Magnetocaloric Effect in Gd$_2$O$_3$@SiO$_2$ Nanocomposite

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Nanocomposite consisting of Gd$_2$O$_3$ nanoparticles embedded in periodical porous silica matrix was investigated with respect to its magnetocaloric properties. Series of field (up to 5 T) dependence of magnetization data were recorded in temperature range 2–52 K. The data were subsequently processed employing Maxwell relation in order to calculate magnetic entropy change ($\Delta S_M$) of the system. Examined nanocomposite exhibited reasonably high value of $\Delta S_M \approx 29$ J/(kg K) at maximal field change 5 T at the temperature of 2 K which suggests that this material could be feasible for cryomagnetic refrigeration applications.

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1. Introduction

Gadolinium based nanoparticles are known as useful material for diagnostics tumor using magnetic resonance imaging (MRI) method. These materials exhibit strong paramagnetic behaviour and high value of $r_1$ relaxivity ($1/T = r$) of 4.8 s$^{-1}$ mM$^{-1}$ at 7.05 T [1]. Besides of their suitable biomedical applications, there is another potential area of such nanoparticle systems applications. Debye in 1926 [2] and Giauque in 1927 [3] independently pointed out that ultralow temperatures could be reached through the reversible temperature change of paramagnetic salts with the alternation of magnetic field. This phenomenon is known as magnetocaloric effect (MCE) and it was discovered by Warburg in 1881. The first experiment on magnetic refrigeration was performed by Giauque and MacDougall in 1933 [4]. With the use of this technology, the temperatures below 1 K were successfully achieved. Many years later the low-temperature MCE was reported in a variety of paramagnetic salts [5]. Unfortunately, low thermal conductivity of this material is detrimental for adiabatic demagnetization applications. Since nanoparticles are characteristic of high surface to volume ratio (in comparison with bulk materials), there is an assumption that such structures would transfer the heat with considerably higher efficiency. However, nanoparticles have long been demonstrated to reduce the thermal conductivity of crystals by scattering phonons [6, 7]. It has been found that the thermal conductivity in nanocomposites is governed by the interface density and that thermal boundary resistance plays a critical role in determining the effective thermal conductivity [8]. On the other hand, several works confirm that embedding of nanostructures into matrix material could result in feasible effects with respect to thermal conductivity of the composite have been published, too. Evans et al. [9] reported that the thermal conductivity of nanofluids and nanocomposites can be significantly enhanced by the aggregation of nanoparticles into clusters. Zhang and Minnich [10] showed that it is possible to affect thermal conductivity of nano-composite by tailoring nanoparticles’ size distribution to scatter broader or narrower thermal phonon spectrum.

According to simulations carried out by Quiao and He [11], for nanocomposite with randomly dispersed nanoparticles, thermal conductivity of matrix material can be enhanced by embedding nanoparticles exhibiting high thermal conductivity. However, the effectiveness of such strategy diminishes as the interfacial thermal resistance between the nanoparticle and matrix material increases. The same study also revealed that the enhancement of thermal conductivity can be affected by the alignment of nanoparticles with respect to the temperature gradient. Further, different nanoparticles have been successfully used to improve thermal conductivity of polymers. For instance, high density polyethylene filled with 7 vol.% nanometer size expanded graphite has double thermal conductivity in comparison with microcomposites at the same volume content [12]. Droval et al. [13] multiplied the thermal conductivity by the factor of six introducing boron-nitride nanoparticles into polymer matrix.

Apparently, heat transfer in nanocomposites is complex phenomenon, where tailoring one contribution often affects another one in a negative way. Thus, properly designed nanocomposite which would combine feasible features like high value of magnetic entropy change along with good thermal stability and conductivity could exhibit suitable properties with respect to magnetocaloric applications. Due to this, we decided to prepare nanocomposite consisting of Gd$_2$O$_3$ nanoparticles embedded in periodical porous silica matrix and to study its MCE properties.

2. Experimental

Investigated Gd$_2$O$_3$@SiO$_2$ nanocomposite was prepared by nanocasting of Gd$_2$O$_3$ nanoparticles in periodic nanoporous silica matrix. The structure of composite has been previously studied and published elsewhere [14, 15].
Commercial MPMS 5XL (Quantum Design) device was utilized to perform magnetic measurements of the Gd$_2$O$_3$@SiO$_2$ nanocomposite. The dependences of magnetization on field magnitude (up to 5 T) were recorded in temperature range 2–52 K with the step of 1 K. The powder sample with the mass of m = 3 mg was encapsulated into a gelatin capsule and inserted into the plastic sample holder. The signals of diamagnetic contributions of gelatin capsule and plastic sample holder were measured and subtracted from experimental data.

3. Results and discussion

Figure 1 obtained by transmission electron microscopy (TEM) shows structure of the examined sample. Blank matrix (without Gd based nanoparticles) with perfectly periodic hexagonal channels is clearly visible in the left part. After incorporation of Gd based nanoparticles inside of periodic matrix, the Gd$_2$O$_3$ nanoparticles are visible as black spots and additionally the perfectly ordered porous matrix is slightly disturbed, right part. Nanoparticles with average size up to 7 nm can be identified from TEM micrographs.

Fig. 1. Transmission electron microscope (TEM) images of Gd$_2$O$_3$@SiO$_2$ nanocomposite: (left part) blank SBA15 hexagonal matrix with size of the pores up to 7 nm; (right part) Gd$_2$O$_3$ nanoparticles embedded in SBA15 matrix.

Figure 2 presents the isothermal $M(\mu_0H)$ data of investigated material. Apparently, the curves obtained at lowest temperatures resemble “S” shape and with increasing temperature are becoming almost linear. This behavior is expected for paramagnetic or superparamagnetic materials. This set of data was used for magnetic entropy change ($\Delta S_M$) calculations in order to reveal magnetocaloric properties of the material.

The Maxwell relation [16]:

$$\left( \frac{\partial M}{\partial T} \right)_{\mu_0H} = \left( \frac{\partial S}{\partial \mu_0H} \right)_T$$

(1)

expresses how change in magnetization induces magnetic entropy change, and vice versa. In the case of isothermal-isobaric process after integration we get [5]:

$$\Delta S_M = \int \left( \frac{\partial M}{\partial T} \right)_{\mu_0H} d\mu_0H.$$  

(2)

For the discrete measurements there is a suitable approximation of Eq. (1) [17]:

$$\Delta S_M \left( \frac{T_{n+1} + T_n}{2}, \mu_0H \right) = \sum \frac{(M_{n+1} - M_n) \mu_0H}{T_{n+1} - T_n} \Delta \mu_0H,$$

(3)

where $M_n$ and $M_{n+1}$ are the magnetization values measured in magnetic field $\mu_0H$ at temperatures $T_n$ and $T_{n+1}$, respectively.

Fig. 2. Isothermal magnetization data of Gd$_2$O$_3$@SiO$_2$ nanocomposite up to applied field of 5 T obtained at temperature range 2–52 K with the step 1 K.

Fig. 3. Magnetic entropy change vs. temperature dependences of Gd$_2$O$_3$@SiO$_2$ nanocomposite for the applied field variations from 65 mT to almost 5 T. For the sake of transparency, only each 10th of 150 curves is displayed.

Figure 3 shows the temperature dependence of magnetic entropy change at different magnetic field variations (up to 5 T) calculated from experimental data displayed in Fig. 2. At higher temperature region, slight increase of $\Delta S_M$ with decrease of the temperature can be observed. However, approaching to lowest temperatures, $|\Delta S_M|$ soars reaching the maximal value of 29 J/(kg K) at 2 K for field variation 5 T, which is the behavior typical of para-
magnetic salts. As it can be seen, no significant peak is present in $|\Delta S_M(T)|$ dependences, which confirms the absence of magnetic phase transition in whole examined temperature range 2–52 K. We would like to note that the existence of local maxima in $|\Delta S_M(T)|$ at 12–15 K and 27–30 K is caused by numeric approximation during experimental data processing and it has no physical origin. Despite of extended research devoted to Gd$_2$O$_3$ nanoparticle systems with respect to their MRI properties [1], studies dealing with magnetocaloric effect in such systems are not available. Table I presents magnetic entropy change maxima reported by other authors for selected Gd based compounds and nanoparticle systems.

**TABLE I**
The comparison of $|\Delta S_M|$ of various Gd based systems.

| System                      | $|\Delta S_M|$ | $T_{\text{peak}}$ | $|\Delta H|_{\text{max}}$ | Ref. |
|-----------------------------|----------------|-------------------|--------------------------|------|
| Gd$_2$O$_3$@SiO$_2$ (nanocomposite) | 29             | 2                 | 5                        | this work |
| Gd$_2$(Si$_2$Ge$_2$) (bulk)    | 19             | 276               | 5                        | [18] |
| Gd (bulk)                    | 10             | 295               | 5                        | [18] |
| Gd$_3$Fe$_5$O$_{12}$ (bulk)   | 2.5            | 35                | 3                        | [19] |
| Gd$_3$Fe$_5$O$_{12}$ (50 nm particles) | 1.6          | 2                 | 3                        | [19] |
| Gd$_3$Fe$_5$O$_{12}$ (35 nm particles) | 3.5          | 2                 | 3                        | [19] |
| GdAl$_2$O$_3$ (nanocapsules)  | 31             | 5                 | 7                        | [17] |

From selected systems, only GdAl$_2$/Al$_2$O$_3$ nanocapsules exhibit higher $|\Delta S_M|$, however at significantly promoted field change of 7 T. Moreover, if we consider that the mass of non-magnetic silica matrix of the composite reduces the values of $|\Delta S_M|$ originating from signal of Gd$_2$O$_3$ nanoparticles, the results of this study suggest that Gd$_2$O$_3$@SiO$_2$ nanocomposites could be promising material for low temperature refrigeration technology.

3. Conclusions

We studied magnetocaloric properties of Gd$_2$O$_3$@SiO$_2$ nanocomposite prepared by nanocasting of Gd$_2$O$_3$ nanoparticles in periodic nanoporous silica matrix with hexagonal symmetry. Isothermal magnetization curves recorded in temperature range 2–52 K pointed to paramagnetic behavior of the material. This was confirmed by the behavior of magnetic entropy change vs. temperature curves calculated for field variations up to 5 T. Reasonable large value of $|\Delta S_M| = 29 J/(kg K)$ was found at 1.8 K for maximal field change of 5 T in the investigated composite, which suggests that this material could be feasible for low temperature refrigeration applications.

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