The Effect of Sintering Temperature on the Structure and Conductivity of the Yttrium Iron Garnet (Y₃Fe₅O₁₂) Nanocrystallite Phase

I. Kashif, Samy A. Rahman*, E. M. Ibrahim* and A. M. Sanad

AL-AZHAR Center for Material Science and Glass research
AL-AZHAR University, Nasr City, Cairo, Egypt 11884

*Physics and Mathematical Engineering Department
Faculty of Engineering Ain-Shams University, Cairo, Egypt

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Abstract

Nano-crystalline Yttrium iron garnet (Y₃Fe₅O₁₂) phase was prepared at various sintering temperature by the usual ceramic method. X-ray diffraction studies indicated the presence of cubic single phase when sample sintering at 1400°C for 12 hours. The Mössbauer spectra indicate the presence of Fe³⁺ in (A) site and (D) site and the ratio of the two peak area ID/IA equal 1.58 for sample sintered at 1400 °C. A dielectric measurement shows that the sample sintered at 1300 °C has higher conductivity. The difference in dielectric behavior is due to factors such as ceramic density, the change of microstructure shape, and presence of mixing phases with difference ratio for sample sintered at 1100 °C and 1300 °C and pure cubic phase for sample sintered at 1400 °C.

Keywords: Nano-crystalline Yttrium iron garnet, X-ray diffraction, Mössbauer effect, dielectric properties.

Introduction

The material yttrium iron garnet YIG is one of the most famous garnets because it used in many applications. Previously, Taketomi, et al. [1-3] found that the preparation of transparent magnetic fluids is necessary for applications of the magnetoptics of magnetic fluids. It was also found that yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) or YIG is suitable for colloidal particles of transparent magnetic fluids [2, 4]. Several researchers have prepared YIG ultra fine particles about 10 nm in size. For example, Abe and Gomi prepared particles by the coprecipitation technique [5], while Matsumoto and Fujii used mist pyrolysis [6, 7]. In homogeneity in the stoichiometry of the particles often occurs with these techniques [6-8]. The alkoxide method readily lends itself to preparing metal oxides, which are hard to synthesize by the conventional techniques (solid-state reactive firing, coprecipitation, sol-gel, etc.) [9]. and it also allows preparation of homogeneous ultra fine particles in stoichiometry [8]. Taketomi et al. have recently prepared YIG powders by the alkoxide method [10]. The cation distribution is important for the preparation of magnetic materials with controlled properties. It is known that the substitution of nonmagnetic ions for iron changes the moment by altering the difference in the number of magnetic ions in tetrahedral and octahedral sites in yttrium iron garnet [11, 12].

The present work attempts to produce powders of YIG by using the direct reaction method at different sintering temperature. The effect sintering temperature on structure and electrical conductivity will be discussed.

Experiment

The sample $\text{Y}_3\text{Fe}_5\text{O}_{12}$ was prepared by direct reaction method. Fe_2O_3 , Y_2O_3 powders were all of 99.99 % purity. After drying powders and milling for 24 hours, the mixture was pressed into the form of pellets. These pellets were calcined at 1000°C for 24 hours, then samples grinding by electrical mill for 4 hours. The mixture was pressed into the form of pellets and heated at sintering temperatures 1100°C , 1300°C and 1400°C , for 12 hours, in an air atmosphere. The pellets were cooled to room temperature.

X-ray diffraction patterns of the samples were obtained at room temperature with Cu K α radiation using Philips x-ray diffractometer model PW3710.

Mossbauer spectra were obtained with a constant acceleration spectrometer with ^{57}Co source (25 mCi) in rhodium matrix. The sample's surfaces were coated with silver paste as a contact material for electrical measurements. The electrical conductivity measured as a function of frequency and temperature. The frequency ranges from 50Hz to 100 KHz and the temperature extends from room temperature up to 600 K using PM6304 LCR meter.

Results and Dissections

The X-ray diffraction pattern of the sintered sample at 1100 °C for 12 hours signified the presence of two crystalline phases. The first phase is α -Fe₂O₃, rhombohedra system with hexagonal indices, which have the unit cell parameters: $a = 5.036$, $c = 13.752$ Å. The α -Fe₂O₃ has a corundum structure. Other crystalline phase is orthorhombic YFeO₃. The unit cell parameters were calculated to be $a = 5.628$, $b = 7.634$ and $c = 5.318$ Å. and its crystal structure is a perovskite-like structure. It should be noted that the strongest diffraction line for both α -Fe₂O₃ and YFeO₃ was observed at 2θ angle at 35.611° indicate the presence of YFeO₃ only [13], and addition to third detected phase was the cubic, garnet-like phase, Y₃Fe₅O₁₂. The unit cell parameter was calculated to be $a = 12.405$ Å. The x-ray density of the cubic phase is, $\rho_{\text{x-ray}} = 4.948$ gm/cm³. The YIG phase constitutes only about one-third of the total volume of the sample.

For the sample sintered at 1200 °C for 12 hours. Indexing of diffraction pattern leads to the suggestion of the presence of two crystalline phases: The first phase, which is dominant, was the cubic YIG phase. The unit cell parameter for the YIG was calculated to be, $a = 12.368$ Å, which is close to the value in the literature [14]. The second crystalline phase was an orthorhombic phase, YFeO₃. It should be noted that the volume fraction of the orthorhombic phase (0.37) was found to decrease as the sintering temperature increased from 1100 to 1200°C for the 12 hours period. The unit cell parameters were found to be $a = 5.560$, $b = 7.596$ and $c = 5.277$ Å.

For the sample sintered at 1300°C for a 12 hours period, the dominant phase was detected as YIG phase, it should be noted that the intensities for these lines were found to be increased although the sintering temperature increased from 1200 to 1300°C. However, it was observed that these lines were shifted towards larger d values, i.e., towards smaller angles. This small shift may correspond to an increase in the unit cell parameter by about 0.04 Å, the unit cell parameter was found to be, $a = 12.404$ Å.

For the sample, which was sintered at 1400°C for 12 hours, as shown in figure 1 all the diffraction lines were identify the product as YIG single phase, which agrees with the standard card number (43-507) ICDD# file. The lattice parameter was found to be $a = 12.404$ Å, and the x-ray density was calculated to be $\rho = 4.949$ g/cm³. The average crystallite size calculated using Sherrer equations. It is equal 59 nm. Such size values classify the studied samples as nanocrystalline materials [14].

Figure 1 The X-ray diffraction pattern of the sintered sample at 1400 °C for 12h

For all samples sintered at different temperature 1100, 1200, 1300 and 1400 °C for 12 hours, the Mossbauer spectra were obtained at room temperature.

For the sample sintered at 1100 °C, three sets of six lines were obtained. The outer lines were ascribed to the iron ions in the yttrium orthoferrite phase. The hyperfine field was about 495 KOe, the isomer shift was about 0.22 mm/s with respect to the metallic iron, and the quadrupole shift was about 0.08 mm/s. the iron ions found exclusively in octahedral sites. The inner two sets of lines were ascribed to the YIG phase, where the iron ions were found at two different sites, octahedral and tetrahedral sites. The hyperfine fields were found to be about 470 and 380 KOe, respectively, the difference between octahedral and tetrahedral fields is about 90 KOe at room temperature. The isomer shifts at room temperature for octahedral (a) and tetrahedral (d) sites were found to be 0.26 ± 0.01 mm/s and 0.06 ± 0.01 mm/s, respectively. Both lines of YIG phase have relatively small quadrupole shifts, about 0.01 mm/s. the relative intensities for the lines of the two phases show that the YFeO_3 phase is, really, dominant in this sample.

For the sample, which was sintered at 1200°C, also three sets of six lines were observed, one set for iron ions at (a) sites in YFeO_3 phase and two sets for the iron in YIG phase. The hyperfine field for octahedral (a) site in YFeO_3 was about 502 KOe, and the isomer shift was about 0.32 mm/s, and the relative intensity of this line was less than the one found in the sample sintered at 1100°C. The increase in the relative intensity of the tetrahedral line may reflect the increase of the garnet phase, and this intensity becomes doubled. The hyperfine fields for iron ions in YIG phase were found to be about 466 and 399 KOe for octahedral and tetrahedral sites respectively. This isomer shifts for both sites were found to be about 0.33 and 0.10 mm/s respectively. The smaller value of the isomer shift for the tetrahedral coordinated iron ions indicates a larger degree of covalence for this sub-lattice [15].

As the sintering temperature increased from 1200 to 1300 °C, the relative intensity for the lines of YFeO_3 phase decay or decreased until 2 %. On the other hand, for iron ions in YIG phase, the intensity of the tetrahedral line increased to be about that of the octahedral line. The hyperfine fields, for both (a) and (d) sites were found to be 469 and 371 KOe, respectively. The isomer shifts for (a) and (d) sites were found to be 0.40 ± 0.01 mm/s and 0.21 ± 0.01 mm/s respectively.

For sample sintered at 1400°C/12 hours, the Mossbauer spectrum exhibits, only, two sets of six Lorentzian lines, as shown in figure 2, which in the pattern of YIG single-phase. The magnetic hyperfine fields at room temperature were found to be 477 and 386 KOe for octahedral and tetrahedral sites, respectively. The isomer shifts for (a) and (d) sites were found to be 0.43 ± 0.01 mm/s and 0.21 ± 0.01 mm/s respectively. From the values of the area ratio of (D) site to (A) site ID/IA , it can be observed that the values of the area ratio increase with the increasing of sintering temperature up to 1.58 at 1400 °C. A Mossbauer spectroscopic result for YIG agrees with that of pervious work [16, 17].

Figure 2 the Mossbauer spectrum for sample sintered at 1400°C/12 hours.

Figure 3 shows the variation of the electrical conductivity versus frequency for three samples. The electrical conductivity shows a dispersion with frequency at relatively low temperatures where σ increases with increasing the frequency. The dependence of the electrical conductivity on the frequency decreases with increasing temperature, and at high temperatures, it becomes frequency independent.

Figure 3 the electrical conductivity versus frequency for samples.

Generally, the AC conductivity can be written as the sum of two components [10, 18, and 19] as

$$\sigma = \sigma_{dc} + \sigma(\omega, T) \quad (1)$$

where (σ_{dc}) is the DC electrical conductivity. The DC electrical conductivity is related to the drift mobility of free charge carriers and independent of frequency in the studied frequency range. The second term $\sigma(\omega, T)$ is related to the dielectric relaxation caused by bound charge carriers. It obeys a power law, which could be written as [20-23].

$$\sigma(\omega, T) = B \omega^s \quad (2)$$

Where ω is the angular frequency, B is temperature dependent parameter and has conductivity units. In addition, s is the frequency exponent.

Figure 4 shows the variation of the exponents S with temperature for all the investigated samples. It is clear that at low temperatures the exponent S decreases rapidly with increasing temperature in all cases. Which agrees with the correlated barrier-hopping (CBH) model [24]. Such values are closely associated with proven carrier transport hopping electrons. It has been established that a value of s close to unity is considered to be associated with the lattice responses [25]. The distinction between lattice and carrier responses is that they correspond to intrinsic and extrinsic process, respectively, due to some impurities or injected carriers as a result of transition metal ions.

Figure 4 the exponents S with temperature for all the investigated samples.

For classical barrier hopping [26, 27] shows a decrease in S with increasing temperature. Therefore, the behavior of σ_0 with frequency and S with temperature, respectively, suggests that the classical barrier hopping model is the most favorable mechanism to describe the conduction mechanism for the samples under investigation.

The AC conductivity in materials has been considered by many authors and different models were proposed to account for its dependence on temperature and frequency [28-30]. They reported that the electrical properties in a periodic field depend not only the mobile (ions or electrons), which give rise to DC conductivity but also on other relatively immobile ions or on dipole, etc. which form part of the network. Also observed that for the AC conductivity in a wide range of materials, including a number in which conduction by hopping is expected. They reported that the exponent s typically cover the range 0.5–1 at room temperature. And proposed the correlated barrier-hopping model (CBH). According to this model, barrier hopping of bipolarons (i.e. two electrons hopping between charged defects D^+ and D^-) has been proposed to interpret the frequency dependence of conductivity.

Figure 5 shows the variation of the AC conductivity ($\ln \sigma$) against the reciprocal of temperature ($10^3/T$) for all the prepared samples at some selected frequencies. It is clear from a figure that the behavior of the AC conductivity is similar for all samples where it increases with increasing temperature in different regions. The change of conductivity in previous regions was due to a change in the conduction mechanism. This behavior is similar to those for many semi conducting materials.

Figure 5 the AC conductivity ($\ln \sigma$) against the reciprocal of temperature ($10^3/T$) for all the prepared samples at some selected frequencies.

It is also observed that at relatively low temperatures (in ferrimagnetic region) the frequency dependence of the AC conductivity is very clear and decreases with increasing the temperature. At high temperatures above Curie temperature (Paramagnetic regions), σ_0 becomes frequency-independent and increases linearly with increasing temperature. According to pervious work [30, 31] the Curie temperature of YIG sample lie around 550 K which is far from the temperature of different regions except the change in final region. Hence the changes are attributed to a change in the conduction mechanism. Moreover, final change is due to Curie temperature and the same change can be observed at the break point in the relation between $\log \sigma_{dc}$ and $1/T(k)$ as shown in figure 6

And all values of σ_{ac} for all composition are found to obey equation (1) which is valid for crystalline materials.

The dielectric function of crystal has a more complex structure, which is related to the distortions of the crystalline lattice, and also the presence of interior interaction, however the crystal oscillation modes depend on the displacement of ions situated in tetrahedral, octahedral and dodecahedral crystallographic positions.

Figure 6 the relation between $\log \sigma_{dc}$ and $1/T(k)$

Conclusions

X-ray diffraction, Mossbauer spectroscopy and AC conductivity measurements at temperatures from 300 to 600 K, were used to study the effect of sintering temperature in YIG. The Mössbauer spectra indicate the presence of Fe^{3+} in (A) site and (D) site and I_D/I_A equal 1.58 for sample sintered at 1400 °C. The XRD results indicate the nanocrystallite cubic phase of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ observed in sample sintered at 1400 °C, while the cubic and orthorhombic phases of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ observed in sample sintered at 1100 and 1300 °C.

From AC conductivity, observed the sample sintered at 1300 °C has higher conductivity. From it can be suggested that the difference in dielectric behavior is due to factors such as ceramic density, the change of microstructure shape, and presence of mixing phases with difference ratio for sample sintered at 1100 and 1300 °C and pure cubic phase for sample sintered at 1400 °C.

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