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Citation: *Appl. Phys. Lett.* **98**, 192503 (2011); doi: 10.1063/1.3589353

View online: <http://dx.doi.org/10.1063/1.3589353>

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Influence of La and Ce additions on the magnetocaloric effect of Fe–B–Cr-based amorphous alloys

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(Received 14 March 2011; accepted 14 April 2011; published online 10 May 2011)

The magnetic entropy change (ΔS_M), temperature of peak ΔS_M (T_{pk}) and refrigerant capacity (RC) in Fe(RE)₈₀B₁₂Cr₈ (RE=La, Ce, or Gd) alloys were studied. Increasing La, Ce, and Gd content led to relatively constant, decrease, and increase in T_{pk} , respectively. Both the phenomenologically constructed universal curve for ΔS_M and field dependence power laws demonstrated that these alloys exhibited similar critical exponents at Curie temperature. With 5% Ce added to Fe₈₀B₁₂Cr₈, T_{pk} could be tuned near room temperature with relatively constant peak ΔS_M . Fe₇₉B₁₂Cr₈La₁ exhibited enhanced RC compared to Gd₅Si₂Ge_{1.9}Fe_{0.1}. The tunable T_{pk} and enhanced RC are needed in active magnetic regenerators. © 2011 American Institute of Physics. [doi:10.1063/1.3589353]

Magnetic refrigeration (MR) offers a competitive alternative to conventional vapor compression refrigeration systems due to its high energy efficiency and environmental friendliness.^{1–3} It employs the magnetocaloric effect (MCE), which is related to the reversible temperature change in a magnetocaloric material (MCM) subjected to varying magnetic field under adiabatic conditions.¹ The Curie temperature (T_C) of MCM plays a significant role in magnetocaloric studies because MCE peaks near T_C . Gadolinium, a well-known MCM, exhibits large MCE with a second order magnetic transition (SOMT) at T_C near room temperature (RT). However, its high cost, poor corrosion resistance, and restricted availability necessitate the development of MCM for near RT MR. An ideal MCM should be low cost and exhibit good refrigerant capacity (RC) and peak magnetic entropy change ($|\Delta S_M^{pk}|$) with little hysteresis. Iron-based amorphous alloys fulfill such requirements. They offer low magnetic hysteresis, high electrical resistivity, enhanced corrosion resistance, good mechanical properties, and tunable T_C by composition variation.^{4–6} In addition, the elements involved are abundant and fabrication costs are reasonable, making them highly competitive. Fe₈₀Cr₈B₁₂ amorphous alloys exhibit promising MCE near RT. Cr additions enhance the corrosion resistance of the alloy.⁷ Gd additions to this alloy have been studied previously⁸ with the aim of tuning the T_C of the alloy. Fe₇₉B₁₂Cr₈Gd₁ alloy displayed enhanced $|\Delta S_M^{pk}|$ (~33% larger than Fe₈₀B₁₂Cr₈) and RC values [~29% larger than Gd₅Si₂Ge_{1.9}Fe_{0.1} (Ref. 9)]. These findings suggest that studies of the effect of rare earths (REs) additions on the MCE of Fe-based amorphous alloys would be useful. The type of RE additions to transition metals (TMs), such as Fe, influences the net magnetic moment of the alloys significantly: Gd and heavy RE contribute to ferrimagnetism while light RE contribute to ferromagnetism, which generally results in a larger net magnetic moment than the former.¹⁰ The magnetism in such alloys depends on the nature of coupling between the RE and TM moments. As the 4f-5d electron exchange interaction at the RE site is ferromagnetic, the an-

tiferromagnetic 5d(RE)-3d(TM) electron interactions result in ferromagnetic coupling of light RE to TM moments and vice versa for heavy RE.¹¹ This present work shows that La, Ce, and our previously studied Gd additions to Fe–B–Cr amorphous alloys influence the temperature of ΔS_M^{pk} (T_{pk}) differently.

Alloys with nominal composition Fe_{80-x}B₁₂Cr₈La_x (x=0, 1, 5, 10, and 15) and Fe_{80-y}B₁₂Cr₈Ce_y (y=2, 5, 10, and 15) were melt spun into ribbons. The ribbons are denoted by their (a) La content as La1, La5, La10, and La15, and (b) Ce content as Ce2, Ce5, Ce10, and Ce15. The amorphousness of the ribbons was confirmed by x-ray diffraction. Magnetic properties were measured by Lakeshore 7407 vibrating sample magnetometer for magnetic fields up to 15 kOe. The magnetic entropy change (ΔS_M) due to the variation in applied magnetic field (H) was determined from $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$. RC is calculated in two ways in this study: (a) RC_{FWHM}: the product of ΔS_M^{pk} times the full temperature width at half maximum of the peak (RC_{FWHM} = $\Delta S_M^{pk} \times \delta T_{FWHM}$), and (b) RC_{AREA}: numerical integration of the area under the $\Delta S_M(T)$ curves, using the full temperature width at half maximum of the peak as the integration limits.

The compositional dependence of $|\Delta S_M^{pk}|$, T_{pk} , and RC_{FWHM} are shown in the main panel of Fig. 1. For both La and Ce series, $|\Delta S_M^{pk}|$ values remains relatively constant for RE content up to 5 at. % and progressively decreases for higher concentrations. The $|\Delta S_M^{pk}|$ for Fe_{80-x}RE_xB₁₂Cr₈ (RE = La or Ce; x=1–5 at. %) alloys compare favorably with the base Fe₈₀B₁₂Cr₈ amorphous alloy.⁷ For higher Gd content, the decrease in $|\Delta S_M^{pk}|$ for the Gd alloy series was larger than those of the La and Ce series (Gd content ≥ 3 at. %). ΔS_M has been shown to be correlated with the magnetic moment of the material in other alloy systems.^{8,12,13} To investigate whether such a relationship holds between $|\Delta S_M^{pk}|$ and the magnetic moment of Fe_{80-x}B₁₂Cr₈La_x and Fe_{80-y}B₁₂Cr₈Ce_y amorphous alloys, the temperature dependence of magnetization was measured below T_C . The low temperature spontaneous magnetization (M_0) was obtained by the linear extrapolation of $M(T^{3/2})$ plots. The experimental $|\Delta S_M^{pk}|$ values were plotted as a function of M_0 in the inset

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FIG. 1. (Color online) Compositional dependence of (a) $|\Delta S_M^{pk}|$, (b) T_{pk} , and (c) RC_{FWHM} for the as-spun ribbons at $H=11$ kOe. (1a) inset: (i) spontaneous magnetization dependence of $|\Delta S_M^{pk}|$ and (ii) compositional dependence of M_0 . (1c) inset: compositional dependence of δT_{FWHM} .

of Fig. 1, a(i) for both alloy series as well as the previously studied $Fe_{80-z}B_{12}Cr_8Gd_z$ ($z=1-11$ at. %) alloys.⁸ $|\Delta S_M^{pk}|$ increases with increasing M_0 , evidencing the abovementioned linear correlation between $|\Delta S_M^{pk}|$ and M_0 . This also attributes to the compositional dependence of $|\Delta S_M^{pk}|$. As La atoms do not exhibit magnetic moment,¹¹ the trend of $|\Delta S_M^{pk}|$ decreasing with higher La concentration in La alloys reflect dilution of the magnetic coupling between the Fe moments. The M_0 values for the Ce alloy series were observed to be lower than the corresponding La alloys in Fig. 1, a(ii). The Ce ion in Fe–Ce alloys was reported to exhibit tetravalent valence state unlike other trivalent RE ions.¹⁴ Hence, the localized $4f$ electron of Ce atom can be easily displaced to the $5d$ conduction band. This results in a further distinct hybridization of $5d$ states with $3d$ states in Fe–Ce alloys, which can lead to lower magnetization in Fe–Ce alloys compared to other amorphous light RE–Fe alloys.^{15,16} For the Gd alloy series, the large magnetic moment of Gd compared to the other RE investigated in this study led to the highest $|\Delta S_M^{pk}|$ value (1 at. % Gd). Its reduced $|\Delta S_M^{pk}|$ for increasing Gd additions is due to the antiparallel coupling between Gd and Fe moments, leading to reduced M_0 for higher Gd content.

The temperature of the peak magnetic entropy change (T_{pk}) can be considered as T_C for low H .¹⁷ T_{pk} shows little variation as La content increases, consistent with earlier reports in amorphous Fe–La binary alloys.¹⁸ The presence of Cr and B in our alloys displaces T_C to higher temperatures

compared to the literature.^{18–20} In contrast, T_{pk} reduces as Ce concentration increases. The Ce alloy series displays lower T_{pk} values compared to the La alloy series.²¹

The magnetic ordering temperatures for Gd and Ce alloys were the highest and lowest, respectively.²² Ce was reported to adopt the tetravalent state in Ce–Fe alloys, which can lead to reduction in the Fe–Fe distance, which in turn reduces T_C ,²³ and thus these alloys exhibit lowest T_C compared to other light RE alloys.²² Gd has been reported to display the largest T_C among all RE,^{22,23} which led de Gennes to correlate this maximum with the maximal value of $4f$ spin in Gd.²⁴ In addition, T_{pk} in the La series showed little variation with La content compared to those of Ce and Gd containing alloys. In contrast, Ce alloys show a monotonic decrease in T_{pk} with increasing Ce content. Unlike the La and Ce series, T_{pk} was observed to increase with higher Gd additions.^{25,26} RC_{FWHM} reduced with increasing RE content, with the Gd alloy series displaying the largest decrease compared to the La and Ce alloy systems. For Ce15, the decreasing trend of RC shows a larger negative slope compared to that of the La15 alloy. To study this reduction in RC_{FWHM} , the compositional dependence of full temperature width at half maximum (δT_{FWHM}) of $|\Delta S_M^{pk}|$ was plotted [inset of Fig. 1(c)]. For RE=15 at. %: δT_{FWHM} increased for the La15 alloy while the Ce15 alloy showed a large reduced δT_{FWHM} among the Ce alloy series. For La alloy series, δT_{FWHM} did not significantly change with La concentration. On the other hand, δT_{FWHM} decreased with increasing Ce concentration. The decrease in RC for the La alloy series could be attributed to the reduction in $|\Delta S_M^{pk}|$ (RC being proportional to $|\Delta S_M^{pk}|$ and δT_{FWHM}) since $|\Delta S_M^{pk}|$ generally plays a dominant role in RC maximization for SOMT materials.²⁷ For the Ce alloy series, the reduced $|\Delta S_M^{pk}|$ and δT_{FWHM} contributes to a much lower RC value, e.g., in the Ce15 alloy. For the Gd series, the large decreasing trend of RC could be attributed to the large reduction in $|\Delta S_M^{pk}|$ with Gd addition.

Literature reports of the properties of MCM are usually published at the maximum available magnetic field in individual laboratories. To compare different literature values, the field dependence studies of ΔS_M^{pk} and RC should be known. The field dependence of magnetic entropy change can be expressed as $\Delta S_M^{pk} \propto H^n$, validated experimentally in several soft magnetic amorphous alloys and some RE-based crystalline MCM.¹⁷ The exponent n is field invariant at T_C or T_{pk} .¹⁷ The field dependence of RC can also be represented by a power law expression: $RC_{FWHM} \propto H^N$. Exponents n (and N) should have similar values for a given alloy series since they are controlled by the critical exponents of the alloy series. As an example, $\Delta S_M^{pk}(H)$ and $RC(H)$ for the La5 and Ce5 alloys are presented in the insets of Fig. 2. The good fits shown aid the determination of the exponents n and N . For the La alloys: $n=0.79 \pm 0.01$ and $N=1.20 \pm 0.01$; and Ce alloys: $n=0.77 \pm 0.03$ and $N=1.20 \pm 0.01$. These values are close to those obtained for Gd alloys ($n=0.75 \pm 0.01$ and $N=1.16 \pm 0.01$).⁸ Both RC_{FWHM} and RC_{AREA} have been predicted to scale with field with the same value of exponent,¹⁷ in good agreement with our experimental results. When $|RC_{AREA}|$ for the La1 and La5 alloy are extrapolated to $H=50$ kOe, values of 386 J kg^{-1} and 356 J kg^{-1} , respectively, are obtained, which are up to $\sim 9\%$ higher than the well-known MCM— $Gd_5Si_2Ge_{1.9}Fe_{0.1}$.⁹ For Ce2 alloys, its $|RC_{AREA}|$ yield 367 J kg^{-1} when extrapolated to 50 kOe,

FIG. 2. (Color online) Universal curves for $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{RE}_x$ where $\text{RE} = \text{La}$ or Ce . Inset: field dependence of ΔS_M^{pk} ($\square$), RC_{FWHM} ($\circ$), and RC_{AREA} ($\triangle$) for (a) La5 and (b) Ce5 alloys. Lines are fits to the power law expressions.

which shows $\sim 3\%$ improvement over $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Fe}_{0.1}$.⁹ A phenomenological universal curve for ΔS_M is used to extrapolate magnetocaloric properties to magnetic fields and/or temperatures which are inaccessible in different laboratories. This aids the performance evaluation of different MCM. Its construction requires the normalization of $\Delta S_M(T)$ with respect to their peaks:¹⁷ $\Delta S' = \Delta S_M / \Delta S_M^{\text{pk}}$ and rescaling the temperature axis θ using two reference temperatures (T_r) such that $\Delta S_M(T_r) / \Delta S_M^{\text{pk}} = 0.6$. The rescaled $\Delta S_M(T)$ curves for La and Ce alloys are presented in the main panel of Fig. 2. The normalized ΔS_M curves collapse nicely onto a single curve for each alloy series, confirming that they exhibit SOMT, that the universal curve is applicable to these alloys and that their critical exponents should be the same.

In summary, additions of La and Ce to Fe–B–Cr amorphous alloys led to different influences on T_{pk} . With increasing RE content, T_{pk} decreases for $\text{Fe}_{80-y}\text{B}_{12}\text{Cr}_8\text{Ce}_y$ but increases for $\text{Fe}_{80-z}\text{B}_{12}\text{Cr}_8\text{Gd}_z$. La additions have little effect on T_{pk} . For $x=1$ and 5 at. % in $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{La}_x$ and $\text{Fe}_{80-x}\text{B}_{12}\text{Cr}_8\text{Ce}_x$ amorphous alloys, T_{pk} can be tuned near RT with $|\Delta S_M^{\text{pk}}|$ comparable to the base $\text{Fe}_{80}\text{B}_{12}\text{Cr}_8$ alloy. Both $\Delta S_M^{\text{pk}}(H)$ and $\text{RC}(H)$ agrees with theoretical predictions of a power law dependence, yielding exponents as 0.79 and 1.20, respectively, for the La alloy series and 0.77 and 1.20, respectively, for the Ce alloys. These are in good agreement with the previous results for the Gd alloy series. $\text{Fe}_{79}\text{B}_{12}\text{Cr}_8\text{La}_1$ alloys exhibit enhanced RC compared to the well-known MCM $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Fe}_{0.1}$.

This work was supported by the U.S. AOARD (Grant No. AOARD-08-4018), program manager, Dr. R. Ponnappan, by the Spanish Ministry of Science and Innovation and EU FEDER (Project No. MAT 2010-20537), the PAI of the Regional Government of Andalucía (Project No. FQM-6462), and the United States Office of Naval Research (Project No. N00014-11-1-0311).

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