Large magnetocaloric effect in fine Gd_2O_3 nanoparticles embedded in porous silica matrix

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Large magnetocaloric effect in fine Gd_2O_3 nanoparticles embedded in porous silica matrix

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The magnetocaloric properties of a composite material consisting of isolated Gd_2O_3 nanoparticles with a diameter of 6–8 nm embedded in the pores of a mesoporous silica matrix have been studied. The fascinating nanostructure and composition were properly characterized by small angle X-ray scattering, X-ray absorption near edge structure, and TEM. Almost ideal paramagnetic behavior of the material was observed in the temperature range of 1.8–300 K. When compared to various nanosystems, the presented composite exhibits an extraordinarily large magnetic entropy change of 40 J/kg K for a field variation of 0–5 T at cryogenic temperature (3 K). Considering only the mass of the Gd_2O_3 nanoparticle fraction, this corresponds to 120 J/kg K. Calculated refrigerant capacities are 100 J/kg and 400 J/kg for the composite and nanoparticles, respectively. Our findings suggest that the combination of the unique porous structure of amorphous silica with fine gadolinium oxide nanoparticles and high value of magnetic entropy change enables to extend the application of the $Gd_2O_3@SiO_2$ composite, to cryomagnetic refrigeration. In addition, the characteristics of the thermomagnetic behavior have been studied using the scaling analysis of the magnetic entropy change. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4963267]

Intensive effort put into the research on magnetic refrigeration in past years was driven by the ambition of replacing less effective and environmentally unfriendly conventional cooling methods. The phenomenon of the change in temperature of the material as a consequence of the magnetic spin realignment under the influence of external magnetic field variation is generally denoted as the magnetocaloric effect (MCE).[1–5] In the last few decades, gadolinium based compounds showed very promising properties with respect to MCE applications. Pure Gd has been considered the de-facto standard for magnetic refrigeration since its application by Brown in a prototype magnetic refrigerator.[2] The focus on Gd-based materials increased abruptly when Pecharsky and Gschneidner[6] discovered the giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$ at room temperature, with a maximum entropy change (ΔS_{pk}) of 20 J/kg K for a field variation from 0 to 5 T. However, the first order nature of the phase transition implied the presence of thermal hysteresis with detrimental influence on energy efficiency, which was also confirmed by experimental data. In general, suppression of hysteresis losses in this kind of material can be achieved by compositional modification or grain size reduction of the material. Provenzano *et al.*[7] decreased these losses by more than 90% by alloying the compound with a small amount of iron.

Rare earth trifluorides can be dissolved in large amounts inside crystalline matrices, which drove the study of the magnetocaloric response of paramagnetic single crystals of non-stoichiometric fluorides $Cd_{0.9}R_{0.1}F_{2.1}$ (R = Gd, Tb, Dy, and Ho), observing a peculiar behavior.[8] The continuous increase in magnetic entropy change (ΔS_M) with diminishing temperature was documented for all the samples. The only exception was $Cd_{0.9}Ho_{0.1}F_{2.1}$ where the unexpected peak of $\Delta S_M(T)$ dependence at low temperatures and high field variations was ascribed to the deviation from the Curie-Weiss law.

An important feature which limits the magnetic refrigerants applications, especially in electronics, is the rate of heat transfer between the refrigerant and its ambient. There is an assumption that nanostructured materials, with their large surface area, should demonstrate faster and more effective heat exchange in comparison with their bulk counterparts. Phan *et al.*[9] compared the MCE in bulk and nanostructured (50 nm and 35 nm) gadolinium iron garnets ($Gd_3Fe_5O_{12}$). The broad peak of $\Delta S_M(T)$ of a bulk sample was found to shift to lower temperatures as the size of the nanostructured samples decreased. Moreover, an increase in the magnitude of ΔS_M was documented with diminishing particle size. This enhancement of MCE is caused by surface spin disorder in nanoparticles.[9,10] However, for other kind of materials, nanostructuring produces a deleterious effect on the magnetocaloric response.[11] As it was demonstrated by numerous authors,[9–12] magnetocaloric properties of nanoscopic and bulk materials may differ significantly. The advantage of nanoparticles (in comparison with bulk materials) is the possibility of tuning their intrinsic properties by tailoring macroscopic parameters like size, shape, and capping layer or hosting matrix. Monte Carlo simulations carried out by Baldomir *et al.*[13] suggest that for a given sample concentration there exists a particle size that produces the largest increase of magnetic entropy, and reciprocally for a given particle volume there exists a sample concentration allowing to produce the largest magnetic entropy change. Hueso

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et al.[14] reported that it is even possible to change the phase transition character by changing the particle size. They found out that the first-order magnetic transition can be minimized and eventually evolves towards a second-order one as the grain size diminishes in $La_{2/3}Ca_{1/3}MnO_3$. All of these effects are considered to be the consequence of the particles' surface layer properties (like spin canting). Due to the decrement of the nanoparticle size, the surface to volume ratio increases and phenomena originating in lattice irregularities start to dominate. However, having an ensemble of nanoparticles as a magnetic refrigerator bed poses numerous technological problems associated with handling the particles, confining them to a certain region of the device even with the presence of a heat transfer fluid, etc. A potential solution to some of these problems is to embed the nanoparticles in a matrix that keeps their individuality (in contrast to compact the particles together, which might make them behave, in some aspects, as a bulk).

In this work, we investigate the magnetocaloric properties of fine (6–8 nm) Gd_2O_3 nanoparticles encapsulated in a periodic nanoporous SiO_2 silica matrix. The prepared composite combines the advantages of nanoporous silica[15] (highly ordered porous structure, large surface area, thermal stability up to 700 °C, preparation with high reproducibility, biocompatibility) with gadolinium oxide in the form of nanoparticles, the production of which is more economic than bulk Gd counterparts. Although these nanoparticles are very promising in biomedicine as contrast agents[16] for MRI diagnostics, they have never been studied from the MCE point of view. With the expectation of a significant influence of particle size on the magnetocaloric properties of the nanoparticle system, we intended to examine the magnetic characteristics of our composite material. We observed a large magnetic entropy change of the system and a high value of the refrigeration capacity at low temperatures. These features along with the fine nanostructure of the composite allow the possibility to extend the Gd_2O_3 nanoparticle applications even in the field of magnetic refrigeration. Especially, the fast evolving area of delicate devices for Micro Electro Mechanical Systems (MEMS) and Nano Electro Mechanical Systems (NEMS) applications currently requires fast and effective cooling methods and materials, where nanocomposites could be essential.[17,18]

The studied $Gd_2O_3@SiO_2$ composite was prepared by nanocasting (wet-impregnation) of pure Gd_2O_3 nanoparticles in periodic nanoporous silica. The inset of Fig. 1 represents a scheme of the investigated material. The SBA-16 silica matrix with cubic symmetry (*Im3m* space group) serves as a nanoreactor which limits the particle growth during their precipitation, thus controlling the nanoparticle size.[19] The porous structure was characterized by small angle X-ray scattering (SAXS) experiments, carried out at B1 beamline (DESY Hamburg) with a beam energy of 12 keV ($\lambda = 1.03$ Å) using a PILATUS detector. SAXS spectra confirm that the mesoporous matrix of the gadolinium-modified sample retained the long-range periodicity with cubic symmetry of the pure silica matrix. The information about the phase composition was brought by the measurements of the X-ray absorption near edge structure (XANES), at DESY Hamburg. XANES spectra confirm the presence of pure Gd_2O_3 nanoparticles. Fig. 1 shows the XANES results of the studied $Gd_2O_3@SiO_2$ sample and the Gd_2O_3 reference. The small differences of the measured sample and reference may be explained by surface effects, which should be larger in the $Gd_2O_3@SiO_2$ in which nanoparticles are embedded in the porous silica matrix. The size of Gd_2O_3 is determined by the size of the cubic pores and additionally confirmed by TEM measurements. Magnetic measurements of the system were performed by using a commercial SQUID magnetometer MPMS 5XL from Quantum Design. The material demonstrated typical paramagnetic behavior in the whole measured temperature span of 1.8–300 K documented by ZFC/FC experimental data displayed in Fig. 1. Since the contribution of the matrix to the magnetic signal of the composite is negligible (in comparison with Gd_2O_3 nanoparticles), we also calculated the magnetization values with respect to the mass of the pure isolated nanoparticles (right y axis). For the determination of the quantity of gadolinium oxide, atomic absorption spectroscopy (AAS) was used and the determined content corresponds to 25% of Gd_2O_3 nanoparticles in the $Gd_2O_3@SiO_2$ composite sample. The magnetic properties of the blank silica matrix were studied in our previous work.[9,15]

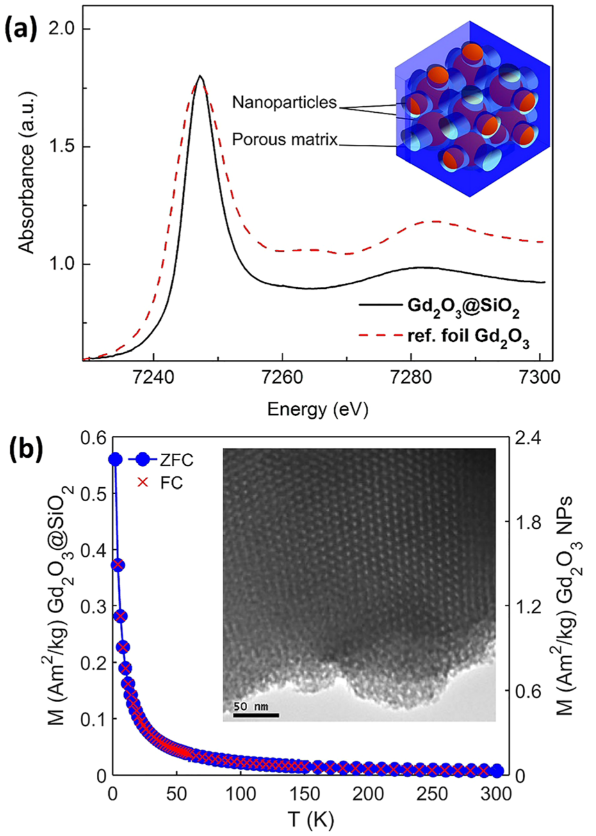

FIG. 1. (a) XANES spectrum confirmed the presence of Gd_2O_3 nanoparticles in the system. Inset: scheme of the composite. (b) ZFC/FC magnetization versus temperature (measured at $H = 10$ mT) of the investigated $Gd_2O_3@SiO_2$ material. Right y axis represents the values of magnetization corresponding to the Gd_2O_3 nanoparticles after excluding the silica matrix mass contribution. Inset: TEM micrograph of blank porous matrix with cubic symmetry.

Isothermal magnetization data recorded for applied magnetic fields up to 5 T in the temperature range of 1.8–40.8 K with a temperature increment of 1 K are shown in Fig. 2(a). The sample exhibits non-saturating $M(H)$ curves with gradual curvature which, together with the lack of

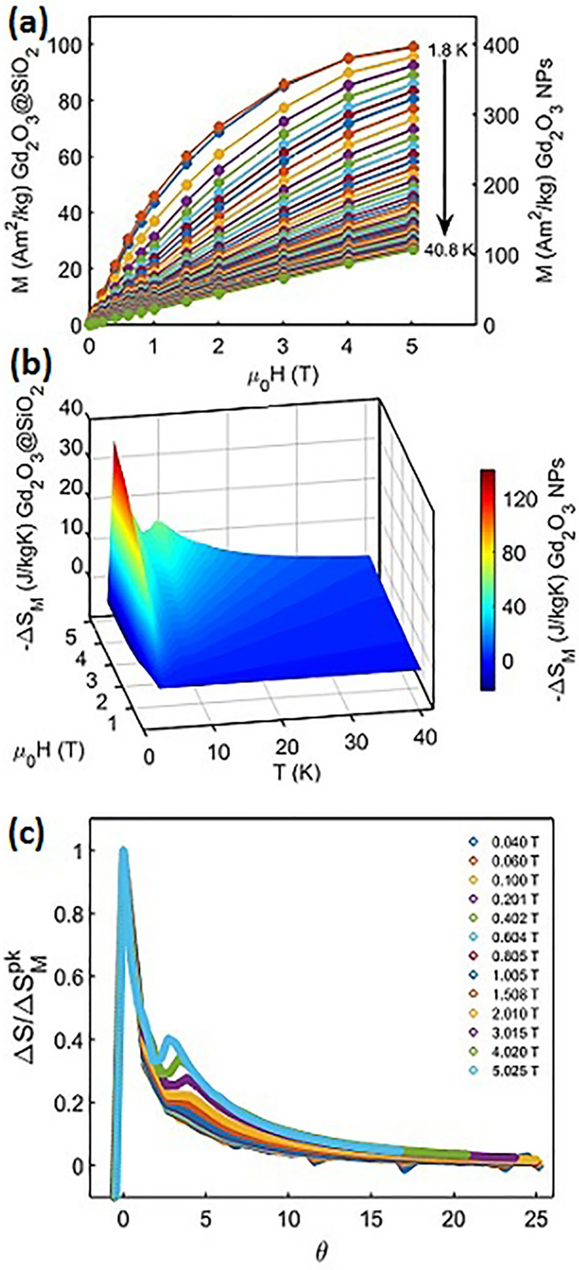

FIG. 2. (a) Isothermal magnetization curves recorded from 1.8 K to 40.8 K, (b) magnetic entropy change of the whole composite and values corresponding to the nanoparticles (colorbar). (c) Collapse of $\Delta S_M(T)$ curves determined for magnetic field variation from 20 mT to 5 T onto a single master curve.

magnetic remanence and hysteresis, suggests a paramagnetic behavior. The set of $M(H,T)$ data was used for the magnetic entropy change calculation. The basis of the relationship between magnetic measurements and the change in entropy is the Maxwell relation[20] $\mu_0(\partial M/\partial T)_{\mathrm{H}} = (\partial S/\partial H)_{\mathrm{T}}$, which for an isothermal-isobaric process after numerical approximated integration yields[4]

$$\Delta S_M\left(\frac{T_{n+1}+T_n}{2}, H_{i_{\max}}\right) = \mu_0 \sum_{i=1}^{i_{\max}} \frac{(M_{n+1}-M_n)_H}{T_{n+1}-T_n}(H_{i+1}-H_i), \tag{1}$$

where M_n and M_{n+1} are the magnetization values measured in magnetic field H_i at temperatures T_n and T_{n+1}, respectively. Fig. 2(b) presents the magnetic entropy change of the whole investigated composite consisting of Gd_2O_3 nanoparticles + SiO_2 matrix as well as the $\Delta S_M(T)$ calculated after considering only the mass contribution of Gd_2O_3 nanoparticles. The maximum of $\Delta S_M(T)$ with extraordinary large values of $\Delta S_M{}^{pk}(T) \sim 40$ J/kg K for a magnetic field variation of 0–5 T was observed at a low temperature of $T \sim 3$ K. Recently, Paul *et al.*[18] investigated the MCE at cryogenic temperatures in Gd_2O_3 nanotubes with average diameter 200 nm, constituting of nanoclusters with average diameter 7.5 nm. The magnitude of $\Delta S_M(T)$ does not exceed 16 J/kg K for maximal field variation of 0–7 T. Li *et al.*[21] studied $GdNi_5$ superparamagnetic nanoparticles of average diameter 15 nm and observed enhanced cryogenic MCE ascribed to high atomic moments and small anisotropy energy barrier induced by small particle size. They established the value $\Delta S_M{}^{pk} = 13.5$ J/kg K at 5 K under a magnetic field change of 5 T. Comparably large values of magnetic entropy change have been reported in $GdAl_2$@Al_2O_3 nanocapsules[4] and oxalate-bridged Gd(III) coordination polymers[22] ($\Delta S_M \sim 32$ J/kg K and $\Delta S_M \sim 48$ J/kg K, respectively), however, at significantly larger field variations of 0–7 T. The occurrence of the peak in Fig. 2(b) is caused by the fact that isothermal magnetization values measured at 1.8 K are lower than the values recorded at 2.8 K. The rest of the $M(H)$ values gradually decrease with increasing temperature, as expected for a standard paramagnetic material. We suppose that surface spin disorder and formation of a spin glass-like state can cause this anomalous effect, similarly as Kodama and Berkowitz[23] and Martinez *et al.*[24] reported. Interestingly, if we did not take into account the mass fraction of the silica matrix, which causes the dilution of the magnetic species by a non-magnetic material and thereby reduces the entropy change per unit mass, the observed $\Delta S_M{}^{pk}(T) \sim 120$ J/kg K contribution of Gd_2O_3 nanoparticles would be extraordinarily high (Fig. 2(b)).

Neither the MCE nor such a high value of magnetic entropy change has ever been measured and detected in Gd_2O_3 nanoparticles. Phan *et al.*[9] reported a similar abrupt increase of $-\Delta S_M(T)$ at low temperatures in nanostructured $Gd_3Fe_5O_{12}$ samples and a shift of the $\Delta S_M{}^{pk}(T)$ towards lower temperatures with diminishing diameter (from bulk down to ~35 nm) of the nanoparticles. They ascribed this phenomenon to the strong effect of the applied magnetic field on the disordered surface spins. In our case of 6–8 nm nanoparticles, this effect is significantly enhanced because of the high surface to volume ratio, thus very high $\Delta S_M(T)$ at very low temperature was observed. Recognizably, a second peak can be observed at $T \sim 9$ K in $\Delta S_M(T)$ experimental data of the composite, Fig. 2(b). This maximum, in contrast with the first one at $T \sim 3$ K, does not appear at lower field variations and becomes apparent at $\Delta\mu_0 H > 1$ T. As its magnitude is significantly lower in comparison with the first one, in the current paper we focus on the examination of the main peak.

Since we ascribe the presence of the $\Delta S_M(T)$ maximum of the Gd_2O_3@SiO_2 material to a second order phase transition (SOPT) from paramagnetic to spin glass-like state, we attempted to employ scaling analysis and consider the dependence of the most relevant magnetocaloric response parameters on the magnitude of magnetic field. It has been shown[25,26] that, in the case of SOPT materials, $\Delta S_M(T)$ curves obtained for different magnetic field variations collapse onto a single master curve. This curve is phenomenologically constructed by normalizing the $\Delta S_M(T)$ curves with respect to their peak, $\Delta S_M{}^{pk}(T)$, and rescaling the temperature axis using a reference temperature,[27] T_{ref} (in our case the one corresponding to $\Delta S_M(T_{ref}) = 0.5\Delta S_M{}^{pk}$). The rescaled temperature axis becomes $\theta = (T - T^{pk})/(T_{ref} - T^{pk})$, where T^{pk} is the $\Delta S_M(T)$ peak temperature. Fig. 2(c) shows processed data of $\Delta S_M(T)$ which obviously collapsed onto a single curve resembling the master curve typical of magnetocaloric materials with a second order phase transition[27] in a temperature interval corresponding to the first $\Delta S_M(T)$ maximum. It is worth noting that the smaller magnetic entropy change peak is also visible in this figure, with a position which is field dependent in the rescaled temperature axis θ. Critical exponents characterizing the second order phase transition temperature could be extracted from the field dependence of the magnetocaloric magnitudes,[25–27] namely, $\Delta S_M{}^{pk}$, T_{ref}, and refrigerant capacity RC, which is the measure of the energy that can be transferred between the hot and cold reservoirs and is defined as[28]

$$RC(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T, \Delta H)dT, \tag{2}$$

where ΔH is the difference between minimum and maximum applied fields. Usually, it is calculated as the full width at half maximum of the $\Delta S_M(T)$ peak times the peak value $\Delta S_M{}^{pk}$. In the case of the SOPT, RC should obey a scaling law[25–27] $RC \propto H^{1+1/\delta}$. The $RC(H)$ data fit for $\Delta H > 1$ T for the investigated material presented in Figure 3 yields the value of $\delta = 2.97$ which is in good accordance with the value $\delta = 3$ corresponding to the mean field theory.[22] Fig. 3 also shows the fit of $\Delta S_M{}^{pk} \propto H^n$ for field variations $\Delta H > 1$ T, which produced $n = 0.68$. Since at the transition temperature[25,26] $n = 1 + 1/\delta(1 - 1/\beta)$, critical exponent $\beta = 0.52$ was calculated for the investigated Gd_2O_3@SiO_2 composite, which agrees well with the mean field theory. Finally, $\Delta = 1.54$ and $\gamma = 1.02$ were calculated employing the relations between critical exponents[26] $\Delta = \beta\delta$ and $\Delta = \beta + \gamma$. However, the value of Δ does not match with the value of $\Delta_{\rm ref} = 0.34$ established from $T_{ref} \propto H^{1/\Delta}$ data fit for field variations above 1 T. The investigation of the peculiar $T_{ref}(H)$ behavior is beyond the scope of this study and it should be related to the presence of the minor peak at higher temperatures.

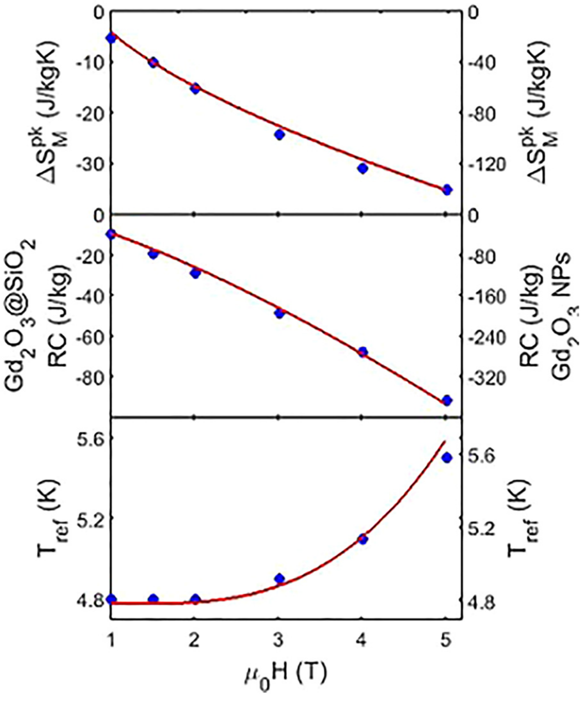

FIG. 3. Field dependence of the peak magnetic entropy change $\Delta S_M{}^{pk}$, refrigerant capacity RC, and temperature at which magnetic entropy change is 20% of the peak (reference temperature T_{ref}). Red curves represent fits of experimental data.

To conclude, magnetocaloric properties of fine Gd_2O_3 nanoparticles, embedded in the periodic nanoporous SiO_2 matrix, were investigated. Large magnetic entropy change $\Delta S_M{}^{pk}(T) \sim 40$ J/kg K was observed for maximum field variation 5 T at low temperatures. Excluding the mass of the non-magnetic silica matrix, extraordinary high value $\Delta S_M{}^{pk}(T) \sim 120$ J/kg K was calculated for the Gd_2O_3 nanoparticles. This finding along with an easy to prepare fine nanostructure could extend the current Gd_2O_3 NPs application to the area of cryogenic refrigeration, e.g., as a material for Nano Electro Mechanical Systems (NEMS).

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