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Comparative study of structure and magnetic properties of micro- and nano-sized $Gd_xY_{3-x}Fe_5O_{12}$ garnet

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ABSTRACT

Gadolinium Yttrium Iron garnet (GdYIG) samples with the chemical formula ($Gd_xY_{3-x}Fe_5O_{12}$) ($x=0.0$, 0.25, 0.5, 0.75, and 1.0) were prepared via two different methods, the standard ceramic method (SC) and the co-precipitation method (CP). The effect of preparation conditions and Gd^{3+} ion substitution on the phase formation, crystal structure, morphology and magnetic properties were studied. Moreover, the initial permeability μ_i and Curie temperature T_c were measured for all investigated samples. It was found that, the lattice parameter increases on addition of Gd^{3+} ion while the porosity decreases for both systems of samples. The crystallite sizes of the samples prepared by the (CP) method are smaller than those prepared by (SC) method. The magnetization M_s decreases while the coercivity H_c increases by increasing the Gd^{+3} concentration in both systems of samples. For the samples prepared by the (SC) method the values of M_s are higher than those prepared by (CP) method. Also, it was found that the initial permeability μ_i and Curie temperature T_c are higher in samples prepared by (SC) method than those prepared by (CP) method. Moreover the magnetic loss (the rate of temperature raise ($\Delta T/\Delta t$) in an AC magnetic field) was measured for all investigated samples, which increased with increasing Gd concentration. Furthermore, it was found that the samples prepared by (SC) method have magnetic loss higher than those prepared by (CP) method.

It was concluded that the preparation method has great effects on the magnetic properties of GdYIG ferrite. The obtained results were explained in the light of Neel's model.

1. Introduction

Rare earth (RE) garnet are complex ceramic oxides, having a cubic crystal structure belongs to the space group $O_h(10)$-Ia3d, and the cations are arranged on three crystallographic sublattices namely c-sites (dodecahedral), a-sites (octahedral) and d-sites (tetrahedral) [1]. RIG, whose chemical formula is $R_3^{3+}Fe_2^{3+}Fe_3^{3+}$, is isostructural with the natural garnets. The rare earth ions, two-fifths of $Fe^{3+}$and remaining Fe^{3+}ions lie on dodecahedral, octahedral, and tetrahedral sites of the garnet structure, respectively. This in which Fe^{3+} ions are coupled *via* antiferromagnetic superexchange interactions [2,3].

Garnet ferrites are employed in a truly wide range of applications such as (magnetic recording, data storage, MW/GHz electronic devices, electromagnetic (EM) absorbers, drug delivery and biomedicine applications) due to their high electrical resistivity and very low magnetic losses, especially in the microwave region [4–6]. Generally, the enhancement and modification of the magnetic and electric properties for garnets can be achieved through three main procedures: the substitution with other cations (such as Y, Nd, Gd, La, etc.) [7], the method and conditions of preparation and the treatment after preparation (such as temperature annealing, magnetic annealing, pressure, and irradiation) [8]. Bertaut and Forrat in 1956, prepared for the first time Yttrium iron garnet, which also referred to as YIG [3]. The Gd magnetic moment is insensitive to the superexchange anisotropy due to the absence of net orbital angular momentum ($L=0$) and also to crystalline field. The dominating interaction between the (a) and (d) sites is superexchange interaction which renders their magnetic moments antiparallel and determines the Curie temperature (T_C) whereas the magnetization of R^{3+} ion sublattice is opposite to the resultant magnetization of Fe^{3+} ion sublattices giving rise to ferrimagnetism [2].

As we are aware, there are no systematic comparative studies about the effect of the preparation conditions on the magnetic properties of the series $Gd_xY_{3-x}Fe_5O_{12}$ ($x=0.0$, 0.25, 0.5, 0.75, and 1.0) in the literatures. So, the motivation in this study is to prepare $Gd_xY_{3-x}Fe_5O_{12}$ using two different methods (standard ceramic and co-precipitation) to trace the effect of preparation conditions and Gd^{3+} ion substitution on the phase formation, crystal

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structure, morphology and magnetic properties of this system.

2. Experimental procedure

The garnet ferrites samples with composition ($Gd_xY_{3-x}Fe_5O_{12}$), where ($x=0$, 0.25, 0.5, 0.75 and 1) were prepared by two methods: the standard ceramic method (SC) and co-precipitation method (CP).

2.1. Standard ceramic method (SC)

Stoichiometric ratios of Fe_2O_3 (99.99%, GFS chemicals), Y_2O_3 (99.99%, REACTION) and Gd_2O_3 (99.99%, SIGMA) were mixed according to the chemical formula ($Gd_xY_{3-x}Fe_5O_{12}$), where ($x=0$, 0.25, 0.5, 0.75 and 1). The components of each sample were mixed carefully to get a mixture of high homogeneity. This mixture was grinded well in a mortar grinder using a machine type (Retsch RM100) to a very fine powder, and then the powder of each sample was presintered at 900 °C for 10 h. The annealed powder for each sample was grinded again and pressed at room temperature, under a pressure of 7.7×10^8 Pa into tablet forms. They were finally sintered at 1400 °C for 12 h and then slowly cooled to room temperature.

2.2. Co-precipitation method (CP)

$Fe(NO_3)_3\cdot9H_2O$, $Y(NO_3)_3\cdot6H_2O$, and $Gd(NO_3)_3\cdot6H_2O$ (99.99%, Alfa Aesar) were used in the (CP) method. The reactant nitrates were weighed for each composition according to their molecular weight and dissolved in bidistilled water. Drops of ammonia solution on the prepared nitrate solution were added till $pH\approx10.5$. The aqueous suspensions were stirred at 500 rpm for 4 h to achieve a good homogeneity. The solution then heated at 75 °C for 3 h producing a dark-brownish precipitate. The precipitation product was separated by filtration. The filtered precipitated was washed several times with distilled water and finally by ethanol. The precipitate was then dried in an oven at 110 °C for 24 h. Finally, in order to form Gd-YIG phase the produced powder was annealed in air at 1200 °C for 3 h.

3. Characterization

The phase identification for the prepared samples was examined by X-ray diffractometer (X'Pert Graphics). The porosity percentage $P(\%)$ was calculated according to the relation: $\boldsymbol{P}\% = [1-\frac{\boldsymbol{D}}{\boldsymbol{D}_x}]100\%$, where D is the density of each composition measured in bi-distilled water using Archimedes' principle and D_x is the X-ray density. Field emission scanning electron microscopy (FESEM) was performed using (FBI Company, Quanta, model FEG – 250) to study the microstructure of samples. The powders were gold coated and the electron microscope was operated at 20 kV excitation potential. The magnetic properties were measured at room temperature using vibrating sample magnetometer VSM (7410 Lakeshore, USA) in a maximum applied field of 20 kOe. Finally, the dependence of initial permeability on temperature was studied by measuring the self-inductance of designed coil filled with the prepared samples. The measurement was taken at $f=10$ KHz and $I=10$ mA from room temperature up to 350 °C using LCR bridge (TEGAM Inc. Model 3550, 42.0 Hz to 5.00 MHz). A programmable furnace is used to control the temperature. The initial permeability was determined by dividing the self-inductance of coil with sample core L_{sample} by that of the coil with air core L_{air}

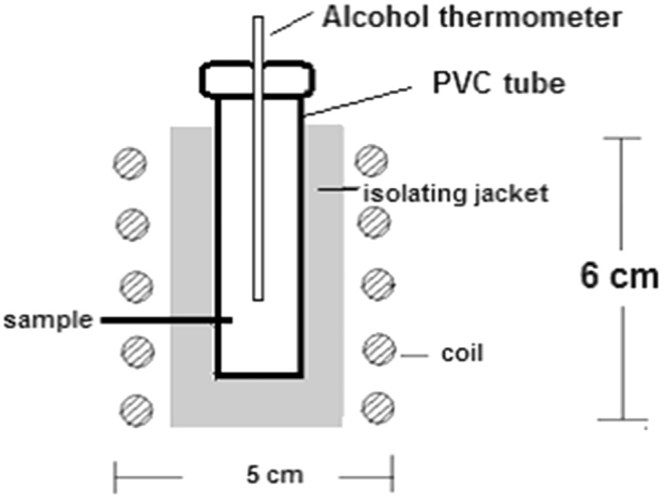

Fig. 1. Exposure set up AMF using the induction heater. The alcohol thermometer, sample holder, insolating jacket and coil dimensions are shown.

$$\mu_i=\frac{L_{sample}}{L_{air}}.$$

The heating ability of the samples under the exposure of AC magnetic field ($F=280$ kHz and $H=13$ kA/m) is measured for the all prepared samples by recording the temperature rise with time using the experimental setup as shown in Fig. 1.

4. Results and discussion

4.1. X-ray analysis

Fig. 2 shows the X-ray diffraction patterns of the formed powders of $Gd_xY_{3-x}Fe_5O_{12}$ prepared by the standard ceramic method (SC) and coprecipitation method (CP) respectively. The planes were indexed compared with JCPDS (Joint Committee on Powder Diffraction Standard) cards of $Y_3Fe_5O_{12}$ (JCPDS 43-0507). It could be seen that the crystallization of the garnet cubic phase structure is formed as the major phase except a small percentage (1.2–2.6%) of perovskite phase (yttrium orthoferrite) ($YFeO_3$). This perovskite phase ($YFeO_3$) was indexed using (JCPDS 39-1489) and its corresponding peaks are shown by small arrow in the figure.

The lattice parameters, a, of all investigated samples were calculated according to the Nelson-Riley formula [9] and are shown in Fig. 3. It is clear that, as the concentration of the Gd^{3+} ions increases, the lattice parameter increases for both systems of samples. This increase could be interpreted due to the larger radius of Gd^{3+} ions (0.938 Å) than Y^{3+} ions (0.858 Å). Furthermore, the samples prepared by the CP method have higher lattice parameter than those prepared by the SC method. This observation could be attributed the change in particle size of the two prepared systems. Where, it is expected that the particle sizes of CP samples are smaller than those of SC samples due to the difference in annealing temperature [10]. As the particle size decreases the repulsive dipolar interactions at its surface increase due to the existence of unpaired electronic orbitals [11]. Furthermore, the existence of oxygen vacancies at the particle surface results the formation for charge compensation. As the ionic radius of Fe^{2+} is greater than that of Fe^{3+} the lattice parameter expands [12].

The average crystallite size was calculated using the Debye Scherrer equation. The variation of the crystallite size and grain size with Gd^{3+}content (x) is shown in Table 1. It is observed that the crystallite sizes of the samples prepared by the CP method are