Room-Temperature Magnetic Refrigerate System Gadolinium-Terbium-Neodymium

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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 ($\Delta S_M$) is large, keeping constant in the cycle temperature range. As is reported, the material with the highest $\Delta S_M$ is Gd, but its $\Delta S_M$ 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 $\Delta S_M$ 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 ($\Delta S_M$) are measured and analyzed. The present results show that the Gd–Tb–Nd system has a comparatively large $\Delta S_M$ 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 $\Delta S_M$ 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 φ2 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 $\Delta S_M$. 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 ($M_0$–$T$) 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 $4 \times 10^{-4}$, $8 \times 10^{-4}$, $12 \times 10^{-4}$, $20 \times 10^{-4}$, $40 \times 10^{-4}$, $60 \times 10^{-4}$, $80 \times 10^{-4}$ 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 $H_{in}$ = $H_{ext}$ – $NMS$, here $H_{ext}$ 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 0.2.7 $M_s$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Gd$<em>{14}$Tb$</em>{26}$</th>
<th>Gd$<em>{15}$Tb$</em>{20}$Nd$_5$</th>
<th>Gd$<em>{15}$Tb$</em>{20}$Nd$_5$</th>
<th>Gd$<em>{15}$Tb$</em>{20}$Nd$_{15}$</th>
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<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>283</td>
<td>267</td>
<td>231</td>
<td>223</td>
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</table>

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is the magnetization. When changing the original magnetization curves as $M_s-H_{int}$ curves, these curves are translated to $M_s-T$ curves under the same inner field. According to the equation $\Delta S_M = \int_{H}^{H_{int}} (\frac{\partial M}{\partial T})_{H} dH$, the tangent of each $M_s-T$ 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 $\Delta S_M$ for Gd$_{75}$TB$_{20}$Nd$_{5}$, here the inner field is from 0 to $8 \times 10^{-4}$ A/m.

Figure 4 is the calculated $\Delta S_M-T$ curves of the Gd–Tb–Nd system. For comparison, results from the Ref. 2) (dotted curves) are also listed. It can be seen that the maximum $\Delta S_M$ (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 that the addition of a small amount of Nd lowers $T_c$ notably, and the temperature range for large $\Delta S_M$ is reduced, while the maximum $\Delta S_M$ 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
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 $\Delta S_M$ 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-refrigeration 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.

### Table 2 Derivatives of $M$–$T$ curves under the different inner field and the calculated magnetic entropy change for Gd$_{75}$Tb$_{20}$Nd$_5$.

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<th>16</th>
<th>24</th>
<th>32</th>
<th>48</th>
<th>64</th>
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<th>$\Delta S_M$ (kJ m$^{-3}$ K$^{-1}$)</th>
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<td>11.5</td>
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<td>7.4</td>
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### 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.

### Acknowledgments

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### REFERENCES


### 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 calculated magnetic entropy change for Gd$_{75}$Tb$_{20}$Nd$_5$.