Magnetocaloric phenomena in Mg-ferrite nanoparticles

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Abstract. A comparative study of magnetocaloric effect (MCE) in superparamagnetic (SPM) regime is reported in two different types of magnesium ferrite nanostructures. The samples were prepared either by microemulsion method as MgFe₂O₄ nanoparticles encapsulated in amorphous SiO₂, or as matrix-less nanoparticles using hydrothermal synthesis in supercritical water conditions. The particle diameter in all prepared samples was obtained from XRD measurements and TEM analysis. All samples show a SPM behavior above the blocking temperature, $T_B$. The entropy change, $\Delta S$ was finally derived from the measurements of magnetization, $M(H,T)$ curves at defined temperature intervals. We observed, that all samples show a broad peak of $\Delta S$ in the temperature range that is fairly above the $T_B$. The values of the $\Delta S$ also depend on the particle size, and they are of about two orders lower than those reported in the famous giant magnetocaloric materials.

1. Introduction
Magnesium ferrite nanoparticles have been of big interest in last years because of their specific physical properties that are employed in various applications (as humidity sensors [1] or catalysts [2]). It was shown recently, that they can be utilized in magnetic cooling [3] because of unique features lacking in the typical MCE materials. In typical MCE materials, the maximum entropy change is concentrated just in the vicinity of the paramagnetic-ferromagnetic transition at the Curie temperature, $T_C$ and decays sharply far from the $T_C$. Whereas it was shown, that magnetic nanoparticles have a broad peak of isothermal entropy change, $\Delta S$ [4]. This peak is extended in the broad temperature range much higher than the $T_B$. In addition, in the common MCE ferromagnets it is cumbersome to tune the $T_C$. However, the blocking temperature $T_B$ can be easily tuned by adjusting the particle size, shape, dispersion and inter-particle interactions [5]. Other advantages of nanoparticles can be e.g. dispersion of nanoparticles in other host matrices, that themselves can be good MCE materials, or large surface area that provides better heat exchange with surroundings. On the other hand, a disadvantage is that the value of $\Delta S$ is rather smaller than in typical giant MCE (GMCE) materials. In this paper, we present a study of the MCE of magnesium ferrite nanoparticles that were prepared either by microemulsion method or by hydrothermal synthesis. The type of preparation has effect on particles size and crystallinity, that affect the values of MCE.
2. Experimental
The first two studied samples are magnesium ferrite nanoparticles embedded in a silica matrix. They were prepared by the microemulsion method [6], and subsequently annealed in order to vary the particle size. The final treatment at 900°C and fast cooling on air was applied for sample marked as Mg900. The sample marked Mg1100P was annealed at 1100°C and cooled down slowly (1°C/min) in a furnace. The samples were then characterized using powder X-ray diffraction (Siemens D5005 diffractometer with Cu anode), HR-TEM (high-resolution transmission microscopy) and SEM (scanning electron microscopy), and Mössbauer spectroscopy. Other two samples of MgFe$_2$O$_4$ are matrix-free (MgF-O3, MgF-O4); they were produced by hydrothermal synthesis in supercritical water without embedding them in an inert matrix. They were characterized by analogous methods. For illustration of the sample morphology, the HR-TEM and TEM images of all samples are shown in Figure 1. The magnetization curves were measured using commercial MPMS7XL device from Quantum Design. The temperature range was chosen above the blocking temperature due to the fact, that below blocking temperature the superparamagnetic magnesium ferrite nanoparticles exhibit hysteresis [7]. Moreover, earlier studies showed that the maximum of ∆S temperature dependence is located much higher than $T_B$ [4], hence the measurements were concentrated in the temperature range between 250-350K.

![Figure 1](image)

Figure 1. The HR-TEM images for a) Mg1100P, b) Mg 900, and the TEM images for c) MgF-O3, d) MgF-O4

3. Results and discussion
The summary of particle diameter, $d$ and blocking temperature, respectively, is shown in Table 1. The $d$ values were estimated from HR-TEM or TEM. The blocking temperature, $T_B$ was determined from the temperature dependence of both the field-cooled (FC) and zero-field-cooled (ZFC) magnetization [6]. The MCE was determined from measurements of the family of $M(H,T)$ curves that is shown for two samples in Figure 2. The ∆S was then numerically calculated by integration of the Maxwell relation:

$$\left(\frac{\partial S_M}{\partial H}\right)_T = \mu_0 \left(\frac{\partial M}{\partial T}\right)_H$$  \hspace{1cm} (1)

The results of these calculations are shown in Figure 3 for different values of the applied magnetic field. The errorbars were estimated from the numerical integration.

In all samples (beyond Mg-FO4) we can observe broad peaks of ∆S (see the arrows), which are a typical feature reported in magnetic nanoparticles. These peaks are not situated in the vicinity of $T_B$, but much higher as expected. This effect has also been observed in cobalt ferrite [4] or zinc ferrite [8] nanoparticles, but the reason has not been explained yet. It seems that peak of ∆S of MgF-O4 is near the $T_B$, that can be due to the relatively large particle size (50nm).
Table 1. Particle size and blocking temperature of the sample

| sample     | Mg900 | Mg1100P | MgF-O3 | MgF-O4 |
|------------|-------|---------|--------|--------|
| \(d\) (nm) | 8     | 21      | 20     | up to 50 |
| \(T_B\) (K) | 10    | 50      | 120    | 240    |

Another reason could be that the peak is also situated much higher than the expected \(T_B\), hence this peak was not observed in our measurements that were done up to 350 K only. The values of entropy change are of same order as in other ferrite nanoparticles [4,8]. If we compare the value of \(\Delta S\) for samples that were encapsulated in SiO\(_2\) with the matrix-free particles, it is easy to see, that \(\Delta S\) for the free MgFe\(_2\)O\(_4\) is 3-4 times higher than for the isolated particles. However, these values were determined from the specific magnetization, hence it is not relevant to compare the values. Taking into account the content of magnesium ferrite in the silica composite (15%) and neglecting influence of the nonmagnetic silica matrix on the value of \(\Delta S\), the samples obtained by microemulsion revealed larger values \(\Delta S\) then those prepared by hydrothermal method. The reason is probably much better crystallinity and size uniformity of the nanoparticles, which in general yield a larger superspin values due to suppression of the surface effects [9]. Moreover, the presence of the silica matrix reduces interparticle interactions, which usually cause undesirable reduction of the saturated magnetization.

Figure 2. The magnetization isotherms of sample Mg900 (left panel) between 50 and 350K, in right panel is sample MgF-O4, the temperature range between 280 and 350K, the temperature measurements are at intervals \(T=10\)K.

We cannot observe peak of \(\Delta S\) in field 1T for all samples. This effect was reported earlier in cobalt ferrite [10]. In small magnetic fields, the peak is located in the vicinity of \(T_B\). Above the blocking temperature, the nanoparticles are superparamagnetic and they are free to have random orientation. Hence the small field does not cause a maximum of \(\Delta\) above the \(T_B\). It is surprising, that for bigger particles (Mg1100), the \(\Delta S\) is smaller. This effect was also observed in cobalt ferrite nanoparticles [4] and the explanation needs further studies. In comparison to the bulk materials that show GMCE (typical values are about 20 J.kg\(^{-1}\).K\(^{-1}\) for field 5T [11]), the values of the entropy change for nanoparticles are quite small. However, using a suitable matrix or materials based on rare earths could enhance the absolute value of the MCE.
4. Conclusions
From the measurements of magnetization curves, we determined the values of magnetic entropy change for magnesium ferrite nanoparticles. Our results confirmed that these MgFe$_2$O$_4$ show a broad peak of $\Delta S$ in the temperature range that is fairly above the blocking temperature. One of the interesting observations is that when the particle size is increasing, the $\Delta S$ is decreasing. To explain this effect further studies are necessary. The nanoparticles embedded in silica show effectively larger value of the $\Delta S$, which is attributed to the reduction of interparticle interaction. In comparison to the nowadays-used magnetic materials that show GMCE, our values of $\Delta S$ are relatively small. On the other hand, their broad temperature range of $\Delta S$ is really promising in comparison to typical GMCE materials, that exhibit a narrow peak concentrated in the vicinity of paramagnetic-ferromagnetic transition. Additional functionalization of the materials in order to enhance the MCE values is in progress.

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