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Optimization of the Fe/Sr Ratio in Processing of Ultra-Fine Strontium Hexaferrite Powders by a Sol-Gel Auto-combustion Method in the Presence of Trimethylamine

S. Alamolhoda[1], S. A. Seyyed Ebrahimi[1] and A. Badiei[2]*

[1]*Center of Excellence in Magnetic Materials, Department of Metallurgy and Materials, University of Tehran, Tehran, Iran*

[2]*Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran*

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Abstract

A novel sol-gel auto-combustion method has been used to synthesize ultra-fine particles of strontium hexaferrite. The gels were prepared from metal nitrates and citric acid by various molar ratios of Fe/Sr and trimethylamine as pH adjusting agent. The results showed that the gel exhibits a self-propagating behavior after ignition in air. The combustion product was calcined at 800°C to form strontium hexaferrite. The obtained powders were characterized by XRD, SEM and FTIR techniques. The optimum molar ratio was Fe/Sr=10 with crystallite size about 37 nm. The FTIR and XRD results showed that the combustion product contains γ-Fe_2O_3 as the main phase and some amount of $SrCO_3$ and α-Fe_2O_3.

Keywords: *Strontium hexaferrite, Sol-Gel, trimethylamine, Combustion, FTIR, XRD.*

Introduction

Strontium hexaferrite, which is a hard magnetic material, has been extensively used as a permanent magnet due to its low cost, relatively high coercivity, corrosion resistance and chemical stability (Huang *et al.,* 2003(38)).

The conventional method of production of this material is solid-state reaction between $SrCO_3$ and Fe_2O_3 at temperatures higher than 1100°C. This method has inherent disadvantages as chemical inhomogenity, coarse grain size and entrance of impurities during milling process (Huang *et al.,* 2003(38), Huang *et al.,* 2003 and Sivakumar *et al.,* 2004). In order to get pure crystalline single domain particles of strontium hexaferrite, different synthesis techniques have been developed, such as: Hydrothermal synthesis (Liu *et al.,* 1999), salt melt method (Guo *et al.*,1997), co-precipitation (Ataie and Heshmati-Manesh, 2001) and sol-gel method (Garcia *et al.,* 2001).

The sol-gel auto-combustion method is one of the pathways for the preparation of nanocrystalline strontium hexaferrite. This route is based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuel, giving a voluminous product with large surface area (Alamolhoda *et.al.*, 2004, Huang *et al.,* 2003). In order to obtain single-phase strontium hexaferrite at lower calcination temperatures, controlling the molar ratio of Fe to Sr is very important. This ratio varies with change in starting materials and with change in method of production (Zhong *et al.,* 1997). In the present study, a solution of metal nitrates and citric acid and trimethylamine has been used to prepare strontium hexaferrite. Then the effect of the Fe/Sr ratio on the powder characteristics has been investigated.

Experimental

$Fe(NO_3)_3.9H_2O$, $Sr(NO_3)_2$ and citric acid of Merck were used as starting materials. The metal nitrates with different molar ratios of Fe to Sr were dissolved together in a minimum amount of deionized water to get a clear solution. Citric acid was added to the solution and then ammonia solution was slowly added to adjust the pH at 7. The solution was slowly heated on a hot plate with continuous stirring to evaporate the water and finally a viscous brown gel was obtained. The gel was heated and automatically burnt with glowing flints. The combustion products with different molar ratios of Fe/Sr were then calcined at 800°C.

The phase identification of the calcined powders was recorded by XRD (X-ray diffractometer) with Cu K_α radiation. The average crystallite size of powders was also measured by X-ray line broadening technique employing the Scherrer formula ($t = 0.9\lambda/\beta\cos\theta$) using the profiles of (114) peak (Huang *et al.,* 2003). In this equation t is the average crystallite size, λ = 1.54Å which is the wave length of Cu K_α radiation, β is the width of (114) peak at half of its maximum intensity and θ is the location of the peak (Cullity, 1978). The combustion product of the specimen with optimum molar ratio of Fe/Sr was characterized with X-ray diffraction pattern and the combustion product of some specimens was characterized by FTIR spectra. The particle morphology was studied by a scanning electron microscope (SEM) as well.

Results and discussion

Figure 1 shows the XRD patterns of the specimens calcined at 800°C with molar ratios of Fe/Sr =12, 11, 10, and 9. The specimen with molar ratio of Fe/Sr=10 is pure hexaferrite while the other specimens have a small amount of residual α-Fe_2O_3. The amount of residual α-Fe_2O_3 in the specimen with molar ratio of Fe/Sr =12 and 11 is more than the specimen with molar ratio of 9. It shows that the presence of strontium ions for the formation of hexaferrite is more necessary than the presence of iron ions. When the ratio of Fe/Sr is higher than the optimum ratio, lack of Sr^{2+} ions causes the formation of α- Fe_2O_3.

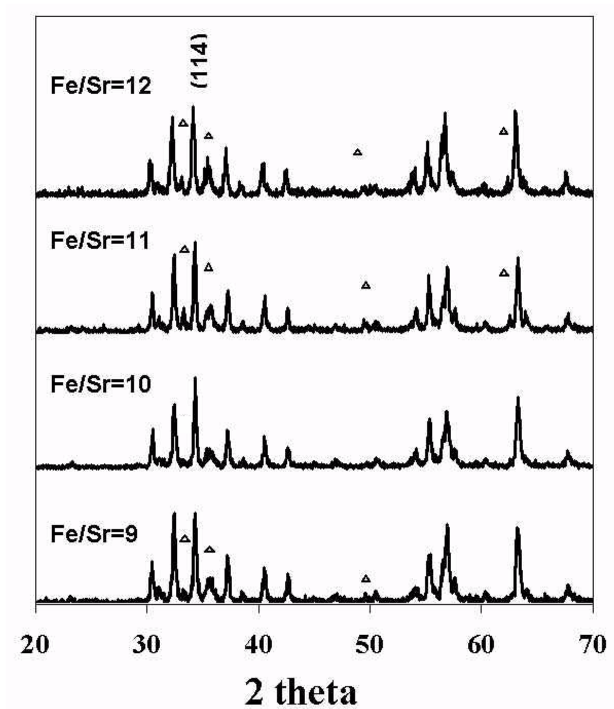

Figure 1. X-ray diffraction pattern of specimens with molar ratios of Fe/Sr equal to 12, 11, 10 and 9 calcined at 800°C for 1 hour (Δ: α-Fe_2O_3).

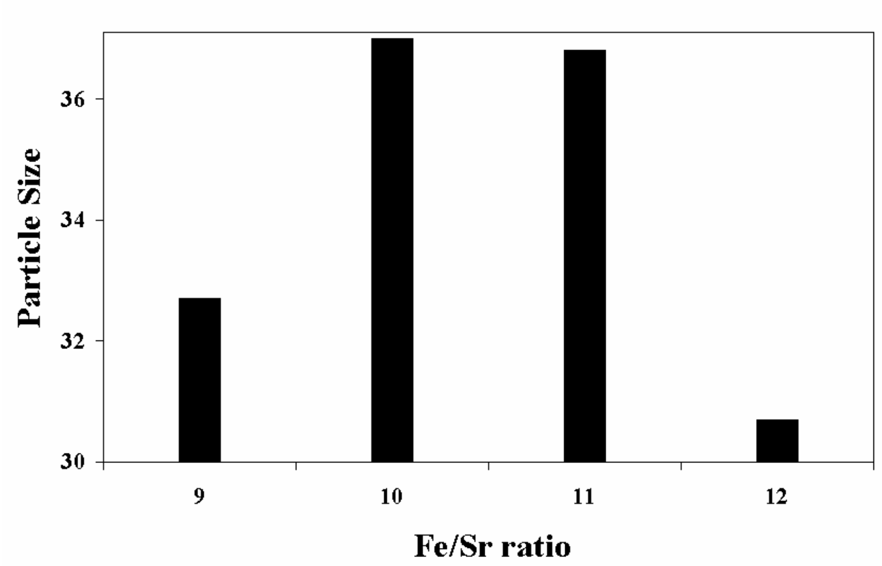

Figure 2. Particle size verse Fe/Sr ratio.

The crystallite size of powders with different molar ratios of Fe/Sr calcined at 800°C, which was calculated from Scherrer formula, was presented in figure 2. It could be observed that the mean particle sizes of samples are about 30 to 37 nm. The specimen with molar ratio of Fe/Sr=10 has the largest particle size at calcined temperature. It can be ascribed to its formation at a lower temperature and increase the crystal size at high temperature.

The X-ray diffraction pattern of the combustion product of the specimen with molar ratio of Fe/Sr=10 was shown in figure 3. It could be observed that γ-Fe_2O_3 is the main phase in the combustion product. The presence of strontium carbonate and α-Fe_2O_3 peaks in the combustion product was observed. The broaden peak width of XRD pattern shows the small particle size of product.

Figure 4 shows the FTIR spectra of the combustion product of specimen for Fe/Sr=10. The IR spectra provide the evidence for the presence of carbonate ions, γ-Fe_2O_3 and α-Fe_2O_3 in the combustion product. The transmittance bands at 1600 cm^{-1} attributed to CO_3^{2-} ions of $SrCO_3$. The vibration bands at 438 and 626 cm^{-1} are belonging to γ-Fe_2O_3 and α-Fe_2O_3, respectively. The comparison of FTIR results with XRD results show that they are in agreement with each other. Finally, in all specimens, the combustion product consists of various percentages of γ-Fe_2O_3, $SrCO_3$ and α-Fe_2O_3.

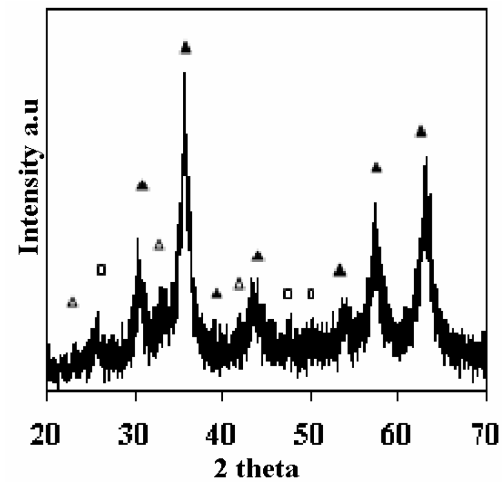

Figure 3. X-ray diffraction pattern of combustion product of the specimen with molar ratio of Fe/Sr=10 (Δ: α-Fe_2O_3, ▲: γ-Fe_2O_3, □:$SrCO_3$).

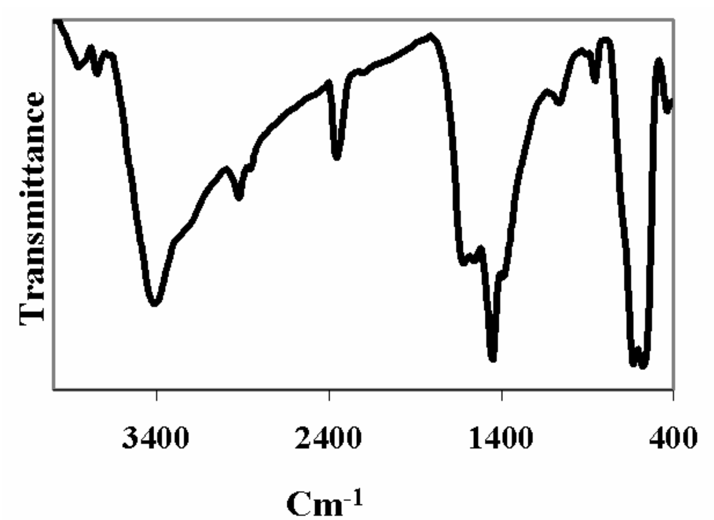

Figure 4. FTIR spectra of the combustion product of specimen with molar ratio of Fe/Sr=10.

The morphology of the particles of strontium hexaferrite could not be observed by SEM in specimens calcined at 800, 900 and 1000°C because the particles were very small. The larger particles were observed at 1100°C for 3 hours. Figure 4 indicates the plate-like particles of strontium hexaferrite with a mean particle size of 3 μm at this temperature.

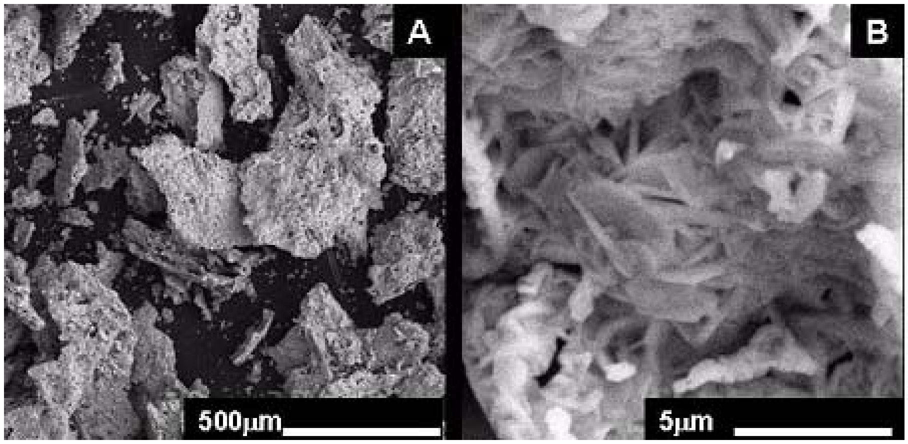

Figure 5. The morphology of the particles of strontium hexaferrite calcined at 1100 C for 3 hours.

Conclusions

A novel sol-gel auto-combustion method has been used to synthesize ultra-fine particles of strontium hexaferrite. The gels were prepared from metal nitrates, citric acid and trimethylamine as pH adjusting agent. The results showed that the nitrate citrate gel exhibits a self-propagating behavior after ignition in air. The combustion product which is a voluminous product with large surface area consists of γ-Fe_2O_3 as the main phase and some amount of α-Fe_2O_3 and $SrCO_3$. Ultra-fine strontium hexaferrite powder with crystallite size of about 37 nm have been produced after calcination of combustion product with the molar ratio of Fe/Sr = 10 in air at 800°C. When the molar ratio of Fe/Sr is not 10, strontium hexaferrite would not be single phase and it would contain some amount of residual α-Fe_2O_3. So the optimum molar ratio of Fe/Sr is 10 in this method.

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