

Y₃Fe₅O₁₂ Prepared by Mechanochemical Synthesis from Different Iron Sources

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ABSTRACT

Yttrium iron garnet, Y₃Fe₅O₁₂ (YIG) powders were synthesized by mechanochemical processing (MCP) from different iron sources (FeO, Fe₂O₃ and Fe₃O₄) mixed with Y₂O₃, followed by a heat treatment. The aim of this work is to demonstrate that MCP followed by annealing at very low temperatures (as compared with the classic solid state reaction) can induce the formation of nanostructured YIG. The effect of iron source on final structure was also studied. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the synthesized powders. The precursors mixed in a stoichiometric ratio to obtain YIG were milled at room temperature in a shaker mixer mill with a ball:powder weight ratio of 10:1. A partial synthesis of YIG was achieved after 9 h of milling time by using the three sources of iron; however, a significant fraction of the product was the perovskite YFeO₃. The largest yield of YIG was obtained by using FeO. In all cases a single garnet phase could only be completely obtained after an annealing process at 900°C, around 400°C lower than the typical temperatures to prepare the material by solid state reaction. An analysis of the microstrain and lattice parameters associated with peak displacements is discussed.

Keywords: Mechanochemistry; YIG; Annealing; Iron Garnet

1. Introduction

Ferrimagnetic garnets have attracted attention as microwave device materials and magneto-optical recording medium for their unique magneto-optical properties [1]. In order to modify these properties, doping with different cations such as bismuth [2,3], lanthanum [4,5], cerium [6], titanium [7], gadolinium [6] and other rare earth cations has been reported.

Garnets are characterized by a compact oxygen array [4] and are assigned to space group Ia3d 8(O_h¹⁰) where the cations are located at the center oxygen polyhedron [2,8]. Due to the possibility to exchange the positions of the cations in the cell, these materials are the basis for many high-technology devices like telecommunications and microwave. The fundamental magnetic properties of YIG are originated from the magnetic ions and their relationship to the surrounding oxygen ions.

Yttrium iron garnet can be synthesized by several methods. The conventional and oldest one is the sintering

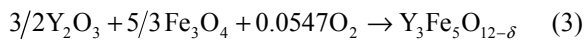
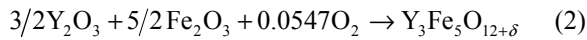
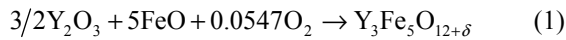
of the corresponding oxides in a furnace at 1400°C (solid state reaction) [3,5]. This process produces large particles and consumes a great amount of energy [9]. This method can produce an intermediate phase, YFeO₃, which has an antiferromagnetic structure. Iron garnet powders can be produced by wet chemical methods such as sol-gel [6-10], coprecipitation [8], chemical vapor deposition [11], thermal plasma spraying [12], etc. A particular method is mechanochemical synthesis which promotes the formation of a new oxide by mechanical activation of precursor's oxides or salts [13]. In spinel ferrites, it leads to a change in the distribution of cations in interstitial sites, thereby modifying the magnetic properties [13,14]. Mechanochemical synthesis of yttrium iron garnet with subsequent heat treatment have been reported in the literature, using annealing temperatures higher than 900°C. Paesano *et al.* [15] reported the successful mechanochemical synthesis of YIG from a mixture of Y₂O₃ and Fe₂O₃ followed by an annealing at 1000°C. Widatallah *et al.* [16] presented a

detailed study of the influence of the milling process on the formation of single phase YIG by mechanochemical synthesis, using similar experimental conditions to those reported by Paesano [15]. Also, M. Niyafar *et al.* [2] used high energy milling to mechanically activate the powder mixture of BiO, Y₂O₃, and Fe₂O₃ and achieve doped Bi-YIG complete synthesis by subsequent annealing at high temperature. All these authors characterized magnetically the obtained powders.

In mechanochemical synthesis experiments in air involving metallic oxides, the reduction of iron oxide phases has been observed to occur in a closed stainless steel container after prolonged milling, and the reaction occurs in a steady-state manner during milling [14,17-20].

2. Experimental Procedure

Fe₂O₃ (Sigma Aldrich, 99% purity), FeO (Sigma Aldrich, 99% purity), Fe₃O₄ (Sigma Aldrich, 99% purity), La₂O₃ (Sigma Aldrich, 99.9% purity), Y₂O₃ (Sigma Aldrich, 99.9% purity) and Gd₂O₃ (Sigma Aldrich, 99.9% purity) powders were used as precursor materials. These powders were mixed in a stoichiometric ratio according to the following equations:



The oxygen (0.0547 mol) in these reactions was calculated from the air contained in the milling vial that was used in the milling process. A total of 5 g of the starting mixtures were loaded with steel balls of 1.27 cm in diameter into a steel cylindrical vial (50 cm³) (steel/steel, S/S) at room temperature in air and milled during 9 hours. The charge ratio (CR) was 10:1. To prevent excessive heating of the vials, the experiments were carried out by alternating 90 min of milling followed by 30 min in standby. Annealing treatments were performed from 700°C to 1000°C in air atmosphere.

Milled powders were characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with CoK α_1 ($\lambda = 1.790300 \text{ \AA}$) radiation. Patterns were collected in a 2θ interval of 20° - 120° with increments of 0.02 (2θ). Rietveld refinement was performed on the X-ray patterns. This method takes into account all of the information collected in a pattern, and it uses a least squares approach method [21] to refine the theoretical line profile until it matches the measured profile.

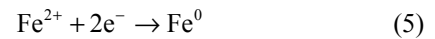
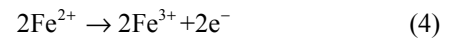
Morphologies of the milling powders were analyzed using a scanning electron microscope, JEOL JSM-6300, working at 15 kV.

3. Results and Discussion

3.1. Mechanochemical synthesis

Figure 1 shows the X-ray diffraction patterns of powder mixtures after 9 hours of milling time for the three iron sources: FeO, Fe₂O₃ and Fe₃O₄. This figure shows the partial formation of perovskite and garnet structures for all the samples.

On the other hand, a widening of the peaks is observed which is associated with a decrease in particle size. In particular, for the mixture FeO + Y₂O₃, a peak is observed after 9 hours of milling at $2\theta = 52.3^\circ$. This reflection is related with the (110) planes of metallic Fe, and suggests the occurrence of the following redox semi-reactions:



But the presence of metallic Fe due to milling media erosion is also possible, because of the hardness of the FeO, higher than those for the other precursors.

The starting stoichiometry corresponds to the YIG formation; therefore, there is an iron oxide excess in the mixture as far as orthoferrite is present.

In addition, results of Rietveld refinements for powder mixtures milled for 9 hours, presented in **Table 1**, show the presence of metallic Fe only for the mixture FeO + Y₂O₃. Nevertheless, it is believed that only with a lack of oxygen the last redox reactions are favored, *i.e.* with only 0.0547 mol of oxygen in the vial, or by heat treatment in inert atmosphere, as will be discussed below.

Besides, **Table 1** shows that YIG formation is favored by starting from Fe²⁺, instead of Fe³⁺ or (Fe²⁺Fe³⁺); in contrast, the mixture with magnetite (Fe²⁺Fe³⁺) privileges the formation of orthoferrite and reactants are undetectable after 9 hours of milling. This perovskite phase is

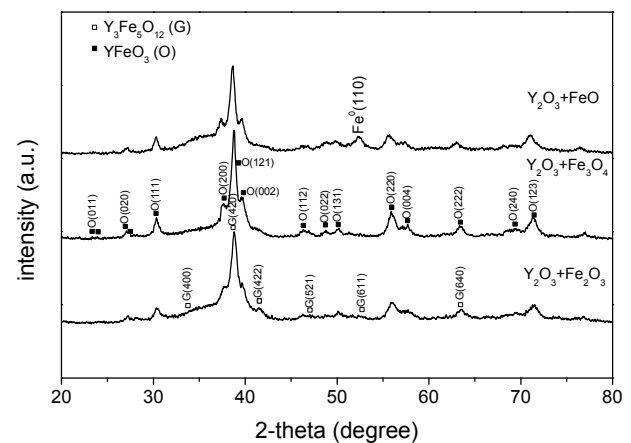


Figure 1. X-ray powder diffraction patterns of different mixtures milled at 9 h.

more stable than YIG according to Bolarín-Miró, *et al.* [13].

Cell parameters are reported in **Table 2** for milled mixtures obtained from different sources of iron. The values for the orthoferrite phase appear closer to reported values [20,22-27]; these results, together with calculated microstrains, as reported in **Table 1**, suggest that the stability of orthoferrite structure is higher than that of the garnet phase; this could mean that YIG structure absorbs all the mechanical strain produced by milling, while orthoferrite remains with the same lattice parameters.

Calculations of the Gibbs free energy [28], *i.e.*, the thermodynamic part of the process states that the most spontaneous reaction (presenting the lowest free Gibbs energy) occurs for the FeO + Y₂O₃ mixture to produce YIG in the presence of oxygen. Less spontaneous reaction, in contrast, corresponds to orthoferrite from Fe₂O₃ and Fe₃O₄.

There is however, the kinetic side which has to be considered. Some results [29,30] indicate that, even when starting from Fe³⁺ sources, Fe²⁺ ions are formed and have a larger diffusion coefficient than ferric ions. In most cases, the formation of the ferrite phase occurs by simultaneous diffusion of both iron cations. Under air atmosphere, Fe²⁺ ions are re-oxidized to the ferric state. It seems that in the case of FeO as a source, where ferrous ions are already present, it would be easier to enhance diffusion and formation of the resulting phases.

3.2. Annealing

The obtained results (**Figure 1**) show that MCP is unable to induce the full formation of YIG as a single phase, independently of the iron source (precursor used). It is therefore necessary to complete the synthesis by means of an annealing process. XRD pattern for mixtures FeO + Y₂O₃ milled and heat treated at temperatures from 700°C to 1000°C are shown in **Figure 2**. The garnet phase is fully formed at 900°C; below this temperature the peaks of the orthoferrite phase are clearly observed while the peaks of the garnet phase just begin to appear at 700°C.

The (110) Fe⁰ peak reflection disappears when temperature is increased up to 800°C. It is also observed an increase in relative intensities and narrowing for all the peaks, both indicators of grain and crystal growth.

In **Figure 3(a)** it can be observed for the starting mixture (Fe₂O₃ + Y₂O₃), that main peaks of both garnet and perovskite phases reach comparable intensities at 800°C, while at 900°C the peak of the perovskite almost completely disappears.

For the Fe₃O₄ + Y₂O₃ mixture shown in **Figure 3(b)**, it is only for $T > 900^\circ\text{C}$ that peaks of orthoferrite phase decrease in intensity and disappear; at 800°C, the perovskite phase still remains and shows a significant proportion in the milled material. Again, the width of the peaks decrease and its height increases for all the peaks, indicating grain and crystal growth.

Table 1. Data from Rietveld refinement of XRD patterns for the mixtures ball-milled 9 h.

Products	(Fe ₂ O ₃ + Y ₂ O ₃) Fe ₂ O ₃ ICDS # 43465		(FeO + Y ₂ O ₃) FeO ICDS # 76639		(Fe ₃ O ₄ + Y ₂ O ₃) Fe ₃ O ₄ ICDS # 20596	
	Weight %	μstrain	Weight %	μstrain	Weight %	μstrain
Fe ₃ O ₄	5.6	0.0022	1.7	0.0008	0	0.0008
Y ₂ O ₃	0.7	0.0008	0.6	0.0008	0.2	0
Y ₃ Fe ₅ O ₁₂	36.5	0.0581	44.6	0.0465	28.2	0.0548
YFeO ₃	57.2	0.0026	49.9	0.0006	71.6	0.0015
Fe	0	0	3.2	0.0008	0	0

Y₂O₃ ICDS # 43465; Y₃Fe₅O₁₂ ICDS # 2012; YFeO₃ ICDS# 43260; Fe ICDS # 64998.

Table 2. Lattice parameters for mixtures after mechano-synthesis.

Reactants	Lattice parameters (Å)				Rietveld parameters		
	YIG ^a	YFeO ₃			Goodness of fit		
	a	a	b	c	Rw	Rexp	χ^2
Fe ₂ O ₃ + Y ₂ O ₃	12.174	5.268	5.559	7.614	19.0	18.2	1.10
FeO + Y ₂ O ₃	12.574	5.295	5.599	7.640	24.9	19.1	1.69
Fe ₃ O ₄ + Y ₂ O ₃	12.290	5.270	5.551	7.612	18.7	18.2	1.06
Reference ^a	12.376	5.281	5.595	7.605	-	-	-

^aY₃Fe₅O₁₂ ICSD #2012 [23]; YFeO₃ ICSD #43260 [20].

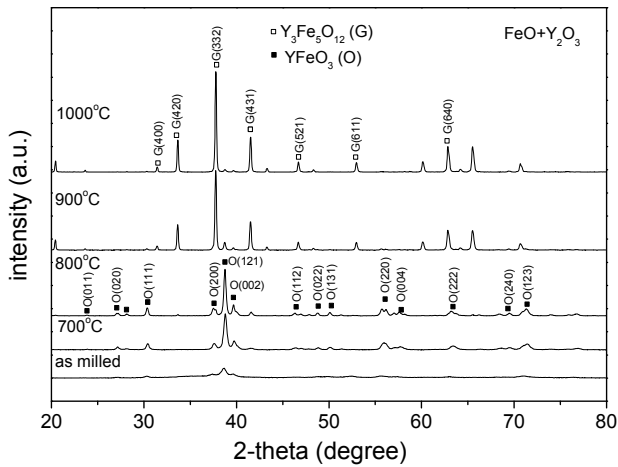


Figure 2. X-ray powder diffraction patterns of milled powders ($\text{FeO} + \text{Y}_2\text{O}_3$) annealed at different temperatures during 3 hours.

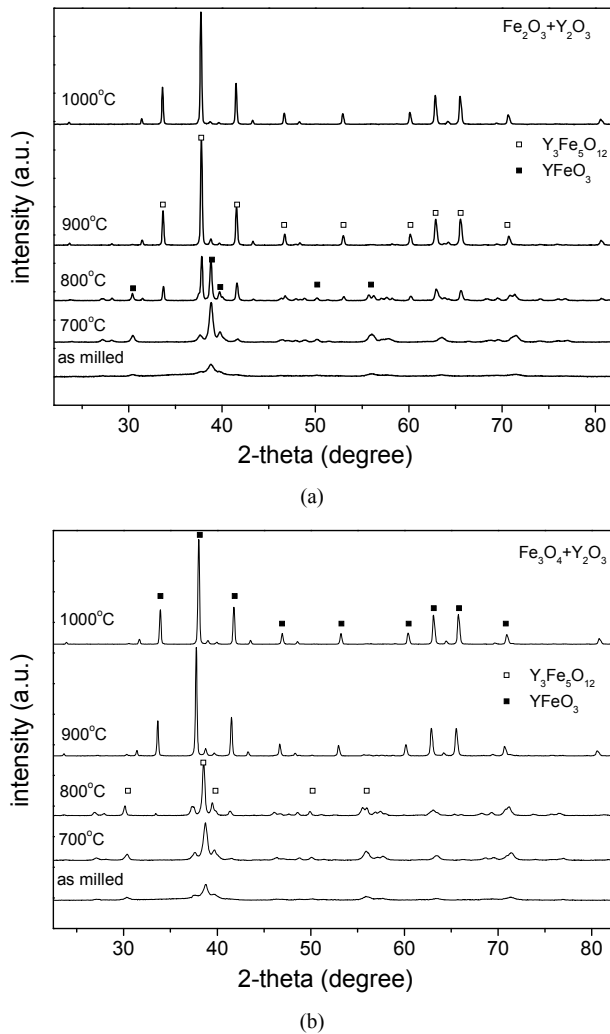


Figure 3. X-ray diffraction patterns of milled powders: (a) ($\text{Fe}_2\text{O}_3 + \text{Y}_2\text{O}_3$) mixture; (b) ($\text{Fe}_3\text{O}_4 + \text{Y}_2\text{O}_3$) mixture, annealed at different temperatures during 3 h.

3.3. Magnetic Characterization

Figure 4 shows the hysteresis loops of powders rich in orthoferrite from different oxide mixtures milled for 9 h.

There are differences in magnetic behaviors for each precursor. The highest saturation magnetization is obtained for $\text{FeO} + \text{Y}_2\text{O}_3$ milled powder mixture. This particular sample showed the presence of Fe^0 in X-ray diffraction analysis. So, if saturation magnetization is additive in weight proportion to each component (according to the mixture theory), an estimation of the total magnetic saturation for each obtained sample can then be carried out. Results of calculations are presented in **Table 3**, as well as the experimental results extracted from the hysteresis loops in **Figure 4**, where is presented the magnetic characterization of different oxides mixtures from different iron oxides after milling for 9 h.

If the experimental and calculated results (**Table 3**) are compared, we can conclude that the calculated values are always larger than the measured ones. This can be due to two possible reasons: first, the measured value is not strictly the saturation value (at the highest applied field there remains a noticeable slope), and second, the YIG content (which is the main component with high saturation magnetization) could be slightly overestimated. The experimental results for coercive field are in the 120 - 300 Oe range, these are characteristic values of small grains with a large concentration of defects.

Figure 5 is a plot of magnetic characterization of YIG obtained from different iron oxides after heat treatment at

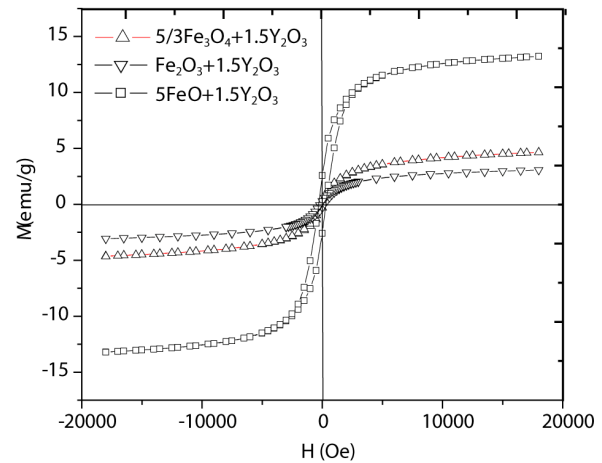


Figure 4. Hysteresis loops at $H_{\text{max}} = 19 \text{ kOe}$ measured at room temperature, for oxide powders milled from ($\text{FeO} + \text{Y}_2\text{O}_3$), ($\text{Fe}_2\text{O}_3 + \text{Y}_2\text{O}_3$) and ($\text{Fe}_3\text{O}_4 + \text{Y}_2\text{O}_3$) mixtures.

Table 3. Magnetization results (emu/g at 19 kOe) [29-32].

Sample	$\text{Fe}_2\text{O}_3 + \text{Y}_2\text{O}_3$	$\text{FeO} + \text{Y}_2\text{O}_3$	$\text{Fe}_3\text{O}_4 + \text{Y}_2\text{O}_3$
Experimental	3.05	13.23	4.63
Calculated	11.64	20.59	10.21

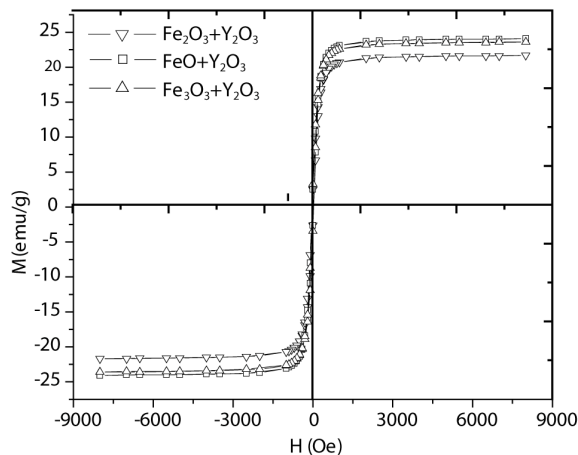


Figure 5. Hysteresis loops measured at room temperature for powders heat-treated at 900°C.

900°C. The highest value obtained is for FeO precursor with saturation magnetization of 24.07 emu/g and coercive force (H_c) of 23.93 Oe, for the others starting oxides the values are (Fe₂O₃) 21.68 emu/g and H_c is 26.8 Oe, and (Fe₃O₄) showed a magnetization of 23.58 emu/g and H_c of 27.37 Oe.

Diminution in values of coercive field with respect to powder samples indicates a relief of defects due to milling, and an increase of crystallite size, in agreement with XRD results.

4. Conclusion

Mechanosynthesis from mixtures of Y₂O₃ with Fe₂O₃, Fe₃O₄ and Fe₂O₃ leads to the formation of a mixture of orthoferrite and garnet phases; a single YIG phase is successfully obtained after annealing at 900°C in all cases. A thermodynamic calculation showed that the (FeO + Y₂O₃) starting mixture produced a slightly larger fraction of YIG, as compared with the other two precursors. The magnetic properties of YIG samples produced by different sources showed minor differences in magnetic behavior; the YIG obtained from (FeO + Y₂O₃) exhibited a M_s value only slightly higher and very close to the reported one.

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