



Article Enhanced Magnetic Cooling through Tailoring the Size-Dependent Magnetocaloric Effect of Iron Nanoparticles Embedded in Titanium Nitride Thin Films

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Abstract: The magnetocaloric effect (MCE) in iron (Fe) nanoparticles incorporated within a titanium nitride (TiN) thin-film matrix grown using pulsed laser deposition (PLD) is investigated in this study. The study demonstrates the ability to control the entropy change across the magnetic phase transition by varying the size of the Fe nanoparticles. The structural characterization carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and scanning transmission electron (TEM) showed that TiN films are (111) textured, while the Fe-particles are mostly spherical in shapes, are single-crystalline, and have a coherent structure with the surrounding TiN thin-film matrix. The TiN thin-film matrix was chosen as a spacer layer since it is nonmagnetic, is highly corrosion-resistive, and can serve as an excellent conduit for extracting heat due to its high thermal conductivity (11 W/m K). The magnetic properties of Fe-TiN systems were investigated using a superconducting quantum interference device (SQUID) magnetometer. In-plane magnetic fields were applied to record magnetization versus field (M-H) and magnetization versus temperature (M–T) curves. The results showed that the Fe–TiN heterostructure system exhibits a substantial isothermal entropy change (ΔS) over a wide temperature range, encompassing room temperature to the blocking temperature of the Fe nanoparticles. Using Maxwell's relation and analyzing magnetization-temperature data under different magnetic fields, quantitative insights into the isothermal entropy change (ΔS) and magnetocaloric effect (MCE) were obtained for the Fe–TiN heterostructure system. The study points out a considerable negative change in ΔS that reaches up to 0.2 J/kg K at 0.2 T and 300 K for the samples with a nanoparticle size on the order of 7 nm. Comparative analysis revealed that Fe nanoparticle samples demonstrate higher refrigeration capacity (RC) in comparison to Fe thin-film multilayer samples, with the RC increasing as the Fe particle size decreases. These findings provide valuable insights into the potential application of Fe–TiN heterostructures in solid-state cooling technologies, highlighting their enhanced magnetocaloric properties.

Keywords: magnetocaloric effect; iron nanoparticles; Fe-TiN heterostructures; isothermal entropy change

1. Introduction

Magnetic refrigeration has gained prominence as a competitive cooling technology due to its tremendous potential for revolutionizing the field of refrigeration and air conditioning. This emerging technology presents a multitude of advantages, such as enhanced energy efficiency, greater environmental sustainability, and improved overall system performance compared to traditional refrigeration systems that depend on compressors and refrigerants [1–3]. Magnetic refrigeration operates on the basis of the magnetocaloric effect (MCE),



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). which can manifest as a change in temperature (ΔT) during adiabatic processes or as an entropy change (ΔS) when a magnetic field is applied in isothermal processes. Magnetocaloric materials (MCMs) exhibit a substantial isothermal entropy change (ΔS) when there is a large change in magnetization with temperature at a constant applied magnetic field (H) [4–6]. Since the discovery of the giant magnetocaloric effect (GMCE) by Pecharsky and Gshneider in 1997, various compound families have been found to exhibit MCE in the vicinity of room temperature [7]. Gadolinium (Gd)-based alloys and intermetallic compounds, La–Fe–Si intermetallic compounds, and Ni-Mn-Ga Heusler alloys have demonstrated exceptional magnetocaloric properties at room temperature [8]. Recent MCE research has primarily focused on rare earth-containing bulk MCMs, as their high magnetic moment per atom correlates with the entropy change. However, due to concerns related to limited supply chains and price stability of rare-earth-based materials, there is a growing interest in developing MCMs that do not rely on rare earth elements [9–11]. The technological significance of nanophase magnetic materials in fields such as magnetic recording, ferrofluid technology, magnetic refrigeration, spintronics, and biotechnology has led to their notable prominence and attention [12–14]. Among these applications, magnetic refrigeration has emerged as a particularly promising area for nanophase magnetic materials [15]. Nanophase MCMs with distinct physical, chemical, or structural characteristics result in synergistic properties that can be exploited for magnetic refrigeration [16]. Previous studies have demonstrated the remarkable properties of MCMs in improving the MCE in different physical forms of the same composition [17,18]. Phan et al. conducted a study comparing the MCE of bulk gadolinium iron garnets (Gd₃Fe₅O₁₂) with nanostructured samples of varying average grain sizes, demonstrating that the MCE magnitude is smaller for nanostructured samples with an average grain size of 50 nm but shows an increasing trend when the grain size is further decreased to 35 nm [19]. In a comparative study of bulk melt-spun ribbons of La–Pr–Fe–Si compounds, Liu et al. reported that the bulk sample achieved a magnetic entropy change of 25.2 J/kg K and an effective refrigerant capacity of 474.1 J/kg, while the melt-spun ribbons showed values of 21.9 J/kg K and 458.5 J/kg, respectively, when subjected to a field change of 0–5 T [20]. In their study, Zhukov et al. demonstrated that the removal of the glass coating in a Ni–Mn–Ga microwire resulted in an increase in ΔT from the range of 0.06–0.08 K to 0.22 K, highlighting the promising potential of glass-coated microwires for magnetic refrigeration due to their favorable surface-to-volume ratio [21]. Despite these promising advancements, there remains a significant research gap concerning the systematic investigation and optimization of MCMs in different physical morphologies. While studies have individually explored the properties of nanoparticles, thin films, or microwires, limited research has focused on a comparative analysis of MCMs with similar compositions in various sizes, shapes, and volumes. Such a comparative analysis is crucial to elucidate the impact of the morphological properties of MCMs on the MCE and to identify the most promising configurations for specific applications. This study aims to bridge this gap in the existing literature by comprehensively investigating and comparing the MCE of nanostructured Fe particles and thin films.

The remarkable MCE exhibited by iron-based nanophase magnetic materials, resulting from their reduced size and single-domain magnetic structure, has opened exciting avenues for efficient magnetic refrigeration [22]. The behavior of magnetic nanoparticles is influenced by finite size and interface effects, which become more pronounced as the particle size decreases, leading to a larger surface-to-volume ratio [23]. Furthermore, the ability to vary particle sizes in nanoparticle systems provides a means to finely control the entropy change across magnetic phase transitions, allowing for precise manipulation of this property [24–26]. These effects greatly influence the thermal properties of magnetic nanoparticles. On the basis of these characteristics, we present the development of a rare-earth-free magnetic material system that demonstrates magnetocaloric effects across a considerably wide temperature range, leveraging its inherent characteristics. This study explores the magnetic and magnetocaloric properties of nanostructured iron (Fe) with different morphologies (nanoparticles and thin film) incorporated in a TiN thin-film matrix. The choice of a TiN thin film as an interlayer between Fe nanoparticles is motivated by its nonmagnetic characteristics, excellent resistance to corrosion, and high thermal conductivity (11 W/m K) [27–29]. Our results demonstrate that the magnetocaloric effect in the Fe–TiN system can be modified by altering the morphology of the Fe within the TiN matrix. The sample with a smaller nanoparticle size (D = 7 nm) exhibited a significant enhancement of isothermal entropy change (ΔS) and refrigeration capacity (RC).

2. Materials and Methods

The deposition of Fe particles on (0001) oriented sapphire and (100) silicon substrates was performed using a multitarget pulsed laser deposition (PLD) system. Sequential ablation was performed on highly pure (99.99%) Fe and TiN targets in an alternating fashion. A krypton fluoride (KrF) excimer laser (Lambda Physik, Germany) operating at a radiation wavelength of 248 nm with a pulse duration of 30 ns was employed for the deposition. The experiments were conducted in a high-vacuum environment of approximately $\sim 5 \times 10^{-7}$ torr. The substrate temperature was maintained at 500 °C using a temperature controller. A thin layer of silver paste was applied to the heater to hold the substrates firmly to ensure the stability of the substrates during deposition. A target-substrate distance of approximately 5 cm was maintained while operating the laser at a pulse rate of 10 Hz with an energy of 750 mJ. The control of iron particle size was achieved by adjusting the number of laser pulses impinging on the Fe target. Table 1 lists the number of laser pulses utilized to deposit Fe nanoparticles of controlled size in the TiN thin-film matrix. In the Fe–TiN sample, the total thickness of TiN was kept constant by applying 800 pulses to the TiN target in each period. A small region of the substrate was masked during deposition to measure film thickness using a Keyence 3D surface profilometer. A schematic representation of the configuration involving Fe nanoparticles embedded in a TiN thin-film matrix is presented in Figure 1. The structural properties of the samples were analyzed using an X-ray diffractometer (Bruker AXS D8 discover series, MA, USA) with a Bruker monochromatic Cu K α radiation, employing θ -2 θ scans. Atomic force microscopy (AFM) (NT-MDT, The Netherlands) was utilized to investigate the volume fraction of the Fe nanoparticles. To obtain more precise information about the shape and size of Fe nanoparticles, cross-sectional scanning transmission electron microscopy (STEM)(FEI, OR, USA) was employed. The cross-sectional samples for the transmission electron microscopy study were prepared by mechanical polishing and followed by Ar ion milling to electron transparency. The magnetic properties of the Fe–TiN systems were characterized using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, CA, USA). In-plane magnetic fields were applied to record magnetization versus field (M–H) curves, while magnetization versus temperature (M-T) measurements were conducted at five distinct fields. In order to account for the combined influence of the substrate and TiN layers in the Fe–TiN heterostructures, the magnetization of the sapphire substrate coated with TiN films of identical thickness without Fe nanoparticles was measured separately, allowing for the subtraction of their collective contribution. For the in-plane M–H and M–T measurements, the surface dimensions of the samples were 3 mm \times 5 mm.

Table 1. Description of sample code, Fe particle size, and magnetic parameters.

Sample	Laser Pulses Fe/TiN	Particle Size (nm)	Fe Volume (10 ^{–8} cm ³)	Fe Volume Percentage	Magnetic Moment (µ _B /atom)	Saturation Magnetization (10 ⁶ A/m)	Coercivity (Oe) at 10 K	Coercivity (Oe) at 300 K
S1	200 pulses Fe/ 800 pulses TiN	7	2.0	2.25	2.03	1.60 ± 0.01	493 ± 4	50 ± 2
S2	300 pulses Fe/ 800 pulses TiN	9	2.2	2.50	2.09	1.63 ± 0.01	550 ± 5	126 ± 2
S3	450 pulses Fe/ 800 pulses TiN	15	10.0	10.00	2.13	1.67 ± 0.01	581 ± 5	321 ± 3
S4	900 pulses Fe/ 800 pulses TiN	Thickness = 12	19.0	20.00	2.17	1.70 ± 0.01	380 ± 3	379 ± 3



Figure 1. Schematic representation of (**a**) Fe nanoparticle embedded in TiN thin-film matrix made using 200 laser pulses, (**b**) Fe nanoparticle embedded in TiN thin-film matrix made using 300 laser pulses, (**c**) Fe nanoparticle embedded in TiN thin-film matrix using 450 laser pulses, and (**d**) Fe thin films (900 laser pulses) buried under TiN film. The dimensions of the substrate, TiN film, and Fe nanoparticles are not to scale.

To avoid errors in data and to check for property reproducibility, a control set of samples was prepared a second time, and the same samples were subjected to repeat measurements, such as XRD, SEM, AFM, TEM, thickness, and SQUID magnetometry. The primary disparity in our experimental data was brought about by an unintentional variation in the two most important deposition parameters (laser energy and substrate temperature) during sample preparations by the PLD method. Therefore, precautions were taken to avoid variation in these parameters that would yield films more than 5% different in terms of thickness, FWHM, particle size, four-point electrical resistivity, and magnetic moments. The films were redeposited if the variation in these characteristics was more than the aforesaid percentage. The absence of an error bar in a given figure means that the data presented are the average data for more than one sample obtained using more than one measurement.

3. Results and Discussion

Figure 2a displays the X-ray diffraction (XRD) pattern obtained from the Fe–TiN multilayer samples grown on *c*-Al₂O₃ substrates with a single-crystal (0001) orientation. The diffraction pattern revealed that the TiN film matrix adopted a rock salt-type cubic structure with a prominent Bragg peak attributed to the (111) plane, with a minor peak along the (222) plane [30]. No discernible peaks corresponding to Fe particles embedded within the TiN film matrix were observed for both sample 1 (S1) and sample 2 (S2). The absence of Fe peaks can be attributed to the relatively low volume fraction of Fe particles,

which measured 2.25% in S1 and 2.5% in S2. In sample 3 (S3) and sample 4 (S4), respectively, there was a clear iron peak at 44.7°, which corresponds to the (110) plane of body-centered cubic (BCC) iron [31]. Using XRD FWHM and the Scherrer formula, as well as image analysis of AFM images, the Fe particle size in samples S1, S2, and S3 was found to be 7 nm, 9 nm, and 15 nm, respectively. Sample S4, made using 900 laser pulses, was a continuous iron thin film (12 nm), as opposed to other Fe–TiN samples, where Fe was observed to be in isolated island form.



Figure 2. (a) XRD patterns of four Fe–TiN multilayer samples: sample 1, sample 2, sample 3, and sample 4. The AFM images of Fe-nanoparticulate samples: (b) sample 1, (c) sample 2, and (d) sample 3.

The thickness of the TiN thin films was maintained at 10 nm for all the samples. The description of the sample code with parameters obtained from structural and magnetic measurements is summarized in Table 1. The size of Fe nanoparticles was confirmed using cross-sectional STEM images. Shown in Figure 3 is the cross-sectional atomic number (Z)-contrast STEM observation of Fe nanoparticles embedded in a five-layered Fe–TiN composite structure grown on a silicon substrate. It is evident from the cross-sectional image that the sample was homogeneous over long lateral distances (Figure 3a). The Fe particles seemed to have an average size of ~7 nm (Figure 3b) with distorted spherical shapes as reflected from the magnified images of two randomly selected particles (Figure 3c,d). The TiN matrix was mostly polycrystalline. The Fe particles were mostly coherent with the surrounding matrix. The slight variation in the shape of the Fe particles was attributed

to the polycrystalline surrounding the TiN matrix with different facets. The growth of Fe nanoparticles took place via the Volmer–Weber island growth mode on TiN buffer due to the predominance of the cohesive force among Fe atoms over the adhesive force between Fe and TiN materials. As shown in Figure 3c,d, the interface between the Fe nanoparticle and the surrounding TiN was atomically sharp, indicating the presence of pure metallic Fe at the surface. Considering the presence of an atomically sharp interface in Fe–TiN, it is reasonable to assume that the Fe nanoparticles embedded in the TiN matrix were unlikely to contain any magnetically inactive Fe–N dead layer.





Figure 4a,b present the isothermal magnetization M-H curves measured at 10 K and 300 K, respectively, for four distinct samples. The coercivity (H_c) of S1, S2, and S3 extracted from M–H graphs is plotted in Figure 4d. There was a negligible change in coercivity with respect to temperature for S4. We can see from Figure 4d that the values of H_c at 10 K for S1, S2, and S3 were 493, 550, and 581 Oe, respectively. As depicted in the figure, the hysteresis disappeared, and superparamagnetism emerged in sample S1 when the temperature exceeded 200 K. Conversely, in sample S2, hysteresis remained evident ($H_c = 126 \text{ Oe}$) even at temperatures up to 300 K. The blocking temperature (T_B) of a particulate system is taken as a temperature at which a transition from a paramagnetic state to a blocked spin-state takes place in a zero field as per the equation $H_c(T) = H_c(0) \left| 1 - \left(\frac{T}{T_B}\right)^T \right|$ [12]. The theoretical T_B of S1 (Fe particle size = 7 nm), S2 (Fe particle size = 9 nm), and S3 (Fe particle size = 15 nm) was 200, 460, and 730 K, respectively, as extracted from the x-intercept of H_c vs. $T^{\frac{1}{2}}$ plots in the inset of Figure 4d. In practice, T_B is measured at a small external field, typically less than coercivity values. The ZFC and FC M-T at 0.05 T showed that, while S2 and S3 had a T_B of ~300 K and >300 K, respectively, S1 had a T_B of around 160 K. This was indeed confirmed by the superimposition of M versus H/T plots (Figure 4c)

above the T_B. The ZFC and FC measurements at 0.1 T revealed that S2 and S3 exhibited magnetic transition temperatures (T_B) of approximately 60 K and 80 K, respectively, while S1 had a T_B of around 30 K. The saturation magnetizations were determined by fitting the experimental data of the high-field magnetization curves to the saturation approach law, $M(T) = M_s \left| 1 - \frac{b}{H^2} \right| + cH$, where b and c are constants [32]. From Table 1, we can observe that the saturation magnetization increased with increasing particle size. As the size of the Fe nanoparticles increases, the enhancement of $M_{\rm s}$ could be attributed to the reduced surface-to-volume ratio [33]. The calculated surface-to-volume ratio for individual iron nanoparticles in S1, S2, and S3 are 4.3×10^8 , 3.3×10^8 , and 2×10^8 , respectively. Using this M_s value, the net magnetic moment of Fe atoms in the nanoparticles was calculated using the formula $M_{Fe} = \frac{M_s/N}{\mu_B}$, where M_{Fe} is the magnetic moment of Fe in terms of Bohr magneton, N is the number of atoms per unit volume (for body-centered cubic Fe, $N = \frac{2}{a^3}$, where a = 0.28665 nm), and $\mu_B = 9.27 \times 10^{-24}$ Am². The magnetic moment was found to be 2.03, 2.09, 2.13, and 2.17 μ_B /atom for S1, S2, S3, and S4, respectively. The lower value of magnetic moment from the theoretical magnetic moment of pure Fe (2.2 μ_B /atom) was due to the formation of dead oxide layers around the surface of the particles.



Figure 4. Magnetization versus applied field relationship for Fe–TiN multilayer sample at (a) 10 K and (b) 300 K. (c) Magnetization as a function of H/T for sample 1. (d) Variation of coercivity as a function of temperature. The inset of (d) represents the fitting with Kneller's law $H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_B} \right)^{1/2} \right]$.

The zero-field-cooled (ZFC) magnetization measurements were conducted by cooling the sample to 10 K without applying an external field and subsequently warming it while measuring the magnetization as a function of temperature. On the other hand, field-cooled (FC) magnetization was obtained by cooling the sample to 10 K in the presence of a magnetic field ranging from 0.01 T to 0.2 T, and then recording the data while heating the sample up to 300 K. Figure 5 shows the ZFC and FC magnetization for S1, S2, and S3 at an applied field of 0.02 T. S4 cannot be compared with nanoparticle samples accurately because of its different structural dimensionality and magnetic features. The ZFC magnetization curve of S4 did not show any specific peak. The temperature where the ZFC and FC curves separated, or the peak temperature in the ZFC curves, could be identified as the T_B of the sample. It is clear from Figure 5 that the ZFC and FC magnetization bifurcated at different temperatures, and we can clearly see the decrease in T_B with smaller particle sizes. The T_B of S1 and S2 at 0.05 T was 295 K and 350 K, respectively.



Figure 5. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature at 0.05 T and 0.1 T for Fe–TiN multilayer samples with different particle sizes: (**a**) sample 1 (7 nm), (**b**) sample 2 (9 nm), and (**c**) sample 3 (15 nm).

It should be noted that T_B depends on various factors, including the duration of the experimental measurement, the strength of the external magnetic field, the anisotropy constant, and the interactions between particles [34,35]. A significant drawback of efficient MCMs is the occurrence of transitional thermal hysteresis. This phenomenon introduces challenges and limitations in their practical applications. This thermal hysteresis introduces efficiency losses and must be considered when designing practical MCMs [36–38]. Above the T_B , the ZFC and FC curves in Figure 5 exhibited overlapping behavior, indicating the absence of magnetic hysteresis in the nanoparticle samples at higher temperatures. The present study employed the indirect method to calculate ΔS , wherein the magnetization of the sample was measured at different external field strengths while varying the temperature. The following formula was used to calculate ΔS using Maxwell's relation [39]:

$$\Delta S(T, H) = \mu_{o} V \int_{H_{i}}^{H_{f}} \left(\frac{\partial M(T, H)}{\partial T} \right)_{H} dH.$$
(1)

The magnetic field-induced isothermal entropy change, denoted as ΔS , is determined by factors such as the vacuum permeability μ_0 , the volume (V) of the material, and the initial (typically zero) H_i and final applied magnetic fields H_{fr} respectively. The isofield FC M–T curves were recorded at five different fields of 0.01, 0.02, 0.05, 0.1, and 0.2 T for each sample to calculate the isothermal entropy change from the Maxwell relation. The change in magnetization with respect to temperature was obtained by differentiating the FC M–Tcurves, as depicted in Figure 6.



Figure 6. *dM/dT* versus temperature plots at 0.2 T for Fe–TiN nanoparticle and thin-film samples.

Typical values of entropy for commonly studied materials, such as Gd alloys and La–Fe–Si compounds, range from 0.1 J/kg K to 45 J/kg K over an applied field of 0.1 T to 7 T [40–43]. For traditional magnetocaloric materials, large dM/dT values near the magnetostructural and magnetic phase transition lead to a significant magnetic entropy change [44–46]. However, these changes are not sustained across wide temperature ranges [47–49]. Magnetic nanoparticles possess a notable advantage due to their ability to adjust the blocking temperature by modifying parameters such as particle size, shape, distribution, and interparticle interaction [50]. The dM/dT values of S1 increased faster than other samples up to 250 K. At 250 K, the dM/dT value for S1 was 8.1×10^3 A/m K, while, for S2, it was 5.9×10^3 A/m K. After 250 K, the slope of S2 increased faster than S1 up to

350 K. The values for dM/dT at 350 K were 9.1 × 10³ A/m K and 8.2 × 10³ A/m K for S1 and S2, respectively. However, none of the Fe–TiN samples exhibited magnetostructural phase transitions at or below room temperature. In Figure 7, we represent the entropy change vs. temperature for all the samples with different Fe particle sizes and the Fe thin-film sample. According to Equation (1), the increase in entropy change can be attributed to a faster rate of change in the magnetization with respect to temperature (dM/dT), as confirmed by the dM/dT vs. T plots in Figure 6.



Figure 7. Temperature dependence of ΔS obtained under applied fields of 0.01 T to 0.2 T for Fe–TiN nanoparticle samples (**a**–**c**) and thin-film (**d**) sample.

When a material undergoes a transition from a paramagnetic state to a blocked state, there is a rapid alignment of the magnetic moments, which contributes to a faster change in magnetization. The weak temperature dependence of ΔS can be attributed to the presence of small Fe particles within the system that exhibit a finite size effect, resulting in a reduction in the Curie temperature of these particles. As the temperature approaches the Curie temperature of these small particles, the activation of ΔS occurs during the second-order phase transition between ferromagnetic and paramagnetic order. The estimation of the total magnetic moment of the Fe nanoparticles can be approximated as follows [51]:

$$m = \sum_{i} N_{i} m_{0, i} \tan h\left(\frac{m_{0, i} B}{k_{b} T}\right).$$
⁽²⁾

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The value of N_i represents the number of particles with a saturation moment $m_{0,i}$, and $B = \mu_0 H$. The expression for the isothermal entropy change of such a particle ensemble can be expressed as follows [51]:

$$\Delta S = -\sum_{i} N_{i} \left(k_{B} ln \cosh \frac{Bm_{0,i}}{k_{B}T} - Bm_{0,i} tan h\left(\frac{Bm_{0,i}}{k_{B}T}\right) \right), \tag{3}$$

where each term has a constant value; $\Delta S_i = -k_B N_i \ln 2$ is the low-temperature limit, while the high-temperature limit is $\Delta S_i = 0$. An inflection point determines the temperature position, denoted as $Bm_{0,i}$, which shifts to higher temperatures as $Bm_{0,i}$ increases. Thus, we enter a region where the entropy change is almost temperature-independent due to the cumulative contributions of these terms. The Curie temperature of ferromagnetic materials and the blocking temperature of superparamagnetic materials are crucial parameters that determine the operating temperature range of a magnetocaloric device. While the Curie temperature is primarily an intrinsic property of a material, the blocking temperature of a material depends on its size at a constant field. The size of Fe nanoparticles in the current study was achieved by altering the number of laser pulses directed at the bulk Fe target during the pulsed laser deposition experiments. The entropy change of N-independent superparamagnetic nanoparticles, characterized by particle moment m, under an external field H and temperature T, can be calculated using the following formula [52]:

$$\frac{T\Delta S}{M_{s}H} = \frac{1}{y} \left[1 - y \text{coth}y + \ln \frac{\sin hy}{y} \right].$$
(4)

By introducing the variable $y = mH/k_BT$, where k_B represents Boltzmann's constant, and M_s denotes the saturation magnetization of the particle system, the equation can be expressed as a constant k when y assumes a specific value. Consequently, the equation can be rewritten as follows [52]:

$$\Delta S = k \frac{M_s H}{T},$$
(5)

where ΔS scales with the reciprocal of the temperature and directly with applied field *H*. As seen from Figure 8a, in our four samples, entropy change scaled with *H*, but all the samples had a weak dependence on temperature. The weak dependence of the entropy change was due to the size distribution of the Fe nanoparticles in the sample. The ΔS adheres to the area sum rule, where it has an upper limit corresponding to the total area under the curve. This rule is expressed by the following equation [53]:

$$\int_0^\infty |\mathbf{s}(\mathbf{T}, \mathbf{H})| d\mathbf{T} = \mu_0 \mathbf{M}_{\mathbf{s}} \mathbf{H}.$$
 (6)

The inclusion of the term "s" (Δ S/V) in Equation (6) is necessary to maintain dimensional consistency between both sides of the equation. This term ensures that the units on both sides of the equation are compatible. The sum rule suggests that, when comparing two materials with identical M_s , the material that exhibits a larger difference in entropy between the adiabatically magnetized and adiabatically demagnetized states at a specific temperature may show a lower entropy change at other temperatures [54,55]. The sum rule ensures the conservation of entropy and provides a fundamental principle for analyzing and predicting the magnetocaloric properties of materials. Integrating ΔS with respect to *T* across the entire temperature range allows for the determination of the $\Delta S-T$ curve area [56]. For instance, for S1, the area under the $\Delta S-T$ curve amounted to approximately 16.5 J/kg when evaluated at a maximum field of 0.1 T. The theoretical limit, or $\mu_0 M_s H$ value, for S1 at 0.1 T was calculated to be 21 J/kg, which is higher than the area value of the $\Delta S-T$ curve. The area sum rule holds significant importance in the case of the Fe–TiN heterostructure as it enables the material to operate effectively over a wide temperature range while remaining consistent with theoretical expectations.



Figure 8. (a) Isothermal ΔS as a function of field. (b) Refrigerant capacity as a function of particle size at various fields for Fe–TiN nanoparticle and thin-film samples.

The refrigerant capacity (RC) was utilized to characterize the cooling capability of Fe–TiN samples. The RC can be derived utilizing the following formula [57]:

$$RC = \int_{T_{min}}^{T_{max}} |\Delta S(T, H)| \times dT.$$
(7)

In Figure 8b, the calculated values of the refrigerant capacity (RC) are presented as a function of sample particle size (D nm) for various magnetic fields up to 0.2 T. It is evident that the RC values exhibited a significant variation, ranging from 38 J/kg for the sample with a particle size of 7 nm to 1.1 J/kg for the thin-film sample under a magnetic field of 0.2 T. These findings indicate that the refrigerant capacity (RC) of the nanoparticles increased as the particle size decreased. Additionally, the nanoparticles demonstrated higher cooling efficiency compared to the thin-film sample. This can be attributed to the higher surface-to-volume ratio of smaller nanoparticles and their ability to undergo a wider entropy change within the experimental temperature range, thereby enhancing their cooling performance. However, if the particles are too small, the magnetic moments and blocking temperature are low. If the particles are big, they tend to coalesce, and the samples eventually become thin-film samples.

The ΔS is plotted in Figure 9a for S1, S2, S3, S4, and Gd samples at an applied field of 0.2 T and a temperature of 300 K. Comparing the maximum ΔS value at 0.2 T and 300 K, we can observe that the ΔS value of S1 (highest among the four Fe–TiN samples) was one-third that of Gd at the same applied field and temperature. However, the cost associated with the production of MCMs is also an important consideration for commercially manufactured magnetic refrigerators. To gain a clearer understanding of the production cost of MCMs, Ucar et al. and Chaudhary et al. reviewed the RC of various MCMs in relation to their cost [42,58]. The joule/dollar value of MCMs was calculated by dividing the RC value by the cost per unit kg of the constituent element for each material. We estimated the cost of Fe nanoparticles and TiN thin-film matrix by considering only the material cost, excluding the fabrication cost. In Figure 9b, the RC of Fe nanoparticles embedded in TiN is compared to other rare-earth and rare-earth-free MCMs in terms of joule/dollar. The joule/dollar value of the Fe nanoparticles embedded in the TiN structure was approximately 150% higher than that of pure Gd. The inclusion of Gd, Pr, Zr, and B elements in the composition led to a reduction in the RC in terms of joule/dollar, indicating a decrease in cost-effectiveness. In contrast, Fe-TiN, FeNiCr, and FeNi are low-cost alternatives to rare-earth MCMs, offering favorable magnetocaloric properties.



Figure 9. (a) Isothermal entropy change at 300 K and 0.2 T for Fe–TiN samples and Gd. (b) Refrigerant capacity in joule/dollar unit for various magnetocaloric refrigerants.

4. Conclusions

Magnetic refrigeration, based on the magnetocaloric effect (MCE), is an emerging solid-state cooling technology that leaves no footprint on the environment. Most of the work on the MCE in the literature is focused on bulk magnetocaloric materials (MCMs) containing rare earth elements since the entropy change scales with magnetic moment per atom, which is high for rare earth elements. However, due to the limited availability and high cost of rare earth elements, efforts are being made to explore rare-earth-free MCMs. The present work demonstrated that nanoparticles and heterostructure systems can be used as an alternative to traditional bulk MCMs due to control over the entropy change across the magnetic phase transition that can be maneuvered by varying particle sizes. The present study focused on the MCE properties of Fe nanoparticles embedded in a TiN thin–film grown on sapphire substrates using pulsed laser deposition. The study reports the isothermal entropy change behaviors of the Fe nanoparticles above their blocking transitions. The isothermal entropy change was measured using an indirect method. In the indirect method, the sample's magnetization was measured as a function of temperature at various external field strengths. Applying Maxwell's relation, the slopes of the M–T curves were used to obtain the magnetic field-induced isothermal entropy change, which was then used to characterize the refrigerant capacity of the magnetic materials.

Our findings showcased a significant negative change in isothermal entropy (ΔS), reaching up to 0.2 J/kg K at 0.2 T and 300 K with a refrigeration capacity as high as 38 J/kg. Additionally, the nanoparticles demonstrated higher cooling efficiency compared to the thin-film sample, which was attributed to the higher surface-to-volume ratio of the nanoparticles and their ability to undergo a wider entropy change within the experimental temperature range. Although the isothermal entropy changes in the Fe nanoparticles embedded in the TiN multilayer are one-third of existing state-of-the-art magnetocaloric materials, the findings are notable because it demonstrates the magnetocaloric effect within a single-element material system. The Fe–TiN system presents additional advantages, such as lower cost and easier tunability of the magnetocaloric effect. The Fe–TiN material system shows promise for next-generation solid-state cooling due to its broad range of usable entropy changes and accessibility. Further research in this field can lead to more efficient and cost-effective cooling solutions in the future.

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