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Structural, magnetic and thermal properties of one-dimensional CoFe$_2$O$_4$ microtubes

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Abstract:

One-dimensional CoFe$_2$O$_4$ microtubes have been prepared via a simple template-assembled sol-gel method. Influence of calcination temperature on structural and magnetic properties, heat capacity and specific heating rate under radiofrequency field 295 kHz was studied. A CoFe$_2$O$_4$ spinel was the main phase in all samples. As the calcination temperature increased, the average crystal size increased from 34.1 to 168 nm and the specific surface area decreased from 85.7 to 8.5 m$^2$·g$^{-1}$. When calcined at 1073 K, porous microtubes with a narrow size distribution in the range between 2.0 and 2.5 µm and a length to diameter ratio exceeding 20 were obtained. The heat capacity of the microtubes calcined at 973 K was 140.81 J·mol$^{-1}$·K$^{-1}$ at 395K, being close to the theoretic value. The sample calcined at 973 K showed highest rate of 0.293 K s$^{-1}$·mg$^{-1}$.

Keywords: Cobalt ferrite; microtubes; magnetic properties; thermal capacity; radiofrequency heating.
1 Introduction

Recently, many researchers have studied different metal oxide morphologies, such as spherical, ordered porous particles, rods, fibers, and hollow structures. The performances of these materials in various applications depend on their chemical composition and surface properties as well as on their textural properties [1-4]. Specially, microtubes play an important role in the miniaturization of components and devices because of their small diameters and high aspect ratios [5]. As their diameter is in the micrometer range, they are more suitable than nanotubes to load guest species such as biomolecules, catalysts, and nanoparticles, which allows to use them in different applications in drug delivery, catalysis, batteries and so on [6]. Currently, hollow metal oxide structures can be prepared with a template method, dry or wet spinning, electrospinning, and centrifugal spinning [7].

Magnetic nanoparticles are the subject of intense research not only for their fundamental scientific interest, but also for their potential applications in magnetic storage media, biosensing applications, catalytic and medical applications [8, 9]. Among the magnetic nanoparticles, spinel cobalt ferrite, CoFe$_2$O$_4$, is a good candidate due to its high saturation magnetization, high coercivity, strong anisotropy and excellent chemical stability [8]. Spinel type ferrite composites provide a novel platform for system integration in reactor engineering [10, 11]. Ferrite microtubes are promising materials for catalytic applications under radiofrequency (RF) heating due to their highly accessible open structures with large specific surface areas, adjustable Curie temperature and moderate magnetic losses in the kHz range [11]. When embedded into catalytic microparticles, they can be used as susceptors of RF heating [12, 13], which provides efficient and fast heat transfer into catalytic sites and flowing fluid [14-17].

The goal of this study is to develop a method to prepare one dimensional cobalt ferrite microtubes by a
template assisted sol-gel synthesis using natural cotton fiber as template. Influence of calcination temperature on the structural and magnetic properties, heat capacity and heating rate in the kHz range of the cobalt ferrites microtubes is presented.

2. Experimental

2.1 Preparation of cobalt ferrite microtubes

Cobalt ferrite microtubes were prepared via a template assisted sol-gel synthesis [18, 19]. Iron (III) nitrate nonahydrate, cobalt (II) nitrate hexahydrate, and citric acid were used as the main raw materials. The metal nitrates were dissolved in ethanol in required molar ratios to prepare solution A. Citric acid was dissolved in ethanol in a separate vessel to produce solution B. Solution B was added into solution A under acutely stir. The resulting mixture was stirred for 4 h and then it was quantitatively titrated by an ammonia solution to a pH of 2.5. The obtained sol was stirred for 24 h then it was absorbed by cotton fibers. These impregnated cotton fibers were dried in an oven at 353 K to get a cobalt ferrite dry gel. The dry gel was calcined at 873, 973, 1073, 1173 and 1273 K for 1 h to produce the corresponding ferrite microtubes. The heating rate during calcination was 2 K·min⁻¹ from room temperature to 573 K and then 5 K·min⁻¹ from 573 to the desired temperatures followed by a dwelling interval of 1 h at that temperature [18]. The cobalt ferrite microtubes are labeled as CF-T hereafter, where index T represents the calcination temperature in K.

2.2 Characterization of CoFe₂O₄ microtubes

The phase composition of the CoFe₂O₄ microtubes was determined using an X-ray diffractometer (X’Pert PRO) with nickel filtered Cu $K_\alpha$ radiation produced at 40 kV and 27.5 mA, at a scanning rate of
5° min⁻¹ and a step of 0.02°. The Scherrer equation was used to calculate the average crystal size \( (D, \text{ nm}) \), and the \( d_{(311)} \) interplanar spacing was determined from the position of the (311) peak using the Bragg equation, also the average lattice constant \( (a) \) were obtained using Bragg’s diffraction condition given by Eq. 1 [20]:

\[
\alpha = \frac{\lambda \sqrt{h^2+k^2+l^2}}{2 \sin \theta_{hkl}} \tag{1}
\]

The specific surface area of CoFe₂O₄ microtubes was determined by nitrogen adsorption at 77 K on a Micromeritics NOVA 1000E nitrogen adsorption apparatus.

The Raman spectra of CoFe₂O₄ microtubes were recorded in the Raman shift of 160-800 cm⁻¹ and carried out on a MKI-2000 spectrometer (Renishaw, UK) with a 532 nm excitation source, equipped with a 1040×256 Renishaw CCD camera, and a laser power of 50mW.

The morphology of CoFe₂O₄ microtubes was characterized by scanning electron microscopy (JSM-6700F, Jeol). Transmission electron microscopy was performed with a Tecnan F20 microscope (Philips) operated at 20 kV using the milled powders of CoFe₂O₄ microtubes.

The magnetization curves of the as-prepared samples were measured by a vibrating sample magnetometer (Princeton Measurements Corporation MicroMag 3900 VSM) equipped with a 2 Tesla electromagnet.

The specific heat capacity of the CoFe₂O₄ microtubes were determined by a STA 449C TG-DSC Analyser (Netzsch Thermische Analyser, Germany) fitted with an appropriate software. The samples (10 mg) were placed in platinum pans that were closed and heated under nitrogen flow of 60 mL/min from 305 to 575K at a heating rate of 5 K/min. Prior to the measurements, the instrument was calibrated under the same experimental conditions, with a sapphire disk (weight: 25.93 mg) [21]. The recommended
sapphire reference heat capacity data from the NIST database was used to adjust the results according to Eq. 2 [22, 23]:

\[
\frac{C_{p,\text{sam}}}{C_{p, \text{std}}} = \frac{H_{\text{sam}}-H_{\text{bsl}}}{M_{\text{sam}}} \div \frac{H_{\text{std}}-H_{\text{bsl}}}{M_{\text{std}}}
\]

where, \( C_p \) is the molar heat capacity, \( M \) is the sample weight, \( H \) is the heat effect. Subscripts bsl, std, sam are referred to an empty vessel, the standard sample (sapphire disk) and the ferrite sample, respectively.

The specific heating rates of the CoFe\(_2\)O\(_4\) microtubes were measured at a frequency of 295 kHz. The sample was placed in a quartz tube inserted along the center axis in a 50 mm RF coil connected to an Easy Heat RF system (Ambrell) operated at a current of 200 A. Prior to the measurements, a slurry of ferrite (10 mg) in deionized water (80 mg) was made to enhance heat transfer towards the temperature sensor. The slurry temperature was measured with a fiber optic sensor (FISO). The specific heating rate was calculated from the initial (linear) part of temperature vs time curves taken into account the specific heat capacities of the ferrite and water in the slurry and their weight fractions.

3. Results and discussion

3.1 Effect of calcination temperatures on the structural properties of the CoFe\(_2\)O\(_4\) microtubes

Figure 1 shows XRD spectra of CoFe\(_2\)O\(_4\) microtubes calcined at different temperatures. The sample calcined at 873 K has amorphous structure. A spinel phase is formed in the 973-1273 K range. The peaks are indexed with the standard pattern reported in JCPDF cards (#22-1086 for CoFe\(_2\)O\(_4\)). Below 1173 K, all samples show a sharp diffraction peak at 35.437º 2 theta, which is ascribed to the (311) plane. However, other peaks are rather wide which indicates that the obtained material has low degree of crystallinity [18].
Also, a minor amount of impurity, cubic Fe$_2$O$_3$, (labeled as A in Figure 1) is detected when calcination temperature is below 1073K. The presence of the cubic Fe$_2$O$_3$ phase can be explained by small discrepancies in molar ratios of metal nitrates or the segregation of metal oxides during the drying step. As the calcination temperature increases, the content of impurity gradually decreases and finally disappears at 1173K.

The average crystal size, interplanar spacing ($d_{311}$) and specific surface area of the microtubes calcined at different temperatures are listed in Table 1. It can be seen that the specific surface area decreases by a factor of nearly eight as the calcination temperature increases from 873 to 1273 K due to progressive aggregation of small crystallites into larger particles. When calcined at 1073 K, the average crystal size and the specific surface area are 66.9 nm and 46.5 m$^2$·g$^{-1}$, respectively. The latter value is nearly 10 times higher than that previously reported for Co ferrites [24]. This indicates that the template-assisted sol-gel
method can improve the specific surface area of the ferrites though it slightly increases the average crystal size at the same time. This is mainly due to the fact that highly porous structure is obtained in the template assisted method. As the calcination temperature increases, the \(d_{311}\) interplanar spacing approaches the value for the bulk \(\text{CoFe}_2\text{O}_4\) material.

Insert Table 1 here

<table>
<thead>
<tr>
<th>Samples</th>
<th>CF-873</th>
<th>CF-973</th>
<th>CF-1073</th>
<th>CF-1173</th>
<th>CF-1273</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average crystal size (nm)</td>
<td>A</td>
<td>34.1</td>
<td>66.9</td>
<td>123</td>
<td>168</td>
</tr>
<tr>
<td>Interplanar spacing ((d_{311}) nm)*</td>
<td>A</td>
<td>2.5228</td>
<td>2.5267</td>
<td>2.5289</td>
<td>2.5292</td>
</tr>
<tr>
<td>Specific surface area (m²·g⁻¹)</td>
<td>85.7</td>
<td>69.8</td>
<td>46.5</td>
<td>13.4</td>
<td>8.5</td>
</tr>
<tr>
<td>Cell parameters (\alpha) (nm)</td>
<td>A</td>
<td>0.837</td>
<td>0.838</td>
<td>0.839</td>
<td>0.839</td>
</tr>
</tbody>
</table>

A – Amorphous

*standard \(d_{311}\) interplanar spacing of \(\text{CoFe}_2\text{O}_4\) is 2.531 nm and unit cell parameters is 0.839 nm.

3.2 Raman spectra study of the \(\text{CoFe}_2\text{O}_4\) microtubes

It is known that \(\text{CoFe}_2\text{O}_4\) has a cubic inverted (or mixed) ferrite structure with a \(O_h^7\) symmetry (Fd3m space group), which gives rise to 39 normal vibrational modes, out of which five are Raman active [25, 26].

\[
A_{1g} + E_g + 3T_{2g}
\] (3)

Lattice distortion, local cation distribution and magnetic ordering can be determined by Raman
spectroscopy [25]. Figure 2 shows room temperature Raman spectra of the CoFe$_2$O$_4$ microtubes calcined at different temperatures. Five peaks with maxima near 684, 609, 466, 301, and 200 cm$^{-1}$ are observed in all spectra. The tetrahedral breath modes at 684 and 609 cm$^{-1}$ are assigned to symmetric stretching vibrations of oxygen atoms with respect to a metal ion in the tetrahedral void [25]. The other low frequency peaks are assigned to vibrations of metal ions in octahedral voids, i.e., $E_g$ and $T_{2g}$ [27]. These modes correspond to the symmetric and anti-symmetric bending vibrations of oxygen atom in the M–O bond in the octahedral voids [28]. The positions of the peaks are in line with the previously reported data [25, 29]. Our data confirm that all as-synthesized samples are CoFe$_2$O$_4$ with a cubic inverse-spinel structure. As the calcination temperature increases, the peaks shift to higher frequencies (Table 2) due to increased crystallite size [27]. The relative intensity of the peaks remained constant, indicating cation redistribution did not occur in the CoFe$_2$O$_4$ microtubes at higher calcination temperatures.

![Raman spectra of CoFe$_2$O$_4$ microtubes calcined at different temperatures.](image)

**Figure. 2** Raman spectra of CoFe$_2$O$_4$ microtubes calcined at different temperatures.

A: CF-873, B:CF-973, C: CF-1073, D: CF-1173, E: CF-1273

Insert here
Table 2. Positions of the peaks in the Raman spectra of the CoFe₂O₄ microtubes calcined at different temperatures[^25,26]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Raman shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₁g (1)</td>
</tr>
<tr>
<td>CF-873</td>
<td>675</td>
</tr>
<tr>
<td>CF-973</td>
<td>675</td>
</tr>
<tr>
<td>CF-1073</td>
<td>680</td>
</tr>
<tr>
<td>CF-1173</td>
<td>682</td>
</tr>
<tr>
<td>CF-1273</td>
<td>684</td>
</tr>
<tr>
<td>Reference</td>
<td>[25]</td>
</tr>
</tbody>
</table>

3.3 Effect of calcination temperature on the microstructure of CoFe₂O₄ microtubes

Figure 3 shows characteristic SEM images of the CoFe₂O₄ microtubes. It can be seen that one-dimensional isolated microtubes are obtained in the template-assembled sol-gel method. Their morphology, diameter as well as the ratio of length to diameter can be changed by increasing calcination temperature. The template consists of isolated fibers with a predominantly parallel orientation (Figure 3(a)). The individual fibers exhibit axial and vein-like texture with a diameter about 25 μm (Figure 3(b)). The most of microtubes have a length exceeding 50 μm and they are separated from each other (Figure...
3(c)). Calcination at 873 K results in amorphous microtubes with a mean diameter of 3-4 μm and a small number of individual crystals (Figure 3(d)). When calcined at 1073 K, the porous microtubes with a diameter in the range from 2 to 2.5 μm and an aspect ratio above 20 are produced. They consist of rather uniform particles with a size about 80 nm (Figure 3(e)). Calcination at 1273 K results in larger particles exceeding 180 nm while the microtube diameter decreases to 2.0 μm (Figure 3(f)).

Insert Figure 3 here
TEM images show that the CoFe$_2$O$_4$ microtubes are formed by individual nanoparticles (Figure 4). The particles form irregular polyhedrons with mean sizes between 20 and 120 nm that are connected by necks. The magnetic attraction force is responsible for agglomeration of particles during calcination and results in this specific shape. As the calcination temperature increases, the amount of amorphous phase decreases and the nanoparticle size increases.
3.4 Effect of calcination temperature on the magnetic properties of CoFe$_2$O$_4$ microtubes

Room temperature hysteresis loops for the CoFe$_2$O$_4$ microtubes calcined at different temperatures are shown in Figures 5(a) and (b) and their magnetic parameters are listed in Table 3.
As the calcination temperature increases from 873 to 1073 K, the saturation magnetization increases, the coercivity monotonously decreases while the Curie temperature remains rather constant. The remnant magnetization first increases and then decreases (Table 3).

It is known that the saturation magnetization in nanoparticles is influenced by both the intrinsic and extrinsic factors [30-33]. The former are composition, preferential site occupancy of the cations, exchange effect, while the latter are microstructure and grain size. The samples with low degree of crystallinity obtained at relatively low calcination temperatures have a high defect density and a higher proportion of surface to internal atoms. In these samples, a relatively larger number of surface atoms is responsible for a disordered state of magnetic moment. Therefore they cannot be easily magnetized when applying an external magnetic field. On the other hand, the existence of defects also hinders the rotation of atomic magnetic moments to the external field direction during the magnetization process. These two factors lead to a lower saturation magnetization. As the calcination temperatures increases, both the particle size and crystallinity increase. This reduces the influence of the thermal disturbance of the surface atoms on the

Figure 5. Magnetization curves of CoFe$_2$O$_4$ microtubes calcined at different temperatures

(a) external field ranged between -20 and 20 kOe; (b) external fields ranged between -2.5 and 2.5 kOe

As the calcination temperature increases from 873 to 1073 K, the saturation magnetization increases, the coercivity monotonously decreases while the Curie temperature remains rather constant. The remnant magnetization first increases and then decreases (Table 3).

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magnetic moment. The magnetic structure becomes more ordered, resulting in a higher saturation magnetization [34]. The exchange interaction between the cobalt ferrite phase and impurity in ferrites decreases as the amount of impurity gradually decreases and finally disappears at higher calcination temperatures. This results in a decrease of the saturation magnetization [30, 35]. Namely, with the increase of calcination temperatures, the variety of particle size and degree of crystallinity would always result in an increase of the saturation magnetization while the exchange interaction in its decrease [32, 35]. It appears that the combined effect of exchange interaction and crystal size levels out a monotonous increase of saturation magnetization in these samples.

Insert Table 3 here

Table 3. Magnetic properties of CoFe$_2$O$_4$ microtubes calcined at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CF-873</th>
<th>CF-973</th>
<th>CF-1073</th>
<th>CF-1173</th>
<th>CF-1273</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetization (emu/g)</td>
<td>52.3</td>
<td>61.4</td>
<td>73.3</td>
<td>76.6</td>
<td>81.2</td>
</tr>
<tr>
<td>Remnant magnetization (emu/g)</td>
<td>19.6</td>
<td>29.0</td>
<td>35.4</td>
<td>33.3</td>
<td>31.2</td>
</tr>
<tr>
<td>Ratio of $M_r/M_s$</td>
<td>0.37</td>
<td>0.47</td>
<td>0.48</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>Coercivity (Oe)</td>
<td>1208</td>
<td>1137</td>
<td>910</td>
<td>731</td>
<td>586</td>
</tr>
<tr>
<td>Curie temperature (K)</td>
<td>803</td>
<td>798</td>
<td>798</td>
<td>798</td>
<td>803</td>
</tr>
<tr>
<td>$\epsilon_p \times 10^{-5}$ (erg/cm$^3$)</td>
<td>A</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Critical particle size (nm)</td>
<td>A</td>
<td>44.0</td>
<td>30.9</td>
<td>28.3</td>
<td>25.2</td>
</tr>
</tbody>
</table>

A – Amorphous
The coercivity of magnetic materials is mainly affected by particle size, magnetic anisotropy, stress anisotropy and magnetic domain structure [36]. As for cobalt ferrite, anisotropy is mainly provided the incompletely quenched orbital angular momentum of the Co$^{2+}$ ions. As the calcination temperature increases, the anisotropy constant of Co$^{2+}$ decreases, which decrease the coercivity of cobalt ferrite. The transition from single to multidomain region occurs at a critical particle size which was estimated by Eq. 4 [37]. The critical particle sizes are listed in Table 3.

\[
d_{cr} = \frac{9e_p}{2\pi M_s} \quad \text{(in CGS units)}
\]

where \(M_s\) is the saturation magnetization and \(e_p\) is the surface energy of the domain wall calculated by Eq. 5 [38].

\[
e_p = \left( \frac{2k_BT_cK_1}{a} \right)^{0.5}
\]

where \(k_B\) is the Boltzmann constant (1.38×10$^{-16}$ erg·K$^{-1}$), \(T_c\) the Curie temperature, \(a\) is the lattice parameter, and \(K_1\) is the absolute value of magnetocrystalline anisotropy constant. The anisotropy constant only slightly changes with composition [37, 38], therefore \(K_1\) was assumed to be constant and equal to 5.10×10$^4$ erg/cm$^2$ [36, 39].

A comparison of average crystal size (Table 1) and critical size (Table 3), suggests that all cobalt ferrite samples have a multidomain structure. Their coercivity is inversely proportional to the grain size [40, 41] (Eq. 6).

\[
H_c = p_c \frac{\sqrt{AK_1}}{M_sD}
\]

where \(p_c\) is a dimensionless factor, \(A\) is the exchange constant. The coercivity data (Table 3) agreed well
with predictions of Eq.6. The remnant magnetization reaches the maximum value of 35.42 emu/g in the sample calcined at 1073 K. This is in line with the data previously reported by Ma [42].

3.5 Heat capacity measurements of CoFe$_2$O$_4$ microtubes

The isobaric molar heat capacity (C$_{p,m}$) of CoFe$_2$O$_4$ microtubes was measured in the 308 – 573 K temperature range (Figure 6). The C$_{p,m}$ data were fitted by a second order polynomial function [21]:

$$Cp = A + B\times T + C\times T^2$$

(7)

The parameter values are listed in Table 4. Weak temperature dependence of the samples calcined at higher temperatures is due to improved crystallinity in samples. The Kopp's law can be used to calculate the specific heat capacity of CoFe$_2$O$_4$ (Eq. 8) [43]:

$$C_v = \sum n_i C_{v,i}$$

(8)

where $n_i$ is the atomicity of element ‘i’ in compound, and $C_{v,i}$ is the specific heat capacity of element ‘i’ in compound. As for CoFe$_2$O$_4$, $C_{v,Co}$, $C_{v,Fe}$ and $C_{v,O}$ are 24.81, 25.10 and 16.70 J·mol$^{-1}$·K$^{-1}$, respectively. The calculated value of specific heat capacity of CoFe$_2$O$_4$ is 141.81 J·mol$^{-1}$·K$^{-1}$.

![Figure 6. Molar heat capacity of CoFe$_2$O$_4$ microtubes as a function of temperature.](image-url)
3.6 Hysteresis loss and specific heating rate of CoFe$_2$O$_4$ microtubes

The hysteresis loss is proportional to the area between the two magnetization curves and it is an important factor in evaluating the performance of materials used as susceptors of RF field [44, 45]. The hysteresis loss can be approximated as a function of coercivity and saturation magnetization [18] (Eq. 9):

$$ P = C_0 \cdot H_c \cdot M_s $$

(9)

where $C_0$ is a constant, which shows the ratio of the actual hysteresis loss to that in the case in which the magnetization curves form a rectangle with edges of $M_s$ and $H_c$. The calculated hysteresis loss (kJ/mol, $M_s \times H_c$) and Experimental hysteresis loss($P$, kJ/mol ) are listed in Table 5.
It can be seen that a good agreement is obtained between the predicted and experimental values of hysteresis loss in the whole temperature range, as the constant $C_o$ hardly varied. A slightly wave of $C_o$ may derives from the choice of boundary value during the integrated process. Also, it can be seen clearly that the higher the saturation magnetization and coercivity, the more heat is produced/cycle of the magnetization reversal process. However, the latter is only true if the external field magnitude can reach the saturation magnetization in the ferrites [11]. Therefore, although these magnetic materials could theoretically produce more heat, in practice there are technical restrictions imposed on the amplitude of the applied field. In this study, the amplitude of magnetic field inside the coil was limited to 500 Oe, therefore, the heating rate is proportional to the actual hysteresis loss inside the coil. The latter is proportional to the area enclosed between the two magnetization curves and two vertical lines corresponding to magnetic field intensity of -500 and 500 Oe.

The experimental specific heating rate of CoFe$_2$O$_4$ microtubes calcined at different temperatures is listed in Table 5. It can be seen that the sample CF-973 exhibits the highest specific heating rate of 0.293

<table>
<thead>
<tr>
<th>Samples</th>
<th>CF- 873</th>
<th>CF - 973</th>
<th>CF - 1073</th>
<th>CF - 1173</th>
<th>CF -1273</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated hysteresis loss ($kJ \cdot m^{-3}, M_s \times H_c$)</td>
<td>66.9</td>
<td>84.83</td>
<td>94.9</td>
<td>76.7</td>
<td>60.8</td>
</tr>
<tr>
<td>Experimental hysteresis loss($P$, $kJ \cdot m^{-3}$)*</td>
<td>50.8</td>
<td>66.2</td>
<td>70.8</td>
<td>59.4</td>
<td>47.4</td>
</tr>
<tr>
<td>Value of $C_o$</td>
<td>0.76</td>
<td>0.78</td>
<td>0.75</td>
<td>0.77</td>
<td>0.78</td>
</tr>
<tr>
<td>Specific heating rate ($K/(s \cdot mg)$)**</td>
<td>0.246</td>
<td>0.293</td>
<td>0.267</td>
<td>0.230</td>
<td>0.179</td>
</tr>
</tbody>
</table>

* Integrated region lies between -5kOe -5kOe,

**A coil with 500Oe field are used to test the heating rate of samples

It can be seen that a good agreement is obtained between the predicted and experimental values of hysteresis loss in the whole temperature range, as the constant $C_o$ hardly varied. A slightly wave of $C_o$ may derives from the choice of boundary value during the integrated process. Also, it can be seen clearly that the higher the saturation magnetization and coercivity, the more heat is produced/cycle of the magnetization reversal process. However, the latter is only true if the external field magnitude can reach the saturation magnetization in the ferrites [11]. Therefore, although these magnetic materials could theoretically produce more heat, in practice there are technical restrictions imposed on the amplitude of the applied field. In this study, the amplitude of magnetic field inside the coil was limited to 500 Oe, therefore, the heating rate is proportional to the actual hysteresis loss inside the coil. The latter is proportional to the area enclosed between the two magnetization curves and two vertical lines corresponding to magnetic field intensity of -500 and 500 Oe.

The experimental specific heating rate of CoFe$_2$O$_4$ microtubes calcined at different temperatures is listed in Table 5. It can be seen that the sample CF-973 exhibits the highest specific heating rate of 0.293
K/(s·mg), which is 1.5 times higher than that of sample CF-1273, also higher than that of CF-1073.

4. Conclusions

One dimensional CoFe$_2$O$_4$ microtubes with the length exceeding 50 µm and with high specific surface area and magnetic saturation have been successfully prepared by the template-assisted sol-gel method. The cobalt ferrite spinel was the main phase for all samples. As the calcination temperature increased, the diameter, specific surface area and coercivity of microtubes monotonously decreased while the average crystal size and saturation magnetization increased. When calcined at 1073 K, a porous cobalt ferrite microtubes with a diameter in the range from 2 to 2.5 µm and an aspect ratio above 20 were produced, which consisted of rather uniform particles with a size about 80 nm, the specific surface area and average crystal size were 46.5 m$^2$·g$^{-1}$ and 66.9 nm. The specific surface area in the microtubes was near 10 times higher than that in the cobalt ferrite nanoparticles obtained at same conditions. The highest saturation magnetization equaled to 81.2 emu/g when calcined at 1273K and the highest coercivity was 1208 Oe at 873 K. The heat capacity was obtained as a function of temperature, value of the microtubes calcined at 973 K was 140.81 J·mol$^{-1}$·K$^{-1}$ at 395K. The microtubed calcined at 973 K, demonstrated the highest specific heating rate of 0.293 K/(s·mg) in RF field of 295 kHz.

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