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Annealing influence on the magnetostructural transition in Gd5Si1.3Ge2.7 thin films

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Abstract
Due to the emerging cooling possibilities at the micro and nanoscale, such as the fast heat exchange rate, the effort to synthesize and optimize the magnetocaloric materials at these scales is rapidly growing. Here, we report the effect of different thermal treatments on Gd5Si1.3Ge2.7 thin film in order to evaluate the correlation between the crystal structure, magnetic phase transition and magnetocaloric effect. For annealing temperatures higher than 773 K, the samples showed a typical paramagnetic behavior. On the other hand, annealing below 773 K promoted the suppression of the magnetostructural transition at 190 K, while the magnetic transition around 249 K is not affected. This magnetostructural transition extinction imparts reflected in the magnetocaloric behavior and resulted in a drastic decrease in the entropy change peak value. Nevertheless, an increase in 25% of the TC and an increasing ΔTFWHM from 23 to 49 K of its operation temperature interval, ΔT, upon annealing, are crucial for future application in magnetic refrigeration.

Keywords
Magnetocaloric effect, Thin Films, Thermal treatment

Disciplines
Electrical and Computer Engineering | Electromagnetics and Photonics | Nanoscience and Nanotechnology

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Influence of Annealing on the Magnetostructural Transition in Gd$_{5}$Si$_{1.3}$Ge$_{2.7}$ Thin Film

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Due to the emerging cooling possibilities at the micro and nanoscale, such as the fast heat exchange rate, the effort to synthesize and optimize the magnetocaloric materials at these scales is rapidly growing. Here, we report the effect of different thermal treatments on Gd$_{5}$Si$_{1.3}$Ge$_{2.7}$ thin film in order to evaluate the correlation between the crystal structure, magnetic phase transition and magnetocaloric effect. For annealing temperatures higher than 500°C, the samples showed a typical paramagnetic behavior. On the other hand, thermal treatments below 500°C promoted the suppression of the magnetostructural transition at 190 K, while the magnetic transition around 249 K is not effected. This magnetostructural transition extinction was reflected in the magnetocaloric behavior and resulted in a drastic decrease in the entropy change peak value (of about 68%). Nevertheless, an increase in $T_c$ was reported, proving that at the nanoscale, heat treatments may be a useful tool to optimize the magnetocaloric properties in Gd$_5$(SixGe$_{1-x}$)$_4$ thin films.

Keywords: Magnetocaloric thin films, Thermal Treatment, Magnetocaloric effect,

I. INTRODUCTION

The recent success in the production of Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ thin films using femtosecond pulsed laser deposition opened new prospects for the optimization of the production process, with the aim of increasing the giant magnetocaloric effect (GMCE) in these nanomaterials [1,2]. It is well known that thin film properties are very

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sensitive to thickness, substrate type, oxygen content, as well as deposition and annealing parameters etc. [3]. For
bulk materials, thermal treatments have been reported in the literature as a very important tool for both the
minimization of secondary phases and optimization of the crystallographic phases responsible for the GMCE
[4–8]. In fact, annealing temperatures below 700 K lead to an increase of the orthorhombic I, O(I), phase hence
minimizing the MCE in Gd₅Si₂Ge₂ [4,6]. This is, in contrast to high temperature annealing, T=1473 K, where the
phase transformation was from the lower volume, O(I), to the higher volume phase, Monoclinic, M, and shown an
increase in the MCE [7].

However, for thin films, i.e. when the dimensions of a material are reduced, their phase diagrams suffer
dramatic changes due to the different diffusion processes. In particular, the phase stabilization temperatures tend
to be significantly smaller, meaning that less energy is necessary to activate the atomic diffusion at the
micro/nanoscale. Hence, in order to unveil the effects of thermal treatments in the still unexplored Gd₅Si₁.₃Ge₂.₇
thin film, we studied the influence of annealing temperatures on the formation/destruction of the different
crystallographic phases and their influence on morphology, structure and magnetic properties.

II. EXPERIMENTAL DETAILS

The preparation details of Gd₅Si₁.₃Ge₂.₇ thin films (~780 ± 25 nm thick) on SiO₂-covered Si substrates using
femtosecond pulsed laser deposition and single crystal target were described in Ref [2]. In order to study the
effects of different annealing temperatures, the samples were wrapped in a tantalum sheet, placed into a crucible,
and introduced in a quartz tube with a zirconium getter to prevent oxidation. Four different temperatures were
chosen for the presented study: 300, 400, 500, and 600°C, with a fixed annealing time of 2 hours in vacuum
(~10⁻⁵ mbar). The samples were fast cooled by immersing the sealed quartz tube in water, in order to quench the
crystal structure. The morphological and structural characterization of the thin films was ensured by Scanning
Electron Microscopy (SEM) and grazing incidence X-ray Diffraction (XRD). The magnetic measurements were
performed in a commercial (MPMS Quantum Design) Superconducting Quantum Interference Device (SQUID)
magnetometer. The magnetic entropy change [-ΔSₘ(T)] was estimated from the measured magnetic isotherms
[M(H)] following the loop method [9].
III. RESULTS AND DISCUSSION

Figure 1a) shows the temperature dependence of magnetization for the Gd₅Si₁₃Ge₂.₇ as-deposited film. On heating (red curve) it is observed that a first-order phase transition (FOPT) occurs from an orthorhombic O(I) ferromagnetic to an orthorhombic O(II) paramagnetic phase at $T \approx 194$ K. However, this transition is incomplete and approximately 33\% of the O(I) phase does not transform into O(II), meaning that at $T>194$ K the film consists of: two thirds [O(II), PM] and one third [O(I), FM] phase, as reported in [2]. At $T \approx 247$ K, a purely magnetic second-order phase transition (SOPT) of the remaining [O(I), FM] phase occurs, changing its magnetic state from the ferromagnetic to the paramagnetic state (at $T > 247$ K).

![Figure 1](image_url)

Figure 1 – (color online) The temperature dependence of the magnetization for the as-deposited sample measured at $H=1000$ Oe; b) Temperature dependence of the magnetization, measured at $H=1000$ Oe, for the samples annealed at: 300, 400, 500 and 600°C; and c) Magnetization as a function of the magnetic field for the same annealing temperatures, measured at 300 K.

The effect of the annealing temperature is shown in Figure 1b). In fact, upon annealing at 300°C and 400°C, the films just present the SOPT at 249 K, previously observed in as-deposited film. Additionally, these annealing temperatures led to the disappearance of the FOPT.

If the annealing temperature is further increased, i.e., above 500°C (Figure 1b), the two magnetic transitions observed in the as-deposited film disappear, and the film exhibit a pure paramagnetic behavior. Figure 1c) represents the $M(H)$ curves measured at 300 K in the samples with different thermal treatments. The magnetic moment is higher in the sample annealed at 400°C.
For the assessment of the nature of the thin film phase transitions and in order to confirm the disappearance of the MST-FOPT with the thermal treatments, the Arrott plots of the as-deposited sample and sample annealed at 400ºC were represented in Figure 2a) and b), respectively. For the as-deposited sample, the H/M vs M² exhibits a different behavior, changing from a negative to a positive slope with the increase of M² resembling an “S” shape. Such behavior is the signature of a first-order phase transition [10,11] and the confirmation that it occurs at Tc~194 K. On the contrary, the H/M vs M² curve of the film annealed at 400ºC shows a monotonous positive slope. Hence, this confirms the second order nature of the magnetic transition at ~ 247 K in the annealed film.

The XRD patterns extracted at 300 K are shown in Figure 3a). The as-deposited sample presents peaks corresponding to both the O(I) phase (Gd₅Si₄) and the O(II) phase (Gd₅Ge₄). After the thermal treatments, there is evidence of the decrease and vanishing of the peaks corresponding to the O(II) phase, such as the reflections: [0 4 0] (24.1°), [2 1 1] (26.5°) and [1 6 4] (61.8°) [12]. Concomitantly, there is an increase in the number of peaks corresponding to the O(I) phase, such as reflections: [2 2 1] (29.1°), [1 3 2] (31.7°) and [1 4 3] (44.5°) [13]. These results confirm the disappearance of the FOPT observed in Figure 1b), which is a direct consequence of the decrease in O(II) phase. The 33.2° and 47.4° peaks appear only after the thermal treatments and there is no correspondence to the O(I)/O(II) phases. Indeed, these peaks correspond to the Gd₂O₃ [14] phase, which may have formed because of the higher reactivity between Gd and O, but in low amounts due to the presence of Tantalum.
and Zirconium getters during annealing process. Many examples of phase transformations induced by annealing process on bulk Gd$_5$Si$_2$Ge$_2$ alloys can be found in the literature [5–7]. In these, several phenomena are responsible for the phase transformation such as, diffusion of Si, due to higher Si content, which may favor the O(I) phase [15] and stress release by the heating process [4].

![Figure 3](image)

Figure 3 – (Color online) a) XRD pattern of the as-deposited film and films annealed at 300°C, and 400°C. The peaks are marked with symbols corresponding to different crystallographic phases; b) Temperature dependence of the $-\Delta S_m$ of the as-deposited film and the films annealed at 400°C under an applied magnetic field change of 50 kOe.

Figure 3b) shows the $-\Delta S_m$ of the as-deposited and annealed (at 400°C) films. The maximum magnetic entropy change, $-\Delta S_m^{\text{max}}$, is 68 mJK$^{-1}$cm$^{-3}$ for the as-deposited at around 193 K. After the thermal treatment, there is a 68% decrease of the $-\Delta S_m^{\text{max}}$ value to 25 mJK$^{-1}$cm$^{-3}$ and occurs at $T \sim 257$ K. This decrease results from the destruction of the [O(II), PM] $\rightarrow$ [O(I), FM] MST that occurs in the as-deposited film at $T \sim 193$ K. Moreover, the temperature at which $-\Delta S_m$ is maximum was found to increase by 25%, i.e., from 193 K to 257 K.

As previously reported, materials presenting coupled magnetic and structural transitions exhibit a much higher MCE because of the extremely large $dM/dT$ value at the transition (which is a critical parameter for the enhancement of the magnetic entropy change) and also because there is an extra entropy change associated with the lattice transformation, $-\Delta S_{\text{lattice}}$ [16]. Therefore the reduction of the $-\Delta S_m^{\text{max}}$ value with annealing temperature was expected since the MST was suppressed. Previously, in Gd$_5$Si$_2$Ge$_2$ bulk material, Pecharsky and co-workers [5,17] found a $-\Delta S_m$ decrease and a $T_c$ increase in samples annealed at 670 and 870 K and attributed such reduction to the formation of the O(I) phase with the annealing. The Full Width at Half Maximum (FWHM) was estimated from the
-\Delta S_m curves and an increase with the annealing process was observed, from 23 to 49 K. The larger FWHM is a signature of a SOPT and in this film, it might also be associated to strain disorder [18]. The refrigerant capacity value (RC = -\Delta S_m^{\text{max}} x \text{FWHM}) was estimated to be \approx 203 \ J kg^{-1} and \approx 160 \ J kg^{-1} for the as deposited and 400ºC annealed film, respectively, with a \Delta H=5T field variation. Hence, despite the large 68% decrease on the -\Delta S_m^{\text{max}}, the thermal treated film shows only a small decrease on its RC (21%) because of its larger FWHM. Simultaneously, a larger FWHM represents an expanded interval of operational temperatures (and closer to room temperature) of a potential magnetic refrigerator/sensor.

IV. CONCLUSIONS

In this work it was found that thermal treatments below 500ºC were responsible for the suppression of the MST in Gd_{5}Si_{1.3}Ge_{2.7} thin films. This was confirmed by the disappearance of the O(II) phase in the XRD measurements. The suppression of the structural phase responsible for the GMCE promoted a 68% decrease in the magnetic entropy change peak value and a 21% decrease in its RC. Nonetheless, there was a 25% increase in T_C, which is closer to room temperature, and a \approx 110% expansion of its operational temperature interval upon annealing. These findings are crucial for future application in magnetic refrigerators/sensor. Hence this work demonstrates that thermal treatments of thin films can be an important tool to promote and optimize the crystallographic phase responsible for the GMCE.

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REFERENCES