Gd$_5$(Si,Ge)$_4$ thin film displaying large magnetocaloric and strain effects due to magnetostructural transition

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**Abstract**
Magnetic refrigeration based on the magnetocaloric effect is one of the best alternatives to compete with vapor-compression technology. Despite being already in its technology transfer stage, there is still room for optimization, namely, on the magnetic responses of the magnetocaloric material. In parallel, the demand for different magnetostrictive materials has been greatly enhanced due to the wide and innovative range of technologies that emerged in the last years (from structural evaluation to straintronics fields). In particular, the Gd$_5$(Six Ge$_{1-x}$)$_4$ compounds are a family of well-known alloys that present both giant magnetocaloric and colossal magnetostriction effects. Despite their remarkable properties, very few reports have been dedicated to the nanostructuring of these materials: here, we report a $\sim$800 nm Gd$_5$Si$_{2.7}$Ge$_{1.3}$ thin film. The magnetic and structural investigation revealed that the film undergoes a first order magnetostructural transition and as a consequence exhibits large magnetocaloric effect ($-\Delta S_{\text{mMAX}} \sim 8.83$ J kg$^{-1}$ K$^{-1}$, $\Delta H = 5$ T) and giant thermal expansion (12000 p.p.m). The thin film presents a broader magnetic response in comparison with the bulk compound, which results in a beneficial magnetic hysteresis reduction. The $\Delta S_{\text{mMAX}}$ exhibited by the Gd$_5$(Si,Ge)$_4$ thin film makes it a promising candidate for micro/nano magnetic refrigeration area.

**Keywords**
Electrical and Computer Engineering, Germanium, Thin film structure, Elemental semiconductors, Magnetic materials, Magnetic films

**Disciplines**
Electromagnetics and Photonics | Engineering Physics | Metallurgy

**Comments**
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Magnetic refrigeration based on the magnetocaloric effect is one of the best alternatives to compete with vapor-compression technology. Despite being already in its technology transfer stage, there is still room for optimization, namely, on the magnetic responses of the magnetocaloric material. In parallel, the demand for different magnetostriective materials has been greatly enhanced due to the wide and innovative range of technologies that emerged in the last years (from structural evaluation to straintronics fields). In particular, the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds are a family of well-known alloys that present both giant magnetocaloric and colossal magnetostriction effects. Despite their remarkable properties, very few reports have been dedicated to the nanostructuring of these materials: here, we report a ~800 nm Gd$_5$Si$_{2.7}$Ge$_{1.3}$ thin film. The magnetic and structural investigation revealed that the film undergoes a first order magnetostructural transition and as a consequence exhibits large magnetocaloric effect (ΔSmMAX ≈ 8.83 J kg$^{-1}$ K$^{-1}$, ΔH = 5T) and giant thermal expansion (12000 p.p.m). The thin film presents a broader magnetic response in comparison with the bulk compound, which results in a beneficial magnetic hysteresis reduction. The ΔSmMAX exhibited by the Gd$_5$(Si,Ge)$_4$ thin film makes it a promising candidate for micro/nano magnetic refrigeration area.

The magnetic materials presenting strong spin-lattice coupling are a powerful set of candidates for multifunctional applications because of their multiferroism, magnetocaloric (MCE), magnetostrictive (MSE), and magnetoresistance (MRE) effects. This coupling is particularly influential on the magnitude of the MCE and MSE.

The Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ family of compounds is a fruitful example of a strongly coupled system that was responsible for the boost in the magnetic refrigeration research at room temperature in 1997. Since then, other material families presenting the Giant MCE (GMCE) were discovered, such as La–Fe–Si$^{2,3}$ and its hydrides$^{4}$ Mn–Fe–P–(As, Ge)$^{5,6}$ and the Heusler alloys based in Ni–Mn–(In, Sn, Sb) compounds.$^{7–10}$ Nowadays, the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds exhibit one of the highest MCE for the broadest temperature range.$^{10–13}$

Besides the GMCE, these materials show colossal magnetostriction,$^{14}$ giant magnetoresistance,$^{15}$ and also spontaneous generation of voltage$^{16}$—their main feature is their multifunctionality. The agile interplay between magnetic and atomic lattice degrees of freedom makes them sensitive materials, capable of undergoing magnetostructural transitions by the variation of external magnetic fields,$^{17}$ pressure,$^{18}$ and/or temperature.$^{15}$

Since the discovery of the GMCE,$^1$ an intense and devoted effort has been focused in the bulk magnetocaloric materials and in macroscale magnetic refrigeration systems. On the other end of the scale spectrum, the nanoscaling processing has just recently been attracting more attention, resulting in an exponential increase of papers published as shown by Miller and co-workers,$^{19}$ but still lagging behind other caloric materials in the nanoscaling race, as Moya and co-workers pointed recently.$^{20}$ From the scientific point of view, the importance to understand the behavior of the magnetostructural coupling with the dimension reduction is crucial. From the magnetic refrigeration point of view, besides the miniaturization of refrigerators, nanostructures can have a great impact by allowing higher operational frequencies on real refrigerators due to their high surface-to-volume ratio that enables faster heat exchange$^{21}$ and higher cooling powers.$^{22}$ Moreover, the wide range of technologies that make use of magnetostriective materials could be empowered by the achievement of strain values in nanostructures such as the ones observed in bulk Gd$_5$(Si,Ge)$_4$ systems. We highlight the sensors/actuators involved in large-infrastructures analysis$^{23}$ and on the straintronics area, where strain is used to mediate magnetoelastic effects towards various applications.$^{24,25}$ Such artificial multiferroic devices, composed of a piezoelectric and a Gd$_5$(Si,Ge)$_4$ magnetostrictive material, have already presented promising properties for energy harvesting purposes at the micrometric scale.$^{26}$
Despite their properties, Gd$_5$(Si$_{1-x}$Ge$_1-x$)$_4$ materials were left behind in the nanoscaling race, whereas an increasing number of works have been published on Gd multilayers, materials and also on the MEMS development and numerical simulations. Concerning the Gd$_5$(Si$_{1-x}$Ge$_1-x$)$_4$ materials, there is only one not-successful report of a Gd$_5$(Si$_{1-x}$Ge$_1-x$)$_4$ thin film. Our group has been developing and optimizing the Gd$_5$(Si$_{1-x}$Ge$_1-x$)$_4$ thin film deposition by femtosecond pulsed laser ablation technique, but, so far, with low amounts of desired phase and no signs of magnetostuctural transition. Nevertheless, the effort devoted to the optimization of the deposition parameters towards the production of a thin film which retains the magnetostuctural transition was finally rewarded resulting in the present work. We have used a femtosecond pulsed laser (9.1 mJ/cm$^2$ laser fluence before focusing and a repetition rate of 1000 Hz) ablation of a multi-grain Gd$_5$Si$_{1.3}$Ge$_{2.7}$ target prepared from high purity materials by Tri-arc method. A thin film ($t = 788 \pm 59$ nm) of the same composition was deposited onto a 1 µm SiO$_2$ layer on the top of a (001) silicon substrate at 200°C and $1.2 \times 10^{-6}$ Torr. The rate of deposition was about 0.65 nm/s.

As expected from the ultrashort laser pulses used for deposition, the thin film has a granular-like morphology [Figure 1(b)], consisting on a stack of nanoparticles with a Lorentzian distribution of diameters: median $\approx$80 nm and a full width at half maximum of $\approx$80 nm [inset of Figure 1(b)]. The thin film chemical composition was inspected by Energy Dispersive Spectroscopy (EDS) analysis [inset of Figure 1(a) and more details in supplementary material] and was found to be similar to the target material with a 5% variation, i.e., Gd$_{5.0(6)}$Si$_{1.3(0.7)}$Ge$_{2.7(0.1)}$.

The structural characterization of the Gd$_5$Si$_{1.3}$Ge$_{2.7}$ thin film as a function of temperature was performed using Synchrotron X-ray diffraction: data collected every 5 K on heating in the [150, 250] K range. Figures 2(a) and 2(b) present the spectra obtained as contour plots. In Figure 2(a), at $T \approx 170$ K, it is clear that the four most intense peaks, associated with (2 3 1), (0 4 2), (1 3 2), and (2 1 2) Miller indices of the O(I) structure, begin to change their relative intensities and positions, whereas at $T \approx 16.5^\circ$ an additional peak emerges. In the same temperature interval, other changes on the peaks intensities occur: the peaks (2 1 1), (0 2 2), (1 1 2) of the O(I) phase are transformed into (1 1 2), (0 2 2), (2 1 1) of the O(II) phase—on heating—as can be seen in Figure 2(b). Such drastic changes of the peak intensities and positions clearly point to a O(I) $\rightarrow$ O(II) structural change in accordance with similar behavior observed in bulk materials.

In the 150–170 K temperature range, the Rietveld refinement reveals the presence of a single phase: Gd$_5$Si$_{1.3}$-type [O(I)] structure. Above $T = 175$ K, an additional structural phase is required for the refinement, namely, the Sm$_5$Ge$_4$-type [O(II)]. From Figure 2(d) it can be observed that the O(II) phase fraction increases continuously from $\approx$11% at 175 K up to 54% at 190 K, where it becomes the majority phase. The O(II) phase fraction stabilizes reaching $\approx$65% of the total volume at 220 K, showing that major changes in the phase fractions occur in the [175, 220] K temperature interval. At room temperature, the major structural phase possesses the following lattice and volume parameters: $a = 0.759(4)$ nm, $b = 1.472(3)$ nm.

**FIG. 1.** SEM cross section (a) and top views (b) of the $\sim$788 ± 59 nm thin film. An EDS spectrum of a representative area is represented in Figure 1(a). The particles diameter histogram is presented in (b) inset.

**FIG. 2.** 2D Contour plot of the collected and analyzed synchrotron x-ray diffracted spectra as a function of temperature ([120, 250] K range) in the [15; 17.6] (a) and [11.5; 14.5] (b) θ interval. Temperature dependence of the two phase fractions present (d) and the majority phase lattice parameters and volume, assigned to the left and right y-axis, respectively (c). The standard deviations for the parameters are not shown on the plots because they are smaller than symbol sizes.
nm, \( c = 0.771(6) \) nm, and \( V = 0.862(7) \) nm\(^3\) which are slightly smaller than bulk counterparts, such as Gd\(_2\)Si\(_1.5\)Ge\(_2.5\) single crystal: 0.7658 nm, 1.4793 nm, 0.77554 nm, and 0.87863 nm\(^3\) (\( \sim 2\% \) higher than the thin film).\(^{47}\) In fact, the shrinkage in nanoparticles unit cell has been observed in previous metallic nanoparticles deposited with a femtosecond pulse laser.\(^{48,49}\) where it was attributed to the nanoparticles intrinsic surface stress\(^{48,50,51}\) (see discussion below). The temperature dependence of majority phase lattice parameters \( (a, b/2, \) and \( c) \) and volume are represented in Figure 2(c), where a giant and anisotropic change of the lattice parameters is displayed at \( T = T_S \approx 190 \) K: \( \Delta a/a = 1.20\%, \Delta b/b = -0.03\%, \) and \( \Delta c/c = -0.40\%, \) leading to a \( \Delta V/V \sim 0.81\% \), similar to bulk counterparts.\(^{47,52}\) Comparing the obtained values with other reported strain effects, one finds that the \( \Delta a/a \) (12000 ppm) is 10 times larger than the recently reported 1300 ppm upper limit on Co\(_1-x\)Fe\(_x\) thin films,\(^{53}\) than the 2000 ppm presented by commercial Terfenol-D,\(^{54}\) being in the same order of magnitude as the recently reported strain values of the shape memory alloys Mn\(_{1-x}\)Fe\(_x\)Ge\(_5\) the improved NiMnGa foams,\(^{8,56}\) and the BiFeO\(_3\) piezoelectric thin films.\(^{57}\)

Figure 3(a) presents the magnetization temperature dependence, on cooling and heating, in the 10–300 K temperature range under a constant applied field of 0.1 T. On heating, two paramagnetic to ferromagnetic transitions are observed: one at \( T = T_S' \approx 194 \) K and a second one around \( T = T' \approx 247 \) K. From Fig. 3, it can be observed that there is an overlap between the cooling and heating curves except in the main stress mechanism in (hetero)epitaxial thin films\(^{65,66}\). This suggestion can be observed in thin films can arise from the preparation method and from strain induced by the substrate-film interface stress (which is the main stress mechanism in (hetero)epitaxial thin films\(^{65,66}\)). Nevertheless, since the produced thin film presents a granular morphology, it should not be neglected the surface stress that naturally occurs in small nanoparticles. Despite the difficulty associated with the complex calculation of the surface pressure of these nanoparticles, it is known that the surface pressure is inversely proportional to its diameter and that it lies in the 1–10 kilobars range for nanoparticles with less than 100 nm diameter.\(^{67}\) Considering that the mean particle size of the nanoparticles in this thin film is \( \sim 80 \) nm, it outcomes that their intrinsic surface stresses can explain the observed results (increase of \( T_C\) and unit cell volume reduction). Furthermore, the observed smoothening of the magnetic responses and the magnetic hysteresis reduction are a plausible consequence of the distribution of surface pressures associated with the different nanoparticles diameters along the film. This suggestion can lead to advanced production methodologies, namely, tuning i.e., after each isotherm the film was warmed up until the PM region (at 300 K) and then cooled down to 100 K and again heated up till the desired temperature. Magnetic hysteresis (highlighted in color in Figure 3(b)) is present in the \( [182, 210] \) K temperature region. Typically in the bulk systems, the metamagnetic transition exhibits a pronounced S-type shape between the two magnetization states\(^{13}\) (see supplementary material for the target sample isotherms\(^{46}\)). In this thin film, the \( M(H)\) curves are smoother leading to a drastic hysteresis reduction when compared with the bulk counterpart. In the literature, this peculiar \( M(H)\) shape has been generally associated with disorder that might be caused by microstrain, structural defects, chemical disorder, etc.\(^{7,68}\) Moreover, the simultaneous observation of a \( T_C\) increase together with the shrinkage of the unit cell are hallmarks of stress and strain presence for the Gd\(_2\)(Si,Ge)\(_4\) materials.\(^{18,61,62}\) Typically, Gd\(_2\)(Si\(_{1-x}\)Ge\(_{x}\))\(_4\) with \( x \sim 0.3/0.4\) compounds present a \( T_C\) pressure dependence of \( \Delta T_C/\Delta P = 1.2–1.5\) K/kilobars.\(^{63,64}\) Considering the \( \sim 13\) K \( T_C\) increase in thin film comparing with bulk, this results in a pressure in the 8–11 kilobars range. This in total accordance with the pressure estimation performed to account with the observed unit cell shrinkage \( \Delta V = V_{\text{bulk}} - V_{\text{film}}\) i.e., by calculating the pressure using the compressibility \( (\kappa = [0.00158, 0.00190])\) kilobars \(^{-1}\)\(^{35}\) and \( P = (\Delta V/V)(1/\kappa)\) a pressure value in the 9–11 kilobars range is obtained. Hence, independent structural and magnetic characterization analysis indicate pressure/stress as the most probable cause for the observed changes in the thin film behavior in comparison with the bulk. Such internal stress in thin films can arise from the preparation method and from strain induced by the substrate-film interface stress (which is the main stress mechanism in (hetero)epitaxial thin films).\(^{65,66}\) Nevertheless, since the produced thin film presents a granular morphology, it should not be neglected the surface stress that naturally occurs in small nanoparticles. Despite the difficulty associated with the complex calculation of the surface pressure of these nanoparticles, it is known that the surface pressure is inversely proportional to its diameter and that it lies in the 1–10 kilobars range for nanoparticles with less than 100 nm diameter.\(^{67}\) Considering that the mean particle size of the nanoparticles in this thin film is \( \sim 80 \) nm, it outcomes that their intrinsic surface stresses can explain the observed results (increase of \( T_C\) and unit cell volume reduction). Furthermore, the observed smoothening of the magnetic responses and the magnetic hysteresis reduction are a plausible consequence of the distribution of surface pressures associated with the different nanoparticles diameters along the film. This suggestion can lead to advanced production methodologies, namely, tuning

FIG. 3. Magnetization as a function of temperature (a) and a focused region in the inset. (b) Magnetization isotherms \( M(H)\) measured in the \([182, 210]\) K temperature range, at 250 K and at 275 K with increasing (lower curves) and decreasing (upper curves) applied magnetic fields. In (b) inset, the \( M(H)\) at 5 K is presented and the magnetization saturation, at \( H = 50\) kOe, is indicated.
the nanoparticle size distribution ensemble (by changing laser parameters\textsuperscript{26}) as a strategy towards magnetic hysteresis reduction, which is of pivotal importance for the efficiency improvement of the magnetic refrigeration process.\textsuperscript{38,69} In contrast with the observations in bulk specimens\textsuperscript{13} it is clear that up to 5 T, the magnetization curves do not achieve a fully saturated state: the saturation magnetization at 5 K is $\mu_{\text{sat}} \sim 6.2 \pm 0.8 \mu_B$, slightly lower than the theoretical $7 \mu_B$. The difference can arise from the presence of small pure Gd amorphous phase(s) amount.

The temperature dependence of the magnetic entropy change ($-\Delta S_m(T)$), plotted in Figure 4(a), was estimated in accordance with Ref. 59. Its peak value is $-\Delta S_{m,\text{MAX}} \sim 8.8 \pm 1.7$ J kg\textsuperscript{-1} K\textsuperscript{-1}, occurs at $T = T_{\text{peak}} = T_{\text{MS}} \sim 192$ K, and the full width at half maximum (FWHM) is $\sim 24$ K for a field variation of $\Delta H = 5$ T. Hence, the refrigerant capacity is $RCP_{\text{FWHM}} \sim 212$ J K\textsuperscript{-1}. Such a large change in the thin film entropy is a consequence of the strong coupling between the magnetic spin and the lattice (as in bulk materials), also illustrated by the occurrence of a simultaneous magnetic and structural transition—magnetostructural transition. Furthermore, it is important to stress that the $-\Delta S_{m,\text{MAX}}$ mass and volume normalization performed are clearly an underestimation of the real $-\Delta S_{m,\text{MAX}}$ of the film, since this normalization assumes that the whole film volume contributes to the entropy change and this is not true. There is a 35% amount of O(I) phase which does not contribute to the $-\Delta S_m$ in the [150, 240] K temperature interval. Recalculating, correcting the 35% volume fraction corresponding to the O(I) phase a $-\Delta S_{m,\text{MAX}}$ corrected $\sim 13.6$ J Kg\textsuperscript{-1} K\textsuperscript{-1} for $\Delta H = 5$ T (see Fig. 4(b)) value is achieved. Such value is lower than that of the $-\Delta S_{m,\text{MAX}}$ bulk ($\sim 43$ J Kg\textsuperscript{-1} K\textsuperscript{-1} for $\Delta H = 5$ T (Ref. 11)), however, it is complemented with a larger FWHM (which constitutes further evidence of strain disorder\textsuperscript{60}) and reduced hysteretic losses. Such reduction can be estimated by averaging the area in between the M(H) curves over the $[T_{c,\text{cooling}} + 20]$K temperature range, resulting in $\sim 12$ J Kg\textsuperscript{-1}, almost three times lower than the value presented by the target sample, $\sim 42$ J Kg\textsuperscript{-1}. Hence, if the hysteretic losses are subtracted to the thin film refrigerant capacity,\textsuperscript{68} the efficient RCP is estimated to be RCP\textsuperscript{eff} $\sim 200$ J K\textsuperscript{-1}. The obtained $-\Delta S_{m,\text{MAX}}$ and RCP values are higher than the observed in manganites thin films, such as La$_{0.6}$Sr$_{0.4}$MnO$_3$,\textsuperscript{30} La$_{0.56}$Sr$_{0.44}$MnO$_3$,\textsuperscript{31} or La$_{0.7}$Sr$_{0.3}$MnO$_3$ on SrRuO$_3$ superlattices;\textsuperscript{29} Gd multilayered films;\textsuperscript{28} or NiMnGa thin films,\textsuperscript{14} being only lower than the epitaxial MnAs and FeRh thin films\textsuperscript{23,26} (see supplementary material for comparative table\textsuperscript{46}). In comparison with the bulk GMC materials,\textsuperscript{10} the thin film presents a lower $\Delta S_{m,\text{MAX}}$. However, its reduced hysteretic losses and broadened $\Delta S_m(T)$ curve ensure a promising RCP (higher than the recent Pt doped NiMnGa\textsuperscript{70} and virtually equal to the Gd$_5$Si$_2$Ge$_3$,\textsuperscript{15} $\varepsilon_{\text{Fe},0.1}$ magnetic refrigerant\textsuperscript{68}). Finally, its higher surface to volume ratio is an advantage towards the enhancement of the heat exchanges velocity occurring in a magnetic refrigerator\textsuperscript{59} thus allowing an increase of the cycling frequency and consequently its cooling power.\textsuperscript{22}

In conclusion, we were able to deposit a Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ thin film which retains the magnetostructural transition as observed in its bulk counterpart. It shows a broader magnetic response than the bulk target, exhibiting a lower $\Delta S_{m,\text{MAX}}$, but a higher FWHM and a large magnetic hysteretic losses reduction. These changes on the magnetic responsive features are associated with the stress distribution on the nanoparticles surface arising from the broader size distribution of nanoparticles. Such properties result in a promising refrigerant capacity at the nanoscale. Simultaneously, a giant thermal expansion was observed across the magnetostructural transition.

In the future, we endeavor to explore the influence of particle size distributions and film thicknesses on the magnetic and structural coupling, the $\Delta S(T)$ curve and the hysteretic losses exploring the nanostructuring process as a strategy to tune the MCE towards the development of nano/micro refrigerators. Their multifunctionality and giant striction features can help the development of high sensitivity restrictive sensors/actuators (due to strain), and bring opportunities for artificial multifunctional materials, such as multilayer deposition with piezoelectric materials.

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