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An investigation on physical properties of strontium hexaferrite nanopowder synthesized by a sol–gel auto-combustion process with addition of cationic surfactant

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Abstract

In this study a novel sol–gel auto-combustion method, using *n*-decyltrimethylammonium bromide as a cationic surfactant, has been used to synthesize strontium hexaferrite nanocrystalline powder. The dried nitrate–citrate gel, prepared from a solution of ferric nitrate, strontium nitrate, citric acid, trimethylamine and cationic surfactant, exhibited an auto-combustion behavior after ignition in air. The formation reaction temperature, phase identification, crystallites size, particles size distribution and morphology of resultant strontium hexaferrite powder were investigated by DTA/TGA, FTIR, XRD, LPSA, TEM and SEM techniques. The results showed that in presence of the cationic surfactant, the combustion intensity increases and the crystallite size decreases. The crystallite size of strontium hexaferrite powder in sample with surfactant calcined at 800 °C was 27.2 nm.

Keywords: Strontium hexaferrite; Nano; Sol–gel; Surfactant

1. Introduction

Strontium hexaferrite has been intensively investigated during the last decades due to its technological interest as a permanent magnet and magnetic recording media. The magnetic properties of this material are largely dependent on the microstructure and its processing routes.[1,2]

Several techniques have been used to prepare strontium hexaferrite, in which wet chemical routes have advantages such as excellent product homogeneity, better compositional control and lower processing temperatures.[3]

Among the different chemical routes, the sol–gel auto-combustion method has received considerable attention because of its relatively simple synthesis scheme. In this route metallic complexes are prepared in an aqueous solution and then heated till form a high viscous gel. The pyrolysis of this gel results in a homogeneous powder. As-burnt powder is then calcined for formation of a single phase strontium hexaferrite.[4]

Addition of cationic surfactant with amphiphilic molecules (hydrophilic head and hydrophobic tail) into precursor solution results in formation of reverse micelles in the gel. Placing the aqueous ions inside these micelles can be effective in controlling the nucleation and growth of the particles (Fig. 1). Due to the existence of surfactant, the surface tension of solution is also reduced, which reduces the energy of the formation of the new phase.[5,6]

In this work, the strontium hexaferrite was synthesized by a sol–gel auto-combustion method and the influences of the addition of cationic surfactant on the synthesis procedure and the physical properties of the resultant nanopowder have been studied.

2. Experimental

Appropriate amounts of ferric nitrate (Merck, ≥98%), strontium nitrate (Merck, ≥99%) and citric acid (Merck, ≥99.5%) powders were dissolved into distilled water. Then trimethylamine solution (Merck, ≥50%) was slowly added to adjust the pH at 7. In another sample the powder of *n*-cetyltrimethylammonium bromide surfactant (Merck, ≥99%) with molar ratio of surfactant to strontium equal to 0.4 was

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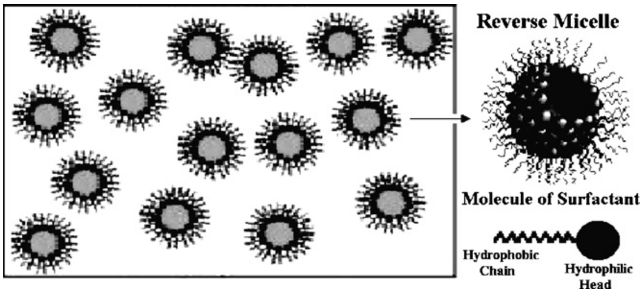

Fig. 1. Placing the aqueous ions inside the reverse micelles.

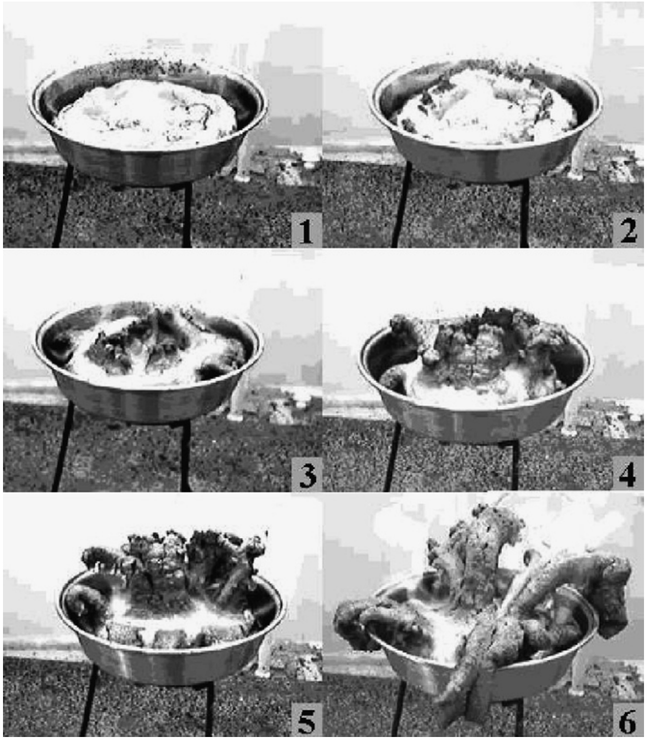

Fig. 2. Self-propagating combustion stages of the citrate–nitrate gel containing cationic surfactant.

also added. The resultant solutions were slowly evaporated until gels formation. These gels were dried and then heated on a plate until the combustion took place automatically. As-burnt powders were calcined at 800, 850 and 900 °C for 1 h for investigation of a temperature at witch single phase strontium hexaferrite could be formed.

The thermal behavior of as-burnt powders was evaluated by simultaneous thermo gravimetric (TG) and differential thermal analysis (DTA). X-ray diffraction (with Cu Kα radiation) was used for phase identification and also determining of the crystallites size by applying the Scherrer formula.[7] Residual organic compounds in as-burnt powders were investigated by Fourier transformed infrared (FTIR) spectroscopy. The particles size distribution was studied by laser particles size analysis (LPSA). The morphology of Sr-hexaferrite powders was also observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

The experimental observations showed that nitrate–citrate gel, in both samples exhibits a self-propagating combustion behavior and after completion of the combustion, a fluffy powder was formed. The whole process was completed within a minute. In sample containing surfactant the combustion had more removal gases and the obtained powder was more voluminous. Fig. 2 shows the ignition of the gel with surfactant. During the combustion, large amount of gases were liberated.

Fig. 3 presents the FTIR spectra of as-burnt powders. The spectrums show the hydroxyl and carboxyl bands of citric acid at about 3420 and 1620 cm^{-1}, respectively. The bands locate at 1380 and 990 cm^{-1}, are related to the nitrate. The bands at 1460, 860 and 690 cm^{-1} are attributed to strontium carbonate. A set of bands fewer than 650 cm^{-1} are also due to the iron-oxide.[8] It is noticeable that in sample prepared with surfactant the bands of citric acid and nitrate are very weak. It reveals that the citrate and nitrate ions take part more complete in the reaction; a reaction in which citrate ion is oxidized and nitrate ion is reduced. It could be deduced that in presence of a surfactant the released heat in the exothermic reaction is sufficient for more complete combustion and conversion of nitrate and citrate ions to metal oxides, because surfactant also plays as a fuel and increases the heat of combustion.

The DTA and TG curves of as-burnt powders in air are shown in Fig. 4. The first exothermic peak in DTA curve is attributed to burning of the residual organic matters, and the second exothermic peak to the formation of Sr-hexaferrite phase. The TG curve also shows two distinct stages of weight loss at same temperatures.[9,10] The formation temperature of Sr-hexaferrite in sample containing surfactant is lower.

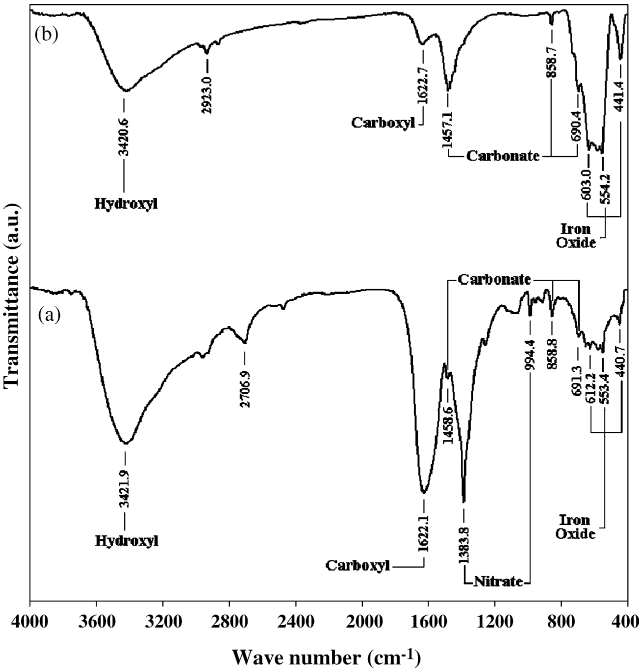

Fig. 3. FTIR spectra of as-burnt powder in samples (a) without surfactant and (b) with surfactant.

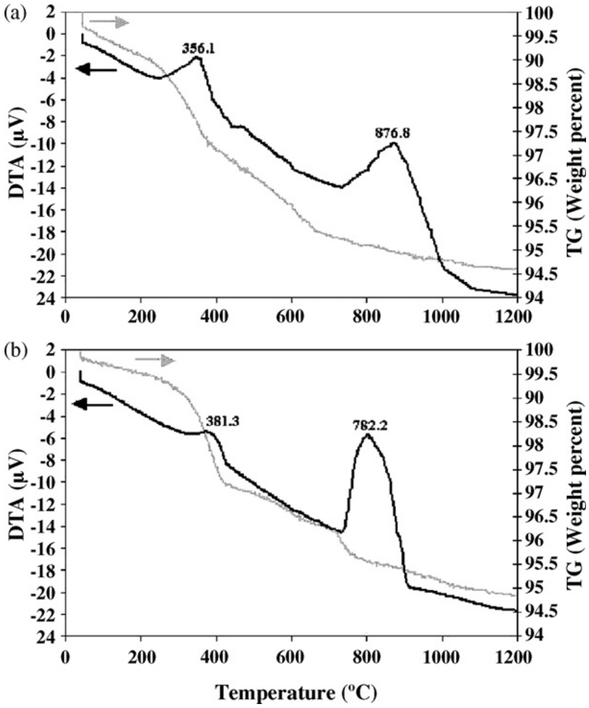

Fig. 4. DTA/TG curves for the as-burnt powders of specimens (a) without surfactant and (b) with surfactant.

The XRD patterns of as-burnt and calcined powders of both samples in various temperatures are shown in Fig. 5. XRD patterns of as-burnt powders show the presence of γ-Fe_2O_3 (maghemite) as a major phase and some $SrCO_3$. In sample with surfactant α-Fe_2O_3 (hematite) phase, could be seen as well. By calcination at 800 °C, a single phase strontium hexaferrite is formed in sample containing surfactant while in sample without surfactant a trace of the α-Fe_2O_3 phase remained but by calcination at 900 °C single phase strontium hexaferrite is formed.

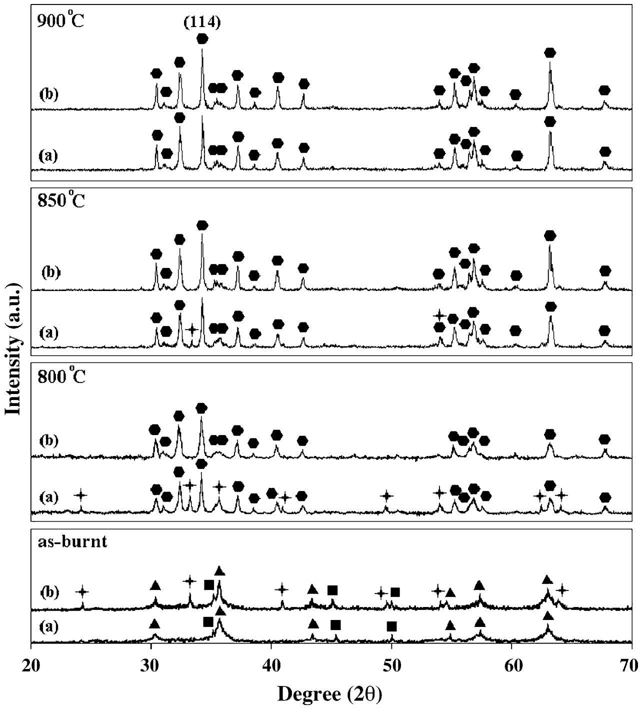

Fig. 5. XRD patterns of as-burnt and calcined powders at various temperatures for samples (a) without surfactant and (b) with surfactant (■ Sr-carbonate; ▲ maghemite; ✚ hematite; ⬢ Sr-hexaferrite).

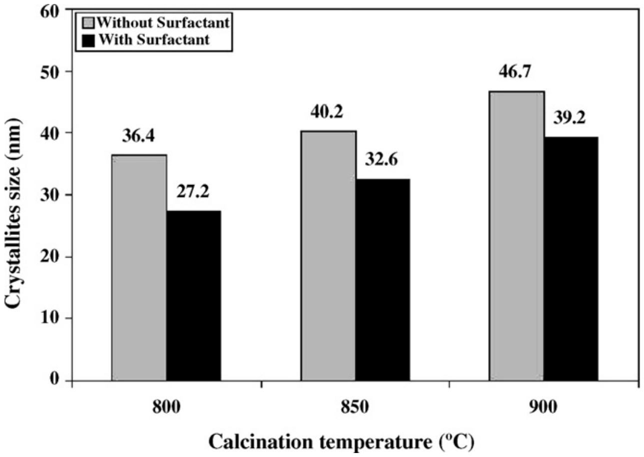

Fig. 6. Comparison of the crystallite size of the synthesized powders at various calcination temperatures in samples prepared without surfactant and with surfactant.

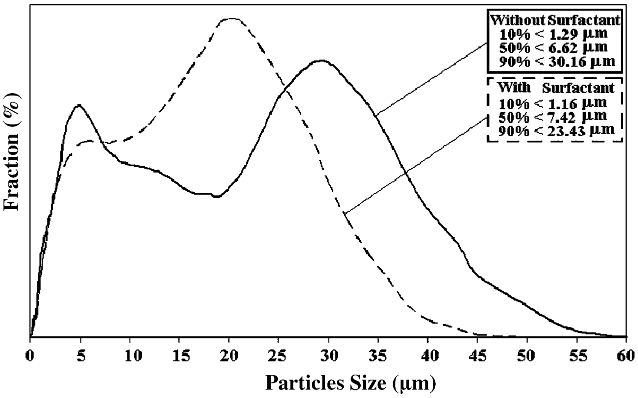

Fig. 7. The particles size distribution of powders without surfactant and with surfactant calcined at 900 °C for 1 h.

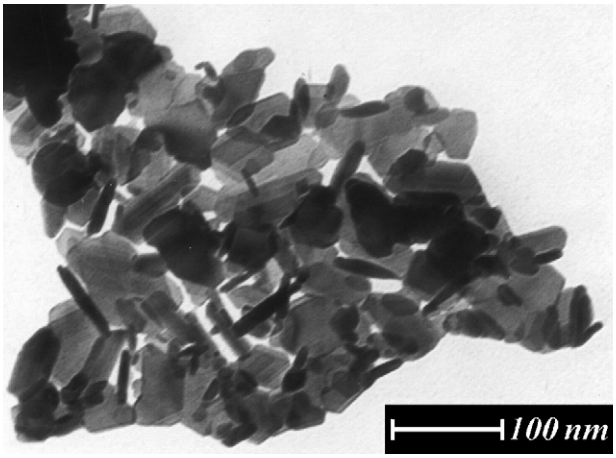

Fig. 8. TEM photograph of the sample synthesized with surfactant, calcined at 800 °C for 1 h.

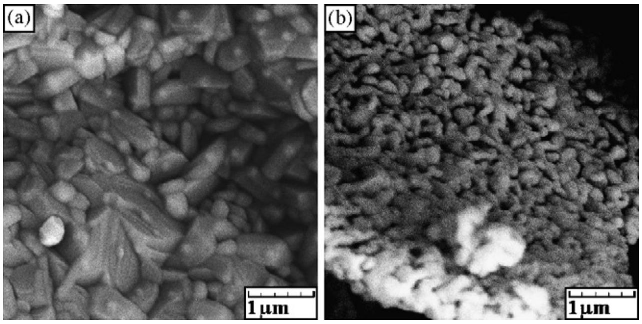

Fig. 9. The morphology of the Sr-hexaferrite powder calcined at 900 °C for 1 h in the specimens (a) without surfactant and (b) with surfactant.

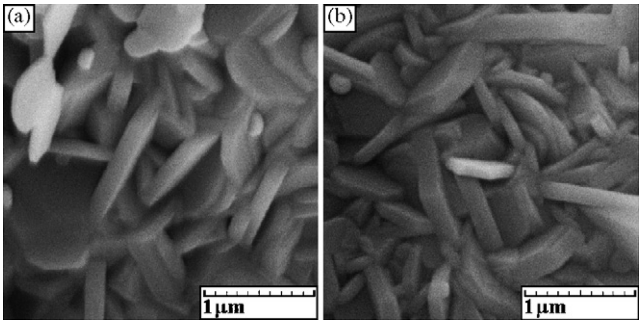

Fig. 10. The morphology of the Sr-hexaferrite powder calcined at 1100 °C for 3 h in the specimens (a) without surfactant and (b) with surfactant.

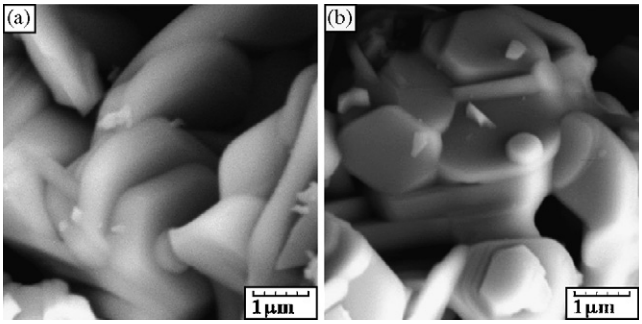

Fig. 11. The morphology of the Sr-hexaferrite powder calcined at 1200 °C for 3 h in the specimens (a) without surfactant and (b) with surfactant.

The crystallite size of strontium hexaferrite powders calcined at different temperatures in both samples are shown in Fig. 6. Crystallite size of single phase Sr-hexaferrite powder in sample with surfactant is about 27.2 nm (by calcination at 800 °C) while in sample without surfactant is 46.7 nm (by calcination at 900 °C).

The particles size distribution of both samples calcined at 900 °C were measured by LPSA technique and are shown in Fig. 7. Note that the curve of particles size distribution for sample with surfactant is narrower. In this sample the formation of micelles in gel controls growth rate of crystallites. Bimodal distribution curve is due to the agglomeration of particles. Since the powders are agglomerated, LPSA shows the sizes, greater than actual amounts.

Fig. 8 shows the TEM photograph of the sample synthesized with surfactant calcined at 800 °C for 1 h which indicates that the powder is completely nanocrystalline.

In Fig. 9 the particles size of the strontium hexaferrite powder has been compared for samples without and with surfactant, both calcined at 900 °C for 1 h. However, the morphology of the particles could be seen much better at the higher temperatures. Then Figs. 10 and 11 show the SEM micrograph of the samples calcined at 1100 and 1200 °C for 3 h, respectively. It is observed that the particles possess a plate-like hexagonal shape. It is also seen that the particles size in sample with surfactant is finer.

4. Conclusions

A nanocrystalline Sr-hexaferrite powder was produced by a surfactant-assisted sol–gel auto-combustion method. The results showed that with cationic surfactant addition into precursor, the calcination temperature decreases from 900 to 800 °C along with the reduction of the crystallites size from 46.7 to 27.2 nm. Particles size distribution of strontium hexaferrite powder is also narrower in sample containing surfactant.

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