Synthesis of strontium hexaferrite nanoparticles prepared using co-precipitation method and microemulsion processing

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Abstract. Strontium hexaferrite (SrFe$_{12}$O$_{19}$) nanoparticles have been prepared with co-precipitation in aqueous solutions and precipitation in microemulsion system water/SDS/n-butanol/cyclohexane, using iron and strontium nitrates in different molar ratios as a starting materials. The mixed Sr$^{2+}$ and Fe$^{3+}$ hydroxide precursors obtained during the reaction between corresponding metal nitrates and tetramethylammonium hydroxide (TMAH), which served as a precipitating reagent, were calcined in a wide temperature range, from 350 °C to 1000 °C in a static air atmosphere. The influence of the Sr$^{2+}$/Fe$^{3+}$ molar ratio and the calcination temperature to the chemistry of the product formation, its crystallite size, morphology and magnetic properties were investigated. It was found that the formation of single phase SrFe$_{12}$O$_{19}$ with relatively high specific magnetization (54 Am$^2$/kg) was achieved at the Sr$^{2+}$/Fe$^{3+}$ molar ration of 6.4 and calcination at 800 °C for 3h with heating/cooling rate 5 °C/min. The prepared powders were characterized using X-ray diffractometry (XRD) and specific surface area measurements (BET). The specific magnetization (DSM-10, magneto-susceptometer) of the prepared samples was measured.

1. Introduction
M-type hexaferrites, with chemical formula of MeFe$_{12}$O$_{19}$, (Me = Ba, Sr and Pb) have been widely used as permanent magnet with great technical importance attracted an extensive attention for the last few decades. It was widely used in the fabrication of computer data storage, high-density perpendicular magnetic and magneto-optic recording, magnetic fluids and certain microwave devices [1,2]. For ideal performance, ultrafine strontium hexaferrite powder ($\approx$ 0.1 µm) with homogeneous particle size distribution and controlled magnetic properties is important [3]. It is difficult to obtain ultrafine and monodispersed particles by the commercial ceramic method (solid-state reaction) which involves the firing of stoichiometric mixture strontium carbonate and $\alpha$-iron oxide at high temperatures (about 1300 °C) [4].

In order to achieve highly homogeneous ultrafine particles of M-type hexaferrite, various techniques were investigated, such as chemical co-precipitation method [5], hydrothermal method, plasma spraying, sol-gel method [6] and microemulsion method [7].

The objective of the present work is to give possible explanation and to investigate the influence of Sr$^{2+}$/Fe$^{3+}$ molar ration and the addition of surfactants on the synthesis of nanocrystalline strontium hexaferrite particles by chemical co-precipitation and microemulsion methods using nitrate precursors.
2. Experimental procedure

Chemical reagents used in this synthesis method were strontium nitrate anhydrous (Sr(NO$_3$)$_2$, 98 %, Alfa Aesar), iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, ACS, 98.0-101.0 %, Alfa Aesar); 25 % aqueous solution of tetramethylammonium hydroxide (TMAH) ((C$_4$H$_{13}$NO), Applichem); cyclohexane (C$_6$H$_{12}$, ACS, 99+ %, Alfa Aesar); sodium n-dodecyl sulfate (SDS) (CH$_3$(CH$_2$)$_{11}$OSO$_3$Na, 99 %, Sigma Aldrich) and 1-butanol (CH$_3$(CH$_2$)$_3$OH, 99 %, Alfa Aesar).

The co-precipitation method and microemulsion method were applied for the preparation of SrFe$_{12}$O$_{19}$ precursors. Prior to synthesis, aqueous solutions of strontium and iron nitrate with various Sr$^{2+}$/Fe$^{3+}$ molar ratios (1/12, 1/8, 1/6.9 and 1/6.4) were prepared.

In co-precipitation method Sr(II) and Fe(II) hydroxide precursors were precipitated during the reaction between the aqueous solution of metal nitrates and 0.5-M aqueous solution of tetramethylammonium hydroxide (TMAH), which served as a precipitating reagent. The precipitation was performed at room temperature and pH value of 12.6. The brownish precursors was washed several times with a mixture of distilled water and ethanol (1:1) and dried at 100 °C.

The microemulsion system used in this study consisted of sodium n-dodecyl sulfate (SDS) as the surfactant, 1-butanol as the cosurfactant, cyclohexane as the continuous oil phase and an aqueous solution of reactants as the dispersed phase. Two microemulsions (I and II) with identical composition and different reagents in aqueous phase were prepared. The aqueous phase in microemulsion I comprised a mixture of strontium and iron nitrate aqueous solutions in the molar ratios from 1/6.4 to 1/12. Although a molar ratio of 1/12 should be sufficient according to stoichiometry, an excess of strontium nitrate was necessary because strontium hydroxide is partially soluble in water [8]. The aqueous phase in microemulsion II comprised the 0.5-M solution of tetramethylammonium hydroxide (TMAH) served as a precipitation agent. The brownish precipitate of metal hydroxides appeared within the nanosized aqueous droplets after the two microemulsions were mixed at room temperature and pH 10.7. The precursor was washed several times with a mixture of distilled water and ethanol (1:1) and dried at 100 °C.

The dried precursors were characterized using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in air with a heating rate of 10 °C/min. Based on the results of these analysis, which will be discussed latter, the dried precursor was calcined in air under different conditions (temperature from 350 °C up to 1000 °C for 3h).

The phase analysis of the calcined particles was done by powder XRD (X-ray diffractometer using CuKα radiation ($\lambda = 0.1542$ nm). The magnetic measurements for the calcined particles were carried using magneto-susceptometer (DSM-10).

3. Results and discussion

The typical TGA and DTA curve of the dried precursor prepared with co-precipitation method and microemulsion method at Sr$^{2+}$/Fe$^{3+}$ molar ratio 1/6.4 are indicated in Figure 1.

The DTA curve of the samples prepared by co-precipitation method indicated an endothermic peak at 116.8 °C and two exothermic peaks at 262 °C and 719.3 °C, respectively. The endothermic peak was due to the vaporization of residual solvent and water from the precursor. The first exothermic peak was associated with the decomposition of residual organic precipitating agent and the second one could be attributed to a phase transition, i.e. the crystallization process of strontium hexaferrite.

On the other hand, when we prepared precursor by microemulsion method, the DTA curve indicated an endothermic peak at 116.4 °C and three exothermic peaks at 255.7 °C, 288.7 °C and 735.1 °C, respectively. The first and the second exothermic peak was associated with the decomposition of residual surfactant and residual organic precipitating reagent, while the third exothermic peak could be attributed to a phase transition and formation of strontium hexaferrite.

The thermogravimetric analyses TGA showed a continuous weight loss from room temperature to about 730 °C. Theoretically, the transformation of the dried precursor hydroxides (Sr(OH)$_2$ and Fe(OH)$_3$) into their oxides (SrO and Fe$_2$O$_3$) and further into hexagonal ferrite structure, at a molar ratio
of Sr/Fe 1/6.4, during the calcination in air led to a weight loss of around 24 %, which was in a good agreement with the experimental results (Figure 1).

Further, to confirm the above results, the precursors obtained in co-precipitation and microemulsion method was calcined from 350 °C up to 1000 °C for 3h and characterized by XRD. Pure single phase strontium hexaferrite (SrFe\(_{12}\)O\(_{19}\)) was obtained when the hydroxide precursor prepared at Sr\(^{2+}\)/Fe\(^{3+}\) molar ration of 1/6.4 was calcined at 800 °C for 3h with a heating/cooling rate 5 °C/min (Figure 2). To estimate the average crystallite size (\(D_{XRD}\)) of pure strontium hexaferrite (SrFe\(_{12}\)O\(_{19}\)) a Debye-Scherrer formula was used. The average crystallite size established from the peak (114) was 30 nm. The prepared samples had a high specific surface area (BET) of around 35 m\(^2\)/g . Mean particle size (\(D_{BET}\)) was calculated from the BET data according to \(D_{BET} = 6/[\rho_{th}S_{BET}]\), where \(S_{BET}\) is the measured surface area and \(\rho_{th}\) is the theoretical density of the compound. The average particle size of the strontium hexaferrite annealed at 800 °C for 3h with a heating/cooling rate 5 °C/min was about 33 nm.

The effect of Sr\(^{2+}\)/Fe\(^{3+}\) molar ratio on the formation of SrFe\(_{12}\)O\(_{19}\) was investigated. Figure 3a shows the magnetic properties of strontium hexaferrite prepared by co-precipitation and microemulsion method with different Sr\(^{2+}\)/Fe\(^{3+}\) mole ratios and calcined at 800 °C for 3h with heating/cooling rate 5
°C/min. With increasing the Sr\(^{2+}/Fe^{3+}\) molar ratio from 1/6.4 to 1/12, the saturation magnetization decreased from 54 to 36 Am\(^2/\)kg due to the formation of nonmagnetic phase α-Fe\(_2\)O\(_3\).

To explain the effect of calcination temperature on the formation of SrFe\(_{12}\)O\(_{19}\), a series of experiments were carried out at different calcination temperatures ranging from 350 °C to 1000 °C. Figure 3b shows the magnetic properties of strontium hexaferrite prepared by co-precipitation and microemulsion method with Sr\(^{2+}/Fe^{3+}\) mole ratio 1/6.4 and calcined at different temperatures for 3h with heating/cooling rate of 5 °C/min. With increasing the calcination temperature the saturation magnetization gradually decreased due to the presence of nonmagnetic phase. Thus, the maximum specific magnetization was obtained for the pure single-phase Sr-hexaferrite samples prepared after the annealing of hydroxide precursors with the Sr\(^{2+}/Fe^{3+}\) mole ratio 1/6.4, at 800 °C for 3h.

Figure 3: The magnetic properties of strontium hexaferrite prepared by co-precipitation and microemulsion method with a) different Sr\(^{2+}/Fe^{3+}\) mole ratios, calcined at 800 °C for 3h and b) Sr\(^{2+}/Fe^{3+}\) mole ratio 1/6.4 and calcined at different temperatures 3h.

4. Conclusion
The observations from TG/TD analysis, XRD and magnetic measurements we can summarized as follows:
- The precursors of nanocrystalline particles of SrFe\(_{12}\)O\(_{19}\) with average particle size around 30 nm and relatively high specific magnetization (54 Am\(^2/\)kg) were successfully prepared by co-precipitation and microemulsion methods using nitrates as starting materials.
- The investigation of the thermochemical properties showed that the precursor could yield SrFe\(_{12}\)O\(_{19}\) at calcination temperature above 730 °C.
- Phase analysis of the final product by XRD confirmed the formation of pure SrFe\(_{12}\)O\(_{19}\) from precursors with Sr\(^{2+}/Fe^{3+}\) molar ratio 1/6.4 after annealing at 800 °C for 3 h with rate of heating/cooling 5 °C/min.

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