Ultra-low temperature sintering and temperature stable microwave dielectrics of (Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{2}O\textsubscript{6} (x = 0–0.09) Ceramics

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ABSTRACT

Novel ultra-low firing (Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{2}O\textsubscript{6} (x = 0–0.09) ceramics have been investigated and systematically designed as promising dielectrics for ultra-low temperature co-fired ceramics applications. The X-ray diffraction patterns indicated that all samples crystallized in a monoclinic structure with a space group of C\textsubscript{2v}. Microstructures and lattice parameters are presented and correlated with the microwave dielectric properties of the ceramics. The Mg\textsubscript{2}O\textsubscript{6} specimen can be well-sintered at 610°C, the resulting ceramic of which featured an \(\varepsilon_r \sim 8.8\), a \(Q \times f \sim 10,300\) GHz and a \(\tau_r \sim 29.7\) ppm/°C. The tunable \(\tau_r\) value can be adjusted to near zero along with a great promotion in the \(Q \times f\) of Mg\textsubscript{2}O\textsubscript{6} by using a small Zn substitution. In addition, excellent microwave dielectric properties (\(\varepsilon_r \sim 9.3\), \(Q \times f \sim 15,300\) GHz and \(\tau_r \sim 3.4\) ppm/°C) were obtained for the (Mg\textsubscript{0.92}Zn\textsubscript{0.08})\textsubscript{2}O\textsubscript{6} specimen sintered at 610°C for 4 h. The specimen is chemically compatible with Al electrodes and could be an ideal ultra-low temperature co-fired ceramics dielectric. Possible applications include the 5G system, particularly with high frequency regions.

1. Introduction

With the progress of today’s wireless communication systems, the requirement of Low Temperature Co-fired Ceramics (LTCC) technology to miniaturize and integrate microwave passive components and devices is more needed than ever. Major requisites for LTCC dielectrics include a low dielectric constant (\(\varepsilon_r < 10\)) to reduce the wave propagation delay of the system, a high \(Q \times f\) value to lower the dielectric loss at high frequency operation, and a near-zero temperature coefficient of resonant frequency (\(\tau_r\)) to limit the resonator frequency shift. For energy conservation, Al (melting point at 660°C) is normally preferred and selected as the electrode material for Ultra-Low Temperature Co-firing Ceramics (ULTCC) applications. Consequently, a < 660°C sintering temperature is required for the dielectrics to prevent the electrode from melting. To this end, glass addition and sol-gel processing are usually employed to reduce the sintering temperature of dielectric ceramics. However, glass-added sintering also degrades the microwave dielectric properties of ceramics. Moreover, a costly, time-consuming, and complex processing is required for the sol-gel method. Most of the ULTCC reveal a negative \(\tau_r\) value [1–3]. To compensate the negative \(\tau_r\) value, dielectrics with a positive \(\tau_r\), which also means a high \(\varepsilon_r\), and a low \(Q \times f\), are often added to the ceramics, resulting in the combined microwave dielectric properties also being distorted, thereby limiting possible applications at high frequency regimes, such as a 5G system [4,5]. For instance, high \(\varepsilon_r\) (>10) dielectrics increase the wave propagation delay of devices for high frequency applications. Therefore, the search for new dielectrics, particularly with a stable \(\tau_r\) for ULTCC applications has become a more urgent issue.

A number of V\textsubscript{2}O\textsubscript{5}-based ceramic families have been studied and reported for LTCC applications over the last decade. For instance, BaV\textsubscript{2}O\textsubscript{5} and Ba\textsubscript{1}V\textsubscript{2}O\textsubscript{1.5}, belonging to the BaO-V\textsubscript{2}O\textsubscript{5} family, have been reported to be good candidates for ULTCC applications [6,7]. The R\textsubscript{2}V\textsubscript{2}O\textsubscript{5} (R = Ba, Sr and Ca), BaO-MO-V\textsubscript{2}O\textsubscript{5} (M = Mg, Zn), and Sm\textsubscript{3}V\textsubscript{2}O\textsubscript{7} (M = Mg, Zn) families have also been found to offer good microwave dielectric properties at ultra-low sintering temperatures [8,9]. Moreover, Mg\textsubscript{3}(VO\textsubscript{4})\textsubscript{2} and BaMg\textsubscript{2}(VO\textsubscript{4})\textsubscript{2} have been proposed as suitable LTCC dielectrics [10–12]. Nevertheless, they possess a large negative \(\tau_r\) which limits their practical applications.

In this paper, a novel ULTCC (Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{2}O\textsubscript{6} (x = 0–0.09) dielectric with a near-zero \(\tau_r\) was investigated. In doing so, the X-ray Diffraction (XRD) patterns and surface morphology were studied. Additionally, the compatibility of co-firing with an Al electrode was also reported.

2. Materials and methods

V\textsubscript{2}O\textsubscript{5}, MgO, and ZnO powders (>99.9%) were mixed according to the (Mg\textsubscript{1-x}Zn\textsubscript{x})\textsubscript{2}O\textsubscript{6} (x = 0–0.09) composition. The powders were ball-milled for 24 h, dried and calcined at 500°C for 2 h. The mixtures, together with PVA binder, were subsequently granulated and uniaxially pressed into pellets with 5 mm in thickness and
11 mm in diameter at 2000 kgf/cm². All samples were then sintered at 520–640°C for 4 h. The subsequent phase identification of the specimens was conducted by XRD pattern analysis using a Siemens D5000 diffractometer (Munich, Germany) with Cu-Kα radiation (at 40kV and 40 mA). Thermal Gravity-Differential Scanning Calorimetry (TG-DSC) analyses (NETZSCH-STA409PC) were employed in analyzing the phase formation of the samples. The microstructures and the compatibility of co-firing with Al were studied using ultra-high resolution scanning electron microscopy (UHR–SEM; HitachiSU-8000) equipped with energy dispersion spectroscopy (EDS, Philips). The Archimedes method was applied to measure the densities of the specimens. Dielectric constants and $Q \times f$ values of the samples were measured using the Hakki-Coleman [13] and Courtney [14] methods on an Agilent 8364A network analyzer (USA). The same technique was applied to measure the $\tau_f$ value and can be expressed by

$$\tau_f = (f_2 - f_1)/[f_1(T_2 - T_1)]$$

where $f_1$ and $f_2$ represent the resonant frequencies at $T_1$ and $T_2$, respectively. All specimens were measured at 25–80°C. Rietveld refinement was completed by using the General Structure and Analysis System(GSAS).

3. Results and discussion

Figure 1 illustrates the TG-DSC curves of the MgV$_2$O$_6$ precursor powders performed by the thermal analyzer. There are two mass losses of the ceramic, the first of which constitutes a total weight loss of 3.7% occurring before reaching 258°C, and the second major weight loss of 10.2% observed during the second stage from 258°C to 450°C. Further increases in the temperature led to no additional obvious weight losses, suggesting that the formation of the MgV$_2$O$_6$ phase was complete. According to the DSC curve, the small endothermic peak appearing at 185°C was most likely caused by free-water evaporation. The second endothermic peak occurring at 245°C along with weight loss was due to the evaporation of crystal water or the decomposition of Mg(OH)$_2$. In addition, an endothermic peak appearing at 415°C was due to the formation of the MgV$_2$O$_6$ phase at the final stage. As can be seen, there are some exothermic peaks observed between 450 and 550°C corresponding to the heat-release process of adjusting the lattice structure in the late stage of the reaction. Based upon the TG-DSC curves, the calcination temperature of the MgV$_2$O$_6$ precursor powders was then chosen to range from 450–550°C.

The XRD patterns of the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_8$ ($x = 0$–0.09) ceramics recorded at room temperature are shown in Figure 2. The specimens exhibited a monoclinic structure with a space group of C$_{2}$/m [11] in accordance with the standard ICDD-PDF #01-071-1651. Additionally, no second phase was detected in all cases, suggesting the formation of a solid solution. With an increase in $x$, peaks shifted to a lower angle due to the replacement of Mg$^{2+}$ (0.72 Å, CN = 6) by the larger Zn$^{2+}$ (0.74 Å, CN = 6). In addition, no peak shift was observed for the (Mg$_{0.93}$Zn$_{0.07}$)$_2$V$_2$O$_8$ specimen at various temperatures, indicating that the influence of the sintering temperature on structure could be excluded. However, the full width at half maximum (FWHM) decreased as the sintering temperature increased, which implies better crystallinity. In order to further clarify the crystal structure of the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_8$ ($x = 0$–0.09) ceramics, GSAS software was used to conduct Rietveld refinements. Table 1 illustrates the resultant refined lattice parameters, molecular volume, reliability factors, and goodness of fit indicators. As seen, the variations of lattice parameters and cell volumes were limited and within 1%, and the goodness of fit indicator values ($\chi^2$) were in the range 0.98–1.28, which suggests that the structural model is valid along with the expected deviations.
Table 1. The refined lattice parameters, molecular volume, goodness of fit, and reliability factors, of the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$ ceramics sintered at 610°C.

| x content | $x = 0$ | $x = 0.01$ | $x = 0.03$ | $x = 0.05$ | $x = 0.07$ | $x = 0.09$ |
|-----------|---------|------------|------------|------------|------------|------------|
| $a$       | 9.29023 | 9.29019    | 9.29119    | 9.29463    | 9.29048    | 9.29328    |
| $b$       | 3.48903 | 3.48252    | 3.46372    | 3.47842    | 3.49837    | 3.50038    |
| $c$       | 6.71728 | 6.71389    | 6.70429    | 6.71229    | 6.72606    | 6.72853    |
| Cell Volume ($\text{Å}^3$) | 202.114 | 202.737    | 201.376    | 201.528    | 202.937    | 203.601    |
| $R_{wp}$(%) | 20.298 | 19.065     | 19.214     | 18.064     | 19.76     | 19.94     |
| $X^2$     | 1.28    | 1.1       | 1.08      | 0.98      | 1.08      | 1.1        |
| $\varepsilon_r$ | 8.8    | 8.1       | 8.8       | 9.0       | 9.3       | 8.7        |
| $\varepsilon_{rc}$ | 9.9    | 9.3       | 9.9       | 9.7       | 10       | 9.5        |
| $V_m(\text{Å}^3)$ | 101.057 | 101.369   | 100.688    | 100.764    | 101.469   | 101.801    |
| $\alpha_0$ ($\text{Å}$) | 18.04  | 17.78     | 17.98      | 17.88      | 18.17     | 17.96      |

reliable refinement results. Moreover, the refined plot of the specimen using (Mg$_{0.92}$Zn$_{0.08}$)$_2$V$_2$O$_6$ at 610°C is illustrated in Figure 3, which shows that the identical results were obtained as those in Table 1. These results also confirmed the formation of a single monoclinic structure phase.

The surface micro-morphology of the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$ (x = 0–0.09) ceramics is presented in Figure 4. A porous microstructure was observed for the (Mg$_{0.92}$Zn$_{0.08}$)$_2$V$_2$O$_6$ ceramic specimen at 520°C. As the sintering temperature was increased, the number of pores decreased and a well-densified morphology was achieved at 610°C. In addition, rapid grain growth occurred at 640°C, indicating an over-sintering temperature for the specimen. Obviously, the grains exhibited a typical polygonal morphology for all specimens. Large grains and small grains co-existed, with both corresponding to a single MgV$_2$O$_6$ phase, as further confirmed by the EDS results (Table 2).

Moreover, specimens with $x = 0$ and 0.01 showed rough grain boundaries, which were improved as $x$ was increased, with smooth grain boundaries being observed for $x > 0.03$, suggesting Zn may aid the sintering process. In addition, the specimen with $x = 0.09$ was found to have an obviously larger grain size and a less uniform morphology compared to that of $x = 0.07$, which may have negative effects on the $Q \times f$ values of the specimen.

The relative densities of the monoclinic (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$ (x = 0–0.09) ceramics sintered at different temperatures are demonstrated in Figure 5. The low relative density of 87%–91% observed for specimens sintered at 520°C was most likely a result of the porous morphology, as shown in Figure 3. However, the density initially increased with increases in sintering temperature, and then decreased after reaching a maximum at 610°C. In all cases, the optimal sintering temperature was 610°C. A high relative density of 95.3% was obtained for the specimen with $x = 0.07$ sintered at 610°C.

Figure 6 illustrates the plots of $\varepsilon_r$ as a function of temperature for the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$(x = 0–0.09) ceramics. The variations in $\varepsilon_r$ were consistent with those of the relative density, indicating that density might be a primary factor affecting $\varepsilon_r$ in this experiment. Moreover, a maximum $\varepsilon_r$ value of −9.3 was achieved corresponding to the highest relative density of 95.3% for the $x = 0.07$ specimen sintered at 610°C. Shannon reported that $\varepsilon_r$ is proportional to the $\alpha_0$ and can be expressed by the Clausius–Mosotti equation [15]:

$$a_0 = \left[ V_m (\varepsilon_{rc} - 1) \right] / \left[ b (\varepsilon_{rc} + 2) \right]$$

where $V_m$ is the molecular volume, $\varepsilon_{rc}$ represents the corrected dielectric constant, and the constant value $b = 4m/3$. According to Eqn. (2), $\varepsilon_{rc}$ increases when $a_0$ increases. As shown in Table 1, the variation of $\varepsilon_{rc}$ is inversely proportional to that of $V_m$ for $x = 0–0.05$, which is because the amount of Zn substitution is small. However, the change in $\varepsilon_{rc}$ becomes consistent with that of $a_0$ at $x = 0.07$–0.09 due to the fact that Zn$^{2+}$ (1.7 Å$^3$) has a larger polarizability than Mg$^{2+}$ (0.651Å$^3$), which dominates the variation of $\varepsilon_r$ in (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$ ceramics.

Figure 7 demonstrates the $Q \times f$ values of the (Mg$_{1-x}$Zn$_x$)$_2$V$_2$O$_6$ (x = 0–0.09) ceramics sintered at various temperatures. Both intrinsic and extrinsic losses are included in the overall measured microwave dielectric losses. Typical intrinsic loss is mainly a result of the lattice vibration modes; extrinsic loss, however, can be related to density, second phases, impurities, surface morphology, and the lattice defects [16,17]. Accordingly, the $Q \times f$ increased with increases in sintering temperature, reaching a maximum at 610°C, which corresponds to the
optimal sintering temperature mentioned earlier, and decreased thereafter. Moreover, the variations of $Q \times f$ for specimens with $x = 0$–0.09 at 610°C was also consistent with those of the relative density, implying that the dielectric loss of specimens was mainly attributed to the extrinsic loss corresponding to the densification of ceramics. Compared to the $x = 0$ specimen, the $x = 0.07$ specimen exhibited a 50% increase in the $Q \times f$ and a maximum value of 15,300 GHz @15.5 GHz could be achieved for the $(\text{Mg}_{0.93}\text{Zn}_{0.07})\text{V}_2\text{O}_6$ specimen sintered at 610°C.

**Table 2.** Corresponding EDS results of Figure 4(d).

| Spot a | Spot b |
|--------|--------|
| Mg K   | Zn K   | V L  | O K   | Mg K   | Zn K   | V L  | O K   |
| Weight%| 10.14  | 2.13 | 44.02| 10.02  | 2.01   | 45.11| 42.86|
| Atomic%| 10.55  | 0.82 | 21.61| 68.33  | 10.43  | 0.78 | 22.15| 67.00|

Figure 4. SEM images of $(\text{Mg}_1\text{Zn}_x)\text{V}_2\text{O}_6$ sintered at (a) 520°C (b) 550°C (c) 580°C (d) 610°C (e) 640°C and of $(\text{Mg}_1\text{Zn}_x)\text{V}_2\text{O}_6$ with (f) $x = 0$ (g) $x = 0.01$ (h) $x = 0.03$ (i) $x = 0.05$ (j) $x = 0.07$ (k) $x = 0.09$ sintered at 610°C.
Figure 5. Relative densities of the (Mg₁ₓZnₓ)₂V₂O₈ (x = 0–0.09) ceramics at different sintering temperatures.

Figure 6. εᵣ values of the (Mg₁ₓZnₓ)₂V₂O₈ (x = 0–0.09) ceramics at different sintering temperatures.

Figure 7. Q × f values of the (Mg₁ₓZnₓ)₂V₂O₈ (x = 0–0.09) ceramics at different sintering temperatures.

Figure 8. τᵣ values of the (Mg₁₋ₓZnₓ)₂V₂O₈ (x = 0–0.09) ceramics at different sintering temperatures.

to the Zn²⁺ substitution for Mg²⁺. By tuning the x to 0.07, the specimen had a τᵣ of −3.64 ppm/°C at 610°C.

The microwave dielectric properties and sintering temperatures of some typical ceramics for ULTCC applications are listed in Table 3. All the dielectrics can be co-fired with aluminum. However, the first four compositions reveal a large τᵣ value that limits their practical applications. In the next two ceramics, the τᵣ was modified to a near-zero value; yet, it still suffers from a high εᵣ, constraining its high frequency applications. In addition, tellurium oxide is toxic and not preferred for use in components. In comparison, the proposed (Mg₀.₉₂Zn₀.₀₈)₂V₂O₈ specimen not only has a near-zero τᵣ, it also exhibits a moderate Q × f and a low εᵣ, making it a very promising dielectric for ULTCC applications, particularly for the high frequency 5G system.

For ULTCC applications, Figure 9 illustrates the EDS line scan and corresponding SEM photo of the interface between the Al electrode and the (Mg₀.₉₃Zn₀.₀₇)₂V₂O₈ specimen co-fired at 610°C. As seen, a sharp decrease in the Al profile at the interface implies that Al did not diffuse into the ceramic during co-firing. Moreover, a very low amount of Mg and V in the Al electrode also suggests that no reaction occurred at the interface. Since the specimen revealed a chemical compatibility with Al, it is

Table 3. Microwave dielectric properties and sintering temperatures of some typical ceramics for ULTCC applications.

| Composition                  | S.T. (°C) | f (GHz) | εᵣ  | Q × f (ppm/°C) | Ref. |
|------------------------------|-----------|---------|-----|----------------|------|
| Ag₂MoO₄                       | 450       | 8       | 17,000 | −133           | [1]  |
| Ag₉Mo₄O₁₆                   | 460       | 9.25    | 13.3 | 25,300 −142    | [2]  |
| Na₂Zn₂(MoO₄)₃               | 500       | 9       | 14   | 8,500 −50      | [2]  |
| Na₂Zn₂(MoO₄)₂                | 590       | 8.1     | 35,800 | −95            | [3]  |
| 0.25Na₂MoO₄                 | 580       | 6.2     | 24   | 13,000 3       | [4]  |
| −0.75Na₂Bl₂O₃MoO₄           | 575       | 25      | 19,300 | −3            | [5]  |
| BaTeO₃                     | 610       | 15.5    | 9.3  | 15,300 −3.4    | This work |
4. Conclusion

The (Mg1−xZnx)V2O6 (x = 0−0.09) ceramics were prepared via the conventional solid-state route. Specimens sintered at 520–640°C for 4 h exhibited a monoclinic structure with a space group of C2/m without evidence of any additional second phase, suggesting the formation of a solid solution. The microwave dielectric properties were correlated to the microstructures, the temperatures, and the relative densities of the ceramics. The (Mg0.93Zn0.07)V2O6 ceramic reveals an εr of 9.3, a Q × f of 15,300 GHz and a τf of −3.4 ppm/°C. The EDS line scan of the (Mg0.93Zn0.07)V2O6 sample co-fired with aluminum also shows an excellent chemical compatibility and is presented as an ideal candidate dielectric for ULTCC applications.

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Disclosure statement

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