Research Article

Effect of Zn Site for Ca Substitution on Optical and Microwave Dielectric Properties of ZnAl_2O_4 Thin Films by Sol Gel Method

Wan Nasarudin Wan Jalal, Huda Abdullah, and Mohd Syafiq Zulfakar

Department of Electrical, Electronic and System Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Correspondence should be addressed to Huda Abdullah; huda@eng.ukm.my

Received 23 May 2013; Revised 2 November 2013; Accepted 6 November 2013; Published 3 February 2014

Academic Editor: Kunpeng Wang

Copyright © 2014 Wan Nasarudin Wan Jalal et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

$\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30) thin films were prepared by a sol gel method. The XRD patterns displayed the characteristic peaks of $(\text{Ca}/\text{Zn})\text{Al}_2\text{O}_4$ with the standard pattern of face-centred cubic (fcc). The addition of Ca decreased the lattice constant from 14.6 nm to 23.2 nm . The optical bandgap of undoped thin film was found to be at 3.84 eV while for doped Ca was observed at 3.50 to 3.73 eV . The substitution of Zn^{2+} by Ca^{2+} in ZnAl_2O_4 thin films was found to increase the crystallite size, grain size, and surface morphology which evidently affect the density and dielectric constant. The $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films were characterized at 20 to 1 MHz frequency to determine the dielectric constant (ϵ_r) and unloaded quality factor (Q_u) using LCR spectrometer. It can be observed that specimen using $\text{Ca}_{0.25}\text{Zn}_{0.75}\text{Al}_2\text{O}_4$ possesses $\epsilon_r \sim 10.41$ and $Q_u \sim 5770$ which is suggested as a candidate material for millimetre-wave applications. Therefore, this ceramic is suggested as a candidate material for GPS patch antennas.

1. Introduction

Microwave dielectric ceramics play important roles in the global telecommunications industry with varieties of applications that have been developed. The microwave dielectric ceramic is widely used for applications that operate in the range of microwave band frequencies between 300 MHz and 300 GHz [1, 2] such as wireless fax, cellular phones, global position satellite (GPS), military radar systems, intelligent transport system (ITS), and direct broadcast satellites. Nowadays, these applications have been operating in the range of millimeter wave due to miniaturization of devices especially as a patch antenna for GPS applications. The miniaturization of GPS patch antennas has become a primary issue in these few years.

Many researchers have tried to study the dielectric properties of ZnAl_2O_4 ceramics such as Wang et al. [3], Surendran et al. [4], Wu et al. [5], and Lei et al. [6–9]. They have found that the ZnAl_2O_4 -based microwave dielectric ceramics have a very extensive prospect research for millimetre-wave applications and GPS antenna in the future with various

dielectric properties. The ϵ_r values of the ZnAl_2O_4 were found in the range of 8.3 [6] to 9.01 [10], while their unloaded quality factor (Q_u) for ZnAl_2O_4 was around $4,590$. These ceramics were prepared by conventional solid state [3] and aqueous gel casting [5] methods, which involved the high sintering temperature (above 1400°C). The sintering temperature above 1400°C cannot satisfy the requirements for the preparation of modern functional ceramics. Thus, the alternative method should be selected in these exploratory studies due to the fact that ZnAl_2O_4 has a large number of material types and phase compositions. Moreover, the preparation of ZnAl_2O_4 ceramic products typically involves heating processes of raw powders material which must undergo special handling in order to control purity, particle size, particle size distribution, and heterogeneity. These factors play important roles in the properties of the finished ZnAl_2O_4 -based microwave dielectric ceramic.

Recently, there are many methods to prepare microwave dielectric ceramics such as solid state mixing reaction of zinc and aluminium oxides [11, 12], coprecipitation [13], hydrothermal [14, 15], microwave hydrothermal [16],

combustion [17], and sol gel methods [18, 19]. Among the various methods, the sol gel method is a useful and attractive technique for the preparation of the ZnAl_2O_4 nanostructure because it offers the advantages of good stoichiometric control and is high homogeneity, producing pure and ultrafine powders and is able to produce thin films at low temperature processing ($<900^\circ\text{C}$) [20, 21]. Furthermore, sol gel is being employed increasingly for the low cost fabrication of ordered high specification materials since its structural and morphological characteristics may be tuned in order to tailor the electrical properties of the material [22]. Therefore, the sol gel method was selected in these exploratory studies of new ZnAl_2O_4 due to having a large number of material types and phase compositions.

In this study, the effects of substitution of Zn^{2+} by Ca^{2+} in the framework of ZnAl_2O_4 on the structural, morphological, and dielectric properties were investigated. The $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30) thin films were prepared by the sol gel method. The effects of the substitution were characterized using X-ray diffraction (XRD), Field-Emission Scanning Electron Microscope (FESEM), Energy-Dispersive X-Ray Spectroscopy (EDX), and ultraviolet visible (UV-Vis) and LCR spectrometer.

2. Experimental Details

Reagent-grade ceramic powders of Zinc acetate dehydrate $\text{Zn}(\text{O}_2\text{CCH}_3)_2$, aluminium nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and calcium nitrate $\text{Ca}(\text{NO}_3)_2$ were selected as starting raw materials for zinc, aluminium, and calcium. The different molar ratios of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.30) were prepared by a sol gel method. Initially aluminium nitrate was dissolved in 60 mL absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) as solvent, followed by ethylene glycols (EG) with designated amount (0.5 mL) was introduced as the chelating agent in the solution. Then, calcium nitrate and zinc acetate were added to the solution. After being kept at around 75°C for 1 h, nitric acid (CA) with amount 0.36 mL is utilized for preparing homogeneous solution. The solution was continuously heated at 75°C with constant stirring on a magnetic stirrer for another 1 h until a clear solution had formed following a chemical reaction. Finally, the solution containing $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ is stirred for 0.5 h at 180°C in order to obtain transparent and stable sol.

Furthermore, the transparent and stable sol of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ would be prepared on the fluorine tin oxide (FTO) substrate by the spin coating technique at 3500 rpm/min for 35 s and treated at 85°C for 15 min. These coating procedures were repeated 10 times to get a result of good thickness and to remove the organic residuals. This technique was carried out in a clean room facility to avoid contamination of particles and to obtain films with good optical quality. The thin films would be kept drying in the air and subsequently were annealed at 500°C for 1 h in air to eliminate the remaining organic matter.

The $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films were characterized by means of the X-ray diffraction (XRD, Siemens D-500). For

FIGURE 1: Synthesis of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films based microwave dielectric ceramics.

Rietveld analysis, the XRD pattern was collected over the range from 20° to 60° , with both selected step scan and step width of 0.0250° . The structural morphology of thin films was then observed by using a Field-Emission Scanning Electron Microscope (FESEM, Zeiss Supra 15 KV) and Energy-Dispersive X-Ray Spectroscopy (EDX), respectively. In the meantime, the optical properties of thin films were examined through recording the absorption spectra using ultra-violet (UV-Vis) double beam spectrophotometer, in the wavelength range of 200–800 nm. The ϵ_r and unloaded quality factor values were measured using an LCR spectrometer (HP 4284A) at frequency range 20 Hz to 1 MHz at room temperature.

3. Results and Discussion

3.1. Structural Analysis. Figure 1 shows XRD patterns of the $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.30) thin films annealed at 500°C for 1 h. It can be seen that the observed diffraction peaks of all samples are corresponding to the standard pattern of face-centred cubic (fcc) ZnAl_2O_4 with dominant peak (311) at 38.66° . The characteristic peaks of the undoped and (Ca/Zn) Al_2O_4 nanostructure were noticed according to the JCPDS files 00-005-0669 and 01-087-0426, respectively. All the observed peaks of ZnAl_2O_4 appearing at $2\theta = 30.72^\circ, 35.65^\circ, 45.36^\circ, 48.64^\circ, 55.25^\circ$, and 58.84° can be indexed as (220), (311), (400), (331), (422), and (511) crystal planes, respectively. The observed diffraction peaks of ZnAl_2O_4 result are consistent with those reported by

FIGURE 2: XRD patterns of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ nanostructure annealed at 500°C for 1 h.

Abdullah et al. [18]. The peaks correspond to $(\text{Ca}/\text{Zn})\text{Al}_2\text{O}_4$ which appeared at 29.375° (422). This peak appeared clearly when the amount of Ca had been increased more than $x = 0.15$. The XRD analyses suggested that the increasing amount of Ca led to the increasing intensity of the diffraction peaks of $(\text{Ca}/\text{Zn})\text{Al}_2\text{O}_4$ [23]. Figure 2 also shows the peaks in the XRD spectra shift to a higher angle implying the formation of $(\text{Ca}/\text{Zn})\text{Al}_2\text{O}_4$. The diffraction peaks shifted, perhaps because the ionic radius of Ca^{2+} (0.99 nm) is larger than Zn^{2+} (0.74 nm) [24]. The shift of XRD diffraction peaks indicates that the lattice parameter (a) was changed.

The crystallite size and lattice parameter of the $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ can be calculated from the XRD data. The crystallite size was calculated from the dominant peak (311) of XRD diffraction lines based on Scherrer's equation using the following hkl peak [25]:

$$D = \frac{0.94 \lambda}{\beta \cos \theta}, \quad (1)$$

where λ is the X-ray wavelength (0.15418 nm) and β is the full width at half-maximum intensity of the diffraction line. The crystallite size of ZnAl_2O_4 is 14.6 nm. The crystallite size increases linearly (15.4 to 23.2 nm) as Ca increases. The increment in crystallite size perhaps was affected by the ionic radii of Zn^{2+} (0.74 nm) [24] smaller than Ca^{2+} (0.99 nm) [26].

The calculated lattice parameters upon the Ca^{2+} substitution of Zn^{2+} were decreased from 8.085 Å to 8.026 Å due to XRD spectra shift to a higher (right) angle. The experimental lattice parameters of ZnAl_2O_4 (8.085 Å) are in good agreement with the reported value $a = 8.083$ Å to 8.095 Å [16, 27], theoretical values (8.05 Å), and JCPDS files 00-005-0669. Normally, the decreases of lattice parameter are able to increase the density.

3.2. Morphological Analysis. The microstructural changes in $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ceramics were studied using SEM and EDX to observe the effects of calcium (Ca) content on the morphologies of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$. The SEM micrographs of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films are shown in Figure 3. We can

see that, in general, all the compositions were well annealed, and the average grain sizes tended to increase. The average grain size of ZnAl_2O_4 is about 37 nm while for doped Ca was found to increase up to 78 nm. The increase in grain size was observed with the increasing content of Ca. The increases in grain size eliminated the porosity. Thus, we suggested that the porosity was eliminated due to grain growth and in line with the increasing of Ca content. It indicates that the bigger grains are Ca and the smaller are ZnAl_2O_4 . Normally, the increases in ceramics grain size considerably improved on the quality factor and dielectric constant [8, 10, 28].

The atomic force microscopy (AFM) was used to analyze the morphology of the surface (Figure 4) with scanning size of $1 \mu\text{m} \times 1 \mu\text{m}$. The average roughness of ZnAl_2O_4 thin films is about 14.9 nm. As x increases, the average roughness increases linearly from 21.5 ($x = 0.05$) to 94.7 nm ($x = 0.30$). The doped samples were identified as rough surface compared to ZnAl_2O_4 . The increment of average roughness and grain size data was parallel with the increment of the crystallite size in XRD data. It is suggested that the increase of surface roughness can promote the increment of dielectric constant (ϵ_r).

3.3. Optical Analysis. The absorption spectra of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ particles in transmission mode were recorded by dispersing the particles uniformly in liquid paraffin, in the wavelength range of 200–800 nm. For a direct bandgap semiconductor material the absorption coefficient near the band edge is given by [29]

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^{1/2}, \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the energy gap and A is constant depending on the type of transition. Equation (2) for any energy can be rearranged and written in the form of

$$(\alpha h\nu)^2 = A^2 (h\nu - E_g). \quad (3)$$

From these equations, it is clear when $h\nu = 0$ and $E_g = h\nu$. The energy gap is determined by plotting $(\alpha h\nu)^2$ against $h\nu$ and finding the intercept on the $h\nu$ axis by extrapolating the plot to $(\alpha h\nu)^2 = 0$ as shown in Figure 5.

The bandgap energy (E_g) of ZnAl_2O_4 was observed at 3.84 eV ($x = 0.00$). As x increases, the optical E_g decreases from 3.73 eV ($x = 0.05$) to 3.50 eV ($x = 0.25$). The optical bandgap analyses suggested that the increasing amount of Ca led to the decreasing optical E_g due to the fact that calcium bandgap (3.2 eV) [30] is smaller than zinc (3.84 eV) [18, 29]. From this experiment, the suggested bandgap of $(\text{Ca}/\text{Zn})\text{Al}_2\text{O}_4$ is between 3.50 eV and 3.73 eV which is applicable as for GPS application [29].

3.4. Microwave Dielectric Properties. The variation of the dielectric constant (ϵ_r) of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ with applied frequency from 20 Hz to 1 MHz is plotted in Figure 6. It can be observed that there is a steady decrease in ϵ_r in applied frequency for each concentration. The dielectric constant (ϵ_r)

FIGURE 3: SEM analysis on $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films.

of pure ZnAl_2O_4 is 8.56, while that for Ca-doped is increased from 8.81 to 10.98. The ϵ_r value of ZnAl_2O_4 (8.56) is in line with that previously reported [31]. The increment is expected since the dielectric constant of Ca is $\epsilon_r \sim 11.95$ [32], which is larger than ZnAl_2O_4 [6, 10]. It suggested that the combination

of ZnAl_2O_4 with Ca is able to increase the ϵ_r values more than 8.52. Furthermore, the largest values of ϵ_r for doped samples are indicating that the ion polarizability of the ZnAl_2O_4 is higher than that of the Ca^{2+} . Thus, the dielectric constant (ϵ_r) of the $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ceramics depended on

TABLE 1: Microwave dielectric properties of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films annealed at 500°C for 1 h.

Ca concentration (x)	Lattice parameter, a ($\text{\AA}$)	Apparent density (g/cm^3)	Dielectric constant ϵ_r	Unloaded Q_u
0.00	8.085	4.61	8.56	4590
0.05	8.081	4.62	8.81	4670
0.10	8.077	4.62	9.29	4890
0.15	8.072	4.63	9.62	5230
0.20	8.066	4.64	10.06	5560
0.25	8.050	4.67	10.41	5770
0.30	8.026	4.71	10.98	5240

FIGURE 4: AFM images of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films.

ionic polarizability (α) of cations and oxygen at microwave frequency [33]. Normally, the changing of ϵ_r values follows the logarithmic mixing rule [34], as follows:

$$\ln \epsilon_r = v_1 \ln \epsilon_{r1} + v_2 \ln \epsilon_{r2}, \quad (4)$$

where ϵ_{r1} and ϵ_{r2} are the dielectric constants of phases with volumes v_1 and v_2 .

Table 1 demonstrates the microwave dielectric properties of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films annealed at 500°C for 1 h. The densities and dielectric constants increased with x increases.

FIGURE 5: Tauc plot to determine optical bandgap from UV-Vis absorption spectrum.

FIGURE 6: Variation of dielectric constant of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ with applied frequency.

Figure 7 illustrates the densities and dielectric constant of the specimens as a function of Ca concentration. With the increase of Ca concentration, the density and dielectric constant were found to increase up to 4.71 g/cm^3 and 10.98, respectively. The increases in ceramics density and dielectric constant were due to the increment of grain size (Figure 3). Figure 7 also shows that the variation of the ϵ_r value was consistent with that of density. We suggest that the ϵ_r of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ceramics is mainly controlled by apparent density.

Table 1 also shows the unloaded quality factor (Q_u) of the $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ ceramics with different degrees of Ca^{2+} substitution. The Q_u is determined from the materials dielectric loss using LCR spectrometer and was characterized

FIGURE 7: Apparent density and dielectric constants of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films.

FIGURE 8: Variation of unloaded quality factor with Ca content (x).

at 20 to 1 MHz frequency using a two-terminal method. This technique is based on the measurement of the dielectric loss constants as a function of frequency of a sample sandwiched between two electrodes [35]. The Q_u was found to increase linearly from 4590 ($x = 0.00$) to 5770 ($x = 0.25$) and decreased thereafter at $x = 0.30$, by increasing the calcium content as shown in Figure 8. This increase of Q_u was attributed to the better density and grain growth of the ceramics with a minor Ca addition. The best Q_u obtained was 5770 for Ca content = 0.25. The degraded Q_u at $x = 0.30$ may be related mostly to the pores structure and grain growth gradually as shown in Figure 3(g). However, Lei et al. [7] and Huang et al. [36] reported that the decrease of Q_u is not only mainly caused by the grain size and pores structure but also affected by intrinsic and extrinsic losses such as the secondary phases, impurities, or the lattice defect. The unloaded quality factor of ZnAl_2O_4 is in line with that previously reported by Surendran et al. [4].

Therefore, we suggest that the relationship between the Q_u and the x value was consistent with the apparent density and dielectric constant with that of the x value. In summary, the minor Zn substitution by Ca improved the microwave dielectric properties of the ZnAl_2O_4 microwave dielectric ceramics. The best composition was $\text{Ca}_{0.25}\text{Zn}_{0.75}\text{Al}_2\text{O}_4$ with microwave dielectric properties of $\epsilon_r = 10.41$ and $Q_u = 5770$. Therefore we consider that the $\text{CaZnAl}_2\text{O}_4$ ceramics have a low dielectric constant ($\epsilon_r < 15$) and high unloaded quality factor and, in particular, are a suitable candidate material for millimeter-wave applications and GPS patch antenna.

4. Conclusion

$\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films were synthesized by sol-gel method, and their optical and microwave dielectric properties were investigated as a function of Co content. The XRD patterns confirmed that the formation of ZnAl_2O_4 and $\text{CaZnAl}_2\text{O}_4$ phase was successfully observed. The XRD data showed that diffraction peaks of all samples were corresponding to the standard pattern of face-centred cubic (fcc). The XRD and SEM indicated that the particle size increased with the increases of calcium. Adding Ca^{2+} by substituting the Zn^{2+} site with different concentration increased the grain size, crystallite size, density, surface roughness, dielectric constant, and unloaded quality factor. However, the bandgap energy (E_g) and lattice parameter of $\text{Ca}_x\text{Zn}_{(1-x)}\text{Al}_2\text{O}_4$ thin films were found to decrease from 3.84 to 3.50 eV and 8.085 to 8.026 Å, respectively, as Ca increased. The specimen with a good combination of $\epsilon_r = 10.41$ and a $Q_u = 5770$ was obtained for $\text{Ca}_{0.25}\text{Zn}_{0.75}\text{Al}_2\text{O}_4$ specimen. Therefore, the composition of $\text{CaZnAl}_2\text{O}_4$ is considered as suitable material for millimetre-wave application and GPS patch antenna.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This project is carried out in Photonic Technology Laboratory, Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, and Department of Physics, Faculty of Science and Technology (FST), Universiti Putra Malaysia (UPM), Malaysia.

References

- [1] Y. T. Lo and S. W. Lee, *Antenna Handbook: Applications*, Chapman & Hall, New York, NY, US, 1993.
- [2] S. Chandrasekaran, S. Ramanathan, and T. Basak, "Microwave material processing-a review," *AIChE Journal*, vol. 58, no. 2, pp. 330–363, 2012.
- [3] X. Wang, W. Lei, and W. Lu, "Novel ZnAl_2O_4 -based microwave dielectric ceramics with machinable property and its application for GPS antenna," *Ferroelectrics*, vol. 388, no. 1, pp. 80–87, 2009.
- [4] K. P. Surendran, N. Santha, P. Mohanan, and M. T. Sebastian, "Temperature stable low loss ceramic dielectrics in $(1-x)\text{ZnAl}_2\text{O}_4$ - $x\text{TiO}_2$ system for microwave substrate applications," *European Physical Journal B*, vol. 41, no. 3, pp. 301–306, 2004.
- [5] J.-M. Wu, W.-Z. Lu, W. Lei, and X.-C. Wang, "Preparation of ZnAl_2O_4 -based microwave dielectric ceramics and GPS antenna by aqueous gelcasting," *Materials Research Bulletin*, vol. 46, no. 9, pp. 1485–1489, 2011.
- [6] W. Lei, W. Z. Lu, X. Wang, F. Liang, and J. Wang, "Phase composition and microwave dielectric properties of ZnAl_2O_4 - Co_2TiO_4 low-permittivity ceramics with high quality factor," *Journal of the American Ceramic Society*, vol. 94, no. 1, pp. 20–23, 2011.
- [7] W. Lei, W. Z. Lu, J. H. Zhu, and X. H. Wang, "Microwave dielectric properties of ZnAl_2O_4 - TiO_2 spinel-based composites," *Materials Letters*, vol. 61, no. 19–20, pp. 4066–4069, 2007.
- [8] W. Lei, W.-Z. Lu, D. Liu, and J.-H. Zhu, "Phase evolution and microwave dielectric properties of $(1-x)\text{ZnAl}_2\text{O}_4$ - $x\text{Mg}_2\text{TiO}_4$ ceramics," *Journal of the American Ceramic Society*, vol. 92, no. 1, pp. 105–109, 2009.
- [9] W. Lei, W.-Z. Lu, J.-H. Zhu, F. Liang, and D. Liu, "Modification of ZnAl_2O_4 -based low-permittivity microwave dielectric ceramics by adding $2\text{MO}-\text{TiO}_2$ ($\text{M}=\text{Co}$, Mg , and Mn)," *Journal of the American Ceramic Society*, vol. 91, no. 6, pp. 1958–1961, 2008.
- [10] C.-L. Huang, T.-J. Yang, and C.-C. Huang, "Low dielectric loss ceramics in the ZnAl_2O_4 - TiO_2 system as a τ_f compensator," *Journal of the American Ceramic Society*, vol. 92, no. 1, pp. 119–124, 2009.
- [11] N. J. van der Laag, M. D. Snel, P. C. M. M. Magusin, and G. de With, "Structural, elastic, thermophysical and dielectric properties of zinc aluminate (ZnAl_2O_4)," *Journal of the European Ceramic Society*, vol. 24, no. 8, pp. 2417–2424, 2004.
- [12] W. S. Hong, L. C. Jonghe, X. Yang, and M. N. Rahaman, "Reaction sintering of $\text{ZnO}-\text{Al}_2\text{O}_3$," *Journal of the American Ceramic Society*, vol. 78, no. 12, pp. 3217–3224, 1995.
- [13] M. A. Valenzuela, G. Aguilar, P. Bosch, H. Armendariz, P. Salas, and A. Montoya, "Effect of calcium addition on zinc aluminate spinel," *Catalysis Letters*, vol. 15, no. 1–2, pp. 179–188, 1992.
- [14] Z. Chen, E. Shi, Y. Zheng, W. Li, N. Wu, and W. Zhong, "Synthesis of mono-dispersed ZnAl_2O_4 powders under hydrothermal conditions," *Materials Letters*, vol. 56, no. 4, pp. 601–605, 2002.
- [15] M. Zawadzki and J. Wrzyszczyk, "Hydrothermal synthesis of nanoporous zinc aluminate with high surface area," *Materials Research Bulletin*, vol. 35, no. 1, pp. 109–114, 2000.
- [16] M. Zawadzki, W. Staszak, F. E. López-Suárez, M. J. Illán-Gómez, and A. Bueno-López, "Preparation, characterisation and catalytic performance for soot oxidation of copper-containing ZnAl_2O_4 spinels," *Applied Catalysis A*, vol. 371, no. 1–2, pp. 92–98, 2009.
- [17] A. Adak, A. Pathak, and P. Pramanik, "Characterization of ZnAl_2O_4 nanocrystals prepared by the polyvinyl alcohol evaporation route," *Journal of Materials Science Letters*, vol. 17, no. 7, pp. 559–561, 1998.
- [18] H. Abdullah, W. Jalal, and M. Zulfakar, "Miniaturization of GPS patch antennas based on novel dielectric ceramics $\text{Zn}(1-x)\text{Mg}_x\text{Al}_2\text{O}_4$ by sol-gel method," *Journal of Sol-Gel Science and Technology*, 2013.
- [19] W. N. Wan Jalal, H. Abdullah, M. S. Zulfakar, S. Shaari, and M. T. Islam, "Characterization and dielectric properties of novel dielectric ceramics $\text{Ca}_x\text{Zn}(1-x)\text{Al}_2\text{O}_4$ for GPS patch antennas," *International Journal of Applied Ceramic Technology*, 2013.

- [20] T. R. Kumar, C. S. N. Selvam, C. Ragupathi, J. L. Kennedy, and J. J. Vijaya, "Synthesis, characterization and performance of porous Sr(II)-added ZnAl_2O_4 nanomaterials for optical and catalytic applications," *Powder Technology*, vol. 224, pp. 147–154, 2012.
- [21] F. Davar and M. Salavati-Niasari, "Synthesis and characterization of spinel-type zinc aluminate nanoparticles by a modified sol-gel method using new precursor," *Journal of Alloys and Compounds*, vol. 509, no. 5, pp. 2487–2492, 2011.
- [22] A. A. D. Silva, A. d. S. Goncalves, and M. R. Davolos, "Characterization of nanosized ZnAl_2O_4 spinel synthesized by the sol-gel method," *Journal of Sol-Gel Science and Technology*, vol. 49, no. 1, pp. 101–105, 2009.
- [23] B. S. Barros, P. S. Melo, R. H. G. A. Kiminami, A. C. F. M. Costa, G. F. De Sá, and S. Alves Jr., "Photophysical properties of Eu^{3+} and Tb^{3+} -doped ZnAl_2O_4 phosphors obtained by combustion reaction," *Journal of Materials Science*, vol. 41, no. 15, pp. 4744–4748, 2006.
- [24] G. Tang, H. Liu, and W. Zhang, "The variation of optical band gap for ZnO: in films prepared by sol-gel technique," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 348601, 4 pages, 2013.
- [25] X. Tian, L. Wan, K. Pan, C. Tian, H. Fu, and K. Shi, "Facile synthesis of mesoporous ZnAl_2O_4 thin films through the evaporation-induced self-assembly method," *Journal of Alloys and Compounds*, vol. 488, no. 1, pp. 320–324, 2009.
- [26] C. L. Huang, J. Y. Chen, and B. J. Li, "Characterization and dielectric behavior of a new dielectric ceramics $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ at microwave frequencies," *Journal of Alloys and Compounds*, vol. 484, no. 1-2, pp. 494–497, 2009.
- [27] L. K. C. de Souza, J. R. Zamian, G. N. da Rocha Filho et al., "Blue pigments based on $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ spinels synthesized by the polymeric precursor method," *Dyes and Pigments*, vol. 81, no. 3, pp. 187–192, 2009.
- [28] Y. C. Chen, "Microwave dielectric properties of $(\text{Mg}(1-x)\text{Co}_x)_2\text{SnO}_4$ ceramics for application in dual-band inverted-E-shaped monopole antenna," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 58, no. 12, pp. 2531–2538, 2011.
- [29] E. Jamal, D. Kumar, and M. R. Anantharaman, "On structural, optical and dielectric properties of zinc aluminate nanoparticles," *Bulletin of Materials Science*, vol. 34, no. 2, pp. 251–259, 2011.
- [30] C. S. Xavier, J. C. Sczancoski, L. S. Cavalcante et al., "A new processing method of $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ powders: photoluminescence and growth mechanism," *Solid State Sciences*, vol. 11, no. 12, pp. 2173–2179, 2009.
- [31] C. W. Zheng, S. Y. Wu, X. M. Chen, and K. X. Song, "Modification of MgAl_2O_4 microwave dielectric ceramics by Zn substitution," *Journal of the American Ceramic Society*, vol. 90, pp. 1483–1486, 2007.
- [32] M. A. Subramanian, R. D. Shannon, B. H. T. Chai, M. M. Abraham, and M. C. Wintersgill, "Dielectric constants of BeO , MgO , and CaO using the two-terminal method," *Physics and Chemistry of Minerals*, vol. 16, no. 8, pp. 741–746, 1989.
- [33] H. Zhang, L. Fang, R. Elsebrock, and R. Z. Yuan, "Crystal structure and microwave dielectric properties of a new $\text{A}_6\text{B}_5\text{O}_{18}$ -type cation-deficient perovskite $\text{Ba}_3\text{La}_3\text{Ti}_4\text{NbO}_{18}$," *Materials Chemistry and Physics*, vol. 93, no. 2-3, pp. 450–454, 2005.
- [34] W. Kingery, H. Bowen, and D. Uhlmann, *Introduction to Ceramics*, John Wiley & Sons, New York, NY, USA, 1976.
- [35] Y. Mobarak, M. Bassyouni, and M. Almutawa, "Materials selection, synthesis, and dielectrical properties of PVC nanocomposites," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 149672, 6 pages, 2013.
- [36] C. Huang, J. Chen, and Y. Tseng, "High-dielectric-constant and low-loss microwave dielectric in the $\text{Ca}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ - $(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ solid solution system," *Materials Science and Engineering B*, vol. 167, no. 3, pp. 142–146, 2010.