Model Analysis of Phase Transformation on Gadolinium-doped Yttrium Iron Garnet

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Abstract. The most suitable model to describe the yttrium iron garnet (YIG) sintering reaction has been evaluated in this study. The sintering reaction at the optimum temperature was predicted by the simulation method. When sintering takes place at a temperature of 1200°C, an intermediate compound of YIP is formed, then at a temperature of 1450°C the formation of YIG reaches a steady state. Sintering at 1450°C for 5 hours resulted in a YIG conversion of about 99.7%. The calculation of the activation energy value of the YIG sintering reaction was carried out based on linear regression technique using the Arrhenius plot. SCM modeling has a deviation tolerance of 0.923 and describes a two-step reaction. The SCM modeling was rated the best compared to other models, and was suitable for describing the true Gd-doped YIG sintering reaction. SCM modeling is considered to be able to describe the actual conditions of the YIG and Gd doped YIG sintering reaction.

Keywords: Garnet, Modeling, Phase conversion, Sintering, Shrinking core model

1. Introduction

Yttrium iron garnet is needed as a circulator part in radar and telecommunication components. Efforts to improve the performance of YIG have been carried out by adding doping materials, for example, the gadolinium element to form Gd-doped YIG. YIG was formed by the sintering process in solid conditions. So far, research on YIG sintering has been carried out by adjusting the sintering temperature, either conducted at a relatively lower temperature than 1200°C, or above 1500°C. In other case, the raw material composition of Fe\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3} and Gd\textsubscript{2}O\textsubscript{3} was adjusted to obtain a single-phase of YIG [1].

Yttrium iron garnet compounds can be formed through the sintering process using Fe\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} as raw materials with a molar composition of 5: 3. The reactions that occur during sintering can be configured through modeling study. A solid-state reaction mechanism has been described in a model called the shrinking core model (SCM) [2]. This modelling uses the main assumption that there is a process that occurs by diffusion or reaction, at the boundary that separates the two zones in the solid. The rate of reaction or diffusion rate is defined as a irreversible or reversible reaction which involves the insertion of foreign compounds into the parent structure and results in significant structural modifications.
to the parent, for example, the insertion of yttrium in the YIG compound. The shrinking core model has been widely used in process technology to describe gas-solid reactions [3]. The reaction mechanism in YIG sintering at a solid state was also studied using the shrink core model [4].

In this study, several models that can describe the YIG sintering process will be investigated. The indication of intermediate product formation prior to the formation of the final YIG product will also be reviewed in this study. It will also be evaluated when intermediate product formation occurs during the YIG sintering process. The addition of Gadolinium as a doping substance in YIG will also be investigated to see if it shows the same trend.

2. Methodology
The actual condition of the YIG sintering reaction needs to be described by modeling the sintering reaction to confirm the reaction mechanism that occurs. So far, the literature data provides information on the conversion of YIG formation up to a temperature of 1250°C. Calculation and simulation methods were carried out to complement the lack of data as a prediction of the sintering reaction at a practical temperature of 1450°C. Based on the simulation data, the product conversion value, reaction rate, reaction rate constant, deviation tolerance and activation energy value are obtained. The simulation value is then compared with the available data, to determine the suitability of the selected YIG sintering modeling.

3. Result and Discussion
3.1. The governing equation
The sintering reaction of YIG is described simply in terms of the solid-state reaction equation according to:

\[ aA(s) + bB(s) \rightarrow cC(s) + dD(s) \]  

The reaction that occurs between solid oxides is assumed to occur at the particle interface at radius \( r \), and is described as moving from the outer surface of the particle to its center during the reaction process. A reaction process occurs at the interface of the core and shell, while the ionic diffusion process occurs at the layer between the reaction interface and the outer particle surface. The application of the assumption of shell and core type reactions shows the ease with which the definition of the conversion of the dominant phase product is only related to the position of the shell and core interface. The conversion of the yttrium iron garnet product is given the symbol \( X(t) \) formulated in a mathematical equation as follows:

\[ X(t) = \frac{n(0) - n(t)}{n(0)} \]  

where \( n \) is the composition of the reacting solid particles (in mol units).

If the reactants are only present in the nucleus, then the amount of reactant in the particle is proportional to the volume of the nucleus, related to the density of the material. The conversion of the reactant particles can be expressed as a function of the radius, according to the following mathematical equation:

\[ X(t) = 1 - \frac{r_i(t)^3}{r_o^3} \]  

where \( r_o \) is the particle radius, and \( r_i(t) \) is the interface radius between the shell and the core at time t. The definition of an inverse function from equation (3) states that the interface position is a product conversion function.

\[ r_i(t) = r_o \left(1 - X(t)\right)^{1/3} \]
Melchiori describes how to calculate the conversion evolution of global particles as a function of a time [4]. The differential equation with respect to time will result in:

$$\frac{dX}{dt} = \frac{3 a}{c_A^0} \left( \frac{1}{\tau_K} + \frac{1}{\tau_D} \right) \frac{c_{B,\text{bulk}}}{b} + \frac{1}{\tau_D} \frac{c_{B,\text{bulk}}}{b}$$

(5)

where $c_A^0$ is the initial molar concentration of A; $a, b$ are the constants of the reaction equation; $D_{BD}$ is the effective diffusion constant B in D; and $h_B$ is the mass transfer coefficient of B.

Finally, by combining equation (4) into equation (5), the variable $r_i$ can be expressed as a conversion function $X$, so that an equation with only one dependent variable can be obtained as follows:

$$\frac{dX}{dt} = \frac{3 a}{c_A^0} \left( \frac{1}{\tau_K} \frac{c_{B,\text{bulk}}}{b} \left(1 - X(t)^3 - \frac{2}{3} X \right) + \frac{1}{\tau_D} \frac{c_{B,\text{bulk}}}{b} \frac{b}{h_B} \right)$$

(6)

Equation (6) above in view of the shrinking core model is an equation which states that the particles are assumed to be spherical. The ion concentration in equilibrium between particles can be expressed in terms of a shrinking nucleus model, which is described by the parameter $c_{B,\text{bulk}}$ as a function of time. If the parameter $c_{B,\text{bulk}}$ is constant, that is, a condition in which a high flow rate of ions is fed to the surrounding particles at a constant composition, then the mathematical equation has the following analytical solution:

$$t = \tau_K \left[ \frac{2}{3} \left(1 - X(t)^3 - \frac{2}{3} X \right) + \tau_M \cdot X \right]$$

(7)

where the parameters $\tau_K, \tau_D, \tau_M$ are the characteristic times associated with kinetic resistance ($\tau_K$), diffusion ($\tau_D$) and external mass transfer ($\tau_M$), respectively.

The value of the characteristic time is related to the importance of each resistance in the reaction process. For example, this means that a high diffusion value $\tau_D$ cannot be ignored, it can even be associated with a low diffusion coefficient. It is useful to understand which type of reaction controller is decisive in determining each characteristic time. If the concentration of reactant $B$ on the pellet surface is constant in time, as well as the temperature of the system, then the parameter $\tau_M$ in equation (7) can be neglected. In this mathematical equation, $\tau_K$ and $\tau_D$ correlate with the importance of kinetic and diffusion resistance. The results of the rearrangement into the form of a non-dimensional mathematical equation, the above equation can be expressed as:

$$\vartheta(X) = \frac{\tau_K}{\tau_K + \tau_D} \left[ \frac{2}{3} \left(1 - X(t)^3 - \frac{2}{3} X \right) \right] + \frac{\tau_D}{\tau_K + \tau_D} \left[ \frac{2}{3} \left(1 - X(t)^3 - \frac{2}{3} X \right) \right]$$

(8)

Next, define another term, namely Thiele's modulus, $\vartheta^2$, which is an equation that expresses a direct relationship between two characteristic times $\tau_K$ and $\tau_D$.

$$\vartheta^2 = \frac{18 \tau_D}{b^2 \tau_K}$$

(9)

The term of Thiele's modulus describes the correlation between catalytic activity and particle size [5]. When the particles have a large size and the reaction rate is very fast, then the diffusion force is only able
to carry the product away from the particle surface. Therefore, only the promoter reactant surface will undergo reaction. Based on the parameters of Thiele's modulus, three criteria can be distinguished for a catalytic activity: diffusive, kinetic, or a transition between the two. In the diffusion regime, the reaction rate is considered faster than the diffusion rate in solids [6]. If the value of Thiele's modulus is sufficiently large, it can be noted that the solution of the shrinking core model follows equation (8) with \( \tau_c = 0 \). In this case, the solution for the shrinking core model can be expressed in non-dimensional numbers.

\[
\theta(X) = 3\left(1 - (1 - X)^{2/3} - \frac{2}{3} X\right)
\]

(10)

It should be noted that the diffusion regime \((\Theta^2 \gg 1)\) means that the value of the kinetic constant as well as the expression of the reaction rate is not important. In the other hand, in the kinetic regime \((\Theta^2 \ll 1)\), the rate of diffusion in solids is faster than the rate of reaction. The kinetic regime is achieved when the diffusion coefficient of \(D_{BD}\) is sufficiently large, while compared to the kinetic constant. In the kinetic regime where \(\tau_D = 0\), the shrinking core model solution can be expressed in terms of a non-dimensional number.

\[
\theta(X) = \left[1 - (1 - X)^{2/3}\right]
\]

(11)

3.2. The shrinking core model

When the sintering reaction is not at optimum conditions, the formation of the YIG product is accompanied by the appearance of a secondary phase, namely yttrium iron perovskite (YIP). The YIP phase can decrease or disappear, when the sintering conditions are carried out at a higher temperature of 1450\(^\circ\)C or the duration is extended to 5 hours, but does not exceed that time interval. This shows that the YIG sintering reaction mechanism is through the YIP intermediate product formation process. The YIG formation reaction takes place in two stages, so that modeling is chosen according to the actual conditions. The evaluation of the formation of the YIP intermediate product as an intermediate product of the YIG sintering reaction was reported by Buscaglia. YIP and YIG phases will be formed during the sintering process when \(\text{Y}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3\) are pressed together at high temperatures [7]. The cross-sectional evaluation results of the sintering product between \(\text{Y}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3\) indicate that the YIG phase is formed on the \(\text{Fe}_2\text{O}_3\) side and YIP is formed on the \(\text{Y}_2\text{O}_3\) side.

The \(\text{Fe}_2\text{O}_3\) component reacts and adheres firmly to the \(\text{Y}_2\text{O}_3\) substrate. Two reaction products detected were the YFeO\(_3\) layer and the \(\text{Y}_3\text{Fe}_5\text{O}_{12}\) layer. The YFeO\(_3\) coating adheres well to both end components. The growth of the YFeO\(_3\) secondary phase layer is not in contact with the \(\text{Y}_2\text{O}_3\) phase. In other words, the compound \(\text{Y}_2\text{O}_3\) does not react directly with YFeO\(_3\). So that there are two faces of the YFeO\(_3\) layer, one grows on the \(\text{Y}_2\text{O}_3\) substrate and the other grows on the \(\text{Y}_3\text{Fe}_5\text{O}_{12}\) substrate. The reaction product is solid, and no impurities have been detected. Observation of differences in Gd-doped YIG and YIG samples showed a finer and denser crystal structure compared to the pure YIG image [8].

In general, sintering up to 1100\(^\circ\)C is dominated by the YIP intermediate product formation reaction. Up to 1100\(^\circ\)C has not shown significant YIG formation [9]. Evaluation of the Ginstling-Brounshtein (GB) model shows that the \(kt\) value tends to be relatively low compared to the Jander model (JDR) and the shrinking core model (SCM). Based on the five selected models, SCM modeling shows the best suitability to describe the yttrium iron garnet sintering reaction compared to other evaluated models. The literature data data plot at 1450\(^\circ\)C is shown as 'figure 1(a)'.

'Figure 1(b)' illustrates the shrinking core model to plot data of YIG reaction rates with and without gadolinium dopant. The YIG phase transformation rate was chosen to follow the diffusive regime. In the actual conditions before the reaction reaches steady state, an intermediate product of YIP is still formed in the first hour of the sintering reaction, so it takes time for the complete conversion to occur. In the curve
above, it can be seen that the actual YIG conversion shows a lower value than the simulation. It is possible that in the first 60 minutes, the reaction mechanism was still dominated by the YIP intermediate-product formation reaction. Then in the next hour, YIP will be converted into YIG products. This is shown at the fifth hour where the YIG conversion approached the simulation result value. The use of the SCM model shows a curve with a steady position at around 0.94. This value looks the best compared to other models with a much lower value.

![Diagram](image1.png)

**Figure 1.** The measured and model based reaction kinetics of garnet at 1450°C

Evaluation of the five models shows that two out of five models show a single reaction, meaning that they cannot represent the real YIG sintering reaction. The other three show a two-stage reaction. Based on the Arrhenius linear regression plot, modeling the two-stage reaction mechanism in the shrinking core model, shows the highest deviation tolerance ($R^2 = 0.923$). Therefore, the shrinking core model is considered capable of describing the phase transformation conditions in the Gd-doped YIG sintering reaction.

The SCM model assumes that the reactants diffuse through the particle interface layer. The reversible reaction occurs at the shell and core interface and depends on the total composition of the reactants and products, as illustrated in 'figure 2'. The interface layer can shift towards the center of the particle, if the global reaction rate is positive. The application of SCM modeling is in accordance with the assumption that changes in the concentration profile of the reactants take place very quickly when compared to changes in the position of the reaction interface.
The study of the sintering reaction rate was carried out by observing the sintering process data from 1000°C to 1250°C [10]. Furthermore, the simulation is carried out at a temperature of 1450°C to predict the sintering conditions at that temperature. The application of KJM modeling is corrected based on the plot of $k_t$ against $t$ ln $(1/(1-\alpha))$ against $t$ (in minutes). Thus, the total value of $k$ will be greater than zero (positive). The shrinking core model (SCM) shows a good correlation factor ($R^2 = 0.923$).

By using the reaction rate curve ($k_t$) of each model against $t$, the values of $k_1$, $k_2$ and $k_{total}$ are obtained. The value of $k_1$ is obtained from the regression of the points at the beginning of the reaction, while $k_2$ is obtained from the regression of points that are close to steady state conditions. Furthermore, an Arrhenius plot between ln $k$ and $1/T$ is made to get the value of activation energy ($E_a$). Table 1 shows the comparison of the activation energy and the deviation tolerance of YIG sintering models.

| Model | $E_a_1$ (kJ/mol) | $E_a_2$ (kJ/mol) | $E_a_{tot}$ (kJ/mol) | $R^2_{tot}$ |
|-------|----------------|----------------|----------------------|------------|
| SCM   | 378           | 380           | 380                  | 0.924      |
| JDR   | 573           | 113           | 594                  | 0.859      |
| GB    | 146           | 44            | 226                  | 0.763      |
| ZLT   | 386           | 0             | 386                  | 0.963      |
| KJM   | 399           | 0             | 399                  | 0.817      |

Although the Zhuralev-Lesotkin-Tempelmen (ZLT) model showed a better $R^2$ value (0.963), ZLT modeling could not be used because it did not configure the YIG formation reaction that took place in two stages. Likewise, the Kolmogorov-Johnson-Mehl (KJM) model obtained a value of $R^2 = 0.816$, which is considered unable to explain the YIG sintering reaction mechanism which takes place in two stages. The ZLT and KJM models both do not show a second reaction mechanism. It does not represent the actual reaction stage and cannot be used to describe the YIG sintering reaction mechanism.
4. Conclusion

The YIG sintering reaction takes place in two stages, through the formation of the YIP intermediate product. The formation of the yttrium iron perovskite phase reaches its maximum value at a sintering temperature at 1200°C, while the formation of yttrium iron garnet reaches its maximum value at a sintering temperature of 1450°C. Sintering carried out at 1450°C for 5 hours resulted in a very significant YIG conversion value of up to 99.7%. The YIG phase transformation rate is predominantly determined by the diffusive regime rather than the kinetic regime. The application of the SCM model is considered to be the best for representing the actual conditions of the yttrium iron garnet, and the gadolinium doped yttrium iron garnet sintering reaction.

References

[1] Wan Ali F F, Othman M A, Ain M F, Abdullah N S, and Ahmad Z A 2013 Studies on the formation of yttrium iron garnet (YIG) through stoichiometry modification prepared by conventional solid-state method J. Eur. Ceram. Soc. 33 pp 1317–24
[2] Yagi S and Kunii D 1955 Studies on combustion of carbon particles in flames and fluidized beds The 5th Symposium on Combustion New York USA pp 231-6
[3] Gbor P K and Jia C Q 2004 Critical evaluation of coupling particle size distribution with the shrinking core model Chem. Eng. Sci. 59 pp 1979-87
[4] Melchiori T 2014 Study of non-catalytic gas-solid reactions- development of single particle model, Disertation Universita Degli Studi di Padova
[5] Thiele E W 1939 Relation between catalytic activity and size of particle Industrial and Engineering Chemistry 31 pp 916–20
[6] Wittrup K D 2007 Chemical and biological reaction engineering Course materials for 10.37 MIT Open Course Ware
[7] Buscaglia V, Caracchio F, Bottino C, Leoni M and Nanni P 1997 Reaction diffusion in the Y2O3–Fe2O3 system Acta Metall. 45 pp 1213–24
[8] Akhtar M N, Yousaf M, Khan S N, Nazir M S, Ahmad M and Khan M A 2017 Structural and electromagnetic evaluations of YIG rare earth doped (Gd, Pr, Ho, Yb) nanoferrites for high frequency applications Ceramics International 43 pp 17032 - 40
[9] Zhao C, Li Y, Shen X, Cao Z, Cao Z, Wen Z, Yuan X, Ma C and Cao Y 2020 Studies on highly dense pure YIG polycrystalline ceramics fabricated by tape-casting method Renmin University of China Beijing 100872
[10] Wan Ali W F F, Othman M A, Ain M F, Abdullah N S and Ahmad Z A 2015 The investigation of the phenomenological YIG phase formation within 1000°C to 1250°C, a kinetic approach J. Am. Ceram. Soc. 99 pp 1-9