Effect of Dy substitution in the giant magnetocaloric properties of HoB₂

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ABSTRACT
Recently, a massive magnetocaloric effect near the liquefaction temperature of hydrogen has been reported in the ferromagnetic material HoB₂. Here we investigate the effects of Dy substitution in the magnetocaloric properties of Ho₁ₓDyₓB₂ alloys (x = 0, 0.3, 0.5, 0.7, 1.0). We find that the Curie temperature (T_C) gradually increases upon Dy substitution, while the magnitude of the magnetic entropy change (ΔS_m) and adiabatic temperature change (ΔT_ad) showed a gradual decrease. On the other hand, due to the presence of successive transitions in these alloys, the peak height of the above magnetocaloric properties tends to be kept in a wide temperature range, leading to a relatively robust figure of merit in a wide temperature span. These alloys could be interesting candidates for magnetic refrigeration in the temperature range of 10–60 K.

1. Introduction
Magnetic refrigeration is an emerging environmentally friendly technology for refrigeration applications, as it does not require to use greenhouse gases and does not depend on conventional gas compression cycles [1–3] while having possible higher cycle efficiency [1,4]. It is based on the magnetocaloric effect (MCE), which consists of the adiabatic temperature change (ΔT_ad) a magnetic material will undergo when a magnetic field is applied/removed adiabatically, but it can also be evaluated in terms of the magnetic entropy change (ΔS_m) this magnetic material will undergo for the same field change, where ΔS_m usually peaks at the magnetic transition temperature (T_magnet).

Recently, our group has unveiled a giant magnetocaloric effect of [ΔS_m MAX] = 0.35 J cm⁻³ K⁻¹ (40.1 J kg⁻¹ K⁻¹) in the vicinity of a ferromagnetic transition at the Curie temperature (T_C) of 15 K for a field change of μ₀ΔH = 5 T in HoB₂ [5]. Due to the closeness of its T_C to the liquefaction point of hydrogen (20.3 K), this material became an attractive candidate for use in low-temperature magnetic refrigeration applications focused on the liquefaction stage of hydrogen. Hydrogen is considered to be one of the most promising replacements for hydrocarbon fuels as a clean energy source [6,7] and in particular liquid hydrogen is widely needed in the space industry [8] and its liquid form is one the suitable way for transportation and storage [9]. In this context, the discovery of magnetic materials with a high MCE effect at low temperatures is imperative for the development of such...
refrigerators working at cryogenic temperatures. Since the magnetocaloric effect peaks at $T_{\text{mag}}$, tuning the $T_C$ of HoB$_2$ to a higher temperature is of extreme interest to examine HoB$_2$-based materials as possible candidates for refrigeration before the liquefaction stage, especially below temperatures of 77 K.

DyB$_2$ orders ferromagnetically at $T_C = 50$ K [10,11] and exhibits a $|\Delta S_M|$ of 0.16 J cm$^{-3}$ K$^{-1}$ (17.1 J kg$^{-1}$ K$^{-1}$) for $\mu_0\Delta H = 5$ T [12]; 9 therefore a partial substitution of Ho by Dy is expected to shift $T_C$ to higher values in the expense of a probable reduction of $|\Delta S_M|$. Also, since both materials exhibit two consecutive transitions, it is interesting to investigate the effect of alloying in the MCE properties of this system. In this work, we study the magnetocaloric properties of Ho$_{1-x}$Dy$_x$B$_2$ alloys ($x = 0, 0.3, 0.5, 0.7, 1.0$) and compare with other well-known materials working at the same temperature span.

All the magnetocaloric properties of the samples are reported in volumetric units (J cm$^{-3}$ K$^{-1}$) as this is the adequate unit when comparing materials for application purposes as there is a volume limit when constructing real applications [13,14]. Therefore, herein all comparisons with other materials is done in this unit by converting it using the ideal density of each material when not provided.

2. Experimental section

2.1. Sample synthesis

Polycrystalline samples of Ho$_{1-x}$Dy$_x$B$_2$ were prepared by an arc-melting process in a water-cooled copper hearth arc furnace under Ar atmosphere. Stoichiometric amounts of Ho (99.9% purity), Dy (99.9% purity), and B (99.5% purity) were weighed and then arc melted several times. During the synthesis trials, we found out that annealing under different conditions did not change the X-ray diffraction patterns of the obtained samples, therefore no annealing was carried out in this work.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the arc-melted samples were investigated using a MiniFlex 600 (Rigaku, Japan) with Cu Ka radiation. The lattice parameters, the volume of the unit cell, and density were obtained by refining the XRD patterns using the FULLPROF [15] software.

2.3. Magnetization measurements

Magnetization measurements were carried out by a superconducting quantum interference device magnetometer contained in the Magnetic Property Measurement System XL (Quantum Design, US). Zero-field cooling (ZFC) and field cooling (FC) measurements at low fields were taken to evaluate the evolution of $T_C$ as a function of Dy content. For the evaluation of $|\Delta S_M|$ the magnetization measurements of the sample under various applied fields ranging from 0.01 to 5 T were performed in ZFC process.

3. Results and discussion

3.1. Crystal structure

Figure 1(a) shows the XRD patterns for the obtained arc melted samples. The main phase peaks can be indexed into a hexagonal $P6/mmm$ AlB$_2$ type crystal structure as shown by the red fitting curves. The remaining peaks are assigned as REB$_3$ unreacted RE or RE$_2$O$_3$ (RE = Ho, Dy) impurity peaks marked by a black square (■), a black star (★), or a black diamond (♦) respectively. The obtained lattice parameters, the volume of the unit cell, and density are summarized in Table 1.

![Figure 1](image-url)

**Figure 1.** Powder XRD patterns and lattice constant evolution for Ho$_{1-x}$Dy$_x$B$_2$ alloys. (a) XRD patterns of the obtained alloys. The red lines show the calculated patterns from Rietveld refinement for the REB$_3$ main phase. The black square (■) marks an REB$_3$ impurity phase, while the black star (★) marks a RE impurity peak and the black diamond (♦) marks a RE$_2$O$_3$ impurity peak (RE = Ho, Dy). (b) The lattice parameters normalized by the value at $x = 0$, as a function of $x$. The black dashed line shows a guide based on Vegard’s law, given by $1 - x + x \left( \frac{a_{RE}}{a_{Ho}} \right)$ where $(a,c)_{Ho}$ is the lattice constants at $x = 0$ or 1.
As shown in Table 1, Dy substitution in the Ho site seems to strongly affect the c-axis length while the a-axis length weakly changes, illustrated in Figure 1(b) where we plot the normalized lattice parameters (a/a_0 and c/c_0) by the value of x = 0. Both c/c_0 and a/a_0 increase with x, roughly following the so-called Vegard’s law (marked by the dashed black line), but with different rates. The observed changes in the lattice constants in Ho_{1-x}Dy_xB_2 suggest that the substitution of Ho by Dy in the REB_2 main phase was successful, and these partially substituted samples can be in the form of a random alloy. We note that in the case of HoB_{2-x}Si_x solid solutions [10] where B site is partially substituted, it has been reported that the expansion rate of a-axis length and c-axis length are comparable to each other. This difference in the change of lattice constants between Ho_{1-x}Dy_xB_2 and HoB_{2-x}Si_x implies that the a-axis and c-axis lengths in HoB_2-based compounds might be closely related to the bonds along axes. Namely, c-axis length seems to be depending on Ho-B bonds and be sensitive to both rare-earth and B-site atoms, while the a-axis length might be more dependent on the B site atom.

3.2. Magnetic properties

The ZFC-FC isofield magnetization (M-T) curves for an applied field of \( \mu_0H = 0.01 \) T and isothermal magnetization (M-H) curves measured at \( T = 5 \) K are shown in Figure 2(a-e, f-g) for each obtained sample, respectively. For the Dy containing samples, the divergence between the ZFC and FC M-T curves becomes more pronounced and a small magnetic hysteresis in the M-H curves is observed, including the end-material DyB_2.

To evaluate the magnetic transition temperatures in this system, the temperature-dependent derivative of the ZFC curves was taken and are shown in the lower panels of Figure 2(a-e). The Curie temperatures that are defined by the peak position in \( \partial M/\partial T \) curves, are marked by the \( T_C \) arrows, showing a systematic increase with Dy content. On the other hand, a second magnetic transition marked by \( T^* \) that is observed at lower temperatures, which is also observed at HoB_2 at \( T^* = 11 \) K [5] and DyB_2 at \( T^* = 15 \) K [12], seems to be almost unchanged by partial substitution of Dy. The origin of \( T^* \) was attributed to a possible spin-reorientation mechanism [12], however, the nature of this transition is still unknown and its investigation is outside the scope of this work. The Dy doping dependence of both transitions is summarized in Figure 3 showing the monotonic increase of \( T_C \) until 50 K, while \( T^* \) remains almost constant.

3.3. Magnetocaloric properties

For evaluating the magnetocaloric effect of the obtained samples, M-T curves in a wide range of applied magnetic fields were measured for all samples, shown in Figure 4(a-e), and \( |\Delta S_M| \) was calculated using the Maxwell relation:

\[
\Delta S_M = \mu_0 \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH
\]

The obtained \( |\Delta S_M| \) for fields up to 5 T is shown in Figure 4(f-j).

| Nominal Dy (x) | a (Å) | c (Å) | V (Å³) | \( \rho \) (g/cm³) |
|---------------|------|------|--------|-------------|
| 0             | 3.283(3) | 3.815(8) | 35.62(4) | 8.696      |
| 0.3           | 3.283(6) | 3.827(1) | 35.77(8) | 8.626      |
| 0.5           | 3.285(7) | 3.832(5) | 35.82(9) | 8.591      |
| 0.7           | 3.287(8) | 3.839(7) | 35.94(7) | 8.540      |
| 1.0           | 3.292(0) | 3.850(6) | 36.14(0) | 8.461      |

Figure 2. Isofield (M-T) ZFC-FC, Normalized temperature-dependent derivatives of the ZFC curves, and Isothermal (M-H) magnetization curves of Ho_{1-x}Dy_xB_2 alloys. (a-e) ZFC and FC curves for all synthesized alloys for an applied field of \( \mu_0H = 0.01 \) T. The lower panels show the derivatives of the ZFC curves normalized by the minimum of the derivative value. The two magnetic transitions \( T_C \) and \( T^* \), are marked by the arrows. (f-g) Isothermal magnetization at \( T = 5 \) K.
Figure 3. Phase diagram between ordering temperature and doping amount ($x$) for Ho$_{1-x}$Dy$_x$B$_2$. The blue filled circles show the evolution of $T_C$ while the orange triangles show $T^*$. While $T_C$ increases monotonically with $x$, $T^*$ remains almost constant.

Due to the presence of the two transitions at $T^*$ and $T_C$, two peaks appear at $|\Delta S_M|$. Therefore, here we will define and compare the maximum entropy change $|\Delta S_M^{\text{MAX}}|$ as $|\Delta S_M(T = T_C)|$, since $T^*$ remains almost unchanged during the whole doping range and is always lower than 15 K while we are interested in the $|\Delta S_M|$ peak shifted toward higher temperature by Dy doping. In this way, the obtained values of $|\Delta S_M^{\text{MAX}}|$ for $\mu_0\Delta H = 5$ T were 0.35, 0.3, 0.18, 0.16 and 0.15 J cm$^{-3}$ K$^{-1}$ for $x = 0, 0.3, 0.5, 0.7$ and 1.0, respectively.

In addition to the change in the magnitude of $|\Delta S_M^{\text{MAX}}|$, an interesting characteristic appears in the $|\Delta S_M|$ curves of Ho$_{1-x}$Dy$_x$B$_2$. That is, since there are multiple transitions in this series of alloys, even though there is a net loss at $|\Delta S_M^{\text{MAX}}|$, the entropy change curve shows an increase of $\Delta T_{\text{FWHM}}$, defined as the region in the entropy curve where $|\Delta S_M| \geq |\Delta S_M^{\text{MAX}}|/2$, leading to a gain in maximum entropy change for higher temperature spans. Such a widening of the $|\Delta S_M|$ curves due to multiple transitions has been commonly observed in materials that show more than one magnetic transition [16–18] and it tends to lead to a high figure of merits. The $|\Delta S_M|$ for all samples for a field change of $\mu_0\Delta H = 5$ T is shown in Figure 5.

Another important property in the magnetocaloric performance of materials is the adiabatic temperature change $\Delta T_{\text{ad}}$. Here, we estimated the $S(T, H)$ (shown in Figure S1.) curves by first calculating the zero-field entropy from specific heat data (not shown here) and then we obtain the field-dependent entropy by subtracting the values of $|\Delta S_M|$ to the zero-field entropy, in the same manner as Refs. [5,19]. For the $x = 0$, we used the

Figure 4. $M$-$T$ curves at a vast range of applied fields and obtained magnetic entropy change for Ho$_{1-x}$Dy$_x$B$_2$ alloys. (a-e) The obtained $M$-$T$ curves measured by ZFC process from $\mu_0\Delta H = 5$ T to 0.01 T. (f-j) Magnetic entropy changes for Ho$_{1-x}$Dy$_x$B$_2$ alloys for $\mu_0\Delta H$ ranging from 1 to 5 T obtained from the $M$-$T$ curves of (a-e). (k-o) Estimated adiabatic temperature change for Ho$_{1-x}$Dy$_x$B$_2$ alloys for $\mu_0\Delta H$ ranging from 1 to 5 T [21]. With the increase of Dy content, the maximum value of $|\Delta S_M|$ decreases from 0.35 J cm$^{-3}$ K$^{-1}$ ($x = 0$) to 0.16 J cm$^{-3}$ K$^{-1}$ ($x = 1.0$).

Figure 5. $|\Delta S_M|$ at $\mu_0\Delta H = 5$ T for Ho$_{1-x}$Dy$_x$B$_2$ alloys.
previously reported data of Ref [5], and for the x = 1 sample, we used the previously reported zero-field specific heat data of Ref [20]. Then, the $\Delta T_{\text{ad}}$ is estimated by taking the horizontal difference between the entropy curves under zero field and final field [21] and the results are shown in Figure 4k-o. Interestingly, the two-peak structure of $|\Delta S_M|$ is also reflected in $\Delta T_{\text{ad}}$ and thus these alloys tend to show high $\Delta T_{\text{ad}}$ in relatively wide temperature range, that is an important characteristic for practical applications [22]. Here we estimated $\Delta T_{\text{ad}}^{\text{MAX}}$ in the same way as $|\Delta S_M^{\text{MAX}}|$, that is $\Delta T_{\text{ad}}^{\text{MAX}} = \Delta T_{\text{ad}} (T = T_C)$. The obtained $\Delta T_{\text{ad}}^{\text{MAX}}$ is 12 K, 11.5 K, 8.6 K, 8.0 K and 7.2 K for $x = 0, 0.3, 0.5, 0.7$ and $1.0$, respectively for $\mu_0\Delta H = 5$ T.

Let us compare the magnetocaloric properties in Ho$_{1-x}$Dy$_x$B$_2$ with those of representative materials that often show prominent magnetocaloric effect with transition temperatures ranging up to 77 K, based on Figure SS of Ref [5]. Here we consider $\Delta S_M$, $\Delta T_{\text{ad}}$ and Temperature averaged Entropy Curve (TEC) as a practical figure of merit proposed earlier [23]. The last value is defined as:

$$\text{TEC}(\Delta T_{\text{ad}}) = \frac{1}{\Delta T_{\text{ad}}^{\text{MAX}}} \int_{T_{\text{ad}}^{\text{MIN}}}^{T_{\text{ad}}^{\text{MAX}}} \Delta S_M dT$$

Where $T_{\text{mid}}$ is chosen to maximize the value of TEC in a given working temperature range of a material ($\Delta T_{\text{ad}}$) (Conventional figure of merits such as refrigerant capacity and relative cooling power are also tabulated in supplementary information).

For this purpose, the values of entropy change of the materials for comparison are converted into volumetric units by using the density contained in the AtomWork [24] database, unless otherwise provided by the authors. Also, the values of TEC (10) and TEC (20) are estimated from the reported entropy curves within the contained references when not reported by the authors. We show the obtained values for $|\Delta S_M^{\text{MAX}}|$, $|\Delta T_{\text{ad}}^{\text{MAX}}|$, $\text{TEC}(10)$, and $\text{TEC}(20)$ in Figure 6a-d. Also, the $\Delta T_{\text{ad}}$ dependence of TEC in selected materials is shown in Figure 6e.

In the temperature range of 15–20 K, HoB$_2$ and Ho$_{0.5}$Dy$_{0.5}$B$_2$ show superior $|\Delta S_M^{\text{MAX}}|$ and $\Delta T_{\text{ad}}^{\text{MAX}}$ for $\mu_0\Delta H = 5$ T, when compared to compounds with similar $T_{\text{mag}}$ such as ErAl$_2$ [25], TmGa$_2$ [26], EuS [27], HoN [28,29], DyNi$_2$ [25] and Ho$_2$Au$_2$In [30]. For the materials with transition temperatures around 30 K, even though Ho$_{0.5}$Dy$_{0.5}$B$_2$ shows similar $|\Delta S_M^{\text{MAX}}|$ to Ho$_2$Cu$_2$Cd [18] and ErGa [31], it has a comparable $|\Delta T_{\text{ad}}^{\text{MAX}}|$ to HoAl$_2$ [32] and ErCo$_2$ [33]. Similarly, Ho$_{0.3}$Dy$_{0.7}$B$_2$ has almost the same $|\Delta S_M^{\text{MAX}}|$ as HoNi [34,35], however with a much larger $|\Delta T_{\text{ad}}^{\text{MAX}}|$. In the case of DyB$_2$, even though it shows almost half of $|\Delta S_M|$ compared to Gd$_8$Ru$_{36}$, its $|\Delta T_{\text{ad}}^{\text{MAX}}|$ is higher and comparable to DyAl$_2$ [37], although both of them are lower than Er$_{0.55}$Ho$_{0.45}$Co$_2$ [38,39]. Furthermore, the TEC in Ho$_{1-x}$Dy$_x$B$_2$ alloys tends to be relatively robust for a higher value of $\Delta T_{\text{ad}}$ due to the multiple transition nature in these materials. This suggests that Ho$_{1-x}$Dy$_x$B$_2$ alloys could support a wide temperature span while keeping the figure of merit and indicate that Ho$_{1-x}$Dy$_x$B$_2$ alloys might be an option for use in magnetic refrigeration ranging from 10 to 60 K as similar materials with $T_{\text{mag}}$ within this range.

4. Conclusions

In this work, we have systematically evaluated the effects of Dy substitution on the giant magnetocaloric effect of HoB$_2$. Even if there is a net loss in the peak value of the $|\Delta S_M|$, the observed two-peak structure in both the magnetic entropy and adiabatic temperature change might indicate these materials could possibly sustain a large working temperature range based on the figure of merit analysis.

![Figure 6](image_url) Figure 6. Maximum entropy and adiabatic temperature change and TEC values for Ho$_{1-x}$Dy$_x$B$_2$ alloys and diverse compounds for $\mu_0\Delta H = 5$ T. (a) $|\Delta S_M^{\text{MAX}}|$ and (b) $|\Delta T_{\text{ad}}^{\text{MAX}}|$ as a function of the magnetic ordering temperature $T_{\text{mag}}$. (c) Values of TEC for $\Delta T_{\text{ad}} = 10$ K and (d) for $\Delta T_{\text{ad}} = 20$ K. (e) TEC as a function of $\Delta T_{\text{ad}}$ for few representative materials with high TEC values. The normal and dashed lines guide the eyes. The TEC values were obtained by using the reported entropy curves within each material reference.
Therefore, these alloys could be an option to work as magnetic refrigerants in the temperature range from 10 to 60 K.

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Disclosure statement

The authors declare no conflict of interest.

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References

[1] Gschneidner KA, Pecharsky VK. Magnetocaloric Materials. Annu Rev Mater Sci. 2000;30:387–429.
[2] Franco V, Blázquez JS, Ipus JI, et al. Magnetocaloric effect: from materials research to refrigeration devices. Prog Mater Sci. 2018;93:112–232.
[3] Tegus O, Brück E, Buschow KJJ, et al. Transition-metal-based magnetic refrigerants for room-temperature applications. Nature. 2002;415:150–152.
[4] Numazawa T, Kamiya K, Utaki T, et al. Magnetic refrigerator for hydrogen liquefaction. Cryogenics (Guild). 2014;62:185–192.
[5] de Castro PB, Terashima K, Yamamoto TD, et al. Machine-learning-guided discovery of the gigantic magnetocaloric effect in HoBx near the hydrogen liquefaction temperature. NPG Asia Mater. 2020;12:35.
[6] Johnston B, Mayo MC, Khare A. Hydrogen: the energy source for the 21st century. Technovation. 2005;25:569–585.
[7] Jones LW. Liquid hydrogen as a fuel for the future. Science. 1971;174:367–370.
[8] Shirron PJ. Applications of the magnetocaloric effect in single-stage, multi-stage and continuous adiabatic demagnetization refrigerators. Cryogenics (Guild). 2014;62:130–139.
[9] Sherif SA, Zeytinoğlu N, Veziroğlu TN. Liquid hydrogen: potential, problems, and a proposed research program. Int J Hydrogen Energy. 1997;22:683–688.
[10] Roger J, Bahjihetskyy V, Guizouarn T, et al. The ternary RE-Si-B systems (RE = Dy, Ho, Er and Y) at 1270 K: solid state phase equilibria and magnetic properties of the solid solution REB₂₋ₓSₓ (RE = Dy and Ho). J Alloys Compd. 2006;417:72–84.
[11] Novikov VV, Matovnikov AV, Volkova OS, et al. Synthesis, thermal and magnetic properties of RE-diborides. J Magn Magn Mater. 2017;428:239–245.
[12] Meng H, Li B, Han Z, et al. Reversible magnetocaloric effect and refrigeration capacity enhanced by two successive magnetic transitions in DyB₂. Sci China Technol Sci. 2012;55:501–504.
[13] Gschneidner A, Pecharsky VK, Tsokol AO. Recent developments in magnetocaloric materials. Reports Prog Phys. 2005;68:1479–1539.
[14] Gottschall T, Skokov KP, Fries M, et al. Making a cool choice: the materials library of magnetic refrigeration. Adv Energy Mater. 2019;9:1901322.
[15] Carvajal J, FULLPROF: A Program for rietveld refinement and pattern matching analysis. Abstr. Satell. Meet. Powder Diffr. XV Congr. IUCr. 1990. p. 127. Toulouse, France.
[16] Zheng XQ, Chen J, Shen J, et al. Large refrigerant capacity of RGa (R = Tb and Dy) compounds. J Appl Phys. 2012;111:07A917.
[17] Zhang Y, Xu X, Yang Y, et al. Study of the magnetic phase transitions and magnetocaloric effect in DyC₂. In compound. J Alloys Compd. 2016;667:130–133.
[18] Yi Y, Li L, Su K, et al. Large magnetocaloric effect in a wide temperature range induced by two successive magnetic phase transitions in HoₓCuxCd compound. Intermetallics. 2017;80:22–25.
[19] Tan X, Chai P, Thompson CM, et al. Magnetocaloric effect in AlFe₂B₂: toward magnetic refrigerants from earth-abundant elements. J Am Chem Soc. 2013;135:9553–9557.
[20] Novikov VV, Matovnikov AV. Low-temperature heat capacity of dysprosium diboride. J Therm Anal Calorim. 2007;88:597–599.
[21] Note that here an assumption that the adiabatic route tracks the horizontal line in S(H,T) is made, and that might not be valid in the case of crossing two successive transitions.
[22] Engelbrecht K, Bahl CRH. Evaluating the effect of magnetocaloric properties on magnetic refrigeration performance. J Appl Phys. 2010;108:123918.
[23] Griffith LD, Mudrýk Y, Slaughter J, et al. Material-based figure of merit for caloric materials. J Appl Phys. 2018. American Institute of Physics Inc. DOI: 10.1063/1.5004173.
[24] Xu Y, Yamazaki M, Villars P. Inorganic materials database for exploring the nature of material. Jpn J Appl Phys. 2011;50:11RH02.
[25] von Ranke P, Pecharsky VK, Gschneidner KA. Influence of the crystalline electrical field on the magnetocaloric effect of DyAl₂, ErAl₂ and DyNi₂. Phys Rev B. 1998;58:12110–12116.
[26] Mo Z-J, Shen J, Yan L-Q, et al. Low field induced giant magnetocaloric effect in TmGa compound. Appl Phys Lett. 2013;103:52409.
[27] Li DX, Yamamura T, Nimori S, et al. Large reversible magnetocaloric effect in ferromagnetic semiconductor EuS. Solid State Commun. 2014;193:6–10.
[28] Yamamoto TA, Nakagawa T, Sako K, et al. Magnetocaloric effect of rare earth mono-nitrides, TbN and HoN. J Alloys Compd. 2004;376:17–22.
[29] Nishio S, Nakagawa T, Arakawa T, et al. Specific heat and thermal conductivity of HoN and ErN at cryogenic temperatures. J Appl Phys. 2006;99:08K901.
[30] Li L, Yi Y, Su K, et al. Magnetic properties and large magnetocaloric effect in Ho$_2$Cu$_2$In and Ho$_2$Au$_2$In compounds. J Mater Sci. 2016;51:5421–5426.
[31] Chen J, Shen BG, Dong QY, et al. Large reversible magnetocaloric effect caused by two successive magnetic transitions in ErGa compound. Appl Phys Lett. 2009;95:132504.
[32] Gil LA, Campoy JCP, Plaza EJR, et al. Conventional and anisotropic magnetic entropy change in HoAl$_2$ ferromagnetic compound. J Magn Magn Mater. 2016;409:45–49.
[33] Wada H, Tanabe Y, Shiga M, et al. Magnetocaloric effects of laves phase Er(Co$_{1-x}$Ni$_x$)$_2$ compounds. J Alloys Compd. 2001;316:245–249.
[34] Zheng XQ, Zhang B, Wu H, et al. Large magnetocaloric effect of Ho$_x$Er$_{1-x}$Ni (0 ≤ x ≤ 1) compounds. J Appl Phys. 2016;120:163907.
[35] Kinami N, Wakiya K, Uehara M, et al. Magnetocaloric effect in single-crystal HoNi with a canted magnetic structure. Jpn J Appl Phys. 2018;57:103001.
[36] Monteiro JCB, Dos Reis RD, Gandra FG. The physical properties of Gd$_3$Ru: A real candidate for a practical cryogenic refrigerator. Appl Phys Lett. 2015;106:194106.
[37] Hashimoto T, Matsumoto K, Kurihara T, et al. Investigations on the possibility of the RAl$_2$ system as a refrigerant in an ericsson type magnetic refrigerator. Boston, MA: Springer US; 1986. p. 279–286. Adv Cryog Eng Mater.
[38] Matsumoto K, Numazawa T. Magnetic refrigerator for hydrogen liquefaction. TEION KOGAKU (J Cryog Supercond Soc Japan). 2015;50:66–71.
[39] Zhu Y, Asamoto K, Nishimura Y, et al. Magnetocaloric effect of (Er$_{x}$R$_{1-x}$)$_2$Co$_2$ (R = Ho, Dy) for magnetic refrigeration between 20 and 80 K. Cryogenics (Guildf). 2011;51:494–498.