Annealing influence on the Magnetostructural Transition in $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ Thin Films

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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 $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ thin film in order to evaluate the correlation between the crystal structure, magnetic phase transition and magnetocaloric effect. For annealing temperatures higher than 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 T_C and an increasing ΔT_{FWHM} from 23 to 49K of its operation temperature interval, ΔT , upon annealing, are crucial for future application in magnetic refrigeration.

Keywords: Magnetocaloric effect, Thin Films, Thermal Treatment

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I. INTRODUCTION

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1 In the Era of devices miniaturization, several materials are being persuaded to scale down the size from bulk
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3 to thin film and/or nanostructures due to new effects and potential functionalities. There are several examples
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5 proving that size can influence dramatically the magnetic, electric and optical functional properties of different
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7 materials in a variety of nanostructures such as thin films, nanorods, nanotubes, nanowires, etc. [1–3]. In the area
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9 of magnetic refrigeration and magnetocaloric materials, size is a more critical parameter since these materials
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11 present a magnetostructural transition that is answerable for the Giant Magnetocaloric Effect (GMCE) [4].
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15 Nevertheless, the recent success in the production of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ thin films using femtosecond pulsed laser
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17 deposition opened new prospects for the optimization of the production process, with the aim of increasing the
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19 GMCE in these nanomaterials [5]. It is well known that thin film properties are very sensitive to thickness,
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21 substrate type, oxygen content, as well as deposition and annealing parameters etc. [6]. For bulk materials,
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23 thermal treatments have been reported in the literature as a very important tool for both the minimization of
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25 secondary phases and optimization of the crystallographic phases responsible for the GMCE [7–11]. In fact,
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27 annealing temperatures below 700 K lead to an increase of the orthorhombic I, O(I), phase hence minimizing the
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29 MCE in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [7,9] bulk material. In opposition, high annealing temperatures, e.g. at $T=1473$ K, where the
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31 phase transformation was from lower volume, O(I), to higher volume phase, Monoclinic, M, promoted an
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33 increase in the MCE as reported in Reference [10].
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37 However, for thin films, i.e. when the dimensions of a material are reduced, their phase diagram suffers
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39 dramatic changes due to the different diffusion processes. In particular, the phase stabilization temperatures tend
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41 to be significantly smaller, meaning that less energy is necessary to activate atomic diffusion at the
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43 micro/nanoscale. Hence, in order to unveil the effects of annealing in the still unexplored $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ thin film,
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45 we studied the influence of annealing temperatures on the formation/destruction of the different crystallographic
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47 phases and their influence on morphology, structure and magnetic properties.
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52 II. EXPERIMENTAL DETAILS 53 54 55

56 The $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ thin films ($\sim 780 \pm 25$ nm thick) were deposited on SiO_2 -covered Si substrates using
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58 femtosecond pulsed laser deposition and single crystal target. The substrate used was a commercial p-type doped
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silicon substrate oriented in the $\langle 100 \rangle$ direction, thermally oxidized on the top (SiO_2) with a 1 micron layer. Further preparation details are described in Ref [5]. 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 annealing temperatures were chosen for the presented study: 573, 673, 773, and 873 K, with a fixed annealing time of 2 hours in vacuum ($\sim 10^{-5}$ 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 $[-\Delta S_m(T)]$ was estimated from the measured magnetic isotherms $[M(H)]$ following the loop method [12].

III. RESULTS AND DISCUSSION

Figure 1a) shows the temperature dependence of magnetization for the $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ as-deposited film. On heating, 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 $T \sim 194$ K. However, this transition is incomplete and approximately 33% of the O(I) phase does not transform into O(II), meaning that at $T \sim 230$ K the film consists of: two thirds $[\text{O(II)}, \text{PM}]$ and one third $[\text{O(I)}, \text{FM}]$ phase, as reported in [5]. At $T \sim 247$ K, a purely magnetic second-order phase transition (SOPT) of the remaining $[\text{O(I)}, \text{FM}]$ phase occurs, changing its magnetic state from the FM to PM state.

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: 573, 673, 773 and 873 K; 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, in magnetization, is shown in Figure 1b). In fact, upon annealing at 573 and 673 K, the films just present the SOPT at 249 K, previously observed in the as-deposited film. Additionally, these annealing temperatures led to the suppression of the FOPT at 194 K.

If the annealing temperature is further increased, i.e., above 773 K (Figure 1b), the two magnetic transitions observed in the as-deposited film suppress, and the film exhibits a pure paramagnetic behavior. Figure 1c) represents the $M(H)$ curves measured at 300 K for samples with different thermal treatments. The magnetic moment is higher in the sample annealed at 673 K.

Figure 2 – (color online) Arrott plots, H/M as a function of M^2 for a) $Gd_5Si_{1.3}Ge_{2.7}$ as-deposited film measured in the [176; 212] K temperature range and b) sample annealed at 673 K measured in the [240; 276] K temperature range.

For the assessment of the nature of the thin films phase transitions and in order to confirm the suppression of the Magnetostructural Transition, MST-FOPT, with thermal treatments, the Arrott plots of the as-deposited sample and sample annealed at 673 K are represented in Figure 2a) and b), respectively. For the as-deposited sample, the H/M vs M^2 exhibits a different behavior, resembling an “S” shape, as M^2 increases. Such behavior is the signature of a first-order phase transition [13,14] at $T_c \sim 194$ K. On the contrary, the H/M vs M^2 curves of the film annealed at 673 K show a monotonous positive slope, confirming the second-order nature of the magnetic transition at ~ 247 K in the annealed film.

The XRD patterns are shown in Figure 3a). The as-deposited sample presents peaks corresponding to both the O(I) phase (Gd_5Si_4) and the O(II) phase (Gd_5Ge_4). After thermal treatments, there is evidence for 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° [15]. 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° [16]. These results confirm the suppression of the FOPT observed in Figure 1b), which is a direct consequence of the decrease of 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 Gd_2O_3 phase [17], which may have formed because of the higher reactivity between Gd and O. This phase is observed just in low amounts due to the presence of Tantalum and Zirconium getters during the annealing process. Many examples of phase transformations induced by annealing process on bulk $Gd_5Si_2Ge_2$ alloys can be found in the literature [8–10,18]. In these, several phenomena are responsible for the phase transformation such as, diffusion of Si which may favor the O(I) phase [19] and stress release by the heating process [7].

Figure 3 – (Color online) a) XRD pattern of the as-deposited film and films annealed at 573 and 673 K. The peaks are marked with symbols corresponding to different crystallographic phases; Inset a): SEM images of the surface of the thin film annealed at 573 K; b) Temperature dependence of the $-\Delta S_m$ of the as-deposited film and the film annealed at 673 K under an applied magnetic field change of 50 kOe.

Figure 3b) shows the $-\Delta S_m$ of the as-deposited and annealed (at 673 K) films. The maximum magnetic entropy change, $-\Delta S_m^{\text{max}}$, is 68 mJ·K⁻¹·cm⁻³ at around 193 K for the as-deposited film. After annealing there is a 68% decrease of the $-\Delta S_m^{\text{max}}$ value, to 25 mJ·K⁻¹·cm⁻³ which now occurs at $T \sim 257$ K. This decrease results from the suppression 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 they present at the transition (which is a critical parameter for the enhancement of the magnetic entropy change) enhanced by the extra entropy change associated with the lattice transformation, $-\Delta S^{\text{lattice}}$ [20]. Therefore, the reduction of the $-\Delta S_m^{\text{max}}$ value with annealing temperature was expected since the MST was suppressed. Previously, in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ bulk material, Pecharsky and co-workers [8,21] 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 treatments [21]. Furthermore, 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 $\Delta T_{FWHM} = 23$ to 49 K. It cannot be neglected that, the larger FWHM is a signature of a SOPT and in this film it might also be associated to strain disorder [22]. The refrigerant capacity value ($RC = -\Delta S_m^{max} \times FWHM$) was estimated to be $\sim 203 \text{ JKg}^{-1}$ and $\sim 160 \text{ Jkg}^{-1}$ for the as deposited and 673 K annealed film, respectively, with a $\Delta H=5T$ field variation. Hence, despite the large 68% decrease on the $-\Delta S_m^{max}$, 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) for potential magnetic refrigerator/sensor. The effect of heat treatments on the phase conversion and consequently on the magnetocaloric properties of some thin films has been recently reported in the literature. For example, in the case of a pure Gd thin film, it was shown that higher temperatures treatments (under pre-gettering conditions) enhance the cubic phases of Gd, which is one of the causes for the higher transition temperature, larger MCE and larger $-\Delta S_m(T)_{FWHM}$ [23]. Similarly, in the case of NiMnGa and $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ thin films, the in-situ or post deposition thermal treatments play a crucial role on their phase stabilization (martensitic and monoclinic phases, respectively) and hence consequently favoring their magnetocaloric properties [24,25].

IV. CONCLUSIONS

In this work it was found that annealings below 773 K were responsible for the suppression of the Magnetostructural Transition in $\text{Gd}_5\text{Si}_{1.3}\text{Ge}_{2.7}$ thin films. This was confirmed by the suppression of the O(II) phase peaks observed 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 Refrigerant Capacity. Nonetheless, a 25% increase in its T_C , which became closer to room temperature, and an increasing of ΔT_{FWHM} from 23 to 49 K in its operational temperature interval were found 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, which is vital for future applications [23–26].

ACKNOWLEDGEMENTS

The authors acknowledge FCT for financial support through the projects: PTDC/CTM-NAN/115125/2009, EXPL/EMS-ENE/2315/2013 and FEDER/POCTIn0155/94. J.H. Belo thanks FCT for the Grant SFRH/BD/88440/2012. A.M. Pereira, I. T. Gomes and A.M.L. Lopes acknowledge the project NORTE-070124-FEDER-000070 for the financial support. A.L. Pires thanks for the Grant: PEst-OE/FIS/UI0275/2014 and Incentivo/FIS/UI0275/2014. Work at Ames Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering. Ames Laboratory is operated for DOE by Iowa State University under Contract No. DE-AC02-07CH11358.

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