EFFECT OF SINTERING PROPERTIES ON THE FORMATION OF YTTRIUM IRON GARNET BY POWDER PREPARATION METHOD FOR MICROWAVE FERRITE RESONATOR ANTENNA

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ABSTRACT

Triyttrium Pentairon (iii) Oxide ($Y_3Fe_5O_{12}$) or familiar called as Yttrium Iron Garnet (YIG) is successfully prepared using a conventional mixed-oxide method of 5:3 Fe to Y ratios. YIG prepared from conventional mixed-oxide usually produced some associated phase which surely will affect electrical properties. In this study, various temperature used in the sintering process to induce associated phases (YIP) to be fully reacting to form single phase of YIG and the effect on resonance frequency is studied for resonator applications. The mixtures of oxide powders are calcined at 1100 ^oC and sintered at various temperatures of (1350, 1380, 1400, 1420 1450 ^oC, respectively). Cubic phase is detected from the formation of YIG. Some other phases such as YIP and hematite also present as secondary phase. However, it is seen that, based on the Rietvield refinement method, the total amount of secondary phase simulated are inversely proportional with sintering temperature. The powder was pressed into cylindrical pellet and tested as a microwave resonator in antenna application. It was found that, on the actual antenna circuit the operating frequencies measured are in the range of 10- 12 GHz for all samples which suitable for X-band. At the end, overall radiation pattern for all samples exhibit an omnidirectional behavior.

ABSTRAK

Triyttrium Pentairon (iii) Oksida (Y3Fe5O12) atau biasa dipanggil sebagai Besi Yttrium Garnet (YIG) berjaya disediakan dengan menggunakan kaedah konvensional-oksida bercampur 5:3 terhadap Fe kepada nisbah Y. YIG yang diselidiki dan disediakan dari konvensional oksida campuran biasanya menghasilkan beberapa fasa sekunder yang pasti akan memberi kesan kepada sifat elektrik. Dalam kajian ini, suhu yang digunakan dalam proses pensinteran dipelbagaikan untuk mendorong fasa sekunder (YIP dan hematite) untuk sepenuhnya bertindak balas untuk membentuk satu fasa YIG. Kesan kehadiran fasa sekunder terhadap kekerapan resonans dikaji untuk aplikasi antenna pensalun dielektrik. Campuran serbuk oksida dipanaskan pada 1100^oC dan disinter pada suhu pelbagai (1350, 1380, 1400, 1420 1450 oC). Fasa kubik dikesan dari pembentukan YIG. Walau bagaimanapun, terdapat fasa sekunder juga seperti YIP dan hematite turut dikesan. Selain itu, berdasarkan kaedah penghalusan Rietvield, jumlah fasa sekunder simulasi adalah berkadar songsang dengan suhu pensinteran. Serbuk telah ditekan ke pelet silinder dan diuji sebagai gelombang mikro penyalun antena. Didapati bahawa, pada litar antena sebenar frekuensi operasi yang diukur adalah dalam julat 10 - 12 GHz untuk semua sampel yang sesuai bagi X-

band. Pada akhir, corak sinaran keseluruhan untuk semua sampel mempamerkan sesuatu tingkah laku kepelbagaian arah.

Keywords: Rietvield refinement. YIG, ferrite resonator, YIP, solid-state processing.

INTRODUCTION

In recent years, the demand for wireless mobile communications has led to the development of antennas from the ceramic materials. Triyttrium pentairon (iii) oxide or yttrium iron garnet (YIG) with chemical formula of $Y_3Fe_5O_{12}$ is identified under magnetic ceramics groups that widely used in microwave regime since its discovery in 1956 [1]. These are due to the high quality factor and low tangent loss (tan δ) as well. Because of these properties, the structure and formation of YIG ceramics have been studied mostly in connection with their behavior in microwave applications [2,3]. Mao and Chen (2003) discovered that through CeO_3 doping, saturation magnetization of YIG is reduced [4]. Rapid development in YIG modification makes this materials are well known to be used in electronic devices such as circulators, optical isolators, and phase shifters in microwave communication applications [5,6].

There a quite number of types of processing can be done to synthesis YIG. Most of them are based on solid state processing, chemical solution deposition, sputtering process, citrate-nitrate gel combustion and etc., [6,7]. However, solid state widely used because of cheaper raw materials and importantly the materials are much stable compare to other processing materials. It is also has advantages including simple technology and low cost although higher synthesis temperature is needed. Industrially, YIG ceramics with mass production are fabricated using conventional ceramic production techniques where both of Yttrium (iii) oxide (Y_2O_3) and iron (iii) oxide (Fe_2O_3) are mixed, calcined and sintered at high temperature. For garnet formation in this given condition such as sufficient sintering temperature i:e 1450 °C (10 h soaking time) [9] which is in conventional mixed-oxide reaction can be described directly by the balanced equations below.

$$(3/2)\ Y_2O_3 + (5/2)\ Fe_2O_3 \rightarrow Y_3Fe_5O_{12}$$

Conventional solid state processing as same with other processing methods couldn't avoid from the processing problems. Mostly said, they are involved of fairly particle distribution that contribute to inhomogeneous mixtures and always involved of high processing temperature to get single crystal materials. Mergen and Qureshi (2009) in their works claims that in order to obtain high density YIG must undergoes sintering process up to 1450 °C for 10 h are required [9]. High density YIG are required to minimize loss in the high frequency regime [1]. Paper of Grosseau et al. (1997) is an excellent paper that outlines the major characteristic of YIG formation with respect to the factors that influence formation of intermediate phase [8].

Dealing with conventional mixed-oxide usually has high potential and chances to obtained intermediate phase or impurities. In this case, Preparation of single phase YIG, intermediate phase such as Fe_2O_3, $YFeO_3$ and Y_2O_3 are remain as impurities unless heated to high temperature. For example Ristic et al. (2003) found $YFeO_3$ that was produced as intermediate phase at low temperature solid-state reaction [10]. The presence of intermediate phases such as yttrium iron perovskite ($YFeO_3$) as discussed by Sztaniszlav et al. (1984) are because of fired at 600 – 800 °C [7]. They conclude that formations YIG from this intermediate phase won't happen because of this intermediate phase are stable.

The qualitative and quantitative analyses of phases present in materials are important analysis to be determine how much and what kind of phases present. To complete this, there are several ways can be done or used to calculate or find the amount or percentage intermediate phases present in materials such as 1) the absorption-diffraction method, 2) Full pattern decomposition, and 3) the Reference intensity ratio [11]. Commonly, quantitative analysis through rietvield refinement is the fastest and reliable tools in quantifying phase contents with several considerations need to be fulfilling as well before run the refinement process. By using rietvield method, calculated pattern from is compared with diffraction pattern. From the calculated profile, percentage of any phases or impurities can be acceptable as the weighted R profile must be less than 10 % while goodness of fit (GOF) need to be less than 4 [12]. Usually if the number exceeded these two conditions, the quality between calculated peaks and observed peaks match aren't good enough and low quality.

This paper, therefore, will address the reduction of secondary phases in YIG through modification of sintering temperature, with belief that the presence of secondary phases in YIG, alike YIP and hematite may impair YIG's performance as a component in DRAs. Rietvield refinement method is used for determination the concentration phases in a mixture after identity of phases present in YIG has been established at various sintering temperature. Any microstructure changes in YIG would clearly observe through FESEM accompanied with element verification by EDX analysis. Other than that, the effects of phases present upon resonator antenna measurements will also be discussed in this paper to observe the behavior of the resonance pattern. The resonance pattern is known to be a strong indicator in projecting the suitability of materials to be used as a component in DRAs at respective band. Meanwhile, radiation pattern exhibit from these materials at the end of this paper gives a view of which type of signal directivity as a DRA's component.

METHODOLOGY

Conventional mixed-oxide method was adopted for synthesizing $Y_3Fe_5O_{12}$ (YIG) from iron (iii) oxide, (Fe_2O_3-95%) powder mixed with Yttrium (iii) Oxide (Y_2O_3-99.0%). The ratios of the mixtures comply are 5:3 of Fe to Y. They are mixing with each other for 24h h in a polyethylene (PE) bottle with ethanol (C_2H_6O) absolute as mixing media and zirconia ball through Heidoph Mixer. Using C_2H_6O solution instead of water could produce better homogeneity and smoother surface structure [13]. The wet slurries were dried in order to evaporate ethanol before calcined at 1100 ^{0}C in air for 6 h. the calcined powders were ground again to eliminated agglomerate. The grounded powders were palletized into cylindrical compacts of 12 mm in diameter and 1.5 mm thickness under uniaxial pressure of 3.5 ton. The green compacts were sintered at various sintering temperature (1350, 1380, 1400, 1420, 1450) for 6 h soaking time. Phase composition of the sintered samples was studied using powder X-ray diffraction analysis (XRD RIGAKU BRUKER D8) using Cu K_α radiation (40 kV, 30 mA) with a wavelength of λ = 1.5405Å. While surface morphology was studied by taking Field Emission Scanning Electron Microscopic (FESEM SUPRA 35VP ZEISS) couple with Energy Dispersive X-ray spectroscopy (EDX) instruments. While for the microwave dielectric characteristic and radiation behaviors were measured using HP8720D Network Analyzer (50 MHz – 20GHz) and Spectrum Analyzer (Agilent 8565E).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for respective YIG formulation sintered at various sintering temperatures (1350 °C, 1380 °C, 1400 °C, 1420°C and 1450 °C respectively) for 6 hours. YIG phase with cubic crystal structure (ICSD 98-005-3762) is the main phase in all samples (ranging from 10°-90° 2-theta). However, other phases that appeared in small quantity are labeled. These phases such as hematite (Fe_2O_3 ICSD 98-006-9763) and yttrium iron perovskite (YIP) with chemical formula of $YFeO_3$ (ICSD 98-000-8038) are also present. Samples that fired at 1420°C, on the other hand, showed nearly free of both secondary phases.

Based on literature, it is reported that the YIP and hematite phase may appear in every 5:3 ratio (Fe/Y) of YIG formulation in solid-state processing. For example Minghao et al. [14] reveals the existence of YIP phases at 33.35° (2Θ) in XRD patterns after sintering at 1400°C. The preparation of YIG through oxidizing atmosphere of conventional solid-state processing will typically be accompanied by YIP as the associated phase [9]. In this instance, YIP and hematite is considered as an intermediate phase formed between the Fe_2O_3–Y_2O_3 reactions to form YIG. Some authors [1,15] also suggested that the formation of YIP is due to the low firing temperatures used to achieve a complete reaction between Fe_2O_3-Y_2O_3.

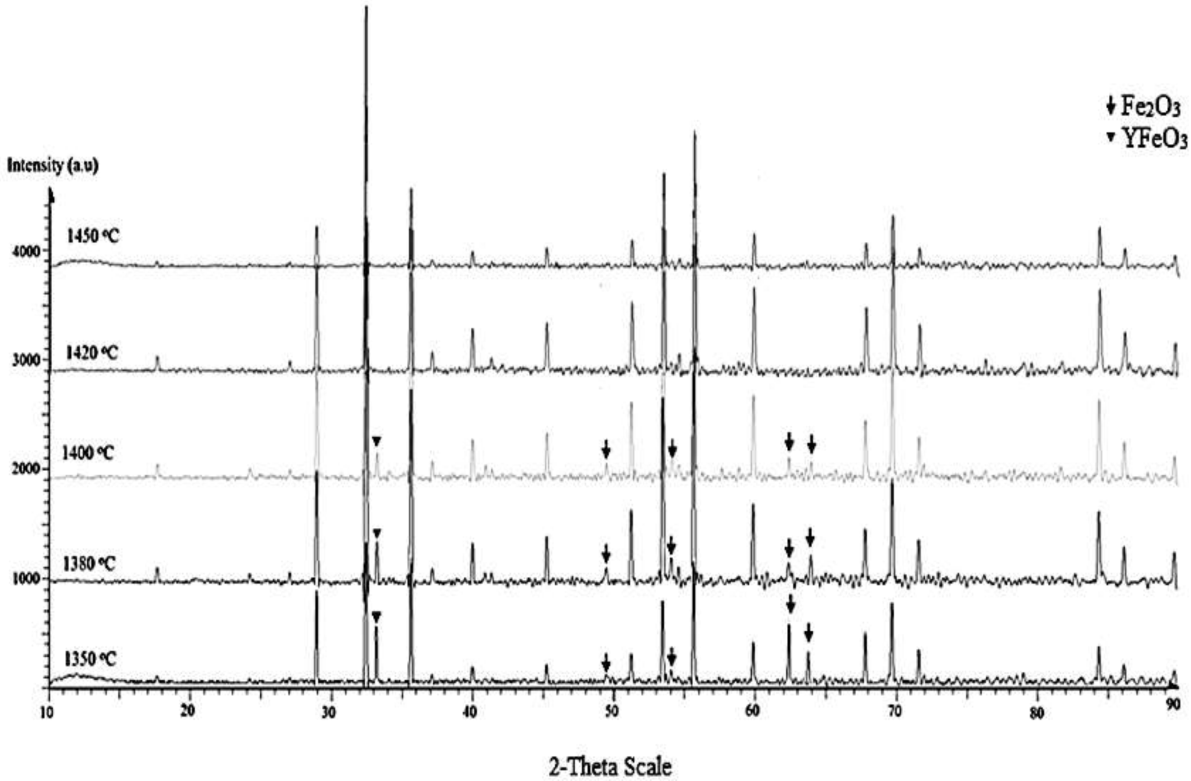


Figure 1: XRD diffracted pattern of 5:3 (Fe/Y) ratio of YIG formulation at respective sintering temperature

It is interesting to observe that diffracted pattern results from Fig. 1 suggest that sintering temperature can be the solution to produce single phase YIG. The modifications of sintering temperature are done into synthesizing YIG are done intentionally to increase the diffusion mechanism of Y_2O_3 to be fully reacting with Fe_2O_3 to form YIG. It is suggested that, temperature does effect solid-solid diffusion between yttria and ferric oxide. It is suggested at high temperature above than 1420°C, materials transport mechanism has occurred. The reaction may occur by a number of mechanisms of mobile ions in O^{2-}, Y^{3+} and Fe^{3+}. Since O^{2-} is having larger ionic radius (126 pm) this ion is expected to have lower mobility than yttrium (Y^{3+}) and iron (Fe^{3+}) cations, with ionic radii of 90 pm and 64 pm, respectively [16].

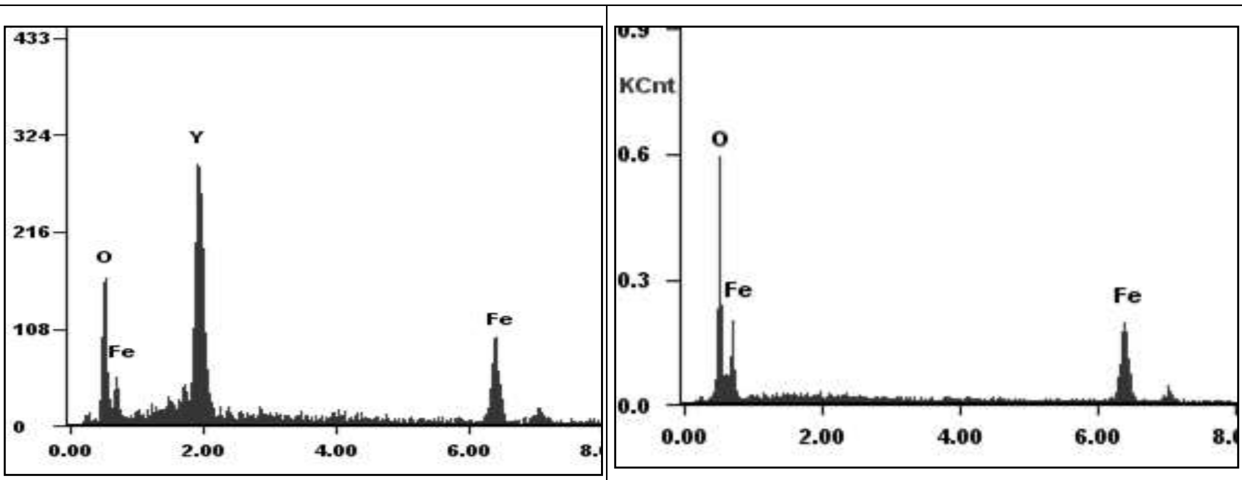
To further confirm this observation, quantitative XRD analysis is carried out through Rietvield refinement method using PANanalytical X'Pert HighScore Plus software. The results can be seen in Table 1. Table 1 shows the matching between diffracted and reference patterns, through the residual (R) values and the goodness of fit values (GOF). This will determine the reliability of the percentage concentration of identified phases obtained during refinement process. For standard and quality measurement, the weighted R profile for each observed peak is found to be within the range as below 10 whereby for GOF are less than 2 [18,19]. If these two criteria are fulfilled then refinement result for phase's identification is acceptable.

It is also observed from Table 1 that the percentages of the secondary phase present are inversely proportional with the levels of sintering temperature. The highest percentage (10.3%) of secondary phases is found in sample that fired at 1350°C. The amount secondary phase however is decreasing up to 40-50 % with increasing temperature. Almost a complete reaction is identified in samples with fired at 1420°C and 1450°C since a very little amount of secondary phase is detected. From these results, it can be safe to conclude that the Rietvield refinement method results in Table 1 exhibits a good agreement with the diffracted patterns shown in Fig. 1.

This observation can also be further confirmed by EDX and FESEM analyses, as depicted in Fig. 2 and Fig. 3, respectively. From the EDX a result (Fig. 3) shows that the darker grains are Fe_2O_3 grains. Meanwhile for grains that represent YIG phases detected in grey color of grains. However, as presented in Fig. 2 it is observed that grains with YIP phases maybe have similar color of grey under FESEM, apparently.

Table 1: Determination of identified phase concentration in XRD diffracted pattern through Rietvield refinement method

Temperatures (°C)	Percentage of $Y_3Fe_5O_{12}$ (YIG) [%]	Total Percentage of Secondary phase identified ($YFeO_3$ & Fe_2O_3) (%)	Peaks profile			
			R expected (error factor)	R Profile (reliability factor)	Weighted R profile	Goodness of fit (GOF)
1350	89.7	10.3	4.9808	4.1155	5.2629	1.1497
1380	95.0	5.0	5.1568	4.6441	5.6264	1.1903
1400	96.4	3.6	4.1764	3.9175	4.6142	0.7470
1420	100.0	0.0	3.1431	2.9976	3.5932	1.3069
1450	98.5	1.5	3.0574	4.1759	3.7316	1.4896



(a) (b)

Figure 2: EDX analysis for (a) Grey grain, and (b) Darker grain respectively

It is noted that, YIP is formed through Fe_2O_3–Y_2O_3 reaction as an intermediate phase for YIG formation since it is not yet completely reacted. However, some authors [10,14,20,21] in their work claimed that YIP phase present because of the presence of excess Y_2O_3, as previously mentioned. Thus, it is believed that in this case, the presence of secondary phases can be reduced through exposing it at high temperature. This also is supported by XRD analysis as shown in Fig. 1. However, for sample which is fired above 1420°C seems to be free from the presence of any secondary phase. This supports the XRD and Rietvield analysis presented earlier. Another interesting observation from Fig. 2 is that very high densification with almost uniform grain size were obtained, compared to previous authors [1,14]. Microstructures from previous researchers [15,18] showed high surface porosity with grains unevenly packed, even though their sintering temperature much higher (1480 °C) compared to the present solid-state sintering at 1420°C.

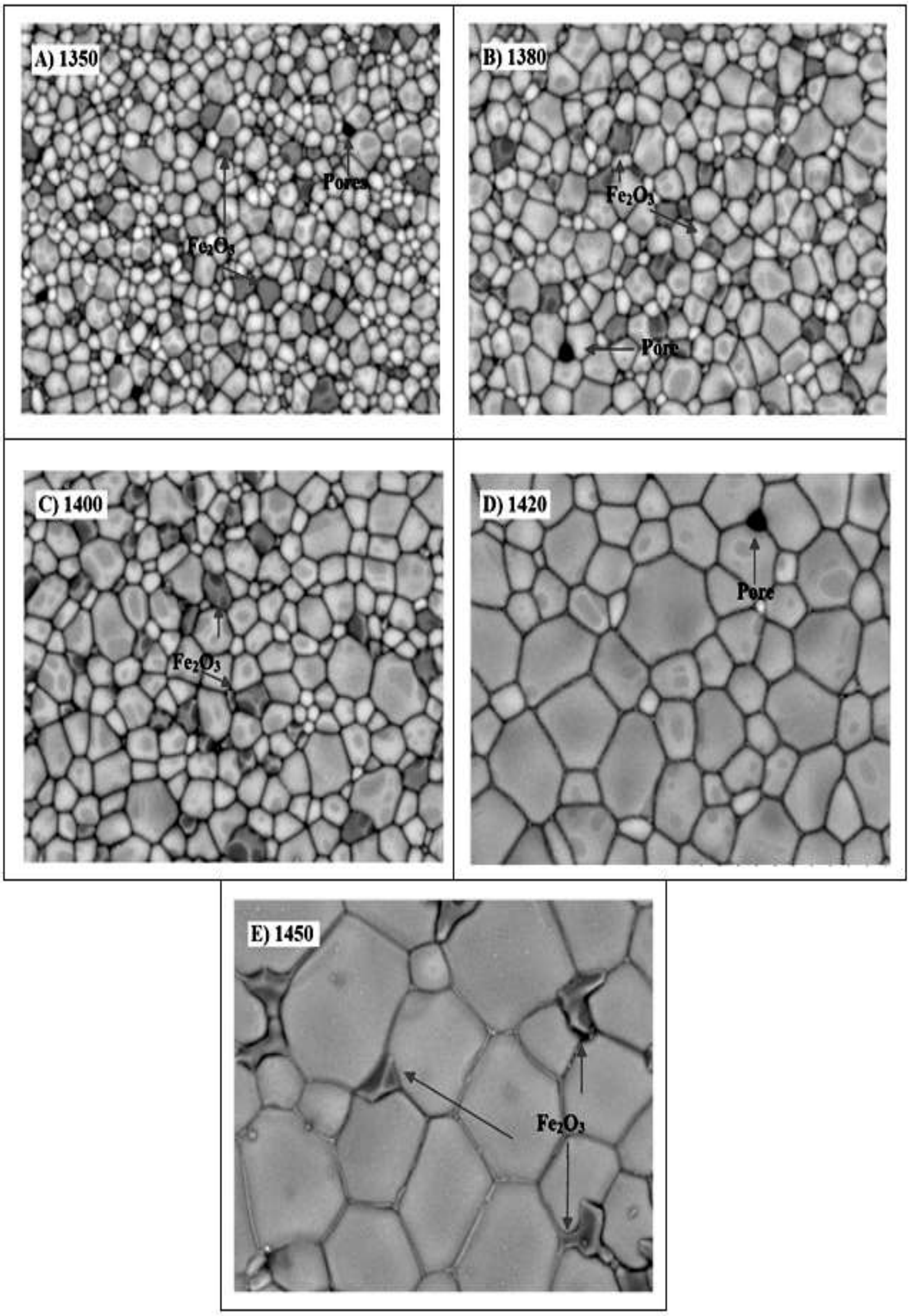


Figure 3: FESEM analysis for samples at various sintering temperature a) 1350°C, b) 1380 °C, c) 1400 °C, d) 1420 °C, and e) 1450 °C respectively

Various factors influence the dielectric properties of sintered samples. As for this case, the presences of impurity associated with grain size were found to be important factors in dielectric response of YIG as resonator. The position of resonator on microstrip is fixed to 32 mm from s11 port (see Fig. 4). This position obey TE_{11} mode for antenna measurement.

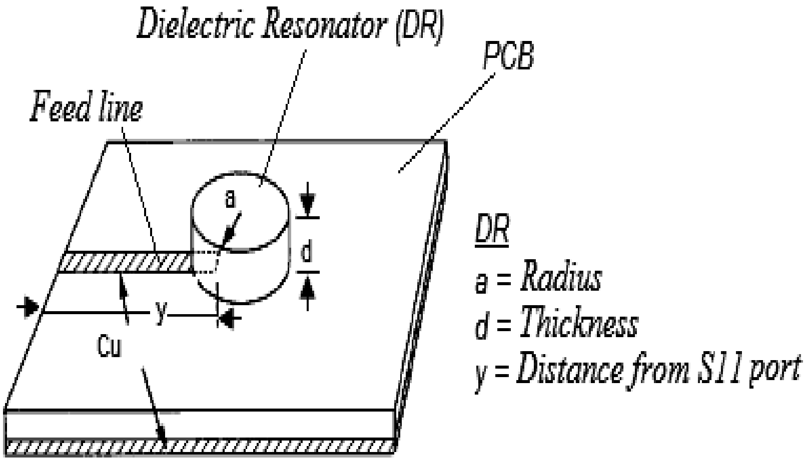
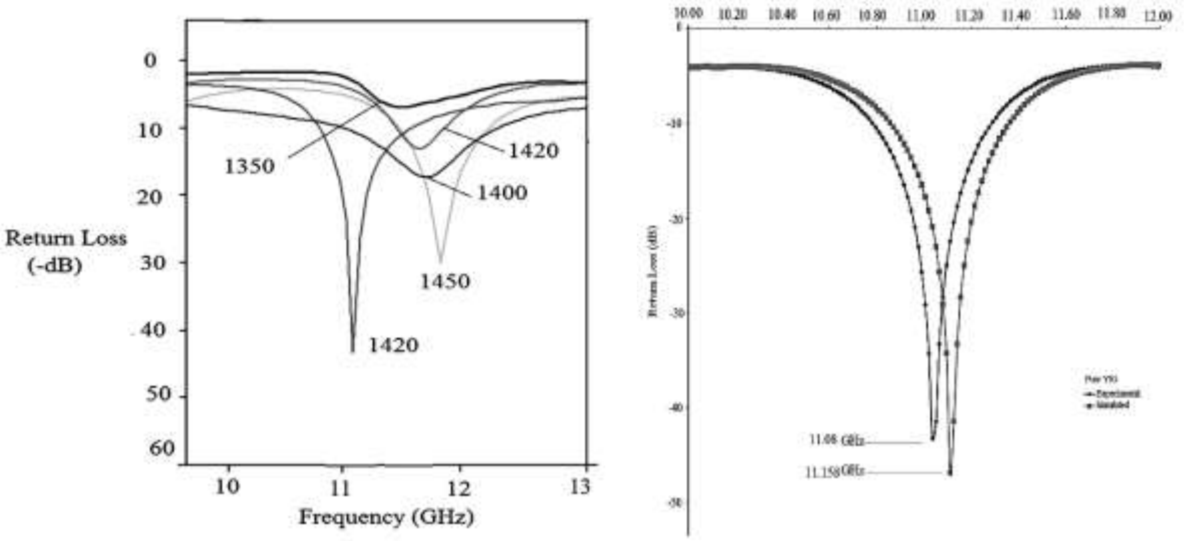


Figure 4: Position of DR in microstrip board



(a)

(b)

Figure 5: Resonance frequency for samples at respective sintering temperature (a) experimental result, and (b) comparison between actual measurement and simulated result of single phase YIG

As for resonator application, the resonance frequency is an important measurement to determine the operation frequency suitable for fabricated ceramics materials. Figure 5(a) shows an overall result of resonance frequency for each sample as different sintering temperature. The result shows that the resonance frequency is existed at different frequencies for each sample. However, the pattern or trend of the resonance shows seems affected by the presence of secondary phases. Based on the result obtained, the operation frequency was found to be in the range of 10.00 to 13.00 GHz. In communication engineering, this frequency range is in the range of X-band. The X-band is a segment of the microwave radio region of the electromagnetic spectrum and its operation is in the range of 8.00 to 12.00 GHz. This means that this kind of resonator fabricated from YIG is suited for satellite communication applications system. For better and accuracy of the resonator measurement, a simulation process through computer simulation technology 2009 (CST) are done with single phase YIG is used for the comparison. The comparison between simulated results and experimental result for single phase YIG is shown in Fig. 5(b). The simulated result is also acceptable with small error because the gap of frequency is closed with each other. The measurement and comparison are take place at -10dB return loss in room temperature.

Table 2 shows the calculated electrical permittivity and the loss tangent for YIG at respective sintering temperature. The calculated values are within the range of 5.000 to 11.000 and 0.0800 to 0.3000 respectively. From this table, shows that dielectric constant is proportional with YIG sintering temperatures. Present of secondary phase secondary phase has contributed to the increasing electrical permittivity of YIG.

Table 2: Electrical characteristic of YIG at various sintering temperature

Sample	Dielectric constant (εr)	Loss factor (tan δ)	Return Loss (dB)		Frequency resonance (GHz)	
			experimental	simulation	experimental	simulation
1350	5.032	0.3081	-7.67	-5.923	11.58	11.710
1380	7.432	0.2247	-12.23	-17.651	11.67	11.793
1400	6.856	0.1983	-18.96	-21.522	11.73	11.912
1420	10.321	0.0892	-43.12	-47.138	11.08	11.158
1450	10.245	0.1318	-30.05	-35.481	11.87	12.021

CONCLUSION

Synthesizing of YIG through solid-state route does produce the secondary phases such as hematite and YIP as byproduct. However modification of sintering temperature which are at 1350°C, 1380°C, 1400 °C, 1420 °C, and 1450°C respectively shows deteriorations of secondary phases. However, this secondary phase does show an effect upon resonator antenna at 10-13 GHz operating frequency. Return loss which indicating the strength of the signal is lower with high amount of percentage secondary phase in YIG. Thus, shows that, secondary phase in YIG did contributed into the signal strength of resonator antenna. Overall result on the radiation pattern exhibit omni-directional behavior.

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