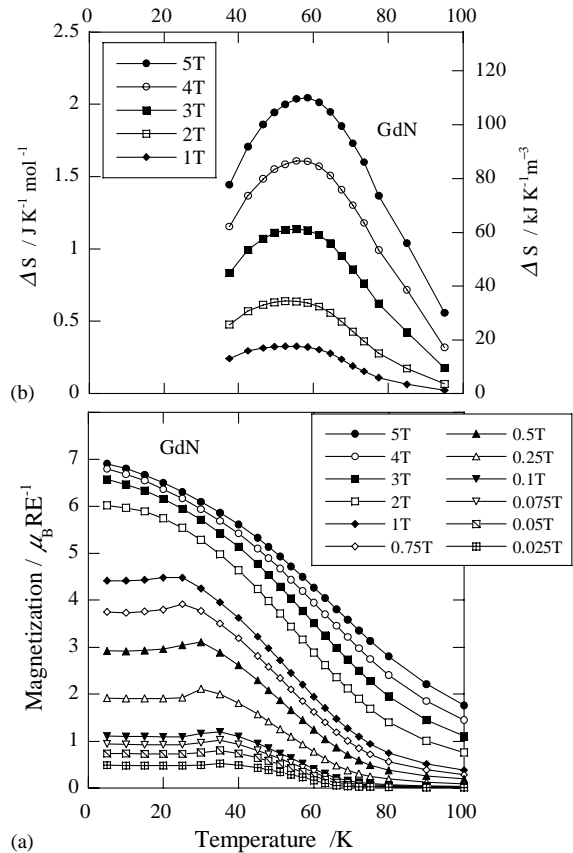


Fig. 7. (a) Magnetization vs. temperature curves at various applied fields. (b) Magnetic entropy change ΔS vs. temperature curve at various fields applied before the demagnetization. Both are for GdN.

lowed by a plateau extending towards lower temperatures. This is caused by the particular magnetism of GdN [23,24]. GdN is classified as displaying metamagnetism, being antiferromagnetic below a low external field and being forced to be ferromagnetic by higher fields. The present GdN sample in fact exhibited such behavior at 35 K or lower temperatures and at 1 T or lower applied fields, so that the present ΔS of GdN was calculated only in the ferromagnetic region.

In Fig. 8, the ΔS versus T curves of GdN, TbN, DyN and HoN induced by the demagnetization from 5 T are compared. First it is noticed that the peak heights do not order according to their atomic numbers like their lattice parameters and magnetic transition temperatures. Both HoN and TbN have far larger ΔS values than those for GdN and DyN that we have already reported. The ΔS values of GdN and DyN evaluated in this work reasonably agree with those evaluated in our previous work. The reproducibility of the data of GdN and DyN was confirmed, including the lattice parameters and magnetic transition temperatures shown in Figs. 2 and 4.

In Table 1, the values of the parameters characterizing HoN and TbN are compared with those reported for materials having their transition temperature in the range from 20 to 70 K. Each ΔS value was read from the maximum

Table 1

Density, rare earth atom density, Curie's temperature T_c , and the maximum value of the magnetic entropy change ΔS at 5 T of the present samples (HoN, TbN) and the reference compounds

Materials	Density (kg m^{-3})	RE density (m^{-3})	T_c (K)	ΔS			Reference
				$\text{kJ K}^{-1} \text{m}^{-3}$	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{J K}^{-1} \text{kg}^{-1}$	
ErNi ₂	1.04×10^4	2.21×10^{28}	6.6	253	6.9	24.2	[4]
ErAl ₂	6.44×10^3	1.69×10^{28}	12	214	7.6	34.4	[3]
HoNi ₂	1.03×10^4	2.20×10^{28}	13	230	6.3	22.3	[4]
DyNi ₂	1.02×10^4	2.20×10^{28}	20	252	6.9	24.7	[4]
HoAl ₂	6.09×10^3	1.67×10^{28}	27	175	6.3	28.8	[3]
ErCo ₂	1.03×10^4	2.18×10^{28}	33	388	10.7	37.5	[5]
(DyHo)Al ₂	6.97×10^3	1.67×10^{28}	46	133	4.8	21.8	[3]
DyAl ₂	5.97×10^3	1.66×10^{28}	56	113	4.1	18.9	[3]
HoN	1.03×10^4	3.47×10^{28}	18	291	5.0	28.2	This work
TbN	9.58×10^3	3.34×10^{28}	44	196	3.5	20.5	This work

point of the ΔS - T curve cited in each paper, and expressed in the table in three kinds of unit; $\text{J K}^{-1} \text{m}^{-3}$, $\text{J K}^{-1} \text{mol}^{-1}$, and $\text{J K}^{-1} \text{kg}^{-1}$. The unit conversion calculation was based on the lattice parameters of each crystal. HoN was found to have a transition temperature at 18 K and should be compared with DyNi₂ with 20 K [4]. The ΔS value of HoN is larger than that of DyNi₂ in terms of both $\text{J K}^{-1} \text{m}^{-3}$ and $\text{J K}^{-1} \text{kg}^{-1}$. TbN has a transition temperature 44 K and should be compared with (DyHo)Al₂ with 46 K [3]. The ΔS value of TbN is larger than that of (DyHo)Al₂ in terms of $\text{J K}^{-1} \text{m}^{-3}$, and almost equal to it in terms of $\text{J K}^{-1} \text{kg}^{-1}$. These high values are ascribed to the high packing density of the RE atoms as already pointed out.

Hydrogen liquefies at 20 K, so that HoN is a very promising candidate for a magnetic refrigerant working just at the liquefaction stage. TbN would also be promising for a refrigerant working at a stage preceding liquefaction. Another two important advantages of the rare earth mono-nitride are now pointed out again. (1) They must be inert towards hydrogen, so that they can work even in direct contact with hydrogen. Recall that some investigators made RE-hydride to react with nitrogen or ammonia to synthesize RE-nitride, which indicates a higher stability of the nitride than the hydride

[25–27]. (2) The magnetic transition of the mono-nitride is an ordinary second-order transition, so that it does not involve a crystal transformation likely to lead to material degradation.

4. Summary

We have synthesized HoN and TbN and evaluated their magnetocaloric effect by calculating their magnetic entropy changes. The ΔS value of HoN is highest at 18 K, $291 \text{ kJ K}^{-1} \text{m}^{-3}$ ($28.2 \text{ J K}^{-1} \text{kg}^{-1}$), which is larger than that reported for the candidate material of the RE-containing intermetallic compound, DyNi₂ having a transition temperature of 20 K. The ΔS value of TbN is highest at 44 K, $196 \text{ kJ K}^{-1} \text{m}^{-3}$ ($20.5 \text{ J K}^{-1} \text{kg}^{-1}$), which is comparable with that of (DyHo)Al₂ having a transition temperature of 46 K. The present results indicate that HoN and TbN are promising magnetic refrigerant materials for hydrogen liquefying systems working below liquid nitrogen temperature.

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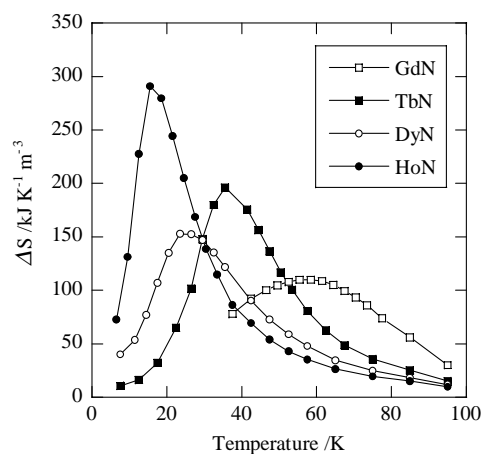


Fig. 8. Magnetic entropy change induced by demagnetization from 5 T to zero-field estimated for GdN, TbN, DyN, and HoN.

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