AIP | Journal of Applied Physics

Magnetocaloric effect in as-cast Gd1−xYx alloys with x=0.0, 0.1, 0.2, 0.3, 0.4

E. S. Lara Pérez, I. Betancourt, J. F. Hernández Paz, J. A. Matutes Aquino, and J. T. Elizalde Galindo

Citation: Journal of Applied Physics **115**, 17A910 (2014); doi: 10.1063/1.4862086
View online: http://dx.doi.org/10.1063/1.4862086
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/17?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Phase diagram and magnetocaloric effects in Ni50Mn35(In1−xCrx)15 and (Mn1−xCrx)NiGe1.05 alloys
J. Appl. Phys. **115**, 17A922 (2014); 10.1063/1.4866082

Large magnetocaloric effect and refrigerant capacity near room temperature in as-cast Gd5Ge2Si2−xSnx compounds
Appl. Phys. Lett. **102**, 192410 (2013); 10.1063/1.4806971

Low hysteresis and large room temperature magnetocaloric effect of Gd5Si2.05− x Ge1.95− x Ni2 x (2x = 0.08, 0.1) alloys
J. Appl. Phys. **113**, 17A916 (2013); 10.1063/1.4795434

Magnetic and magnetocaloric properties of the new rare-earth–transition-metal intermetallic compound Gd3Co29Ge4B10
J. Appl. Phys. **111**, 07E333 (2012); 10.1063/1.3677658

Magnetic property and magnetocaloric effect of Gd(In) solid solutions
J. Appl. Phys. **103**, 07B323 (2008); 10.1063/1.2830684

You don't still use this cell phone
or this computer
Why are you still using an AFM designed in the 80's?
It is time to upgrade your AFM
Minimum $20,000 trade-in discount for purchases before August 31st
Asylum Research is today's technology leader in AFM
dropmyoldAFM@oxinst.com
OXFORD INSTRUMENTS
The Business of Science®

[This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to] IP: 132.248.12.211 On: Thu, 23 Apr 2015 18:45:39

JOURNAL OF APPLIED PHYSICS **115**, 17A910 (2014)

Magnetocaloric effect in as-cast $Gd_{1-x}Y_x$ alloys with x = 0.0, 0.1, 0.2, 0.3, 0.4

E. S. Lara Pérez,[1] I. Betancourt,[2] J. F. Hernández Paz,[1] J. A. Matutes Aquino,[3]
and J. T. Elizalde Galindo[1,a)]
[1]*Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez, Ave. Del Charro 450 norte, 32310 Ciudad Juárez, Chihuahua, Mexico*
[2]*Departamento de Materiales Metálicos y Cerámicos, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México D.F. 04510, Mexico*
[3]*Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, 31109 Chihuahua, Mexico*

(Presented 7 November 2013; received 23 September 2013; accepted 17 October 2013; published online 21 January 2014)

In this report, we present the magnetocaloric effect of $Gd_{1-x}Y_x$ alloys ($0.0 \leq x \leq 0.4$) prepared by arc-melting from high purity Gd and Y precursors in inert atmosphere. The formation of $Gd_{1-x}Y_x$ solid solutions was verified by means of X-ray diffraction analysis across the compositional series; also, residual secondary phases Gd and Y were present. Magnetic characterization performed by Vibrating Sample Magnetometry at a maximum applied field of 3.0 T showed a drastic reduction of the magnetization saturation (from 233 emu/g for x = 0.0 to 183 emu/g for x = 0.4), due to a dilution effect of the Y alloying, together with a marked Curie temperature decrease from 296 K to 196 K between x = 0.0 and x = 0.4. The second-order character of the magnetic transition was established by Arrot plots for all the cases. On the other hand, the magnetic entropy variation, determined from numerical integration of Maxwell relation displayed excellent values above 5.30 J/kg K for alloys with $x < 0.3$ due to the steep transition of the thermomagnetic curves.
[http://dx.doi.org/10.1063/1.4862086]

INTRODUCTION

Recently, magnetic refrigeration based on the magnetocaloric effect (MCE) has been a topic of great interest for minimizing environmental impact and global warming.[1–5] A key advantage of magnetic refrigeration is that it does not use chlorofluorocarbons causing ozone layer depletion. Although magnetic cooling to achieve ultralow temperatures dates back to early past century, the interest in its use at near room temperature operation puts the attention on the search for new materials or on the improvement of current ones. Over the past few years there have been many studies of magnetic refrigeration, where ferromagnetic materials, such as Gd, have been used as the magnetic refrigerant.[6] However, since the value of magnetic entropy variation ΔS_M of ferromagnetic materials shows a peak near the Curie transition, T_C, and ΔS_M decreases as the temperature separates away from the T_C temperature, the working temperature region of magnetic refrigeration with ferromagnetic materials has been restricted to short operational temperature ranges. In order to apply room-temperature magnetic refrigeration techniques to practical use, the working temperature region must be greater than 30 K.[7] To solve this problem, it is necessary to increase the working temperature range of magnetocaloric materials by the use of layered structures of magnetic refrigerants with different T_C. This subject has been the focus in most of the recent work on MCE, where some materials like Gd-Si-Ge based compounds and others, such as $(La_{1-x}Ca_x)MnO_3$, $MnFeP_{1-x}As_x$, and $La(Fe,Si)_{13}$, have attained interesting advances.[4,5,8–11]

This work presents a systematic study on the magnetocaloric effect and T_C dependence on composition for as-cast $Gd_{1-x}Y_x$ alloys with x = 0.0, 0.1, 0.2, 0.3, and 0.4 as possible candidates for layered-structure magnetic refrigerants.

EXPERIMENTAL

Raw material ingots of Gd and Y, from Alfa Aesar, with a purity of 99.9%, for both of them, were used to produce small buttons of $Gd_{1-x}Y_x$, with x = 0.1, 0.2, 0.3, and 0.4, by arc melting under Ar atmosphere. The buttons were turned and re-melted three times to ensure homogeneity. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert MPD diffractometer with Cu-Kα radiation in a 2θ ranging from 20° to 90°, with a step size of 0.016° and time per step of 30 s. Hysteresis loops and thermomagnetization curves for as-cast alloys were measured on a Quantum Design Versalab system in fields up to 30 kOe at temperature over a temperature interval ranging from 50 to 350 K. The magnetic entropy variation ΔS_M was determined by numerical integration of the Maxwell relation based on isothermal magnetization curves measured in a range of temperatures around the T_C, as

$$\Delta S_M = -\mu_0 \int_{H_1}^{H_2} \frac{\partial M}{\partial T} dH, \tag{1}$$

where μ_0 is the vacuum permeability and T is the temperature.[12] The refrigerant capacity (RC), defined as the amount of heat transferred between the hot and cold sinks in an ideal refrigeration cycle,[1] was calculated for all the alloys by numerical integration of the area under the $-\Delta S_M$ vs T curve.[13,14]

[a)] Author to whom correspondence should be addressed. Electronic mail: jose.elizalde@uacj.mx.

TABLE I. Cell parameters and magnetic properties of as-cast $Gd_{1-x}Y_x$ alloys with x = 0.0, 0.1, 0.2, 0.3, and 0.4.

Material	a (Å)	c (Å)	M_S (emu/g)	T_C (K)	$(dM/dT)_{max}$	$-\Delta S_M$ ($Jkg^{-1}K^{-1}$)	RC (Jkg^{-1})
Gd	3.621(2)	5.776(5)	233	296	0.21	5.43	289
$Gd_{0.9}Y_{0.1}$	3.636(2)	5.701(4)	231	269	0.29	5.50	284
$Gd_{0.8}Y_{0.2}$	3.647(2)	5.725(3)	214	245	0.20	5.35	282
$Gd_{0.7}Y_{0.3}$	3.712(3)	5.765(4)	218	218	0.18	4.82	271
$Gd_{0.6}Y_{0.4}$	3.665(1)	5.808(3)	183	196	0.09	4.24	232

RESULTS AND DISCUSSION

The formation of $Gd_{1-x}Y_x$ solid solutions across the compositional series was verified from X-ray diffraction patterns (not shown) indicating hexagonal crystalline structure according to ICDD PDF 01-089-2924, also, secondary phases Gd and Y were present at the minority. Cell parameters for the Gd-Y solid solution were calculated by using UNITCELL software.[15] The obtained values are presented in Table I. It was found that cell parameters were not strongly affected by increment of Y content.

The hysteresis loops measured at 50 K for $Gd_{1-x}Y_x$ alloys are shown in Figure 1. A marked reduction of the saturation magnetization is manifested for increasing Y content due to a dilution effect caused by the incorporation of non-magnetic Y atoms. A resume of properties is shown in Table I. Thermomagnetic *M vs T* curves ($H = 100$ Oe) for all the alloys within the temperature range from 150 to 350 K are displayed in Figure 2, for which T_C values were determined at the maximum of the derivative dM/dT. In general, it can be observed a steep transition of the thermomagnetic curves, with only the $Gd_{0.6}Y_{0.4}$ alloy displaying a smooth transition. The T_C values were determined as 296, 269, 245, 218, and 196 K for x = 0, 0.1, 0.2, 0.3, and 0.4, respectively. The inset in Figure 2 shows the T_C as a function of the yttrium content, for which a lineal tendency of T_C with composition can be observed, characterized by a reduction rate of 2.5 K for each 1% of Y concentration. This behavior affords the possibility for a precise control of T_C in order to establish the temperature range where these Gd-Y alloys could be useful for magnetic refrigeration applications.

Isothermal magnetization curves were measured for all $Gd_{1-x}Y_x$ alloys in the temperature range of 150 to 300 K. The magnetic field was applied in a very slow sweep rate to ensure an isothermal-like process. Figure 3 shows (a) isothermal magnetization curves and (b) Arrot plots for the $Gd_{0.7}Y_{0.3}$ alloy, as example. The progressive evolution of these curves to linear behavior denotes a typical ferromagnetic transition in the vicinity of T_C. The Arrot plots[16] presented in Figure 3(b) shows positive slopes for all isothermal curves, indicating that the Gd-Y alloys undergo a second order Curie transition. Same behavior was recorded for all the remaining alloy samples.

The calculated values for the temperature dependence of ΔS_M for all the $Gd_{1-x}Y_x$ alloys are shown in Figure 4. It is observed that all curves display a caret-like shape indicating that the magnetic phase transition near T_C is a second-order phase transition,[17] which is consistent with the Arrot plots (Fig. 3). ΔS_M values slightly increases initially from $x = 0.0$ to $x = 0.1$, followed by a marginal reduction for $x = 0.2$ and noticeable decrements for $x > 0.2$, as indicated in Table I. In addition, RC values for the alloys are also exhibited in Table I, for which interesting values between 232 and 289 J/kg are manifested, well comparable with the maximum RC = 289 J/kg corresponding to pure Gd ($x = 0.0$). The ΔS_M behavior can be attributed to the steepness of the *M vs T* plots, quantified by means of the maximum of the dM/dT

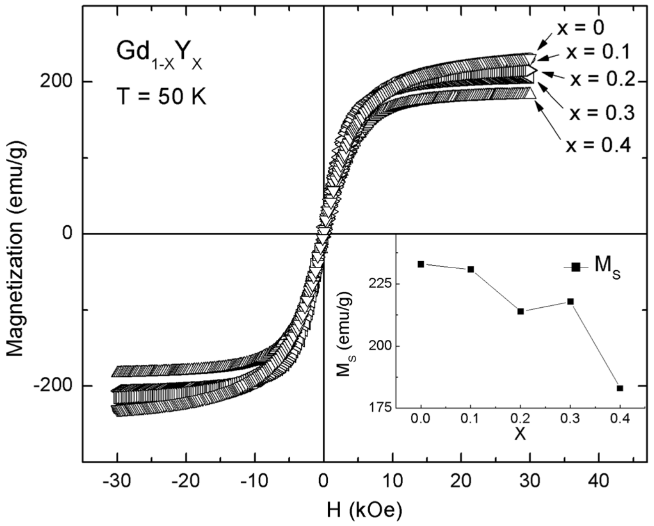

FIG. 1. Hysteresis loops of $Gd_{1-x}Y_x$ alloys measured at 50 K with $H_{max} = 30$ kOe. The saturation magnetization M_s as a function of the compositional series is shown in the inset.

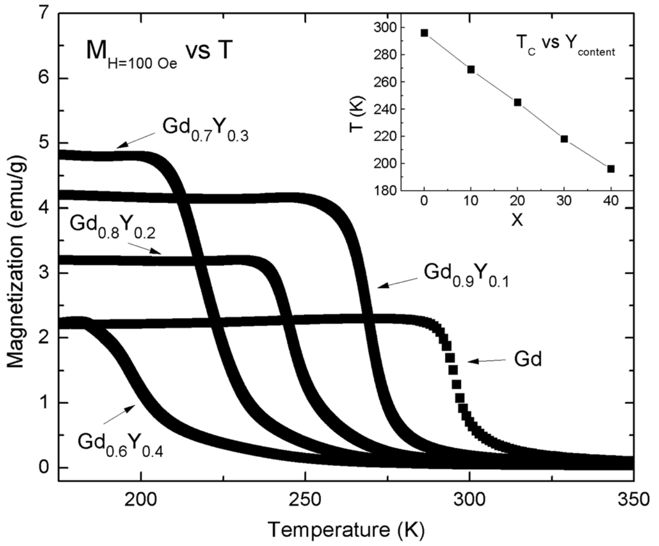

FIG. 2. Thermomagnetic curves, *M vs. T*, for $Gd_{1-x}Y_x$ alloys ($H_{max} = 100$ Oe). Curie temperature across the compositional series is shown in the inset.

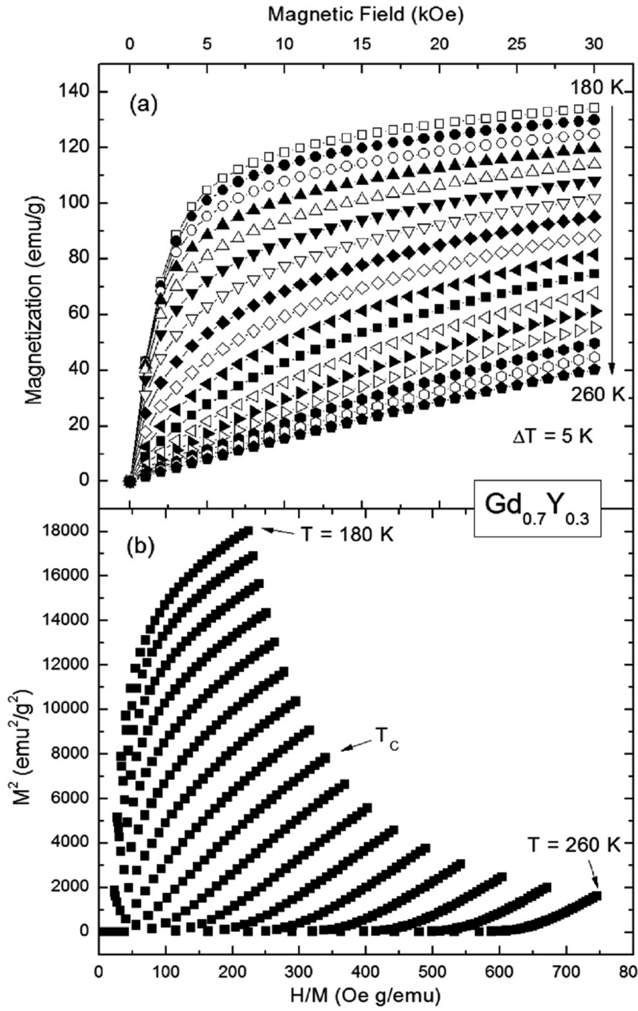

FIG. 3. (a) Isothermal magnetization curves and (b) Arrot plots for the $Gd_{0.7}Y_{0.3}$ alloy.

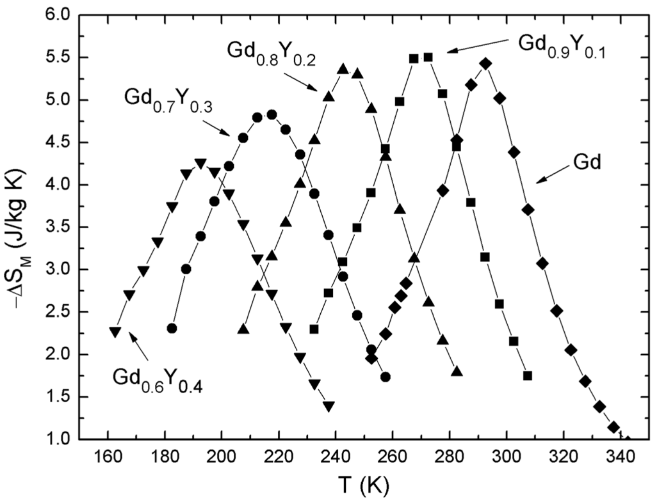

FIG. 4. Magnetic entropy variation ($\Delta H = 30$ kOe) as a function of temperature for $Gd_{1-x}Y_x$ alloys.

curves. This maximum is included in Table I for each alloy. Those maximums are very similar for $x = 0.0$, 0.1, and 0.2 (except for $x = 0.1$, which exhibits an enhanced dM/dT peak), while for $x > 0.2$, a reducing tendency is manifested (in fact, the lowest slope corresponds to $x = 0.4$). This behavior is consistent with the observed ΔS_M dependence on Y content. Hence, the entropy variation in these Gd-Y alloys seems to be mainly driven by *M vs T* rate of change around T_C, rather than the total magnetization variation when the alloys go through the magnetic transition at T_C.

CONCLUSIONS

The magnetocaloric effect of as-cast $Gd_{1-x}Y_x$ alloys ($x = 0.0$–0.4) (quantified by means of magnetic entropy variations at $\Delta H = 30$ kOe) was found very similar for x values up to 0.2, whereas marked reductions were recorded for $x > 0.2$. The observed entropy variation dependence on composition for these Gd-Y alloys was ascribed to the rate of change of the *M vs T* curves around T_C. On the other hand, the Curie temperature resulted strongly dependent on Y composition, with a linear dependence characterized by a reduction rate of 2.5 K for each 1% of Y added to the alloys. The maximum entropy variation was of −5.5 J/kg K for the $Gd_{0.9}Y_{0.1}$ alloy with a $T_C = 269$ K.

ACKNOWLEDGMENTS

This research was supported by UACJ research fund and CONACYT-PROINNOVA project with registry number 1901329. JTEG wants to dedicate this work to his loved ones Valkyria and José.

[1] K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[2] N. A. de Oliveira and P. J. von Ranke, Phys. Rep. **489**, 89 (2010).
[3] J. Lyubina, K. Nenkov, L. Schultz, and O. Gutfleisch, Phys. Rev. Lett. **101**, 177203 (2008).
[4] V. K. Pecharsky and K. A. Gschneidner, Jr., Appl. Phys. Lett.**70**, 3299 (1997).
[5] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).
[6] S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
[7] S. Kito, H. Nakagome, T. Kobayashi, A. T. Saito, and H. Tsuji, in *Cryocoolers*, edited by S. D. Miller and R. G. Ross, Jr. (International Cryocooler Conference, 2007), Vol. 14, pp. 549–553.
[8] Z. B. Guo, J. R. Zhang, H. Huang, W. P. Ding, and Y. W. Du, Appl. Phys. Lett. **70**, 904 (1997).
[9] F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[10] A. M. Tishin, J. Magn. Magn. Mater. **316**, 351 (2007).
[11] E. Brück, J. Phys. D: Appl. Phys. **38**, R381–R391 (2005).
[12] A. M. Tishin, "Magnetocaloric effect in the vicinity of phase transitions," in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, The Netherlands, 1999), Vol. 12, pp. 395–524.
[13] S. N. Jammalamadaka, S. S. Rao, S. V. Bhat, J. Vanacken, and V. V. Moshchalkov, J. Appl. Phys. **112**, 083917 (2012).
[14] A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (Institute of Physics Publishing, Bristol, Philadelphia, 2003), p. 406.
[15] T. J. B. Holland and S. A. T. Redfern, Mineral. Mag. **61**, 65 (1997).
[16] A. Arrot, Phys. Rev. **108**, 1394 (1957).
[17] X. C. Zhong, P. F. Tang, Z. W. Liu, D. C. Zeng, Z. G. Zheng, H. Y. Yu, W. Q. Qiu, H. Zhang, and R. V. Ramanujan, J. Appl. Phys. **111**, 07A919 (2012).