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Room-Temperature Magnetic Refrigerate System Gadolinium-Terbium-Neodynium

Zhang Xiyan, Yang Ling, Zhou Shijie *, Qi Linlin and Liu Zhinong

The Institute of Rare Earth and Informational Materials, Southwest Jiaotong University, Chengdu 610031 P.R. China

A system of magnetic materials suited for a room temperature magneto-refrigeration, Gd–Tb–Nd, has been investigated. Samples were melted in an argon-protected high-frequency magnetic induction furnace. Magnetization curves were measured with a vibrating-sample magnetometer, in order to obtain the magnetic entropy change. Experimental results show that the Curie temperature (T_c) of the present system is near room temperature and decreases as the Tb and Nd contents increase. By addition of a small amount of Nd, the magnetic entropy change is comparable with that of Gd–Tb, and the transition temperature changes greatly. Therefore Nd can be used as a working temperature regulator. The Gd–Tb–Nd system is a prospect for realizing a large-scale room-temperature refrigeration in low magnetic fields.

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1. Introduction

Because it is more efficient than freezing air and because it produces no environment pollution, magneto-refrigeration has aroused great interest. Those magneto-refrigerative materials with a transition temperature around room temperature are crucial in the development of magneto-refrigerators and magneto-conditioners. However, there remain many problems, among which the most important is to find a kind of magnetic material that has a considerable magneto-calorific effect. Room temperature magneto-refrigeration employs the Ericsson cycle, which requires that the magnetic entropy change (ΔS_M) is large, keeping constant in the cycle temperature range. As is reported, the material with the highest ΔS_M is Gd, but its ΔS_M changes sharply with temperature, so it can not be used in the Ericsson cycle. Many researchers have studied compounds of rare earth elements with transition metals, that commonly have a lower ΔS_M than that of Gd. Some of researchers have studied the magneto-calorific effect of rare earth alloys, and they think the alloys of Gd with other rare earth metal are suitable for use in a room temperature magneto-refrigeration.[1–5]

On the basis of the former researches, this paper studies the magneto-calorific effect of the Gd–Tb–Nd system that is intended for room temperature use. The magnetic entropy changes (ΔS_M) are measured and analyzed. The present results show that the Gd–Tb–Nd system has a comparatively large ΔS_M in a wide temperature range. Compared with the entropy–temperature figures of the Gd–Tb system in the Ref.[2] it was found that the addition of a small amount of Nd influences the transition temperature greatly, while ΔS_M is kept at the same level, which proves that Nd is an excellent work temperature adjuster.

2. Experiment Method

Starting materials with purity above 99.9% were mixed stoichiometrically, and melted in a high-frequency magnetic induction furnace under argon protection. Each sample was melted for several times to make it homogeneous. The results of microstructure examination by microscope and X-ray diffraction showed that the samples were homogeneous solutions.[6]

Cylinders of $\phi 2$ mm × 2 mm were cut from the cast. Magnetic properties were measured with a vibrating-sample magnetometer to obtain the Curie temperature (T_c) and ΔS_M. Liquid nitrogen was used to control the temperature from above room temperature to 213 K.

3. Experimental Results and Analysis

3.1 The curie temperature

Since measuring temperatures are around T_c, we can calculate T_c according to the measuring temperatures on the magnetic curve. The method is to measure the curves of magnetization versus temperature (M_s-T) under low magnetic field ($H < 4 \times 10^{-4}$ A/m), the cross point of axis x and the tangent of the curve is T_c, as Table 1 shows.

3.2 Magnetization curves

In the temperature range (> 20 K) around T_c, a set of temperatures are chosen with suitable intervals. Under each temperature, magnetization of each sample is measured under 4×10^{-4}, 8×10^{-4}, 12×10^{-4}, 20×10^{-4}, 40×10^{-4}, 60×10^{-4}, 80×10^{-4} A/m respectively. In each set of the curves, the transition from the paramagnetic to the ferromagnetic state with temperature variation is obvious as shown in Fig. 1.

3.3 Calculation of magnetic entropy change

The demagnetization effect should be considered when the magnetic entropy change is calculated. The actual magnetic field is $H_{in} = H_{ex} - NMs$, here H_{ex} is the external magnetic field, H_{in} is the inner magnetic field of the samples, N is the demagnetization coefficient, which is found to be 0.27,[7] Ms

Table 1 Estimated magnetic transition temperature (T_c) of samples.

Composition	$Gd_{74}Tb_{26}$	$Gd_{75}Tb_{20}Nd_5$	$Gd_{25}Tb_{70}Nd_5$	$Gd_{25}Tb_{60}Nd_{15}$
T_c (K)	283	267	231	223

*Graduate Student, Southwest Jiaotong University. Present address: The Dep. of Materials Eng., Southwest Jiaotong University, Chengdu 610031, P.R. China.

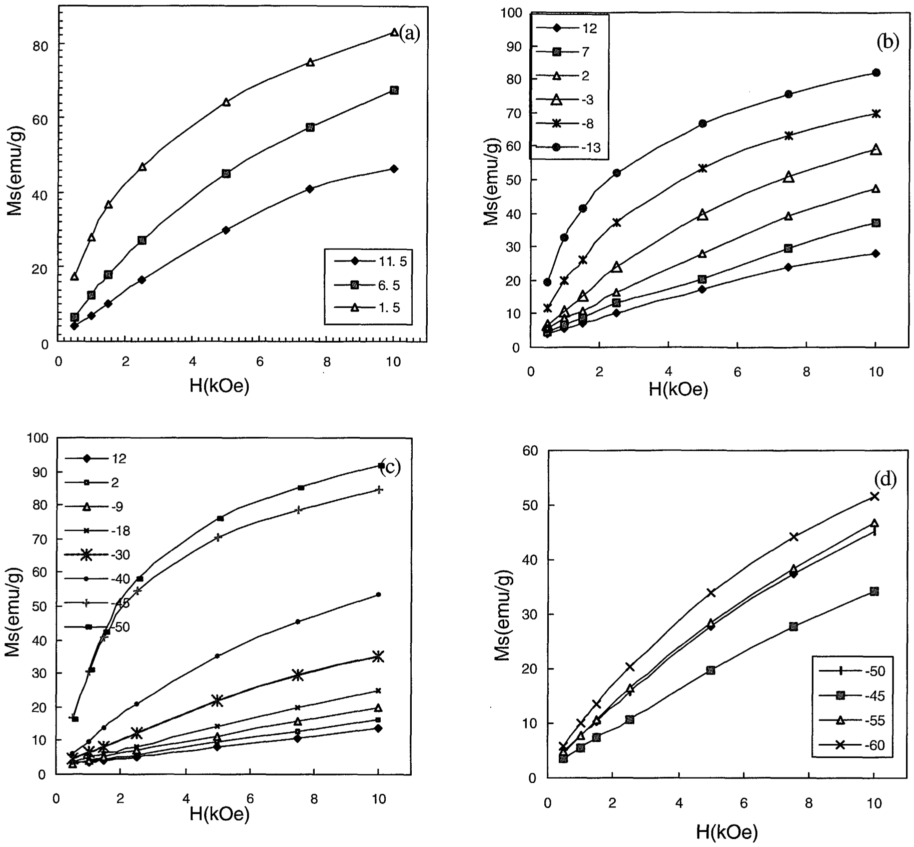

Fig. 1 Fig. 1(a) is the magnetization curves of $Gd_{74}Tb_{26}$, Fig. 1(b) is the magnetization curves of $Gd_{75}Tb_{20}Nd_5$, Fig. 1(c) is the magnetization curves of $Gd_{25}Tb_{70}Nd_5$ and Fig. 1(d) is the magnetization curves of $Gd_{25}Tb_{60}Nd_{15}$.

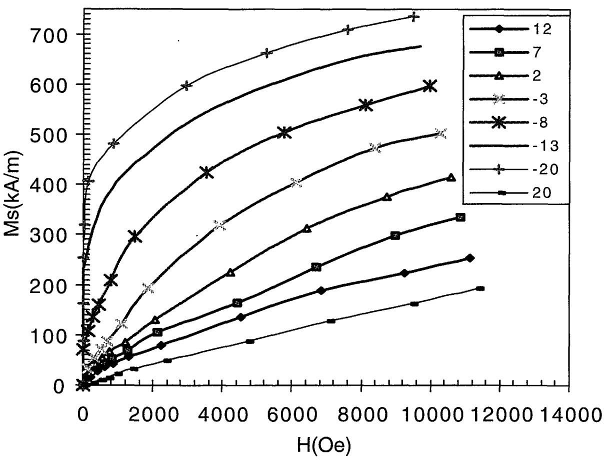

Fig. 2 M-H_{int} curves of $Gd_{75}Tb_{20}Nd_5$ as a function of temperature.

is the magnetization. When changing the original magnetization curves as Ms-H_{in} curves, these curves are translated to Ms-T curves under the same inner field. According to the equation $\Delta S_M = \int_0^H (\partial M/\partial T)|_H \mathrm{d}H$, the tangent of each Ms-T curve is made, and its integration with the inner field is the magnetic entropy change. Figures 2 and 3, and Table 2 show the procedure of calculation of ΔS_M for $Gd_{75}Tb_{20}Nd_5$, here the inner field is from 0 to 8×10^{-4} A/m.

Figure 4 is the calculated ΔS_M-T curves of the Gd–Td–Nd system. For comparison, results from the Ref.[2] (dotted curves) are also listed. It can be seen that the maximum ΔS_M (24 kJ/m^3·K) of $Gd_{75}Tb_{20}Nd_5$ is comparable to that of $Gd_{80}Tb_{20}$, but T_c is lowered by about 283 K, which means

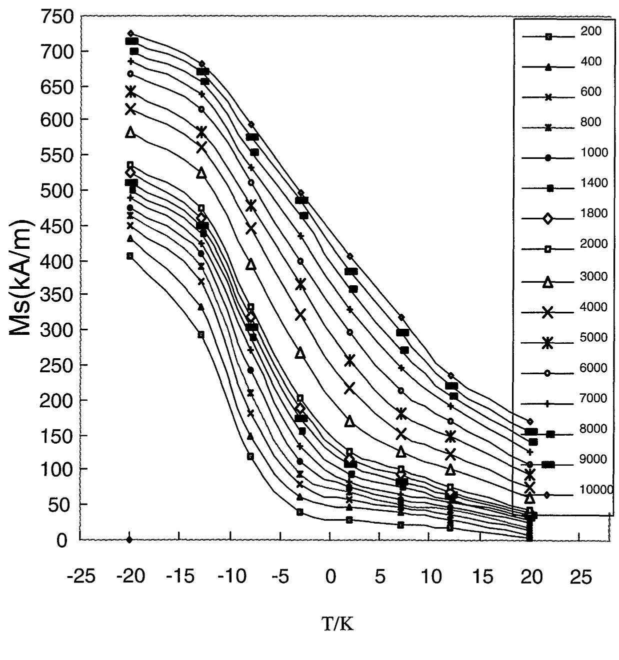

Fig. 3 Ms-T curves of $Gd_{75}Tb_{20}Nd_5$ as a function of magnetic field.

that the addition of a small amount of Nd lowers T_c notably, and the temperature range for large ΔS_M is reduced, while the maximum ΔS_M remains comparable to that of a pure Gd. This is advantageous for magneto-refrigerations with a very wide range of temperature.

Also seen from Fig. 4, the addition of Nd not only lower T_c, but when its amount is increased, the magnetic entropy

Table 2 Derivatives of M-T curves under the different inner field and the calculated magnetic entropy change for $Gd_{75}Tb_{20}Nd_5$.

	H/KA·m^{-1}											
T/K	1.6	3.2	4.8	6.4	8	16	24	32	48	64	72	ΔS_M/kJ·m^3·K^{-1}
253	14	11.5	10	10	9.5	7.4	7	6.8	6.7	5	6	6.33
256	15	9	9	7.5	8	7.5	7	7	6.5	5.5	5.5	6.19
258	17	15	12	10.5	10	10	8.5	8.5	7.5	7	7.5	7.74
260	23	22	22	21	18	17	15	13	12	11	10	12.54
261	30	31	30	31	30	23	22	20	16	18	14	18.34
262	35	38	42	40	34	30	26	22	19.5	20	17	21.79
263	40	40	42	40	40	28	27	26	24	24	18	24.34
264	32	36	40	40	34	30	28	25.5	25	22	18.5	23.85
265	25	26	30	30	30	29.5	27	26	22	19	19	21.77
267	17	18	20	23	27	26	26	25	21.5	18	19	20.08
268	12	16	19.5	20	25	26	26	25	21.5	18	19	19.75
270	8.5	10	11	13	15	20.5	21	21	20	20	19.5	17.025
273	0	1.5	1.5	2	5	15	18	20	18.5	20	20	14.4
278	1.6	1.3	3	4	3	3.3	7	11	15.5	16.5	16	9.433
285	1.5	2.5	2.5	2.5	2.5	5	5	6	7.5	10	12	5.83

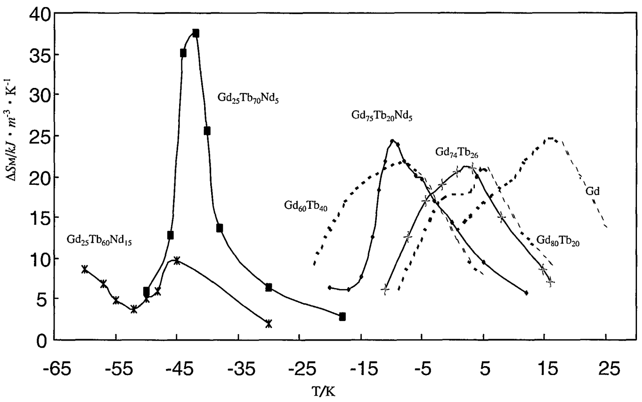

Fig. 4 ΔS_M-T curves of Gd–Tb–Nd system ($B = 1$ T, solid-experimental results, dashed-from Ref. 2)).

change reduces, as for $Gd_{25}Tb_{60}Nd_{15}$. This is due to an electron-layer structure of Nd and the interaction integration among the spin system of Nd, Gd and Tb.

Experimental results show qualitatively that T_c of Gd–Tb–Nd alloys is in the range of high temperature, and their ΔS_M is rather large. A small amount of Nd acts as a working temperature regulator.

If a proper composition is selected, the combination of this system would achieve a high and a constant magnetic entropy change in a large temperature scale, which would satisfy the Ericsson cycle.

Much work has indicated that Gd–Tb alloys can be utilized as wide-temperature-range magneto-refrigerate materials. Research has proceeded to the point of designing appropriate equipment. The present study of the Gd–Tb–Nd system enriches knowledge in this field, as well as helping to develop a more profound understanding of how the different element structures affect the interaction integration of the spin system, which can be applied in materials selections and equipment designs.

4. Conclusion

Magnetic properties of the Gd–Tb–Nd system alloys have been measured with a vibrating-sample magnetometer. The results show that the Curie temperature (T_c) of this system is in the range of room temperature, while the increase of Tb and Nd lowers T_c. When the concentration of Nd is low the magnetic entropy change is comparable to that of Gd–Tb alloys. A small amount of Nd addition of lowers T_c notably, so it can be used as an efficient working temperature regulator. Gd–Tb–Nd alloys with a proper composition can hopefully realize a large-scale room temperature magneto-refrigeration.

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Appendix

A1 is a table of the estimated magnetic transition temperature (T_c)of samples.

A2 is a table of the estimated derivatives of M-T curves under the different inner field and the caculated magnetic entropy change for $Gd_{75}Tb_{20}Nd_5$.