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# Temperature stable low loss ceramic dielectrics in (1-x)$ZnAl_2O_4$-x$TiO_2$ system for microwave substrate applications

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**Abstract.** The microwave dielectric properties of $ZnAl_2O_4$ spinels were investigated and their properties were tailored by adding different mole fractions of $TiO_2$. The samples were synthesized using the mixed oxide route. The phase purity and crystal structure were identified using X-ray diffraction technique. The sintered specimens were characterized in the microwave frequency range (3–13 GHz). The $ZnAl_2O_4$ ceramics exhibited interesting dielectric properties (dielectric constant ($\varepsilon_r$) = 8.5, unloaded quality factor ($Q_u$) = 4590 at 12.27 GHz and temperature coefficient of resonant frequency ($\tau_f$) = −79 ppm/°C). Addition of $TiO_2$ into the spinel improved its properties and the $\tau_f$ approached zero for 0.83$ZnAl_2O_4$-0.17$TiO_2$. This temperature compensated composition has excellent microwave dielectric properties ($\varepsilon_r$ = 12.67, $Q_u$ = 9950 at 10.075 GHz) which can be exploited for microwave substrate applications.

**PACS.** 72.80.Sk Insulators – 77.22.-d Dielectric properties of solids and liquids – 77.84.Dy Niobates, titanates, tantalates, PZT ceramics, etc. – 77.84.Bw Elements, oxides, nitrides, borides, carbides, chalcogenides, etc.

## 1 Introduction

Ceramic substrates find a wide range of applications in wireless access circuits that use millimeter waves for 3rd generation cell phones, blue-tooth equipped devices, wireless LAN, optical communications as well as peripheral electronic devices. Ceramic substrates should ideally have a low permittivity (to minimize cross-coupling with conductors and to shorten the time for the electronic signal transition) if they are to be used as advanced substrate materials in microwave integrated circuits (MIC) [1]. The typical characteristics needed for a dielectric substrate are: (a) low dielectric constant, (b) low dielectric loss and (c) matching coefficient of thermal expansion to that of the material attached. These substrate materials also ought to exhibit high $Q$ factors in order to maintain overall high-$Q$ circuits by lowering power dissipation. Typical dielectric properties of some commonly used low-dielectric constant ceramic substrates show less reliable properties for MIC application [2]. For an ideal microwave substrate material the temperature coefficient of resonant frequency ($\tau_f$) should be close to zero. Alumina [3] and Forsterite [4] are two good candidates for substrate applications but their high negative temperature coefficient of resonant frequencies put constraints on their use in temperature stable microwave devices such as oscillators. Hence the search for new substrate materials with optimum balance of the dielectric properties is considered as a big challenge in the research of microwave materials.

Compounds with the general formula $AM_2O_4$[A = Mg, Zn, Co, Ni, Cu; M = Al, Ga, Fe] are referred to as spinels [5], which belong to the face centered cubic symmetry group $Fd\overline{3}m$. Their cubic cell contains a close packed array of 32 oxygen atoms with cations in the tetrahedral and octahedral interstices. In the normal spinel structure, tetrahedral sites are occupied by divalent cations whereas octahedral sites are occupied by trivalent cations [6]. The aluminate spinel materials were reported to be ideal candidates for serving as radiation resistant matrices in nuclear bombardment experiments and as a support for Pt and Pt-Sn catalysts because of their high thermal stability and low acidity. Furthermore, a recent survey revealed that zinc aluminate spinels were also finding versatile application in industrial ceramics [7], as a second phase in glaze layers of white ceramic tiles to improve wear resistance and mechanical properties and to preserve whiteness. This has been supported by an increasing number of

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**Table 1.** Properties of pure and doped $ZnAl_2O_4$ and $TiO_2$.

| Material | Density ($g/cm^3$) | Sinter Temp. | % Density | Cell Parameter $a$ (Å) | $c$ (Å) | $\varepsilon_r$ | $\tau_f$ (ppm/°C) | $Q_u \times f$ (GHz) |
|---|---|---|---|---|---|---|---|---|
| $ZnAl_2O_4$ Pure | 4.38 | 1425 | 95.6 | 8.0899 | -- | 8.5 | –79 | 4590 × 12.27 |
| $ZnAl_2O_4$ + 1 mole % $CaCO_3$ | 4.37 | 1400 | 95.4 | 8.0902 | -- | 8.5 | –81 | 4730 × 12.27 |
| $ZnAl_2O_4$ + 1 mole % $SnO_2$ | 4.42 | 1400 | 96.5 | 8.0913 | -- | 8.7 | –85 | 4240 × 12.26 |
| $ZnAl_2O_4$ + 1 mole % $Eu_2O_3$ | 4.35 | 1450 | 94.9 | 8.0841 | -- | 8.2 | –72 | 3950 × 12.29 |
| $TiO_2$ (Rutile) Pure | 4.00 | 1500 | 93.8 | 4.5911 | 2.9599 | 104.2 | +411 | 5070 × 3.47 |
| $TiO_2$ + 1 mole % $Fe_2O_3$ | 4.09 | 1500 | 96.0 | 4.5928 | 2.9588 | 105.1 | +398 | 7770 × 3.46 |
| $TiO_2$ (Rutile) Sol-Gel Route | 3.69 | 1300 | 86.6 | 4.5824 | 2.9441 | 93.3 | +423 | 3540 × 3.50 |

research papers in the literature. The mixture characteristics of $ZnAl_2O_4$-$TiO_2$ have also been studied although the emphasis was on exploring the possibility of developing ultra filtration membranes. The aim was to increase the electrical interaction of the $ZnAl_2O_4$ and $TiO_2$ layers with the filtered ionic species [8,9]. In a recent publication [10], a group of Dutch researchers attempted to measure its dielectric constant but their results throw no light on the dielectric loss behavior of these ceramics. The present investigation revealed that $ZnAl_2O_4$ is a high $Q$ dielectric with negative $\tau_f$. It has been previously reported that it is possible to tune the $\tau_f$ of materials by making solid solutions or mixtures of positive $\tau_f$ material with a negative $\tau_f$ material [11,12]. Hence we carried out a detailed study on the mixture characteristics of $ZnAl_2O_4$ with $TiO_2$, which has high positive $\tau_f$ and high dielectric constant, in an effort to tune the temperature coefficient of resonant frequency to zero. The present paper reports the microwave dielectric properties of $ZnAl_2O_4$ spinels, and tailors its properties by making molar mixtures with $TiO_2$ to form $(1-x)ZnAl_2O_4$-$xTiO_2$ in an effort to develop an alternate substrate material composition for applications in mobile communication devices.

## 2 Experimental

The $(1-x)ZnAl_2O_4$-$xTiO_2$ ceramics were prepared by the conventional mixed oxide route. High purity ZnO and $Al_2O_3$ (purity 99.9%; Aldrich Chemical Co.) were used as the starting materials for the synthesis of $ZnAl_2O_4$ spinels. The chemicals were weighed according to the stoichiometric compositions and were ball milled in a polyethylene bottle using zirconia balls in deionized water for 24 hours. The slurry was dried at 100 °C in a hot air oven and was calcined at 1100 °C for 4 hours. The phase purity of the spinel was established using the X-ray diffraction technique. It was then ball milled with anatase $TiO_2$ (Aldrich 99.9% pure) according to the formula $(1-x)ZnAl_2O_4$-$xTiO_2$ ($x = 0.0, 0.1, 0.12, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.20, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9$ and $1.0$) for 24 hours using deionized water as the mixing medium. The slurry was dried and was then ground well in an agate mortar. Four wt% of poly vinyl alcohol (PVA) was added as the binder, mixed well and ground to a fine powder. It was then pressed into cylindrical disks of about 14 mm diameter and 6–8 mm thickness in a tungsten carbide die under a pressure of about 150 MPa. These compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 1 hour to expel the binder before they were sintered in the temperature range 1375–1425 °C for 4 hours in air at a heating rate of 10 °C/hour. Adding a dopant such as $CaCO_3$, $SnO_2$ and $Eu_2O_3$ did not show any significant improvement in the densification or quality factor of the spinels (see Tab. 1). Hence the $ZnAl_2O_4$ was prepared without any dopants. However $Fe_2O_3$ dopant was always added to $TiO_2$ since it improves the quality factor [17]. In synthetic spinels, a disordered distribution of cations exists systematically [6] in such a way that a fraction of trivalent aluminium ions occupy tetrahedral sites for zinc. So the sintered samples were annealed at 1000 °C for 5 hours. The well-polished ceramic pellets with an aspect ratio (D/L) of 1.8 to 2.2 (found to be the best for maximum separation of the modes) were used for microwave measurements. The bulk density of the sintered samples were measured using the Archimedes method. The powdered samples were used for analyzing the X-ray diffraction patterns using Cu $K_\alpha$ radiation (Rigaku, Japan).

The dielectric properties $\varepsilon_r$ and $\tau_f$ of the materials were measured in the microwave frequency range (3–13 GHz) using a network analyzer HP 8510C (Hewlett-Packard, Palo Alto, CA). The dielectric constant $\varepsilon_r$ was measured by the post resonator method of Hakki and Coleman [13] and the dielectric sample was end

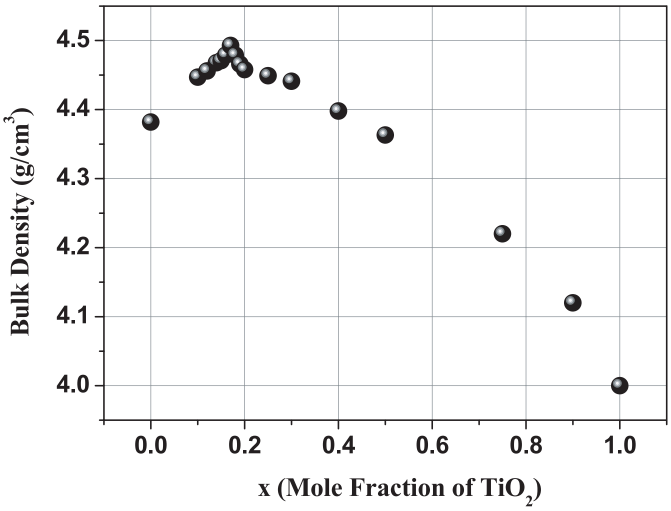


**Fig. 1.** Variation of the bulk density of $(1-x)ZnAl_2O_4$-$xTiO_2$ with $x$.

shorted with copper plates coated with gold. The microwave is coupled though $E$-field probes as described by Courtney [14]. The $TE_{01\delta}$ mode of resonance, which is least perturbed by the surrounding field variations was used for measurements. The unloaded quality factor $Q_u$ of the $TE_{01\delta}$ resonance was determined using a copper resonant cavity [15] whose interior was coated with silver and the ceramic dielectric is placed on a low loss quartz spacer. The unloaded quality factor is calculated using the equation

$$Q = \frac{f}{\Delta f} \tag{1}$$

where $f$ is the resonant frequency when the sample is placed centrally symmetric to the microwave cavity and $\Delta f$ is the 3dB bandwidth. The temperature coefficient of resonant frequency is measured by noting the variation of the $TE_{01\delta}$ resonant mode with temperature in the range 20–80 °C, when the sample was kept in the end shorted position. Then $\tau_f$ is given by

$$\tau_f = \frac{1}{f} \times \frac{\Delta f}{\Delta T} \tag{2}$$

where $\Delta f$ is the variation in resonant frequency from room temperature and $\Delta T$ is the difference in temperature.

## 3 Results and discussion

The density of pure $ZnAl_2O_4$ was measured to be 4.38 g/cm$^3$ which is around 96% of its theoretical density [5] (4.58 g/cm$^3$). The theoretical density of $TiO_2$ (rutile) is 4.26 g/cm$^3$. Figure 1 represents the variation of bulk density of $ZnAl_2O_4$ as a function of $TiO_2$ concentration. The $TiO_2$ was only densified up to 93.8%. It has been reported [16] that the densification behaviour of $TiO_2$ is hindered due to the anatase to rutile phase transition consequent to the reduction of $Ti^{4+}$ to the $Ti^{3+}$ state. It is

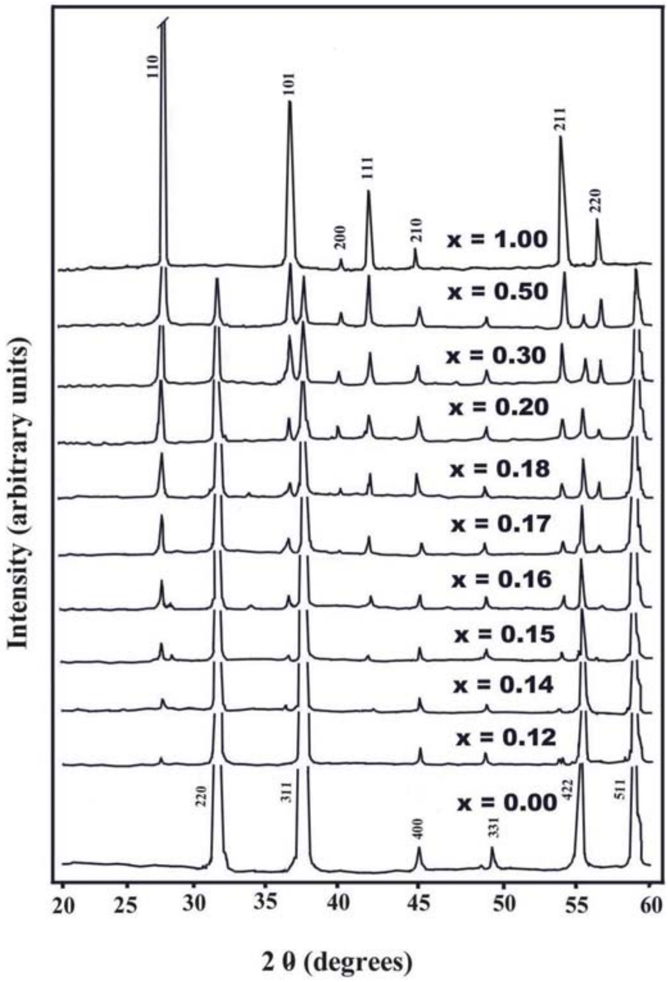


**Fig. 2.** Powder diffraction patterns of $(1-x)ZnAl_2O_4$-$xTiO_2$ mixed phases for $x = 0.0$, 0.12, 0.14, 0.15, 0.16, 0.17, 0.18, 0.2, 0.3, 0.5, 1.0.

believed [17] that addition of dopants with valancies 2 and 3 improves densification, since they can compensate any oxygen vacancies that may form during sintering. We used anatase titania as the starting material in this investigation, and then it is doped with 1 mole % additive $Fe_2O_3$ which improved the densification process. The densification performance of $TiO_2$ sample prepared from alkoxide sol-gel route was very poor (see Tab. 1).

Figure 2 represents the XRD patterns recorded from samples for $x = 0.0$, 0.12, 0.14, 0.15, 0.16, 0.17, 0.18, 0.2, 0.3, 0.5 and 1.0 in $(1-x)ZnAl_2O_4$-$xTiO_2$. The powder diffraction pattern of $ZnAl_2O_4$ is indexed as per JCPDS File Card Number 5-669. The crystal structure of $TiO_2$ (rutile) is tetragonal. The powder diffraction pattern of specimen for $x = 1.0$ is identical with JCPDS File Card Number 21-1276 for $TiO_2$ (rutile). The XRD pattern suggests that $ZnAl_2O_4$ will not form a solid solution with $TiO_2$, which has been one of the reasons behind selecting them for preparing ultrafiltration membranes [8]. The variation of physical and dielectric properties of the

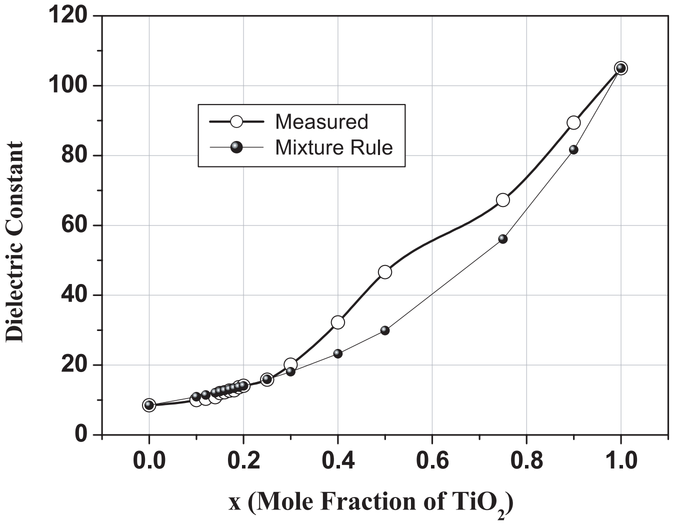


**Fig. 3.** Variation of the dielectric constant of $(1-x)ZnAl_2O_4$-$xTiO_2$ with $x$.

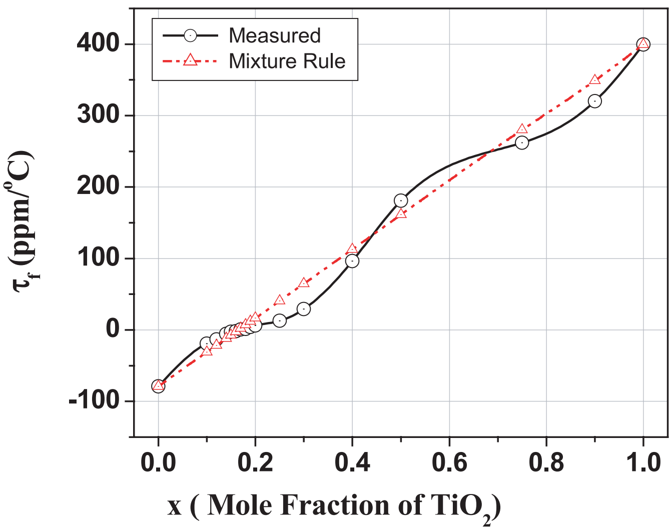


**Fig. 4.** Variation of the temperature coefficient of resonant frequency of $(1-x)$ $ZnAl_2O_4$-$xTiO_2$ with $x$.

mixture compositions were proportional to the variation of the molar concentration of the contributing phases.

The microwave dielectric properties of zinc aluminate spinel are found to be quite interesting since the dielectric loss factor of this ceramic is low enough for microwave substrate applications. The measured dielectric constants were corrected for porosity [18]. The dielectric constant of pure zinc aluminate is 8.5 while that for $Ca^{2+}$, $Sn^{4+}$ and $Eu^{3+}$ doped spinels are 8.5, 8.7 and 8.2 respectively. The variation of the dielectric constant of $ZnAl_2O_4$ with $TiO_2$ addition is plotted in Figure 3. The dielectric constant shows reasonably good agreement with the following logarithmic mixing rule [19] for smaller values of $x$, while it shows noticeable deviation as the value of $x$ increases. The dielectric constant of the mixture is given by

$$\ln \varepsilon_r = v_1 \ln \varepsilon_{r1} + v_2 \ln \varepsilon_{r2} \tag{3}$$

where $\varepsilon_{r1}$ and $\varepsilon_{r2}$ are the dielectric constants of phases with volumes $v_1$ and $v_2$. It must be remembered that this mixture rule does not have any physical implication but is introduced as a curve fitting construct. Furthermore, the behavior of the dielectric constant of $ZnAl_2O_4$ with $TiO_2$ does not follow any other mixture rules for random binary phase materials. The dielectric constant of pure $TiO_2$ is 104 while that doped with $Fe_2O_3$ is 105.1 (Tab. 1). The dielectric constant of the $TiO_2$ sample made of chemically derived powder is only 93.2. The lower dielectric constant of this sample made from powder obtained from chemical method is due to its poor densification. Very recently, van der Laag et al. [10] reported that $\varepsilon_r$ of $ZnAl_2O_4$ was 9.46 at a frequency of 10 MHz, where the dielectric constant would be higher than that measured at microwave frequency.

The temperature coefficient of resonant frequency ($\tau_f$) of pure $ZnAl_2O_4$ is −79 ppm/°C while that for $Ca^{2+}$, $Sn^{4+}$ and $Eu^{3+}$ doped samples are −81, −85 and −72 ppm/°C respectively. In one of our previous reports it has been shown that variation of $\tau_f$ in a random mixture is proportional to the molar variation of the constituent phases [12]. Hence the $\tau_f$ of the mixture phases can be computed using a general mixture formula [20]

$$\tau_{f(eff)} = v_1 \tau_{f1} + v_2 \tau_{f2}. \tag{4}$$

The variation of $\tau_f$ of the mixed phases of $ZnAl_2O_4$-$TiO_2$ was plotted in Figure 4 from which it is obvious that the variation of mixed phases varied around the straight line corresponding to the rule of mixtures. The value of $\tau_f$ for $x = 0.16$ is −1.9 while that for $x = 0.18$ is +1.5 ppm/°C, from which one can interpolate that the zero $\tau_f$ composition will be around $x = 0.17$ in $(1-x)ZnAl_2O_4$-$xTiO_2$ mixture. We measured the $\tau_f$ of $0.83ZnAl_2O_4$-$0.17TiO_2$ as 0.74 ppm/°C which can be approximated as zero $\tau_f$ composition within the limits of experimental error. However, the error of the experimental value from the zero $\tau_f$ value predicted by the rule of mixtures (0.825 $ZnAl_2O_4$-0.165 $TiO_2$) given by equation (4) is marginal. Furthermore, there was no additional phase formation detected consequent to the chemical reaction between $ZnAl_2O_4$ and $TiO_2$ throughout the complete range of mixtures. On the other hand, additional phase formation of $MgTi_2O_5$ was observed in a recent report [4] on substrate material when rutile was added to high $Q$ forsterite, which resulted in anomalous behavior of $\tau_f$ in the mixture.

The resonant frequency of the dielectrics in the mixed phase measured using a microwave cavity was plotted in Figure 5 (inset) with respect to the molar addition of $TiO_2$ into the spinel. The resonant frequency of samples with the same dimensions should decrease linearly from $ZnAl_2O_4$ to $TiO_2$ rich compositions, which have larger dielectric constants. The nonlinear variation of the resonant frequency is due to the slight variations of dimension of the ceramic samples, since the resonant frequency depends on the sample dielectric constant and dimensions.

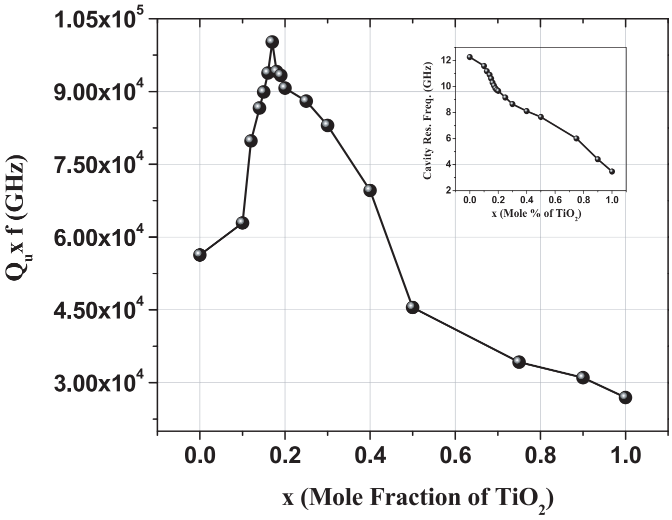


**Fig. 5.** Variation of the unloaded quality factor and resonant frequency of $(1-x)$ $ZnAl_2O_4$-$x TiO_2$ with $x$.

The unloaded quality factor of pure $ZnAl_2O_4$ is reasonably good (Tab. 1) and is well above that of many of the conventional low dielectric constant materials. Doping with $CaCO_3$ improved the $Q$ factor slightly but $SnO_2$ addition deteriorated it (Tab. 1). The addition of $Eu_2O_3$ also decreased the dielectric quality factor of the material. The variation of unloaded factor of the various mixture phases are plotted in Figure 5 as a function of the increasing $TiO_2$ content. It must be noted that the microwave quality factor, which depends greatly on the synthesizing conditions, porosity, grain morphology etc. does not show any specific relationship with the rule of mixtures. The product $Q_u \times f$ is maximum ($Q_u = 9950$ at 10.075 GHz) around $x = 0.17$ in $(1-x)ZnAl_2O_4$-$x TiO_2$ where the $\tau_f$ assumes minimum value. It is worthwhile to note that the intermediate phases show better quality factors compared to the end phase components, which is very rare in dielectric mixtures. From Figure 5, it is clear that the drop in quality factor is more for the $TiO_2$ rich compositions. It is well known that the anatase to rutile phase transition around 700 °C was a major source of concern in its dielectric loss quality, since it involves collapse of the relatively open anatase structure. This collapse takes place by a distortion of the oxygen framework and shifting of the majority of $Ti^{4+}$ ions, by rupturing two out of the six Ti-O bonds to form new bonds [21]. Shannon [16] suggested that doping with aliovalent additives or sintering in reduced atmosphere can accelerate oxygen vacancy formation and expedite the anatase to rutile transformation. In our experiment doping of $TiO_2$ with $Fe_2O_3$ yielded a better quality factor (see Tab. 1) even though it is less than the quality factor reported by Templeton [17] et al. The $TiO_2$ samples derived from sol-gel precursor also showed a poor microwave quality factor.

The above discussion revealed that the composition 0.83 $ZnAl_2O_4$-0.17 $TiO_2$ is an ideal temperature stable, high $Q$ dielectric resonator, which is comparable to many of the conventional low dielectric constant microwave dielectrics such as $Al_2O_3$. In spite of its high quality factor at microwave frequency range, the $\tau_f$ of sintered alumina [3] is –60 ppm/°C and being a well-known refractory, its processing temperature is high. But the new $0.83ZnAl_2O_4$-$0.17TiO_2$ rutile-spinel mixture composition is advantageous over $Al_2O_3$ in respect to temperature compensation which is a necessary requirement for microwave dielectric substrate applications.

## 4 Conclusion

Low dielectric constant, face centered cubic ceramics based on $ZnAl_2O_4$ were synthesized using mixed oxide route. The $ZnAl_2O_4$ spinels have low dielectric constant, high quality factor and negative temperature coefficient of resonant frequency in the microwave frequency range (3–13 GHz). The addition of dopants such as $CaCO_3$, $SnO_2$ and $Eu_2O_3$ did not considerably improve their properties. The dielectric constant was increased with the molar addition of $TiO_2$ into the spinel to form mixtures based on $(1-x)ZnAl_2O_4$-$x TiO_2$ ($x$ = 0.0, 0.1, 0.12, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.20, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9 and 1.0). The analysis of the crystal structure based on powder diffraction suggested that no additional phase was formed in the entire range of mixture formation. The densification was improved and the quality factor reached a maximum value of $Q_u = 9950$ at 10.075 GHz for $x = 0.17$ in $(1-x)ZnAl_2O_4$-$x TiO_2$. The resonant frequency remained unchanged with temperature for the composition with $x = 0.17$. This temperature stable dielectric property is an important requirement for fabricating temperature stable oscillators and filters in microwave circuits. Furthermore, unlike in the forsterite-rutile mixture where additional phases formed, resulted in fluctuating values of $\tau_f$, we observed no chemical reaction between spinel and rutile to form additional low $Q$ phases in the mixture. The $0.83ZnAl_2O_4$-$0.17TiO_2$ dielectrics with $\varepsilon_r = 12.67$, excellent quality factor and temperature stability is proposed as a suitable microwave substrate material. This composition is advantageous over alumina due to its temperature stability and lower preparation temperature.

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