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Research articles

The frequency dependence of magnetic heating for $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles

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The study addresses the role of frequency of the AC magnetic field on heating of $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles. We observe (i) a superlinear dependence of specific absorption rate as a function of frequency at the body temperature and (ii) the presence of a maximum temperature at which the magnetic heating stops. This self-limiting mechanism of the magnetic heating can be used in various applications such as magnetic fluid hyperthermia or catalysis.

1. Introduction

Magnetic nanoparticles have been extensively studied in recent years in the context of biomedical applications, particularly for magnetic fluid hyperthermia (see reviews [1–3] and references therein). This cancer treatment modality exploits the ability of magnetic nanoparticles to accumulate in the target tumor and to heat under the influence of an AC magnetic field. To prevent the undesired eddy currents that may be harmful for surrounding healthy tissues the AC field should be within a low frequency range, usually below 500 kHz [2]. Another problem is the overheating resulting in thermoablation and uncontrolled tissue damage. It can be avoided in self-regulating (or self-controlled) hyperthermia [4,5] using magnetic nanoparticles with an intrinsic mechanism that limits the increase of temperature. This type of "smart" nanoparticles can be also useful in other fields where certain temperature regime is critical, e.g. in nanocomposite systems with magnetic-field-controlled catalytic activation.

A promising family of compounds for self-regulating magnetic heating is $La_{(1-x)}Sr_xMnO_3$ (LSMO) whose Curie temperature can be tuned by Sr content [4,6–9]. The magnetic heating dependence of LSMO nanoparticles on the Sr content, the magnetic field amplitude [7], and the size of nanoparticles [9] has been investigated, while reports on frequency dependence are still lacking.

In this study we analyze the physical mechanism that limits the heating at high frequency of the AC magnetic field on LSMO nanoparticles with $x = 0.25$. This Sr/La ratio has been chosen because it is set in a region of the phase diagram for La-Sr series far from the mixed phases and has a Curie temperature close to room temperature.

2. Synthesis and measurement techniques

The $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles were synthesized following the Pechini method in which lanthanum nitrate, strontium nitrate and manganese acetate were dissolved in a citric acid solution. The solution was mixed and heated at 70 °C for 1 h to obtain a transparent solution, then ethylene glycol was added to provide the polymerization. A light pink gel was obtained after 2 h. The gel has been placed into the furnace for 4 h to evaporate the organic compounds and then heated at 700 °C during 4 h for calcination yielding black powder. The structural characterization was performed on a Bruker D8 advance machine with Cu-Kα radiation ($\lambda = 1.54{,}056$ Å), where a single phase of $La_{0.75}Sr_{0.25}MnO_3$ with lattice parameters a = b=5.5053 Å and c = 13.3864 Å was found. The diffraction pattern is presented in Fig. 1. The morphology visual-

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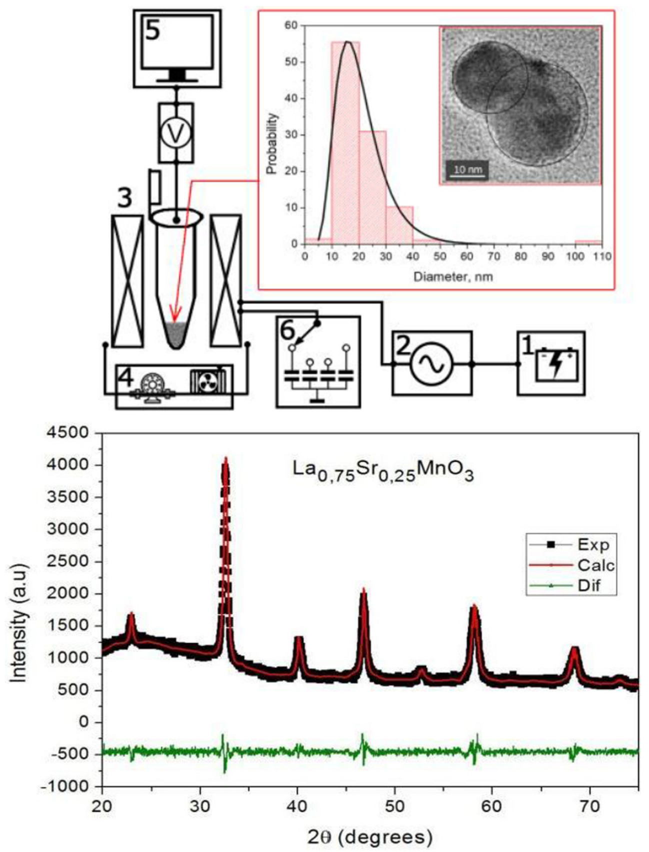

Fig. 1. a) Equipment for SAR measurement.1. Power supply; 2. generator; 3. solenoid; 4. water cooling system; 5. data acquisition and monitoring system, 6. reconfigurable capacitor system. Inset: TEM image of $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles with size distribution histogram b) X-ray diffraction pattern for nanoparticles (λ = 1.54056 Å). Black dots: experimental data; red line: theoretical data; green line: difference.

ized by Transmission Electron Microscopy (TEM) on a High Resolution Transmission Electron Microscope JEOL 2100F-200KV TEM showed a log-normal distribution, with mean size $\langle D \rangle$ = 21 nm, most probable value D_m = 17 nm and standard deviation Δ = 11 nm. The particle size distribution and the corresponding fitting to the experimental data are presented in Fig. 1.

The magnetic properties of the nanoparticles were studied with a Lake Shore 7407 vibrating sample magnetometer (VSM). The experimental setup for calorimetric measurements consists of an AC magnetic field module, a water cooling system and a PC data acquisition system (Fig. 1). The AC magnetic field module is comprised of the 400 W power supply, the generator connected in series with the oscillating circuit that, in its turn, includes the reconfigurable capacitor system and the solenoid providing magnetic field in the working volume with the inner diameter 7 mm. Due to the reconfigurable capacitor system there is the possibility to adjust the frequency in the vicinity of the oscillating circuit resonance frequencies corresponding to the series of values: 150, 200, 250, 300 kHz.

A conventional parameter for quantitative characterization of magnetic heating is the Specific Absorption Rate (SAR), i.e. the ratio of the dissipated power to the mass of the particles [10]:

$$SAR = C\frac{M}{m}\frac{dT}{dt}, \tag{1}$$

where C is water specific heat capacity, $\frac{dT}{dt}$ is the rate of heating on the initial part of the curve, and $\frac{M}{m}$ is the ratio of the water mass to the mass of nanoparticles. SAR value is of practical importance since it allows for calculating the amount of the nanoparticles and magnetic field exposure.

Due to a specific property of studied nanoparticles, i.e. the temperature limit of magnetic heating, the conventional Box-Lucas method [10], based on approximation of the heating curve with the dependence $(1 - \exp(-t/\tau))$, where τ is a characteristic time constant of the system is irrelevant. A variation of the *corrected slope method* [10] was used that takes into account the non-adiabatic measurement conditions. To estimate thermal losses of the system the cooling curve after the field switch-off was also measured. The real value of dT/dt in Eq. (1), at any given temperature can be obtained as a sum of slopes of heating and cooling curves [7].

3. Results

The magnetic hysteresis curves measured at various temperatures are shown in Fig. 2. The Curie temperature $T_c \sim 367$ K is somewhat higher than the Curie temperature $\sim$330 K for bulk-like particles with the same Sr content [4]. The ZFC-FC measurements show that the blocking temperature even for quasistatic measurements (time of measurement $\sim$1 h) is close to the Curie temperature thereby making these nanoparticles metastable in the range of temperatures 30–50 °C.

The suspension of 20 mg of magnetic nanoparticles in 0.1 ml of distilled water was heated by AC magnetic field with amplitude of 100 Oe for 400 s when the AC field was switched off and the cooling curve was recorded to estimate the heat power losses in the system (Fig. 3). The increment of the saturation temperature (corresponding to the top plateau) became smaller with increasing frequency showing the temperature limit at around 70 °C.

4. Discussion

In order to quantitatively characterize the heating of the samples the SAR values were calculated according to eq.1. The temperature increasing rate $\frac{dT}{dt}$ at the temperature 37 °C was obtained following the procedure described in Section 2. The frequency dependence of *SAR(f)* is shown in the Fig. 3, inset.

The theory of magnetic fluid heating in AC magnetic field [11] gives the following frequency dependence:

$$SAR \sim \frac{(2\pi f \tau_m)^2}{1 + (2\pi f \tau_m)^2}, \tag{2}$$

where f is the frequency of AC magnetic field, τ_m is the characteristic time of magnetization relaxation. In the limit $(f\tau) \ll 1$ the Eq. (2) is close to a quadratic law that agrees with the experimental data (Fig. 3, inset).

This superlinear frequency dependence of the initial slope is in striking contrast to the behavior of the heating curves at higher temperatures: the increments of the saturation temperature corresponding to equal steps of 50 kHz tends to zero. Thus the mechanism limiting the magnetic heating with the maximum temperature $\sim$70 °C (Fig. 2) is not related to the saturation of the dependence (2) at high frequencies $(f\tau) \gg 1$; therefore an alternative mechanism should be provided.

In this context the temperature dependence of hysteresis loops in Fig. 2 is helpful: both the saturation magnetization and coercive field decrease with increasing temperature leading to the drop of the hysteresis loop area.

In summary, the mechanism of self-limiting heating of $La_{0.75}Sr_{0.25}MnO_3$ nanoparticles at high frequency range >200 kHz is related to the drop of hysteresis losses at higher temperatures rather than to the effect of finite magnetic relaxation time τ_m.

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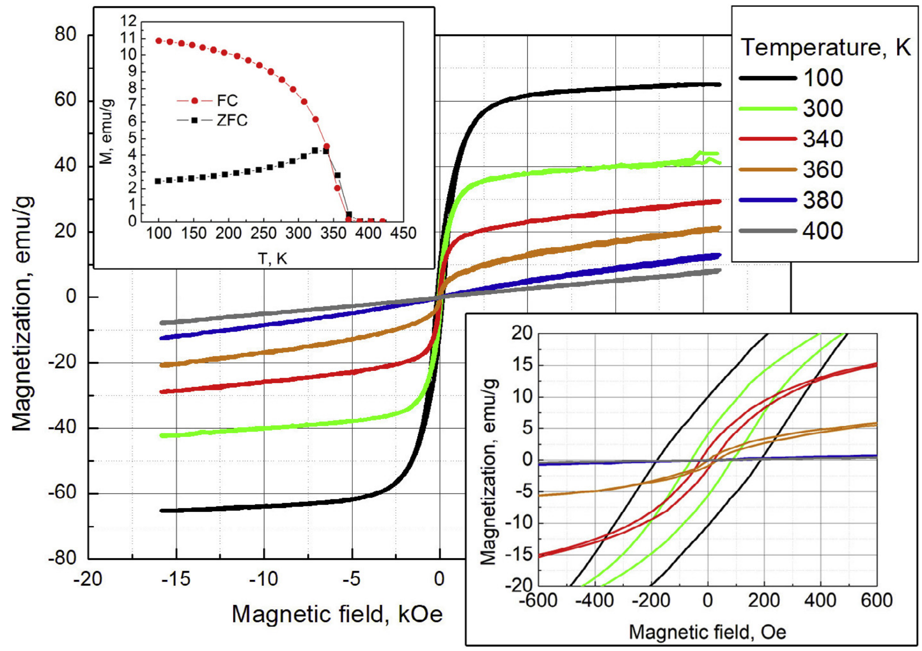

Fig. 2. Magnetization curves of LSMO nanoparticles at various temperatures. The inset in the upper left corner shows the ZFC-FC curves (the static magnetic field was 50 Oe). The inset at the lower right shows the zoom of the low field region.

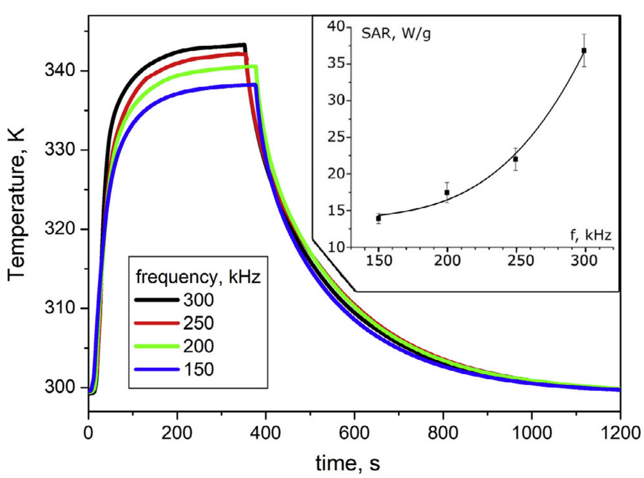

Fig. 3. The heating/cooling curves of the suspension of LSMO nanoparticles measured at various frequencies. Amplitude of AC magnetic field is 100 Oe. Inset. The dependence of SAR on frequency. The dots are experimental data, the curve is a quadratic approximation.

Therefore in the body temperature range the dependence *SAR(f)* is superlinear that enables one to adjust the heating regime. This principle can be used for self-regulating magnetic hyperthermia and catalysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmmm.2017.11.126.

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