Complex permeability, Curie temperature and activation energy as a function of microstructure evolution in a mechanically alloyed $Y_3Fe_5O_{12}$ single-sample.

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ABSTRACT

We report on an investigation to unravel morphological and magnetic-property dependence on sintering temperature for mechanically alloyed $Y_3Fe_5O_{12}$ single-sample. The sample was sintered at various sintering temperatures from 600°C to 1400°C. The dependence of the complex permeability, Curie temperature and activation energy on the microstructural evolution was studied respectively. The complex permeability showed an increasing trend parallel to the grain growth of the sample. How this correspondences depends on the relationship between ordered magnetism and the microstructure of the sample was duly explained. The Curie temperature was independent of the grain growth and remained almost constant over the grain changes. Additionally we found that two stages of activation energy sensitively influenced the sample grain growth, hence influencing the magnetic properties.

INTRODUCTION

In recent years, great interest on yttrium-iron garnet (YIG) has been focused on the dependence of physical and chemical properties on the grain size. For this reason, there is a renewed interest in the development of new techniques to produce particles in different sizes, sufficiently monodispersed and with a good degree of homogeneity. Generally, YIG powder can be prepared either by using a solid state method such as ball milling, high energy ball milling (HEBM), mechanical alloying (MA) or by using a chemical method such coprecipitation, sol-gel, microemulsion etc.

However, among the methods mentioned above, the MA method has attracted much interest in recent years due to its simplicity in the preparation of various interesting solid-state materials. MA milling is used for the preparation of nanocrystalline powders and takes advantage of perturbation of surface-bonded species by pressure to enhance thermodynamics and kinetic reactions at room temperature or at least much lower temperatures than normally required to produce a pure metal (Suryanarayana, C. 2001; Fathi, M.H. and Zahrani, E.M. 2009). This is due to the energy transferred from the milling media to powder particles which are continuously submitted to fracture and cold welding processes that will define their final morphology. The energy transfer to the powder particles in these MA mills takes place by a shearing action or impact of the high velocity balls with the powder. The size of the nanoparticles depends on several factors namely milling speed; type and size distribution of balls; ball to powder weight ratio; milling atmosphere and so on (McCormick, P.G., et al., 1998). This process has the advantage to produce large quantities of material and is already a commercial technology. However, contamination from balls should be taken care of.

In the ferrite industry, it is desirable to produce samples with low loss and high permeability. However, Ref. (Roess, E. 1982) has pointed out that it is impossible to obtain both high permeability and very low loss material. For this reason, there is a renewed interest in the development of new techniques to produce particles in different sizes, sufficiently monodispersed and with high homogeneity to achieve the best compromised low loss-high permeability combination.

The earliest work on correlating grain size and permeability was carried out by Ref. (Guillaud, C. 1957) on manganese zinc ferrite. Ref. (Guillaud, C. 1957) related the inflection at 5 µm to a change from a domain rotation mechanism to a wall movement mechanism. He considered the limitation at about 20 µm to be due to the presence of pores included in grains. Permeability appears to increase with increasing grain size by assuming
the other factors, such as porosity, to remain constant. If high magnetic permeability is desired without regard to high magnetic losses, the presence of grain boundaries will act as an impediment to the domain wall movement. The fewer the number of grain boundaries present, the larger the grains and the higher the permeability. The lack of bifurcation during processing, presence of pores, and greater chemical inhomogeneity also prevent the attainment of high permeability. Ref. (Tseng, T.J. and Lin, J.C. 1989) and (Ravindran, P. and Patil, K.C. 1987) also confirm that the permeability increased when the grain size increased.

Ref. (Hahn, H.T. 1991) reported a decrease in permeability with porosity in nickel zinc ferrite. Meanwhile, Goldman (1990) claimed that if pores can be suppressed or located at the grain boundaries, the permeability would increase with grain size. Guillaud (1957) noticed that resistivity in the bulk material was dominated by grain boundaries via his study on grain boundaries (Guillaud, C. 1957). He also discovered the importance of Ca\(^{2+}\) which segregated at the grain boundaries as a useful additive in reducing eddy current losses. The thickness and chemical composition of the grain boundary are two important factors in determining the magnetic properties of ferrites. Ref. (Akashi, T. 1961) showed that addition of a sensibly amount of SiO\(_2\) to CaO could increase resistivity and lower losses, due to an increase in grain boundary resistivity.

Ref. (Ishino, K. and Narumiya, Y. 1987) summarizes the requirements for low-loss ferrites at frequencies up to 1 MHz. The researchers noticed the following combinations of chemical and microstructural aspects to be important:

(i) Suppression of electron hopping from Fe\(^{3+}\) to Fe\(^{2+}\) inside the grains,
(ii) Insulating films surrounding the grain boundaries by the addition of Ca\(^{2+}\) and Si\(^{2+}\),
(iii) Small and homogenous grain size,
(iv) Reduction of pores for increased density as it creates a demagnetizing field and increases flux density.

Pores should be concentrated at the grain boundaries.

Ferrites with nanometer-sized grains exhibit a much higher coercivity than samples having micron-sized grain size (Pal, M. and Chakravorty, D. 1999). This is due to the fact that nanometer-sized particles are not likely to have any grain boundary contribution; however, sintering introduces the effects of grain boundary and some microstructural defects, thereby resulting in higher values of coercivity. The coercive force is the property most sensitive to porosity and grain size. The increase in coercive force with porosity is linear at low porosity and deviates at higher level (Smit, J. and Wijn, H.P.J. 1954). High porosity samples contain smaller particles, which have larger coercive force. It is correlated with Neel’s theory, which states that the demagnetizing effect will increase due to non-magnetic inclusions including pores (Treble, T.S. and Craik, T.J. 1969). Morphological properties are acknowledged as the major factor which influences changes of magnetic properties in ferrites. For several past decades, studies of the relationship between morphological properties and magnetic properties of soft ferrites have been focusing only on the product of the final sintering temperature largely neglecting the parallel evolutions of morphological and magnetic properties. Previously, we have reported the evolution of microstructure-magnetic properties in NiZn ferrites (Syazwan Mustaffa, M., et al., 2013; Ismail, I., et al., 2013; Ismail, I. Hashim, M. 2012; Idza, I.R., et al., 2012; Ismail, I. et al., 2012; Ismail, I., M. Hashim, 2011), to the best of our knowledge no study has been found in the literature attempting to correlate the microstructure with the magnetic properties of Y\(_3\)Fe\(_5\)O\(_{12}\) bulk single-sample produced by mechanically alloyed nanosized powders and later subjected to sintering temperature from 500°C up to 1400°C. This study is aimed at evaluating the microstructural evolution and its effect especially on the complex permeability properties of Y\(_3\)Fe\(_5\)O\(_{12}\) prepared by the mechanical alloying method. We also analysed the activation energy involved during the sintering process and observed its influence on the microstructural changes.

**Methodology:**

To synthesize YIG powders by using high energy ball milling or mechanochemical reaction, Y\(_2\)O\(_3\) and \(\alpha\)-Fe\(_2\)O\(_3\) were used as precursor reagents. The high energy milling was carried out in a SPEX 8000D machine for 2 hours with the ball-to-powder ratio 10:1. The as-milled powders with particle sizes ranging from 50 to 180 nm were compacted into a toroid sample which had an outer diameter of 15 mm and an inner diameter of 10 mm with 2.5 grams in weight by uniaxial pressing at 3 tonne. One green toroid sample was repeatedly annealed in an ambient temperature from 600°C to 1400°C and this heating process is denoted as single-sample sintering. The density of the sample was measured using the Archimedes principle. The surface morphology of the samples was then observed by using a Nova Nano 230 Field Emission Scanning Electron Microscope (FeSEM). An Agilent HP4291B Impedance/Material Analyzer (Figure 4.6) was used to measure the complex permeability of the samples. The measurements were carried out in the frequency range of 10 MHz to 1 GHz at room temperature. The complex permeability is represented by the complex permeability components which are real permeability, \(\mu'\) and magnetic loss factor, \(\mu''\) as shown in equation (1) below:

\[
\mu' = \mu' - j\mu''
\]

(1)
Curie temperature measurements were carried out in order to determine the transition temperature from ferromagnetic to paramagnetic state. Before the measurement, atoroidal YIG samples which had been sintered at 9 different temperatures (600-1400°C) were each wound with 20 turns of 150 cm insulated copper wire with both ends scraped with a sand paper. The samples were heated in the box furnace and connected to an Agilent HP4294A Precision Impedance/Material Analyzer. For each sample, the value of inductance, $L_s$, was recorded from the analyzer at a frequency of 10kHz from room temperature up to 310°C after every increment of 20°C. The Curie temperature point was obtained by plotting $L_s$ value at 10 kHz versus temperature graph. A drastic drop of the $L_s$ value can be seen and the intersection point on the temperature axis indicates the Curie temperature.

RESULTS AND DISCUSSION

3.1 Complex Permeability Measurement:

The room temperature real permeability, $\mu'$, of the single-sample of YIG was measured from 10MHz to 1.8GHz (Fig.1). It can be observed that the $\mu'$ value increases to a maximum value and then decreases rapidly to a very low value. The $\mu'$ value at 10MHz changes linearly with increasing sintering temperature. The observed increase of $\mu'$ with sintering temperature can be attributed to the increased grain size, which correspondingly reduces the porosity and grain boundaries inside of the samples. As mentioned earlier, porosity and grain boundaries, as well as impurities will impede the domain wall movement, thus influencing the permeability of the sample (Xu, Z., et al., 2009).

Furthermore, an increase in the sintering temperature will result in a decrease of magnetic anisotropy, reducing the hindrance to the movement of domain walls, thus increasing the value of $\mu'$. (Gupta, N., et al., 2005). The $\mu'$ spectra also show the ferromagnetic resonance in our testing frequency range. These, according to Snoek’s Law, give the relation $\mu'f = $ constant, where $f_r$ represents the ferromagnetic resonance frequency. Snoek’s Law states that the higher the values of $\mu'$, the lower is the value of the ferromagnetic resonance frequency. The sloping part of $\mu'$ spectra also indicate that ferromagnetic resonance was occurring at a frequency inside the testing range.

Table 1 shows the results for the initial permeability, $\mu_i$, value for the single-sample sintering. The initial permeability is qualitatively the magnetization response at very low exciting fields. The $\mu_i$ value was found to vary with sintering temperature, where the sample sintered at 1400°C has the highest real permeability value of 36.0. This agrees with the expectation that permeability of samples increases with increasing sintering temperature.

It is also known that magnetization in ferrites is contributed by spin rotation and domain walls displacement. Considering Fig. 5(a) and the relatively small $\mu'$ and average grain size values for sintering temperature $\leq$ 1000°C in Table 1, most of the grains corresponding to sintering temperature 1000°C and below are single-domain grains. Therefore the permeability for samples sintered at 1100°C upward is probably dominated by both spin rotation and domain walls forming multi-domain grains, while for samples sintered below 1000°C the permeability is contributed only by spin rotation. Thus the increasing trend of $\mu'$ can be attributed to the increase in density and grain size and the decrease in porosity with sintering temperature (Table 1). The large grains diminish the number of grain boundaries, therefore reducing the hindrance to the domain wall motion. Moreover, pores become fewer, thus lessening the impediments to the domain-wall movement. Generally the permeability of polycrystalline garnet ferrite ceramics is due to two different magnetizing mechanisms, which are spin rotation and domain wall movement. This relationship can be described as (Hossein, A.K.M.A., et al., 2006): 

$$\mu_i = 1 + X_w + X_{\text{spin}}, \quad (2)$$

where $X_w$ is the domain wall susceptibility; $X_{\text{spin}}$ is intrinsic rotational susceptibility. Meanwhile the $X_w$ and $X_{\text{spin}}$ may be written as follow:

$$X_w = 3\pi M_s^2 D/4\gamma \quad (3)$$

and

$$X_{\text{spin}} = 2\pi M_s^2/\gamma. \quad (4)$$

where $M_s$ is the saturation magnetization, $K$ is the total anisotropy, $D$ is the average grain diameter, and $\gamma$ is the domain wall energy. From the formulae given, the domain wall motion is affected by the grain size and enhanced with the increase of grain size. The initial permeability is therefore a function of grain size and magnetization as tabulated in Table 1. Larger grains tend to consist of a greater number of domain walls. As the
number of walls increases with the grain sizes, the contribution of wall movement to magnetization increases. The effect of sintering causes the grains to grow and provides more spaces for the domain movement which is reflected in the increase of initial permeability as seen in Table 1.

Fig. 1: Real permeability measured at room temperature in range of 10 MHz to 1 GHz for single-sample sintering

Table 1: Sintering temperature, average grain size and initial permeability, $\mu_i$, at 10MHz for single-sample sintering, measured at room temperature.

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Average grain size (µm)</th>
<th>Density (g/cm³) ± 0.1</th>
<th>Initial Permeability, $\mu_i$ at 10MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.16</td>
<td>4.09</td>
<td>0.8</td>
</tr>
<tr>
<td>700</td>
<td>0.17</td>
<td>4.18</td>
<td>0.9</td>
</tr>
<tr>
<td>800</td>
<td>0.18</td>
<td>4.27</td>
<td>1.0</td>
</tr>
<tr>
<td>900</td>
<td>0.28</td>
<td>4.39</td>
<td>2.93</td>
</tr>
<tr>
<td>1000</td>
<td>0.33</td>
<td>4.51</td>
<td>4.90</td>
</tr>
<tr>
<td>1100</td>
<td>0.60</td>
<td>4.59</td>
<td>6.62</td>
</tr>
<tr>
<td>1200</td>
<td>1.14</td>
<td>4.63</td>
<td>11.5</td>
</tr>
<tr>
<td>1300</td>
<td>1.68</td>
<td>4.70</td>
<td>21.6</td>
</tr>
<tr>
<td>1400</td>
<td>2.71</td>
<td>4.74</td>
<td>36.0</td>
</tr>
</tbody>
</table>

Besides that, the increase in the sintering temperature leads to a decrease in the magnetic anisotropy by decreasing the internal stress and crystal anisotropy, hence the hindrance to the domain wall motion reduces, thereby increasing the value of the magnetic permeability (Verma, A., et al., 2005).

The results for the magnetic loss factor, $\mu''$, at different sintering temperatures are shown in Fig. 2. The loss factor arises due to a lag between the magnetization or flux induction and external applied field (Gupta, N., et al., 2005). The same trend with magnetic real permeability is observed in the case of magnetic loss factor with respect to the frequency. The sample shows the increase of loss factor with increasing frequency, attaining the maximum value at particular frequency and decreases with a further increase in frequency. As can be observed, the loss factor value is increased as the sintering temperature increased. Ref. (Otsuki, E., et al., 1991) reported that the larger grain size increases the eddy current loss because the domain wall movement is easier in the larger grain. Thus eddy current is induced. Besides that, the fraction of grains that are occupied with domain walls increases in the larger grain thus increasing the eddy current and hysteresis losses. The main types of loss encountered in ferrites are the hysteresis loss, eddy current loss and residual loss. The grain size increased with increasing sintering temperature, therefore the domain wall will easily moves in the larger grains. Hysteresis loss can be minimized if one reduces the hindrance to domain wall motions by reducing the pinning centre to the domain walls movement such as volume fraction of pores, impurities and dislocations, and internal strain inside the samples (Kotnula, R.K., et al., 2010). Besides that, the hysteresis loss becomes less important at high-
enough frequencies due to spin rotation at high frequency. The eddy current losses is more important at higher frequencies as a circulating current is induced in the sample due to changing magnetic field, leading to energy losses. However, in polycrystalline YIG, the eddy current losses can be neglected due to high resistivity (~$10^{14}$Ωcm). Residual loss plays an important role in the high frequency range, therefore to reduce the losses, the complex permeability has to be made to peak at the high frequency as possible and this can be achieved using fine-grained samples. Losses at high frequency are always associated with rotational or spin resonance. This resonance involves energy absorption during its occurrence, followed by dissipation of energy to the lattice in the form of heat (Smit, J. and H.P.J. Wijn, 1954).

**Fig. 2:** Magnetic loss factor, $\mu''$ from 10 MHz to 1 GHz measured at room temperature for single-sample sintering

**Curie Temperature:**

The Curie temperature of the single-sample which was sintered at various temperatures is shown in Fig.3. The single-sample sintering yielded nearly same value of Curie temperature, i.e $\sim 267\pm 5$°C, which is slightly lower than the Curie temperature reported by Ref. (Gilleo, M.A. and S. Geller, 1958) which is 272 °C. The difference is believed to be due to experimental error. Curie temperature is defined by the vanishing temperature for the spontaneous magnetization of the material.

The Curie temperature depends on the superexchange interaction (Rao, A.D., et al., 1999), where it depends strongly on the distribution of Fe$^{3+}$ ions in octahedral and tetrahedral sites which changed the magnetization. It is also depends on the distance between those ions in both of the sites. Since significant magnetization occur only in well-formed crystalline phase, the single-sample YIG did not show any value of Curie temperature for samples sintered at 600°C to 800°C due to incomplete crystal structure (Table 2).
3.3 Activation Energies of the Microstructure Evolution:

Coble’s theory (Coble, R.L., 1961; Shinde, T.J., et al., 2008) mentioned that from the behavior of particle growth, the activation energy of grain growth can be predicted using the Arrhenius equation below:

\[ \frac{d(\ln k)}{dT} = \frac{Q}{R T^2} \]

where \( k \) is the specific reaction rate constant, \( Q \) is the activation energy, \( T \) is the absolute temperature, and \( R \) is the ideal gas constant. The value of \( k \) however can directly be related to grain size according to Ref. [30].

Integration of Eq. (5) would result in the equation below:

\[ \log D = (-Q/2.303R)1/T + A \]

where \( A \) is the intercept on the log \( D \) vs \( 1/T \) plot and \( D \) is the grain size. By using Eq. (6), one can obtain a best fitted straight-line plot of grain size where a plot of log \( D \) versus the \( 1/T \) is as shown in Fig. 5. This method was adopted from Ref. (Li, X. and G. Wang, 2009). We obtained two slopes of \(-Q/2.303R\) of the lines and the values of the activation energy of grain growth (\( Q \)) can be calculated from the Arrhenius plot in Fig. 4 having 2 stages of activation energy which are 17.33kJ/mol and 93.09kJ/mol. These two stages of activation energy show a significant shift of the grain growth process and can be associated with grain size. As we recall, the starting powder of the samples is in nanometer size having been processed via mechanical alloying. During the low sintering temperatures, the activation energy was lowered due to the effect of nanosized particles. The small particles stimulated the growth reaction by having a large surface area. Higher activation energy was needed in order to continue the growth of grains. The shift of activation energy can also be correlated with the microstructural evolution that affects the magnetic properties of the samples. The low activation energy

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**Fig. 3:** The Curie temperature results for the single sample after sintering, at various temperatures.

**Table 2:** Curie temperature value of single-sample sintering as a function of various sintering temperatures.

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Curie Temperature for single-sample sintering ± 5 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>267</td>
</tr>
<tr>
<td>1000</td>
<td>267</td>
</tr>
<tr>
<td>1100</td>
<td>267</td>
</tr>
<tr>
<td>1200</td>
<td>266</td>
</tr>
<tr>
<td>1300</td>
<td>263</td>
</tr>
<tr>
<td>1400</td>
<td>263</td>
</tr>
</tbody>
</table>
(sintering temperature from 600 to 1000°C) which was due to the smaller size of starting powders which were initially mechanically alloyed, reducing their dimensions into the nanosized region. This caused the surface area of the starting powders to be increased and lower down the activation energy. Since the sample has been sintered repeatedly, causing it to have a thermal history and higher activation energy needed for the second stage of the grain growth.

**Fig. 4:** Plots of log D versus the reciprocal of absolute temperature (1/T)

Density remains almost the same but the grain size were increasing with the sintering temperature as can be seen in Fig. 5 and Table 1. The grain growth effect has influence the formation of domain wall and initial permeability was observed to rise significantly within this temperature range. Looking at the microstructure of the sample sintered at 1000°C, it could be deduced that the shape and size of grains contributed dominantly to the coercivity through shape anisotropy. No in-grain domain wall was formed for this sintering temperature. A columnar shape of grains formed during this stage and it is not favorable for the magnetic moment rotation compared to the equiaxed grain shape in the samples sintered at 1100°C and above. Fig. 5 shows micrographs of single-sample sintered at 1000°C, 1100°C and 1200°C respectively. The picture clearly shows the shape grain-changes in the samples which contributed to the rise of complex permeability of the sample.
Fig. 5: SEM micrographs of YIG single-sample sintered at: (a) 1000°C, (b) 1100°C and (c) 1200°C.

Conclusions:
Real permeability corresponded to the increase of sintering temperature. Increased grain size (due to sintering process) resulted in increase of $\mu'$. Domain walls dominated the grain, giving rise to the sample sintered above 1100°C. This effect was also observed with the loss factor. The Curie temperature for YIG single-sample was 267°C; it remained the same even with changes in grain size. This shows that Curie temperature is independent of microstructural effects and relies only on exchange forces. Interestingly, two stages of activation energy were found using the Arrhenius equation. The lower activation energy was due to the higher reactivity of nanometer-sized starting powder. Reduced surface reactivity from repeated sintering of the single-sample caused higher activation energy needed for the grain growth.

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REFERENCES

Akashi, T., 1961. Effect of the addition of CaO and SiO$_2$ on the magnetic characteristics and microstructures of manganese–zinc ferrites (Mn$_{0.68}$Zn$_{0.21}$Fe$_{2.11}$O$_{4+\delta}$), Transactions of the Japan Institute of Metals., 2: 171-176.
Ismayadi Ismail et al., 2014
Australian Journal of Basic and Applied Sciences, 8(3) March 2014, Pages: 474-482

Ismayadi Ismail, M. Hashim, 2011. Structural and magnetic properties evolution of fine-grained Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ series synthesized via mechanical Alloying, Australian Journal of Basic and Applied Sciences, 5(11): 1551-1561.

Ismayadi Ismail, I., M. Hashim, K.A. Matori, R. Alias, J. Hassan, 2012. The transition from paramagnetic to ferromagnetic states as influenced by evolving microstructure of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. Journal of Superconductivity and Novel Magnetism., 25(5): 71-77.

Ismayadi Ismail, I., M. Hashim, 2012. Sintering temperature dependence of evolving morphologies and magnetic properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ synthesized via mechanical alloying. Journal of Superconductivity and Novel Magnetism., 25(5): 1551-1561.


Li, X. and G. Wang, 2009. Low-temperature synthesis and growth of superparamagnetic Zn$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ nanosized particles, Journal of Magnetism and Magnetic Materials., 321: 1276-1279.


