# STRUCTURE AND MAGNETIC PROPERTIES OF STRONTIUM HEXAFERRITE NANOPOWDERS PREPARED BY MECHANOCHEMICAL SYNTHESIS

C. MICLEA, C. TANASOIU, C.F. MICLEA, A. GHEORGHIU*, I. SPANULESCU*, M. CIOANGHER, C.T. MICLEA*
NATIONAL INSTITUTE FOR MATERIALS PHYSICS, Bucharest-Magurele, ROMANIA
*HYPERION UNIVERSITY, Faculty of Physics, Str. Calarasi 169, Bucharest, ROMANIA

## 1. INTRODUCTION

Hexagonal ferrites are the most important hard magnetic materials used for high quality permanent magnets. They are of particular interest for application in recording media as well as in high quality permanent magnets. There are several unconventional methods used to prepare fine particle materials including coprecipitation, hydrolysis of metalorganic complexes, spray pyrolysis, sol-gel route, glass crystallization, hydrothermal synthesis, and mechanical alloying. The particle size can be experimentally controlled either by the preparation method or by the milling process. This process introduces a considerable number of defects and mechanical stresses which leads to the degradation of the coercivity. These can, to a great extent, be removed by a proper thermal annealing so that coercivities in excess of 4500 Oe were reported for strontium ferrites nanopowders but the reversal mechanism of magnetization and the origin of coercivity are not yet clear. Therefore, more experimental studies are necessary in order to have a deep insight into this.

## 2. OBJECTIVES

- To synthetize strontium ferrite nanopowders by mechanochemical process, starting from pure iron and strontium oxides;
- To obtain coercive forces as high as possible for such thermally treated nanopowders in order to check, experimentally, the Stoner-Wohlfarth theoretical prediction for magnetization reversal process in ensembles of magnetic noninteracting particles;
- To obtain permanent magnets of high quality and high magnetic parameters from nanopowders by sintering the powders to highly densified ceramic bodies.

## 3. EXPERIMENTAL

Mechanochemical synthesis of oxidic materials has received increased attention in recent years. It represents a new an and reliable method to prepare nanopowders. We have started with strontium and iron oxides as raw materials of p.a. purity and having a particle size distribution in the 1-6 μm range. Stoichiometric batches of 50 g of oxides, corresponding to the formula $SrO \cdot 6Fe_2O_3$ were weighted and loaded into hardened steel jars of 500 ml together with steel balls of 10, 15 and 20 mm diameters, corresponding to a balls/oxides weight ratio of 5:1. Four jars ("the planets") were mounted in their places on the sun wheel of a Retsch PM 400 planetary ball mill, operating at a rotation speed of the sun wheel of 350 $min^{-1}$ and a speed ratio of 1:-2. Centrifugal forces carry the balls in the direction in which the jars are rotating and the differences between the speeds of the grinding jars and the balls result in strong frictional forces. On the other hand the Coriolis forces act on the balls and displace them from the jar walls and make them fly through the interior of the jar and impact against the sample on the opposite wall of the jar, thus releasing considerable impact energy. In this way the *impact* and *frictional forces* result in a high degree of pulverization and comminution of the powders in the nanosize range.

## 4. RESULTS

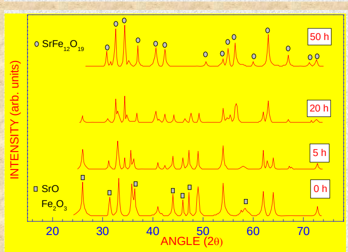


*Figure 1*
*XRD pattern of mechanochemicaly activated powder for different milling time*

The mechanochemical synthesis produces fine grained powders and skips the calcinations step, as a result of physico-chemical changes of constituent oxides intimately mixed and milled in a high energy planetary ball mill for different times. Fig. 1 shows the XRD patterns of mixed oxide powders mechanically activated for different times, up to 50 hours. The initial mixture of oxides (0 h) shows only the peaks corresponding to strontium oxide and $\alpha$-$Fe_2O_3$. After 5 hours of milling some faded peaks, characteristics to strontium ferrite, begin to appear being visible at 2θ=34.10, 42.50 and 63.10. After 20 hours of milling the strontium ferrite is synthesized in a much higher amount with intense peaks at 32.30, 34.10, 37.10, 56.80 and 63.10. Finally, after 50 hours the $SrFe_{12}O_{19}$ compound is completely synthesized. The morphology of the milled powder after 50 hours of milling is illustrated in Fig. 2. One may appreciate that the grain size is situated somewhere around 50 nm. The magnetic properties of the synthesized nanopowders by mechanical activation were measured at room temperature. Very low values were recorded: 0.45 kOe for $H_C$ and 42 emu/g for $\sigma_S$. In order to remove all these a thermal annealing was necessary. Consequently, we annealed the nanopowder at different temperatures between 700 and 1100 $^oC$ for different times and the results are shown in Fig. 3 for coercive field. The coercive field starts to recover slowly in time even at lower temperatures and this process becomes faster with increasing temperature. At 1000 $^oC$ and above the recovery is complete after one and a half hour where both curves intersects each other. However, the temperature of 1000 $^oC$ can be considered as an optimum for annealing since HC reaches its maximum value of 6600 Oe and remains practically constant even for prolonged times. The full curve of coercive field recovery as a function of temperature up to 1200 $^oC$ is shown in Fig. 4. As for magnetization, its recovery as a function of annealing temperature is shown in Fig. 5. One can see that at 1000 $^oC$ the specific magnetization reaches a high value but not its maximum. These annealed nanopowders can be used for checking experimentally the theoretical prediction of Stoner Wohlfarth (SW) theory. Magnetization reversal by coherent rotation was indeed experimentally observed in nanosized hard ferrites. In order to make an ensemble of noninteracting nanoparticle we prepared an isotropic sample of nanopowder dispersed in a nonmagnetic matrix of a rather, initially, fluid resin at a packing fraction of 0.01 and was immersed in an ultrasonic bath and stirred for 30 minutes until the resin starts hardening. An example of demagnetizing curve of such a sample after saturation in a field of 2T is illustrated in Fig. 6 together with the calculated one using SW model for an ideal ensemble of spherical noninteracting single domain particle. One can see that both curves are in good agreement up to the reverse fields of -5 kOe after which a small discrepancy for $H_C$ of about 10% between the theoretical value of 7400 kOe and the experimental one of 6600 Oe was observed. This may be assumed as being due either to the fact that the particles are not ideal spheres or that the nucleation is favored at local surface defects and at the sharp edges and corners of the particles. Isotropic samples from this nanopowder were pressed and sintered at 1200 $^oC$ for 3 hours. Dense ceramics of more than 97 % of theoretical density were formed as shown, in Fig. 7 on a polished and thermally etched surface. One can see that the crystallite size of ceramics ranges between 0.2 and 1 μm so that the great majority of grains are still below the single domain size. The main magnetic characteristics of such magnets were evaluated from the hysteresis loop shown in Fig. 8. As can be seen these characteristics are as follows: coercive field $H_C$=4600 Oe, $B_r$=2100 Gs and a maximum energy product $(BH)_{max}$=1.85 MGsOe.

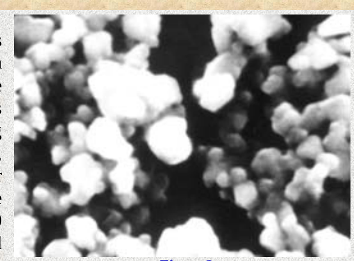

*Figure 2*
*Morphology of strontium ferrite powder obtained by mechanochemical synthesis after 50 hours of milling*

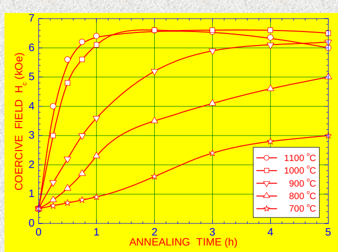


*Figure 3*
*Effect of annealing time on coercive field of strontium ferrite powder subjected to different annealing temperatures*

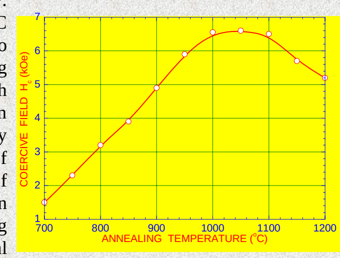


*Figure 4*
*Effect of annealing temperature on coercive field of strontium ferrite powder produced by mechanochemical synthesis*

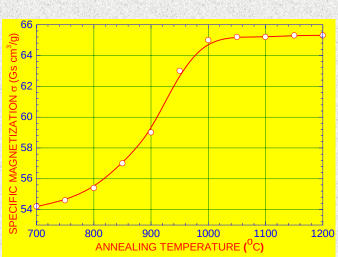


*Figure 5*
*Effect of annealing temperature on magnetization of strontium ferrite powder produced by mechanochemical synthesis*

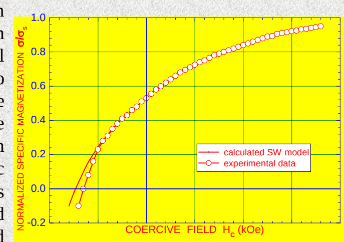


*Figure 6*
*The experimental demagnetization curve for strontium ferrite nanopowder annealed at 1000°C and dispersed in a nonmagnetic matrix at a packing fraction of 0.01 and the calculated one using S-W model*

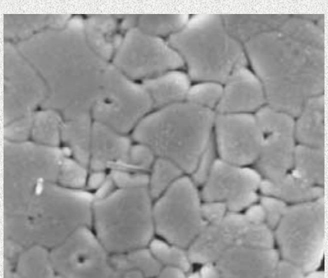

*Figure 7*
*SEM image of the polished and termally etched surface of an isotropic sample of strontium ferrite magnet sintered at 1200 °C for 3 h*

## 6. SUMMARY

Strontium ferrite powders with an average grain size of 50 nm were synthesized by mechanochemical process after 50 hours of milling in a high energy planetary ball mill. During this process a great amount of different types of defects were introduced into particles but they were nearly completly removed by a suitable thermal annealing at 1000 $^oC$ for one and a half hour.

Magnetic properties of such nanopowders were determined in the case of noninteracting state by dispersing them into a nonmagnetic matrix of resin. Coercive fields of 6600 Oe and magnetization of 65 emu/g were recorded in such samples.

Permanent magnets were produced from such nanopowders by pressing isotropic samples and sintering at 1200 $^oC$ for 3 hours. Their magnetic characteristics were: $H_C$=4600 kOe, $B_r$=2100 Gs and $(BH)_{max}$=1.85 MGsOe.

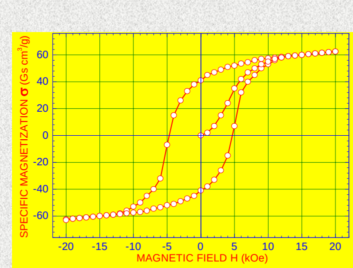


*Figure 8*
*Hysteresis loop of an isotropic strontium ferrite magnet sample in a maximum magnetic field of 2 T*