

SAMARIUM-IRON GARNET NANOPOWDER OBTAINED BY CO-PRECIPITATION

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Abstract— In this work, samarium-iron garnet nanopowder ($\text{Sm}_3\text{Fe}_5\text{O}_{12}$) was obtained and characterized by TG/DTA, XRD, SEM and EDS. The synthesis of this magnetic material was carried out by the co-precipitation method, using hydrated chlorides of the rare-earth elements and ferrous sulfate. PVA was added to the calcined powder in order to facilitate the production of a toroidal compact specimen, which was submitted to sintering in the range of 1200 °C to 1400 °C, to establish a correlation of its magnetic properties with morphology.

Keywords—garnet, co-precipitation, magnetic properties and nanomaterial.

I. INTRODUCTION

Billions of soft ferrites are used in every conceivable electronic devices. Rare-earth garnet-structure ferrites, $\text{R}_3\text{Fe}_5\text{O}_{12}$ (where R is yttrium or rare-earth cation), have attracted great attention for applications such as both microwave devices and magnetic recording media (Sugimoto, 1980; Rodic *et al.*, 1999).

Recently, garnets are widely used in microwave communication through mobile and satellite communications and are of significant interest for numerous applications, including magnetic materials, lasers, phosphorescent sources, and electrochemical devices (Waerenborgh *et al.*, 2004).

The garnet materials possess unique optical, thermophysical and mechanical properties, in particular, excellent creep and radiation damage resistance, fracture toughness, moderate thermal expansion coefficients, high thermal conductivity and energy-transfer efficiency (Waerenborgh *et al.*, 2004).

Samarium-iron garnet ($\text{Sm}_3\text{Fe}_5\text{O}_{12}$) is of considerable interest for its potential use as a broadband material in microwave application (Cunningham and Anderson, 1960).

In this work, this material was synthesized by co-precipitation method and its magnetic properties were studied. The resulted garnet shows nanometric size and better magnetic properties than others prepared by traditional methods.

Co-precipitation is a chemical route which plays a crucial role in preparing the final product by minimizing

problems associated with diffusion, impurities and agglomeration. In solid state methods, mechanical mixing of oxides followed by calcination, result in final products with worst electrical, mechanical and magnetic properties (Lax and Button, 1962; Horvath, 2000; Dionne, 1971; Adair, 1991).

II. EXPERIMENTAL PROCEDURE

The synthesis of the material was carried out by the co-precipitation method, using as reagents the rare-earth element hydrated chlorides ($\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, purity 99%, Aldrich) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, purity 99%, Reagen). These solutions were all mixed together in a 500 mL recipient and the pH of the total solution was kept in the range 2 - 3.

This solution was heated up to 6 °C under intensive agitation for about 30 minutes, followed by KOH addition to increase the pH value in 10 - 11 range, while allowing easy elimination of the K^+ ions, by simple washing of the precipitate with distilled water (Adair, 1991).

Thermodynamic analysis (Caffarena and Ogasawara, 1999) shows that the final pH for co-precipitation method shall be in the range 9 - 12, so the synthesis has been repeated three times with pH values from 10 to 11.

The co-precipitated solids were separated from the initial solution by vacuum filtration, after several washings with distilled water, until Cl^- and SO_4^{2-} anions were no more detectable by test reactions with AgCl and BaSO_4 , respectively (Morita and Assumpção, 1972).

The drying of the precipitate was carried out according to Reed's recommendation (Reed, 1991) with initial drying inside a desiccator for 24 hours, followed by heating at 75 °C for 4 hours. The dried co-precipitate was submitted to thermal analyses using Shimadzu 50H Differential Thermal Analyzer and Shimadzu TGA-50 Thermogravimetric Analyzer (Sorrel, 1991).

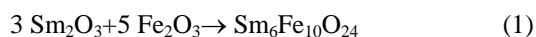
Subsequent calcination (Halloran, 1991) of co-precipitates was carried out under conditions suggested by thermal analysis, corresponding to heating up to 1000°C (rate of 5 °C/minute); holding time of 4 hours, followed by natural cooling down inside the furnace.

The powder was characterized (JCPDS, 1977) by X-ray fluorescence (Philips model PW2400), scanning electron microscopy (Zeiss SEM model DSM 940A and

Oxford-Link EXL II EDS Module), X-ray diffraction (Philips PW3170 X-Ray Diffractometer, copper K_{α} [$\lambda = 1.542 \text{ \AA}$] radiation, generator at 40 kV and 40 mA, scanning 2θ angles from 10 to 100°).

Ring shaped compacts (2.0 cm outer diameter, 0.8 cm inner diameter and 0.4 cm height) were produced by dry pressing of the calcined powder, to which was added as a binder an aqueous solution containing 15 wt % of PVA (polyvinyl alcohol), in a suitable amount corresponding to 2 wt% of the total compacted mass. A total of 50 pieces were produced for each batch.

Ten compacted pieces were sintered at 6 different firing temperatures (1200 °C, 1250 °C, 1300 °C, 1350 °C, 1400 °C and 1450 °C) in order to promote formation of the desired samarium-iron garnet, according to the reaction 1:



The firing was performed in the following heating schedule: $4^\circ\text{C}/\text{minute}$ up to 400°C , a 400°C plateau for 1 hour, $8^\circ\text{C}/\text{minute}$ up to the final sintering temperature, where the sample was kept during 5 hours, in air. The cooling down inside the furnace was carried out at a rate of $8^\circ\text{C}/\text{minute}$ down to 800°C , where the sample was kept during 1 hour, before the final cooling down to the room temperature, at the same rate. Figure 1 shows the thermal profile of the ceramic firing for different sintering temperatures.

Magnetic properties of the sintered samples were determined by using magnetic hysteresisgrapher (Walker Scientific model AMH-20): each ceramic ring received a varnished copper AWG 29 wire winding, to provide a solenoid (magnetically analyzed under 60 Hz frequency and 25 Oe maximum magnetic field). The microstructure of the sintered toroids (rings) was analyzed by scanning electron microscopy (SEM). They were mounted on aluminum supports and coated with a film of gold.

III. RESULTS AND DISCUSSION

Results of thermogravimetric (TGA) and differential thermal analysis (DTA) are shown in Fig. 2. There is not any DTA peak below 500°C and the TGA information reveals the formation of mixed oxide, firstly as an amorphous phase that converts to crystalline phases during the latter heating. DTA revealed an exothermic peak at 946°C associated to the transformation of the samarium and iron (III) amorphous mixed oxides into the crystalline ones.

The powder was calcined at 1000°C and the X-ray diffraction pattern of the product confirmed this transformation (Fig. 3), giving rise to intermediate compounds (SmFeO_3 , Fe_2O_3 and Sm_2O_3), a feature meaning that greater time and temperature are needed, in order to achieve full conversion of the material to true iron garnet (Forterre, 1991; Gasgnier *et al.*, 1998).

Figure 4 shows the X-ray diffraction pattern of the mixed oxide sintered at different temperatures in the 1200-1450°C range. At 1200°C (Fig. 4-a), 1250°C

(Fig. 4-b) and 1300°C (Fig. 4-c) remained samarium orthoferrite, Sm_2O_3 and Fe_2O_3 phases. At 1350°C (Fig. 4-d), the XRD pattern indicate the presence of $\text{Sm}_3\text{Fe}_5\text{O}_{12}$, Sm_2O_3 and orthoferrite. It is seen that complete formation of the samarium-iron garnet only occurred at elevated temperatures at 1400°C (Fig. 4-e) according to JCPDS 23-526 data.

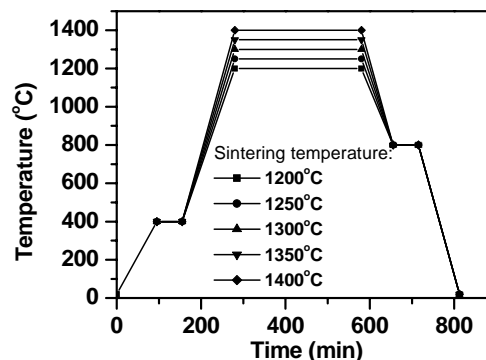


Figure 1. Thermal background for sintering ceramic rings at 1400°C .

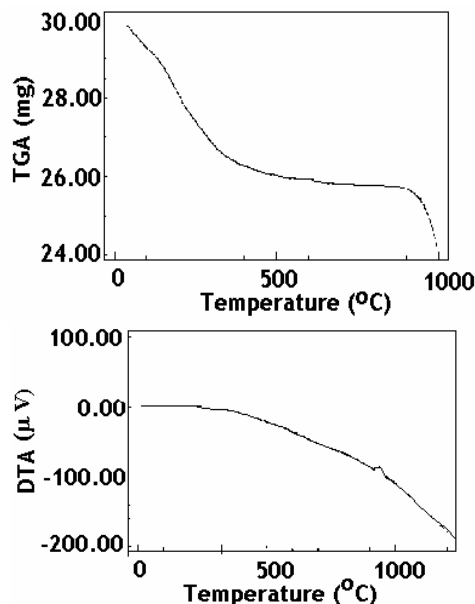


Figure 2. TGA and DTA of co-precipitated samarium and iron hydroxides, in air, with heating rate of $10^\circ\text{C}/\text{min}$.

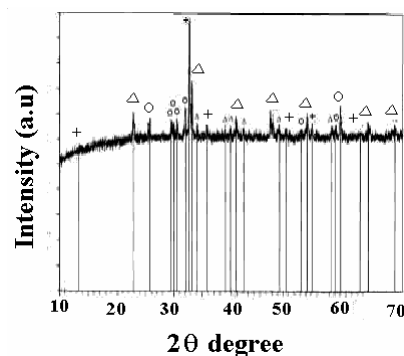


Figure 3. X-ray diffraction pattern of the ceramic pieces, corresponding to samarium-iron garnet formation, where: Δ SmFeO_3 , \circ Fe_2O_3 and \square Sm_2O_3 .

IV. CONCLUSIONS

The most important results of the work are those related to formation of the samarium-iron-garnet nano powder (150 nm) by co-precipitation method, according to the previous studied thermodynamic analysis.

The magnetic properties of this soft ferrite can be associate to this microstructure and the following correlations were observed:

- The grain-size increased from 2.0 μm to 4.2 μm in the 1200-1400 $^{\circ}\text{C}$ range;
- The coercive force decreased from 7.16 Oe to 4.72 Oe in the 1200 – 1400 $^{\circ}\text{C}$ range, as the result of the grain growth as expected;
- Hysteresis losses, maximum magnetization and the magnetic remanence presented maximum at 1350 $^{\circ}\text{C}$.

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