

# The effects of hydrothermal temperature and time on structure and magnetic properties of lanthanum-substituted zinc ferrites

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Received: 26 October 2018 / Accepted: 18 January 2019 / Published online: 11 March 2019 © Springer-Verlag GmbH Germany, part of Springer Nature 2019

#### Abstract

The ZnFe<sub>2</sub>O<sub>4</sub> and ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> zinc ferrites had been prepared by the hydrothermal method. The detection method using in this investigation was X-ray diffraction, scanning electronic microscope, Fourier transformed infrared spectrometer (FTIR), and vibrating sample magnetometer. The results indicated that the samples had spinel structures. This study revealed that the crystallite size, lattice constant, and X-ray density of samples were decreased, while prolonged holding time and increased temperature, whereas the crystallite size was increased with the temperature increasing. Four absorption bands were observed in FTIR spectra and assigned to the corresponding site bonds. The saturation magnetization ( $M_S$ ), coercivity, magnetic moment, and anisotropy constant (K) were affected by the holding time and temperature. Anisotropy constant proved dependence on the temperature, and it increased with the enhancement of temperature.

## 1 Introduction

Cancer diseases and cardiovascular are the two leading causes of death worldwide. In the present, cancer is commonly treated by the combination of surgery, radiation therapy, and chemotherapy. However, surgical treatment is only suitable for patients with tumors which have not yet metastasized, and chemotherapy kills normal cells as well as cancerous. These side effects have great limitation in their application. Magnetic nanoparticles (MNPs) are perceived as promising materials for magnetic resonance imaging agents, biomedical drug carriers, magnetic hyperthermia [1-3], etc, due to their superior magnetic properties and high specific surface. MNPs can also be targeted to tumor site in a magnetic field, which had importance in cancer therapy [4]. In this regard, MNPs have shown great potential in targeted drug delivery for cancer treatment [5]. For example, in magnetically targeted drug delivery, carriers comprising

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of coated MNPs loaded with anti-cancer drug are injected into the patient body via the human circulatory system, or are able to transport pharmaceuticals to a specific site in the body when facilitated by an external magnetic field [6, 7]. The latter, it can prolong the drug at the relevant cells, and more concentrated doses of drug. The researches on the MNPs of crystallite size, morphology, magnetic properties, and biocompatibility have become an attractive field of biomaterial in recent years. Researchers studied on homogeneity particle size and size distribution, morphology, and agglomerate size of the most important parameters in MNPs by the synthesis process of MNPs [8-10], different transition metal cations [11–13], surface modification technology of material [14, 15], and has yielded the certain result. Zhang et al. found that grain size and maximum magnetization increased with the increasing sintering temperature and Yang et al. found that  $H_c$  and  $M_S$  varied with increasing sintering temperature [16, 17], MNPs were coated with multifunction polymers that can be used to improve the conglomeration and reduce the side effects on normal cells and tissues [18, 19]. Some experiments demonstrate that longlasting hyperthermia could effectively induce the apoptosis of tumor cells, and finally suppress the tumor growth within a certain period of time [19–21].

The research background of this paper is based on the preparation of zinc ferrites magnetic materials for tumor therapy by magnetic hyperthermia. Based on the works in the literature, research of size, morphology, and magnetic

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properties for  $ZnFe_2O_4$  ferrites was studied with different prepared methods. Some researchers reported that induces structural modification as well as improvement in magnetic properties by the introduction of rare-earth elements [22, 23]. However, at present, there were no detailed articles about lanthanum (La)-doped zinc ferrites magnetic were synthesis by hydrothermal, which intrigued by our interest to prepared samples of  $ZnLa_{0.5}Fe_{1.5}O_4$  by hydrothermal. The  $ZnFe_2O_4$  and  $ZnLa_{0.5}Fe_{1.5}O_4$  zinc ferrites had been prepared through hydrothermal method on the condition of the diverse parameters, and the influence of temperature and holding time on microstructure and magnetic properties of zinc ferrites was studied.

## 2 Experimental details

ZnFe<sub>2</sub>O<sub>4</sub> and ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> zinc ferrites were synthesized by hydrothermal method. FeCl<sub>3</sub>·6H<sub>2</sub>O (ferric chloride), La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (lanthanum nitrate), and ZnCl<sub>2</sub> (zinc chloride) were used as the starting chemical reagents without any further purification for the synthesis. Aqueous solutions of ferric chloride, zinc chloride, and lanthanum nitrate are prepared by adding 40 ml of deionized water and all the solutions were added and mixed thoroughly using a magnetic stirrer for 30 min, and 0.25 ml of NaOH of 2 mol/l was dropwised into the previous solution under stirring continuously at room temperature, until the pH of the solution stabilized 10. After tending a stable pH value, after some time of inactivity, the upper clear liquid was removed, and the remnant mixture was transferred to Teflon lined sealed stainless steel autoclaves and kept inside an oven for 12 h at different temperatures, 170 °C, 180 °C, 200 °C, respectively, and maintained at 180 °C for 10 h, 11 h, and 13 h, respectively. The autoclave was taken from the oven and natural cooling to room temperature. Then, the sample was washed thoroughly three times using by deionized water and anhydrous ethanol, respectively, and the sample dried in the oven for 24 h at a temperature of 80 °C was obtained the dried sample. The dried sample was grinded in a mortar and pestle until fine powder of ZnFe<sub>2</sub>O<sub>4</sub> and ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> was obtained.

Techniques such as X-ray diffraction (XRD), Fourier transformed infrared spectrometer (FTIR), scanning electronic microscope (SEM), and vibrating sample magnetometer (VSM) were used to characterize the prepared  $ZnFe_2O_4$  and  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoferrites at room temperature. For all the samples, the XRD powder patterns were recorded on Rigaku D/max 2550 diffractometer using the Cu K $\alpha$  as radiation source to analyze the prepared samples as the  $2\theta$  position from 20° to 80°. The functional groups and chemical bonds existing in prepared samples were identified on Nicolet iS10 spectra in the wavenumber range of

4000–400 cm<sup>-1</sup>. A pellet was created of 95% KBr with 5% prepared nanoferrites for FTIR spectral analysis. The morphology microstructures were investigated with a QUANTA 650FEG scanning electronic microscope (SEM). Magnetic measurements of prepared samples were performed using a PPMS-9VSM with an applied magnetic field of -15 kOe to 15 kOe.

## 3 Results and discussion

#### 3.1 XRD analysis

Figure 1 shows the XRD spectra of the samples of ZnFe<sub>2</sub>O<sub>4</sub> and ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> at 180 °C with different holding times, and Fig. 2 shows the XRD spectral of the samples of ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> for 12 h with different temperatures, respectively. The main reflection planes (220), (331), (400), (422), (511), and (440) are appeared in Figs. 1 and 2, which matched well with the JCPDS date (#22-1012). However, for the sample at 200 °C, some less intense impurity phases were found in XRD spectra, which matched well with the JCPDS date (#36-1481). The result indicated that La(OH)<sub>3</sub> was existence. The reason may be higher doping concentration and leads to the increase of potential barrier for  $La^{3+}$  ion to enter into spinel crystal lattice. Consequently, a small amount of La La<sup>3+</sup> was remained, and La(OH)<sub>3</sub> was formation. Besides, La<sup>3+</sup> ion-substituted zinc ferrites  $(ZnLa_{0.5}Fe_{1.5}O_4)$  nanoparticles had a stronger diffraction intensity and sharp diffraction, compared with zinc ferrite  $(ZnFe_2O_4)$ . The results indicated that crystallite size of  $ZnLa_{0.5}Fe_{1.5}O_4$  was larger than crystallite size of  $ZnFe_2O_4$ , which may be due to the substitution of relatively smaller



Fig. 1 Powder XRD date for ZnLa $_{0.5}$ Fe $_{1.5}$ O<sub>4</sub> and ZnFe $_2$ O<sub>4</sub> with different holding times at 180 °C



Fig.2 Powder XRD date for  $ZnLa_{0.5}Fe_{1.5}O_4$  with different temperatures

ionic radius size Fe (0.64 Å) ions with larger ionic radius La (1.06 Å) ions. It was also verified that crystallite size of the samples was calculated using Scherrer formula [24], and the results are given in Table 1.

The lattice constant  $a_t$  was calculated using the software and further confirmed by the following relation [25], and the results are given in Table 1.

The X-ray density for all composition was calculated [26], the results are given in Table 1.

Based on the data in Table 1,  $\rho_{X-ray}$  of  $ZnFe_2O_4$  and  $ZnLa_{0.5}Fe_{1.5}O_4$  at 180 °C increased, while increasing holding time, it was due to a reduction in volume.

Figure 3 displays variation of true lattice constant  $a_t$  against holding time. It showed that lattice constant  $a_t$  of ZnFe<sub>2</sub>O<sub>4</sub> and ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> decreased with increasing holding time, which was in good agreement with the literature [27]. It can also be seen that the lattice constant  $a_t$  of ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> was greater than that of ZnFe<sub>2</sub>O<sub>4</sub>, it may be rare earth of La ion getting substituted in the lattice [28].



Fig. 3 ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> of lattice constant  $a_t$  with different holding times at 180 °C

Figure 4 shows  $ZnLa_{0.5}Fe_{1.5}O_4$  and  $ZnFe_2O_4$  of crystallite size with different holding times at 180 °C. According to the Ostwald Ripening theory [29], extending the holding time can effectively promote the crystallite size growth, this explained that crystallite size of  $ZnFe_2O_4$  increases with the increasing holding time. Nevertheless, crystallite size of  $ZnLa_{0.5}Fe_{1.5}O_4$  decreased with the increasing of holding time. The reason was maybe that mismatch of small size  $Fe^{3+}$  (0.64 Å) ion was substituted by large size  $La^{3+}$  (1.06 Å) and formed the crystalline anisotropy, which leaded to the creation of volume strain of the crystallite with holding time increasing [30]. The crystallite size decreased with prolonging holding time, which leaded to the volume strain relaxed, and balanced between volume strain and crystal anisotropy was achieved [11].

Figure 5 displays both the crystallite size *D* increased and true lattice constant  $a_t$  against temperature risen. It was worth to note that the crystallite size was strongly affected by the temperature. Higher temperature resulted the more

Table 1	Lattice constant
$a_{\rm t}$ , cryst	allite size D, cell
volume	V and X-ray density of
ZnLa <sub>05</sub>	$Fe_{15}O_4$ and $ZnFe_2O_4$

Composition	Tempera- ture (°C)	Holding time (h)	Lattice con- stant, $a_t$ (Å)	Crystallite size, D (nm)	Volume (Å <sup>3</sup> )	X-ray density $\rho_{X-ray}$ (g/cm <sup>3</sup> )
ZnFe <sub>2</sub> O <sub>4</sub>	180	10	8.4436	6.1	601.98	5.3195
ZnFe <sub>2</sub> O <sub>4</sub>	180	11	8.4425	6.3	601.74	5.3230
ZnFe <sub>2</sub> O <sub>4</sub>	180	12	8.4413	6.4	601.49	5.3250
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	10	8.4612	15.0	605.75	5.4218
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	11	8.4513	14.9	603.63	5.4409
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	12	8.4474	14.6	602.79	5.4485
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	13	8.4454	14.3	602.37	5.4523
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	170	12	8.4513	13.7	603.63	5.4409
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	200	12	8.4440	16.1	602.07	5.4550



Fig.4 ZnLa\_{0.5}Fe\_{1.5}O\_4 and ZnFe\_2O\_4 of crystallite size with different holding times at 180  $^{\circ}\rm C$ 



Fig. 5 ZnLa $_{0.5}$ Fe $_{1.5}$ O<sub>4</sub> of lattice constant  $a_t$  and crystallite size D with different temperatures

vapor pressure in the Teflon reactor and the greater pressure on the crystal cells, which limited the growth of crystal cell and reduced the lattice constant  $a_t$ . However, for crystallite size, the increasing rate of nucleation rate was slower than that of crystal growth rate as temperature increasing and the granularity of crystallite size was bigger. Another reason was the higher probability of crystallite collision with higher the temperature, which was prone to form large-scale particles.

#### 3.2 FTIR spectroscopy

The FTIR spectrum of the prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoferrites is shown in Figs. 6 and 7. The FTIR spectrum of Fig. 6 indicated that  $ZnLa_{0.5}Fe_{1.5}O_4$  and  $ZnFe_2O_4$  were basically consistent. It indicated that  $La^{3+}$  successfully replaces  $Fe^{3+}$  and enters the lattice without changing the crystal structure. The FTIR spectrum showed two absorption bands which were the characteristic absorption bands



Fig. 6 FTIR spectra of the prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoferrites with different holding times



Fig. 7 FTIR spectra of the prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoferrites with different temperatures

of spine nanoferrites. The lower frequency absorption band  $\nu_1$  lied in around 420 cm<sup>-1</sup>, corresponding to the band that was the intrinsic stretching vibration of the between the oxygen ion and octahedral site metal ion (Fe–O). Higher frequency absorption band  $\nu_2$  lied in around 560 cm<sup>-1</sup>, corresponding to the band that was the intrinsic stretching vibration of the between the oxygen ion and tetrahedral site metal ion (Zn–O) [31]. Compared to the values of  $\nu_1$ , the values of  $\nu_2$  were higher. Because of the normal mode in ferrite spine, the vibration of the octahedral cluster was lower than that the tetrahedral cluster for the shorter bond length of the tetrahedral (Zn<sup>2+</sup>) clusters than that of the octahedral (Fe<sup>3+</sup>) clusters [32,

Table 2 EDS pattern of the sample at temperature 180  $^{\circ}\mathrm{C}$  and holding time 10 h

Element types	O (%)	Fe (%)	Zn (%)	La (%)
Theoretical weight%	22.65	29.62	23.15	24.58
EDS	24.09	31.49	24.73	19.69



Fig. 8 SEM image of the  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoparticles at temperature 180  $^\circ C$  and holding time 10 h

33]. Besides, the two weak absorption bands of  $\nu_3$  and  $\nu_4$  were observed in the FTIR spectra, which were in around 880 cm<sup>-1</sup>, and 1050 cm<sup>-1</sup>, respectively. Divalent ions Zn<sup>2+</sup> in the A-sites leaded to the band  $\nu_3$  generation [34]. The presence of complexes Fe<sup>4+</sup>–O<sup>2-</sup> and/or La<sup>4+</sup>–O<sup>2-</sup> was duo to the band  $\nu_4$  assigned to the tetravalent metal ion-oxygen. The electron hopping between the La<sup>3+</sup> and Fe<sup>3+</sup> ions may cause the tetravalent ions of La<sup>4+</sup> and Fe<sup>4+</sup> produce [35–37].

#### 3.3 Morphology characterization

The morphology of  $ZnLa_{0.5}Fe_{1.5}O_4$  for the temperature 180 °C and holding time 10 h was observed by SEM. Figure 8 shows the SEM image of  $ZnLa_{0.5}Fe_{1.5}O_4$  sample. The Nano measurer software was used to calculate the particle size. The average particle size of the sample was 19 nm, which was approximate with the Scherrer formula result (15 nm). In addition, EDS analyses showed that the sample was composed of O, Fe, Zn, and La elements. As shown in Table 2, the elements of EDS analyses were close to the stoichiometric ration. These results indicated that  $La^{3+}$  ions were successfully introduced into the zinc ferrites (Fig. 9).



Fig. 9 Elemental analysis by EDS spectrum of the ZnLa $_{0.5}$ Fe $_{1.5}$ O<sub>4</sub> nanoparticles at temperature 180 °C and holding time 10 h



Fig. 10 Hysteresis loops for  $ZnLa_{0.5}Fe_{1.5}O_4$  samples at 180 °C with different holding times

## 3.4 Magnetic analysis

The obtained magnetic hysteresis loops by VSM for the as-prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  nano-ferrite samples at different holding times and different temperatures are shown in Figs. 10 and 11, respectively. The values of saturation magnetization ( $M_S$ ) for all samples at different holding times and different temperatures are listed in Table 3. Results depicted that the curves have a small coercivity and saturation magnetization, which was characteristic of the soft magnetic materials.

Figure 10 shows that the saturation magnetization value of the prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  nanoferrite was 34, 16.0, and 4.7 emu/g at different holing times, 10 h, 12 h, and 13 h, respectively. The saturation magnetization for the samples decreased with increasing the holding time. In the previous XRD analysis, we had already known that crystallite size of  $ZnLa_{0.5}Fe_{1.5}O_4$  decreased with increasing holding



Fig. 11 Hysteresis loops for  $ZnLa_{0.5}Fe_{1.5}O_4$  samples at 12 h with different temperatures

time. With holding time prolonging, the crystallite size of the samples decreased, which increased the surface effect [30]. The structure at the surface is distorted and the atoms on the surface are strained to produce various interatomic spacing, low coordination numbers, and vacancies which in turn breaks the exchange bonds of the surface atoms leading to spin disorder [38]. Crystallite size of the sample decreased due to increase holding time, and decreasing crystallite size leaded to the increase of spins disordering which resulted in the reduction of saturation magnetization. Besides, Fig. 10 shows that the saturation magnetization value of the prepared  $ZnLa_{0.5}Fe_{1.5}O_4$  (D=14.6 nm) and  $ZnFe_2O_4$  (D=6.4 nm) was 16 and 13 emu/g, respectively. It can be found that the influence of crystallite size on saturation magnetization was not significant. The observed behavior could be attributed to the factors: In the spinel ferrite, the saturation magnetization is dominated by the super-exchange interactions between the tetrahedral (Zn-sites) and octahedral (Fe-sites) sites cations. La<sup>3+</sup> ions were not magnetic, because La<sup>3+</sup> ions were zero magnetic moment, and La<sup>3+</sup> ions do not take part in the exchange interactions to the nearest neighboring ions. Hence, it will decrease the number of magnetic linkages occurring between tetrahedral and octahedral cations.

Figure 11 shows that the  $M_{\rm S}$  value of the prepared ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> nanoferrite was 35, 16.0, and 16.2 emu/g at different temperatures, 170 °C, 180 °C, and 200 °C, respectively. Results showed that saturation magnetization of the sample at 170 °C was higher compared with the samples at 180 °C and 200 °C. The observed behavior could be attributed to two the factor: the irregularity of magnetic moment arrangement in crystal increased with the advance of temperature in action. Thus, the value of saturation magnetization was reduced. On the other hand, with increasing temperature, the crystallite size of the samples increased, and increasing crystallite size leaded to the decrease of spins disordering which resulted in the increase of saturation magnetization value changes up and down randomly.

The values of coercivity for the samples for different holding times at 180 °C are listed in Table 3. The coercivity of the samples increased, while the holding time prolong. It could be due to the presence of magnetic multi-domain in the sample. In the multi-domain region, the variation of coercivity with the crystallite size can be expressed as the following equation [30]:

$$H_{\rm C} = e + \frac{f}{D},\tag{1}$$

where 'e' and 'f' are constants and 'D' is the crystallite size.

Hence, the coercivity increases, as the crystallite size decreases in the multi-domain region.

However, we have observed that coercivity increased with the temperature (crystallite size increase with the increase temperature). It may be formula single domain at particular temperature (170 °C and 200 °C). In a single domain region, the variation of coercivity with the crystallite size was expressed as the equation [30]:

$$H_{\rm C} = g - \frac{h}{D^2},\tag{2}$$

where g and h are constant. Hence, coercivity increases with the increase in crystallite size in the single domain region.

The magnetic moment  $n_{\rm B}$  per atom in Bohr magneton units ( $\mu_{\rm B}$ ) could be calculated using the following relation [39]:

Table 3 Saturation
magnetization $(M_S)$ , coercivity
$(H_{\rm c})$ , remnant magnetization
$(M_{\rm r})$ , magnetic moment $(n_{\rm B})$ ,
and anisotropy constant $(K)$

Composition	Tempera- ture (°C)	Holding time (h)	$M_{\rm S}$ (emu/g)	$M_{\rm r}$ (emu/g)	$H_{\rm c}$ (Oe)	$n_{\rm B}~(\mu_{\rm B})$	K (erg/Gauss)
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	10	34	3	23	1.722	814.58
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	12	16	0.3	153	0.811	2550
ZnFe <sub>2</sub> O <sub>4</sub>	180	12	13	0.3	32	0.562	433.33
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	180	13	4.7	0.1	157	0.238	768.64
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	170	12	35	1.2	46	1.772	1667.80
ZnLa <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	200	12	16.5	0.46	165	0.836	2835.9

$$n_{\rm B} = \frac{M \times M_{\rm S}}{N \times \beta},\tag{3}$$

where *M* is the molecular weight, *N* is the Avogadro's number and  $\beta$  is the conversion factor to express the magnetic moment per atom in Bohr magnetons (it value is  $9.27 \times 10^{-21}$  erg/Gauss). The obtained values of  $n_{\rm B}$  are given in Table 2. It was clear that  $n_{\rm B}$  varies similar to  $M_{\rm S}$ , and this was considered as an indicator of the total magnetization for the samples [35, 36].

The anisotropy constant *K* can be evaluated using the following equation [35, 36]. The obtained values of *K* are listed in Table 3:

$$H_{\rm C} = \frac{0.96K}{M_{\rm S}}.\tag{4}$$

Results showed that the values of anisotropy constants (*K*) for the samples  $ZnLa_{0.5}Fe_{1.5}O_4$  increase with the temperature increasing. The anisotropy constants of the nanoparticles depend on the crystallite size [40]. It (*K*) increases with the temperature increasing (as the crystallite size increases with the temperature) due to minimization of the surface effect. The value of *K* for the samples  $ZnLa_{0.5}Fe_{1.5}O_4$  and  $ZnFe_2O_4$ , our result for un-doped sample was small comparable to the  $La^{3+}$  doped samples. It may be surface effect and cation distribution combined effects of value *K*.

### 4 Conclusion

ZnLa<sub>0.5</sub>Fe<sub>1.5</sub>O<sub>4</sub> nanoparticles were synthesized by hydrothermal method with different reaction conditions, including reaction temperature and reaction holding time, which causes appreciable changed in the structural and magnetic properties. The lattice constant and crystallite size were dependent for the samples with holding time and temperature. The lattice constant and crystallite size for the samples decreased with the increase of holding time at 180 °C. The lattice constant of the samples decreased with the temperature increasing, while the crystallite size increased with the temperature increasing. The magnetic properties were influenced surface effect for the samples at different holding times and temperatures. Anisotropy constant increases with the increasing of crystallite size, and it increased with the temperature increasing.

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**Funding** This work were supported by the planned Science and Technology project of Hunan Province, China (2016TP1028) and supported by the double first-class discipline construction program of Hunan province.

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