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# Tuning Strontium M-type Hexaferrite Nanopowders Coercive Field through pH Control

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**Abstract**—Monophasic strontium M-type hexaferrite powders have been successfully synthesized using a citrate precursor sol-gel method. The effect of the pH of the starting solution on the structural and magnetic properties was studied. XRD analysis, SEM imagery and magnetometry measurements were carried out to characterize the obtained powders. Results showed that pH value had an insignificant effect on the saturation magnetization  $M_s$ , the remanence  $M_r$  and the  $M_r/M_s$  ratio. It has also been noticed that the lattice parameters  $a$  and  $c$  were slightly affected by the pH variation. The coercive field  $H_c$  and the crystallite size  $D$  were affected by the pH value reaching a maximum value of  $H_c = 0.68$  T. SEM imagery revealed that the particles shape and size were strongly dependent on pH value.

**Index Terms**—hard magnetic materials, hexagonal ferrites, nanopowders.

## I. INTRODUCTION

Strontium M-type ferrite (SrM) belongs to the class of hexagonal ferrites (hexaferrites) with magnetoplumbite structure. They exhibit a wide range of interesting properties such as: high Curie temperature, cheap raw materials and large magnetocrystalline anisotropy [1]. Many synthesis routes are used to obtain hexaferrite, amongst which the citrate precursor sol-gel method – which is a chemical route – has shown that the obtained materials exhibits excellent magnetic properties. In this method, the metal cations are intimately mixed since the early stages of the synthesis in a solution and then chelated by the carboxylic groups of citric acid. The hard magnetic material is obtained after dehydration and calcination of the precursor [2–4].

The effect of pH on the structural and magnetic properties of the powders has been studied but yet its effect is not clearly understood and further investigation is required. Lee and Fang [5] have reported that a solution with a pH = 7 yields optimum properties of barium hexaferrite (BaM) powder. Yu and Huang [6, 7] have confirmed that a pH  $\geq 7$  for the starting solution is necessary to obtain pure single domain barium hexaferrite powders. On the other hand, Xu *et al.* [8] have reported that nanoparticles of barium hexaferrite with optimum structural and magnetic properties have been synthesized from a starting solution of pH = 10. Xu *et al.* [9] have shown that very fine monophasic strontium hexaferrite nanoparticles as fine as 40 nm in diameter have been obtained from a solution at a pH = 12. They have noticed that the particles size, the saturation magnetization  $M_s$ , the remanence  $M_r$ , and the  $M_r/M_s$  ratio decreased by increasing the

pH value while the coercive field  $H_c$  increased. In this paper, we report a systematic study of the structural and magnetic properties of SrM powders synthesized from a solution having a pH varying from 1 to 10.

## II. EXPERIMENTAL PROCEDURE

The citrate precursor sol-gel method was used to synthesize the powders [2–4]. In a 200 mL beaker, an amount of iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3$ ) was dissolved in deionized water. A solution of ammonia was then added in excess to allow the iron(III) hydroxide ( $\text{Fe}(\text{OH})_3$ ) to precipitate. The latter was then filtered and washed with deionized water to get rid of the residual ammonia solution. In order to allow a good homogenization, the solution was continuously stirred at 60–70°C with citric acid with a ratio of 2:1 of citrate to metal ion to dissolve the obtained iron(III) hydroxide ( $\text{Fe}(\text{OH})_3$ ). Strontium hydroxide ( $\text{Sr}(\text{OH})_2$ ) was then added and the pH was adjusted to values ranging from 1 to 10 by adding ammonia solution. The temperature was set to 80–90°C till the formation of a transparent gel.

The gel was further dried in a furnace at 160°C for 2 hours, and black foam was formed. The latter was crushed and put back in the furnace for 2 hours at 450°C to eliminate any residual organic compounds. Afterwards, the crushed powder was mortared and calcined at 900°C for 2 hours to form the magnetoplumbite phase.

Using a Bruker D2 PHASER diffractometer XRD analysis was conducted and the diffractograms were analyzed with the Rietveld refinement method using MAUD software [10]. The magnetic properties were measured by means of a LakeShore vibrating sample magnetometer model 7400 at room temperature in a maximum field of 1.9 T. SEM images were obtained using a Thermo Fisher FEI

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Magellan 400 scanning electron microscope.

### III. RESULTS AND DISCUSSION

XRD patterns of the synthesized powders at different pH values after a calcination at 900°C presented in Fig. 1 show that monophasic SrM powders were obtained at low pH values (from 1 to 4). Some traces of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), not exceeding 2–3 %, were observed at some pH values (5 and 10). The presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> seems not related to pH but rather to preparation inconsistencies.

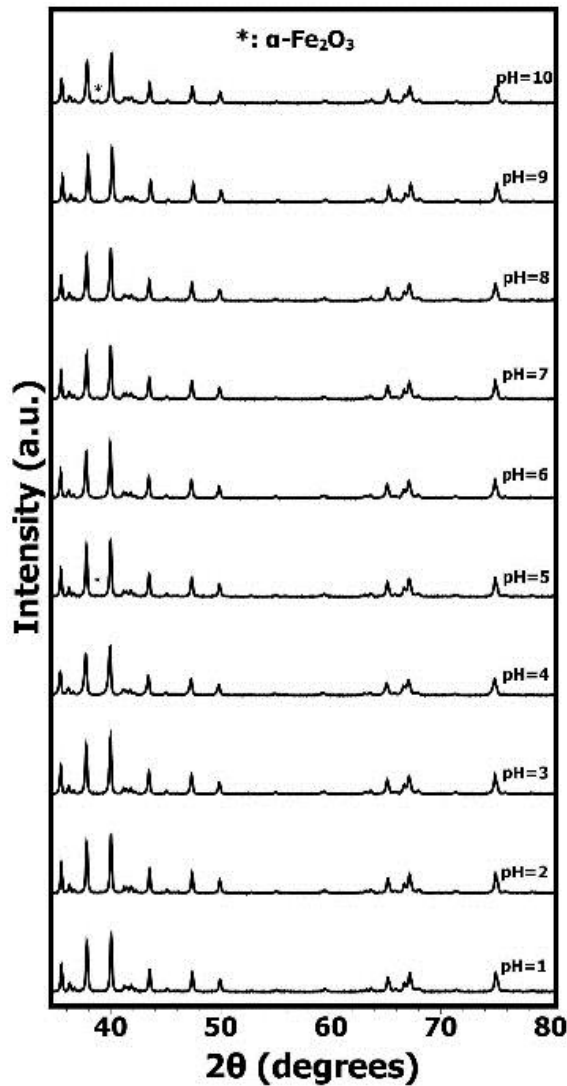


Fig. 1. XRD patterns of synthesized SrM powders prepared at different pH values and calcined at 900°C.

Obtaining monophasic SrM nanopowders for all pH values is not in consistence with the findings of Wu *et al.* [9] who reported the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at all pH values except for pH = 12 as well as the findings of Masoudpanah *et al.* [11] who noticed that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> the vanishes at pH values above 9.

It is worth to note that the synthesis method we used consists of dissolving iron(III) hydroxide and strontium hydroxide in a citric acid solution, with a ratio of citric acid to metal ions of 2:1. The freshly precipitated Fe(OH)<sub>3</sub> and Sr(OH)<sub>2</sub> are soluble in heated water and citric acid which ensures the obtainment of Fe<sup>3+</sup> and the Sr<sup>2+</sup> ions. The excess of the added citric acid ensures the total chelation of the metallic Fe<sup>3+</sup> and the Sr<sup>2+</sup> ions by the carboxylic groups. This results in a precursor with uniformly distributed Fe<sup>3+</sup> and Sr<sup>2+</sup> ions after dehydration and elimination of residual organic compounds. After calcination, the so obtained precursor allows the formation of well crystallized uniform powder particles as well as the complete transformation into a hexagonal structure [7].

Table 1 represents the lattice parameters  $a$ ,  $c$  and  $D$  (crystallite size which refers to the size of single crystalline domain and it is deduced from the Rietveld refinement of the XRD patterns) of the SrM powders obtained at different pH values. The results show that raising the pH value does not affects  $a$  and  $c$  lattice parameters but on the other hand, and in contrast to the findings of Masoudpanah *et al.* [11], the crystallite size deduced from XRD seem to be independent of the pH value of the starting solution since the scattering is within the error bars.

Table 1. Lattice parameters  $a$ ,  $c$  and  $D$  (crystallite size) of SrFe<sub>12</sub>O<sub>19</sub> obtained at different pH values.

	$a$ (nm)	$c$ (nm)	$D_{XRD}$ (nm)
1	0.587432	2.301963	127 ± 20
2	0.587565	2.302610	139 ± 20
3	0.588155	2.306061	114 ± 20
4	0.588866	2.309165	90 ± 20
5	0.588002	2.304734	121 ± 20
6	0.588315	2.306732	110 ± 20
7	0.587942	2.304083	103 ± 20
8	0.587883	2.304302	100 ± 20
9	0.586393	2.296827	90 ± 20
10	0.587318	2.302051	93 ± 20

From the SEM images represented in Fig. 2, it is obvious that the powders nanoparticles are under the theoretical single-domain size which is around 460 nm [12]. The hexagonal shape is clearly obtained for all the pH values.

At low pH values (from 1 to 3) the shape of the particles is almost spherical, and the particles tend to agglomerate. The obtained shape maybe explained by the large number of Fe<sub>2</sub>O<sub>3</sub> during the SrM hard phase formation at low pH values as reported by Wu *et al.* [9]. Increasing the pH values (above 4) leads to a more defined platelet-like particles with clear edges (flat hexagonal prisms) showing that large pH promotes growth perpendicular to  $c$ .

However, except for pH = 1, the powders particle size is inhomogeneous and it is clear that the powders are made of very small and larger particles and this becomes more obvious for pH = 10 which is not in consistence with what is reported by Wu *et al.* [9].

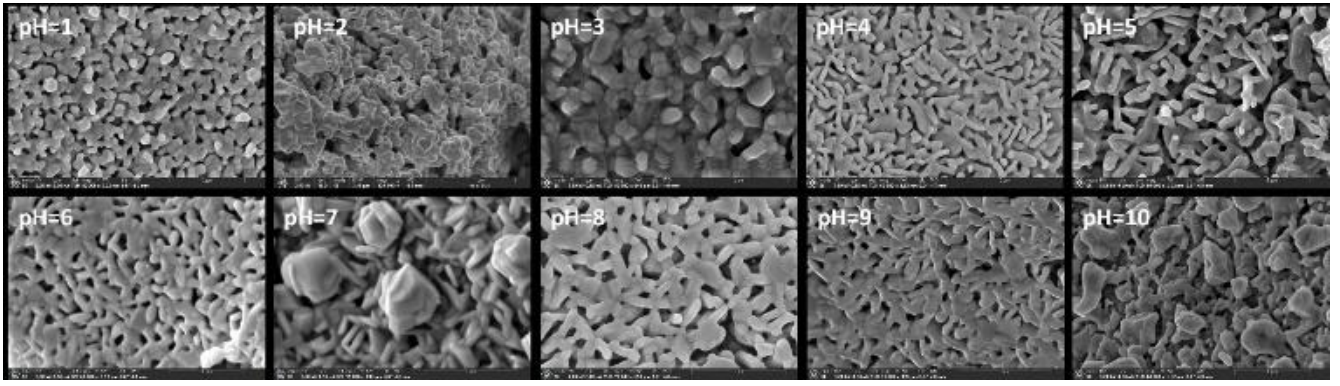


Fig. 2. SEM images of synthesized SrM powders prepared at different pH values and calcined at 900°C.

Table 2 shows the magnetic properties at room temperature of SrM nanopowders prepared at different pH values. The hysteresis loops of these materials are presented in Fig. 3.

Table 2. Saturation magnetization ( $M_s$ ), remnant magnetization ( $M_r$ ), coercive field ( $H_c$ ) and  $M_r/M_s$  ratio of SrFe<sub>12</sub>O<sub>19</sub> obtained at different pH values.

pH	$M_s$	$M_r$	$H_c$	$M_r/M_s$
1	66	36	0.68	0.54
2	64	35	0.59	0.54
3	67	36	0.58	0.54
4	62	33	0.57	0.54
5	66	35	0.62	0.54
6	64	34	0.59	0.54
7	66	35	0.55	0.53
8	60	32	0.59	0.54
9	64	35	0.55	0.54
10	63	34	0.61	0.54

Increasing the pH value seems to have no effect on the values of  $M_s$  and  $M_r$  which can be explained by the absence of any secondary or nonmagnetic phases in all samples even though traces of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have been detected (Fig. 1) in samples of pH = 5 and pH = 10 but its contribution is insignificant nevertheless.

Regardless of the pH value, the ratio  $M_r/M_s$  is constant and its value is equal to 0.54. This value is commonly observed in the M-type hexagonal ferrites. Referring to Stoner-Wohlfarth theory [13], the squariness ratio of an assembly of particles with a single easy axis uniformly distributed in space should be 0.5. The slightly higher value recorded is due to a slight underestimation of  $M_s$ , as the maximum field applied is equal to the anisotropy field  $H_K = 2K_1/\mu_0 M_s$ .

$H_c$  on the other hand, shows a different behavior. It actually decreases by increasing the pH value which is confirmed by Yu *et al.* [7]. A maximum value of  $H_c = 0.68$  T is obtained at pH = 1 which represents 77% of the theoretical value of isotropic SrM ( $H_c = 0.48H_K = 0.88$  T [14]). This value is to our knowledge the highest  $H_c$  value ever reported for a strontium hexaferrite powder. For all samples, all grains are smaller than the single-domain limit, the fact

that increasing the pH leads to a decrease in the homogeneity of the particles size and shape observed in Fig. 2, contributes to the decrease in the coercive field. Indeed, when the particles grows perpendicularly to the easy axis, a perpendicular shape anisotropy will be added and reduce the total anisotropy, so is seem logical that equiaxial particles exhibits the highest coercivity.

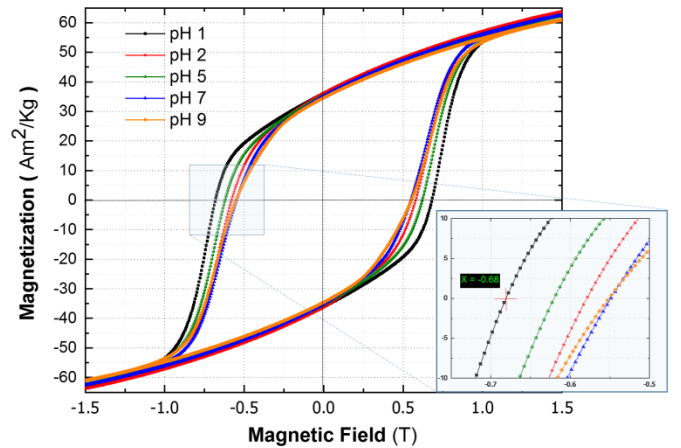


Fig. 3. Magnetization loops of SrM powders prepared at different pH values and calcined at 900°C.

#### IV. CONCLUSION

This study has revealed that the pH of the starting solution has an effect on the coercivity of the final powder by influencing the particles size and shape. A starting solution without any NH<sub>4</sub>OH addition and a pH = 1 has resulted in a powder with a maximum field of 0.68 T which then decreased by increasing the pH value. The crystallite size also showed a decrease by increasing the pH in the starting solution. The particles size, shape and homogeneity have shown a strong dependence on pH. On the other hand,  $M_s$ ,  $M_r$ ,  $M_r/M_s$ , the lattice parameters  $a$  and  $c$  have been relatively constant when the pH value varied. It was also shown that the presence of hematite may be totally avoided at any pH by meticulous adjustment of molar ratio of all components.

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