

Proceeding Paper

Investigation of Transition Metal Ions Cu^{2+} and Mg^{2+} Doped Zinc Aluminate (ZnAl_2O_4) and Their Structural, Spectral, Optical, and Dielectric Study for High Frequency Applications [†]

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Abstract: Zinc Aluminate is an excellent dielectric material suitable for a variety of technological applications due to its high-quality factor, low dielectric loss and appreciable conductivity. Here in this study, the preparation of $\text{Zn}_{1-x}\text{M}_x\text{Al}_2\text{O}_4$ ($\text{M} = \text{Cu}^{2+}, \text{Mg}^{2+}; x = 0, 0.10$) powders were carried out using the citrate-based combustion route. The structural, spectral, optical, stoichiometry composition and dielectric performance of the synthesized nanoparticles were evaluated to explore the substitution effect of Cu^{2+} and Mg^{2+} ions. It was confirmed from XRD results that all the samples exhibited monophase spinel structure. The estimated average crystallite size is calculated to be 23 nm. The functional groups identification of the samples was monitored by FTIR spectroscopy. Scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy analysis (EDAX) was utilized to confirm the composition of the samples. UV-Visible absorption spectroscopy demonstrated decrement in the band gap due to doping. Impedance spectroscopy displayed improved dielectric properties for the doped samples. The Cole Cole plots enlightened about the relaxation processes and provided information about the complex electrical behavior of the material. It was established that non-Debye relaxation was found to be prominent in the investigated aluminates. From the electrical parameters obtained, it displays the semiconducting nature of the zinc aluminate particles and it can be utilized for high frequency applications such as ceramic capacitors, resonators, and filters in high frequency electronics. Overall, Zinc Aluminate is a versatile material with potential application in various fields of science and electronics.

Keywords: sol-gel; band gap; dielectric constant

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1. Introduction

The crystal structure of zinc aluminate is known as the spinel structure, which is a type of face-centred cubic (FCC) crystal lattice. The structure of Zinc Aluminate consists of tetrahedral spaces occupied by divalent ions and octahedral spaces occupied by trivalent ions, respectively, in a face centered cubic arrangement. The ratio of tetrahedral to octahedral sites is 1:2 in spinel structure, resulting in a chemical formula of ZnAl_2O_4 . The tetrahedral sites in zinc aluminate are neighbored by four O_2 ions, while the octahedral sites are neighbored by six O_2 ions. The cations in the structure are arranged in such a manner that creates a 3D network of shared edges and corners, resulting in a high degree of structural stability. The spinel structure of zinc aluminate is characterized by a high degree of symmetry, with a cubic unit cell and lattice constant of approximately 8.1 Å. The crystal

structure of zinc aluminate is similar to other spinel compounds, such as magnesium aluminate (MgAl_2O_4) and iron aluminate (FeAl_2O_4), which have the same crystal structure but different cation compositions.

The spinel structure of zinc aluminate is important for its properties and applications, such as its excellent thermal stability, high melting point, and electrical properties. The structure also plays a key role in determining the material's behaviour in different environments, making it an important consideration in various fields of science and engineering [1]. Copper Cu^{2+} and Magnesium Mg^{2+} doped zinc aluminate has a spinel crystal structure, with copper ions (Cu^{2+}) and magnesium ions (Mg^{2+}) substituted for some of the zinc ions (Zn^{2+}) in the lattice. The material's dielectric behavior, such as its dielectric constant and tangent loss, can get affected by exact doping level of copper and magnesium which are important for electronic applications [2]. The material's high thermal stability and resistance to moisture and humidity also make it suitable for use in harsh environments [3]. There are several methods to synthesize Zinc Aluminate nanoparticles including mixed oxide method, citrate-nitrate method, hydrothermal synthesis and combustion methods. Among all, combustion technique is one of the most efficient routes and human friendly method to develop spinel oxide materials in a short span of time with less utilization of energy.

Here we report the synthesis of Cu^{2+} and Mg^{2+} doped ZA through sol-gel method. The ongoing study aims to scrutinize the effect Cu^{2+} and Mg^{2+} ions on structural and dielectric behavior of ZnAl_2O_4 with general formula $\text{Zn}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ (ZAC) and (ZAM) $\text{Zn}_{1-x}\text{Mg}_x\text{Al}_2\text{O}_4$ ($x = 0.0, 0.1$). The ionic radius of Cu^{2+} and Mg^{2+} are 0.73 \AA and 0.72 \AA , respectively; therefore, they can displace Zn^{2+} (0.74 \AA) without deformation of the spinel cubic structure and hence maintain a monophase. Thus, the current study gives an insight on various properties like the optical and dielectric properties of the synthesized samples.

2. Materials and Methods

For synthesis of zinc aluminate ZA, ZAC and ZAM through combustion method, zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Loba chem), aluminium nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (Loba Chem), cupric nitrate trihydrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Loba chem), magnesium nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Loba chem), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), distilled water H_2O and ammonia solution were used as precursors. The metal nitrates were weighed according to their stoichiometric ratios and dissolved in distilled water which was used as a solvent to form a precursor solution followed by addition of fuel or chelating agent such as citric acid to the precursor solution and it was mixed thoroughly. The ratio of fuel to metal nitrate was taken in 2:1 ratio. Ammonia solution was added to the above mixture to sustain $\text{pH} \approx 8$. The redox mixtures were heated with the help of a magnetic stirrer provided with a hot plate at $100 \text{ }^\circ\text{C}$, to initiate the combustion reaction which results in a highly exothermic flame that rapidly heats and evaporates the solvent, burns the fuel and converts the metal salts into the desired metal oxide product. After the completion of combustion process the resulting products were collected and dried to remove any remaining solvent or fuel. The powders were then calcined at high temperature typically $800 \text{ }^\circ\text{C}$ to remove any residual carbon and to promote crystallization. The physical and electrical characterizations were carried out for the sintered powders.

The synthesized aluminates were characterized to know the phase purity and crystalline structure with the help of X-ray Diffraction technique (XRD: D8 Advance Bruker AXS, Germany). The study on vibrational modes and identification of functional groups in the prepared aluminates in the range of $400\text{--}4000 \text{ cm}^{-1}$ was done using Fourier-transform infrared (FTIR-SHIMADZU) spectra. The energy band gap was estimated using UV-Vis spectrophotometer (SHIMADZU, UV 3600 PLUS, JAPAN). The stoichiometry analysis was done using Scanning Electron Microscope (SEM with EDX) (Model: TESCAN VEGA3 XMU). The dielectric performance was explored using an Impedance analyzer (Hioki IM3570). For Dielectric studies the powder samples were mixed with PVA binder (5%)

and it was then pressed into pellets at the desired pressure using the 13 mm pelletizer. The pellets were well polished to obtain a smooth surface and it was further sintered at 1000 °C for 5 h.

3. Results and Discussion

3.1. P-XRD Analysis

The identification of crystalline phases, structural defects or impurities and phase purity present in the prepared aluminates was monitored by powder X-ray diffraction (PXRD) method. Figure 1 depicts the XRD spectrum of ZnAl₂O₄ (ZA), Zn_{0.9}Cu_{0.1}Al₂O₄ (ZAC) and Zn_{0.9}Mg_{0.1}Al₂O₄ (ZAM) synthesized by employing a sol–gel-based combustion route. The observed pattern with planes (111), (2 2 0), (3 1 1), (4 0 0), (331), (4 2 2), (5 1 1), (4 4 0), (620) and (533) which is in accordance with JCPDS Card No. 05–0669 [4]. It is evident that the spinel structure of undoped as well as Cu, Mg doped Zinc Aluminates were not distorted by the inclusion of the small amount of dopants. The crystallite size is calculated using Scherer's equation,

$$D_{XRD} = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

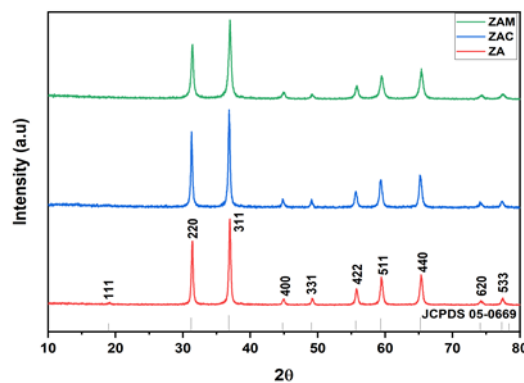


Figure 1. XRD Diffractogram of (ZA), (ZAC) and (ZAM)-left (b) Enlarged (311) peak of (ZA), (ZAC) and (ZAM)-right.

From the above equation 'D' denotes the crystallite size, 'k' is the shape factor whose value is 0.9 (constant), 'λ' is the wavelength source of Cu-Kα which takes the value 1.5405 Å and Full Width Half Maxima (FWHM) of the diffracted peaks is denoted by β. Table 1 represents the calculated parameters from XRD spectrum. The crystalline size was measured by using the Debye Scherrer's formula and was evaluated size was found in the range of 21–24 nm. We can observe that the Zinc Aluminate particles indicated an increase in average crystallite size for Cu²⁺ and Mg²⁺ samples when compared to the mother sample[5].

Table 1. Structural parameters of ZA, ZAC and ZAM synthesized through the Sol gel method.

Parameters	Crystallite Size D(nm)	Lattice Parameter (a = b = c) Å	Dislocation Den- sity (δ=)10 ⁻³	Interplanar Spac- ing d (Å)	Volume of the Unit Cell v = a ³
ZA	22.818	8.0809	1.9205	2.436	527.69
ZAC	23.048	8.0597	1.8823	2.430	523.54
ZAM	22.920	8.0598	1.9034	2.431	523.56

3.2. Functional Group Analysis

Figure 2 depicts the FTIR spectra of synthesized powders of ZnAl_2O_4 (ZA), $\text{Zn}_{0.9}\text{Cu}_{0.1}\text{Al}_2\text{O}_4$ (ZAC) and $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{Al}_2\text{O}_4$ (ZAM). The peak around $600\text{--}700\text{ cm}^{-1}$ can be assigned to vibrational stretching of aluminium-oxygen (Al-O) at octahedral site. While the peak around $400\text{--}500\text{ cm}^{-1}$ can be assigned to vibrational stretching of zinc-oxygen (Zn-O) at tetrahedral site. The sharp nature of the bands defines the porosity of the synthesized samples. The presence of bands at 2354.27 cm^{-1} is due to CO_2 absorbed from air. The absorption of the H_2O molecule on the surface is characterized by the presence of -OH stretching band at 3437.87 cm^{-1} . The bands at 1627 cm^{-1} represents symmetric stretching and at 1408 cm^{-1} can be attributed to asymmetric stretching of C-H [5,6].

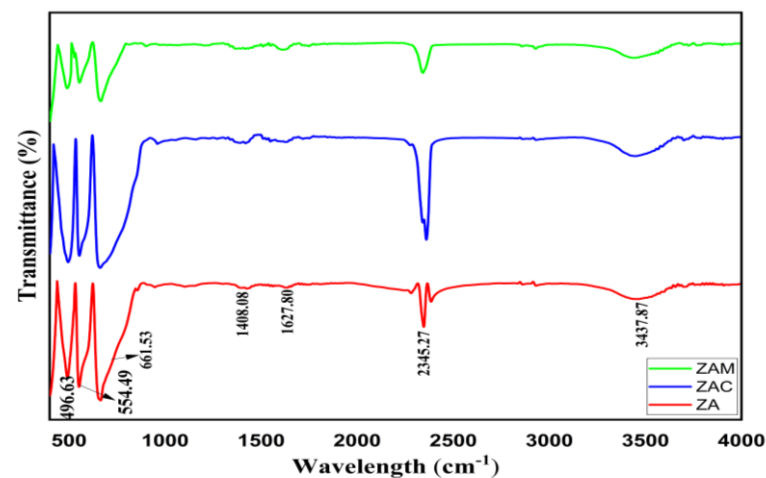


Figure 2. FTIR spectra of (ZA), (ZAC) and (ZAM).

3.3. EDAX Analysis

Energy Dispersive X-ray Analysis (EDAX) is a powerful technique that is commonly employed for the determination of the stoichiometric composition of a material. From Figure 3a–c the EDAX analysis shows peaks which correspond to Zinc (Zn), Aluminium (Al), Copper (Cu), Magnesium (Mg) and Oxygen (O) and shows the existence of all the ions present in the ZA, ZAC and ZAM compounds. Thus, it was confirmed that there were no other impurities.

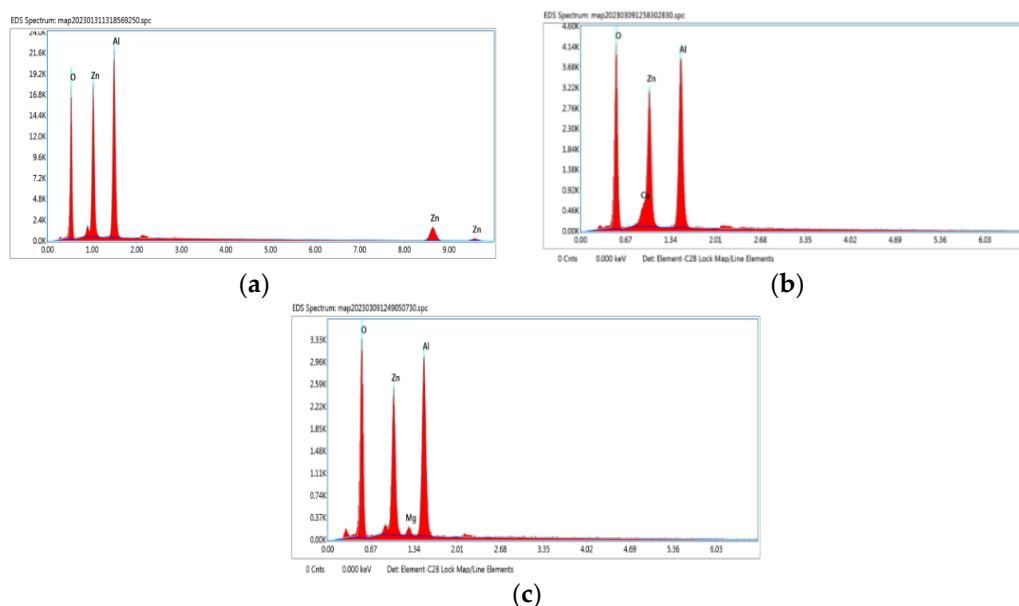


Figure 3. EDX Spectra of (a) ZA (b) ZAC & (c) ZAM Samples.

The percentages of each element of ZA, ZAC and ZAM are obtained from energy dispersive X-ray spectrum.

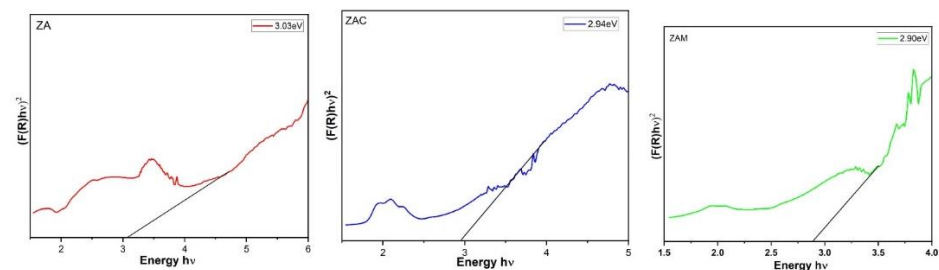
3.4. UV-DRS Analysis

The optical property of ZA, ZAC and ZAM particles in DRS mode and the spectrum was recorded by measuring the absorption of light in the 200–800 nm wavelength range. The energy gap of semiconducting materials, is usually estimated using the equation

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

where α is the absorption coefficient, h is the planks constant, ν is the frequency of the incident light, E_g the energy band gap and A is constant which depends on the optical properties of the synthesized compound. The above relation can be modified as $(\alpha h\nu)^2 = A^2(h\nu - E_g)$.

From Figure 4, by plotting $(F(R)h\nu)^2$ against $h\nu$ and bringing the straight line region of the curve to x-axis $(\alpha h\nu)^2 = 0$ the energy gap of the material can be calculated as shown in figure. The optical band gap value is evaluated to be 3.03 eV, 2.94 eV and 2.90 eV for ZA, ZAC and ZAM samples obtained from Kubelka-Munk plot. We observed a decrement in band gap decreases, which occurs due to various factors like doping with impurities, defects in the crystal structure or changes in the stoichiometry of the material. The figure indicated a redshift which indicates the quantum confinement effect due to reduction in size of Zinc Aluminate particles [7]. Therefore, understanding the causes of decrement in the optical band gap is essential for exploring the electrical properties as well as the optical behavior of the material for specific applications.

**Figure 4.** Kubelka-Munk Plot of ZA, ZAC and ZAM.

3.5. Dielectric and Electric Modulus Measurements

3.5.1. Dielectric Constant and Tangent Loss

The spinel-aluminate's dielectric properties relies mostly upon several factors like the stoichiometry composition of the compound, applied electric field, preparation methods and the temperature etc. This study aims to explore dielectric performance of Zinc aluminate samples which is measured at room temperature from 10 Hz to 20 MHz frequency range. The value of dielectric constant (ϵ') can be estimated by using the following relation.

$$\epsilon' = \frac{Cd}{A\epsilon_0}$$

where C denotes the capacitance of the capacitor filled with the material, d denotes the pellet thickness, A denotes the cross-sectional area of the calcined pellet. The permittivity of free space is given by ϵ_0 at a given frequency. The frequency Vs dielectric constant ϵ' 's shown in Figure 5.

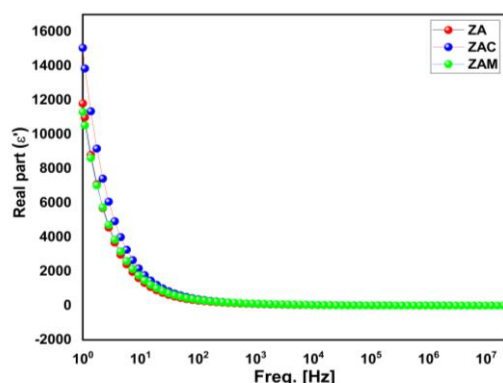


Figure 5. Frequency dependent dielectric constant (ϵ') of (ZA), (ZAC) and (ZAM)

The dielectric constant for Cu and Mg doped ZA particles depends on the electric field applied and also on the amount and distribution of copper and magnesium ions in the material. From Figure 5, It can be visualized that, at the low-frequency regime, the ϵ' is high and at higher frequency regime it is low which may be correlated with Maxwell–Wagner (M–W) model which is in accordance with Koop’s theory [8]. In general, the of Cu and Mg doped ZnAl_2O_4 increases with increasing frequency due to the polarization of the material at high frequencies. Also, from Figure 5, it is quite clear that in high frequency portion the value of dielectric constant increased for Mg doped ZA particles but found to be decreased for Cu doped ZA particles. Overall, the dielectric constant of Cu and Mg doped ZA particles can vary based on the concentration of the dopant, specific synthesis methods and processing conditions used.

Figure 6 shows the room temperature measurement of tangent loss ($\tan\delta$) of zinc aluminate particles. The presence of relaxation peaks in the mid frequency regime with decline in the loss tangent in lower and higher frequency regions was noticed. The decrement in tangent loss ($\tan\delta$) can be related to Koop’s theory which suggests that at lower frequency region the loss is high and it declines as the frequency increases. A similar behavior was obtained for all the zinc aluminate samples. The relaxation peak observed for ZAM sample at the mid-frequency region is because of the formation of additional defect states within the energy gap, which can increase the energy dissipation in the material or space charge polarization effect [8]. From Figure 6, It can be seen that at higher frequency the loss tangent δ for both Cu and Mg doped ZA particles increases slightly from pure ZA at a higher frequency region. Therefore, from the obtained dielectric parameters, combination of high dielectric constant and minimum loss makes them suitable for their use in high-voltage ceramic capacitors and microwave devices. Hence, careful selection of the dopant concentration makes it a potential candidate for several applications.

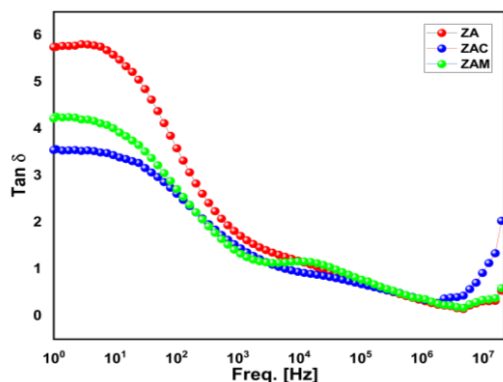


Figure 6. Frequency dependent Tangent loss ($\tan\delta$) of (ZA), (ZAC) and (ZAM).

3.5.2. Cole-Cole Plot

Figure 7 shows the Cole–Cole plotted between real and imaginary part of electric modulus at different frequencies. Cole–Cole plot provides information about the electrical properties of the material clearly and dielectric relaxation behavior of the material such as the presence of multiple relaxation processes. The Cole–Cole plot can provide insight into the nature of the electrical nature of the material based on the shape obtained. It can be seen that all the samples exhibit half semicircle, depressed semicircle and an arc attached to the semicircle. The centers of all the samples were lying below the real axis which denotes the presence of non-Debye type relaxation behavior in zinc aluminate samples. The presence of semicircles followed by an arc indicates the material has multiple relaxation mechanisms. The figure shows the measured Cole–Cole plots of under different frequencies which exhibits partial semicircle and a depressed semicircle followed by an inclined straight line [9]. The presence of half semi-circle and depressed circle at lower frequency regime corresponds to the presence of capacitive behavior and resistive behavior in higher frequency regime and the arc suggests the presence of boundary layer or interface between the material and its environment. From the plot we can infer that the resistance of grain boundary contribution is larger than the grains for all the samples. The arc may represent the

The decrease in diameter of the semicircle with respect to doping Cu and Mg in the host lattice denotes decrease in the samples resistance and increase in electronic conductivity of the sample. Therefore, by analyzing the shape and position of the Cole–Cole plot, researchers can give valuable information about the material's electrical properties and how they change with frequency. This information can be used to optimize the material's performance for specific high frequency applications like antennas or filters.

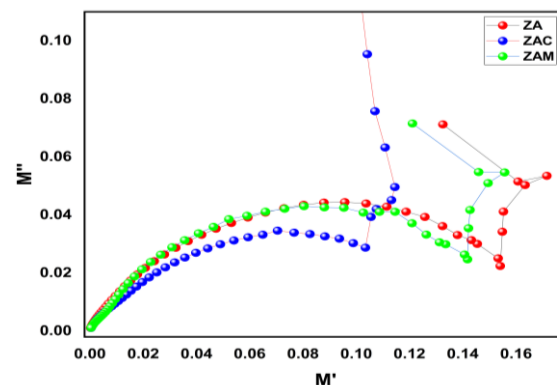


Figure 7. Cole-Cole Plot Of ZA, ZAC and ZAM Samples.

4. Conclusions

In Conclusion, the replacement effect of Cu^{2+} and Mg^{2+} on the structural and optical as well as the dielectric parameters of zinc aluminate (ZnAl_2O_4) was studied and found to be a promising material for low frequency applications. The XRD of aluminates displayed their single-phase spinel structure and it was observed that the substitution of Cu and Mg content decreases the lattice parameter (8.09–8.05 nm) and an increase in crystallite size (21–23 nm) was observed when compared to the parent sample. The transmittance band in the range 554 cm^{-1} for the octahedral O_h site and 661 cm^{-1} for the tetrahedral T_d site of aluminates was confirmed by FTIR spectra. The purity and presence of elements in the ZA, ZAC and ZAM samples were confirmed by EDAX spectrum. From the optical band gap results which was estimated by using Kubelka-Munk function, it was observed that with the substitution of Cu and Mg in the mother sample a decrement in band gap value (3.03–2.90 eV) was observed, which in turn indicates a redshift in zinc aluminate samples. Room temperature frequency dependence of the dielectric constant ϵ' , Cole Cole plot and tangent loss ($\text{Tan } \delta$) was analyzed for all the samples and the obtained results have been

reported. The results showed that Mg doping significantly improves the dielectric properties making it suitable for high frequency applications. From the Cole-Cole plot it was found that both grains and grain boundaries both contributed in the conduction process. The temperature dependent dielectric and impedance behavior will be extended in the ongoing studies in future.

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