Effect of a minute substitution on the structure and microwave dielectric properties of novel LiCoVO₄ ceramics for ULTCC applications

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ABSTRACT
The feasibility of novel LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) microwave dielectrics for ULTCC (ultra-low temperature co-fired ceramics) applications was investigated. Continuous solid solutions were formed as expected in the whole composition range and can be indexed in the cubic system with the Fd3m space group. The Raman spectrum of the specimen was also analyzed. All samples can be sintered into dense ceramics (relative density > 97%) at the temperature 650°C. The variation of structure parameters resulted from minutely substituting Co with Mg or Zn has significant effect on the microwave dielectric properties of the specimen. The relative density and dielectric polarizability have significant impact on the εr of the specimens. Q × f value is dominated by the density and packing fraction of the ceramics. The τf, however, was mainly controlled by the bond-valence of the samples under a minute substitution. Specimen with 0.01 mol% Zn-substitution at 650°C revealed the highest Q × f of 53,000 GHz along with an εr of 13.2 and a τf of ~57.5 ppm/°C. It also exhibited a good Al-cofiring chemical compatibility.

1. Introduction
To develop a highly integrated microwave devices for today’s communication system, LTCC (Low temperature co-fired ceramics) technology has been commonly used for ceramic process in the scientific and industrial fields for decades. Consequently, dielectrics with Ag electrodes can be fired at a temperature lower than 961°C (the melting point of silver) and a great cost down can be achieved [1–3]. Energy saving, however, is still a global issue and becomes more significant in these days. Considering Al is also a good electrode material and has a melting point of 660°C even lower than that of Ag, the dielectrics that can be co-fired with Al is so-called LTCC (Ultra-low temperature co-fired ceramics) were widely investigated and reported in the last decade for energy saving [4–7]. The use of LTCC can definitely further reduce the energy consumption particularly in the manufacture. Glass mixture addition is commonly used to lower the sintering temperature of the specimens; however, it also deteriorates its microwave dielectric properties [8–11]. Therefore, intrinsic LTCC materials are more desired for practical applications. The most popular LTCC materials can be grouped into two families which are molybdate- and tungstate-related oxides [12–18]. Some of them known as intrinsic LTCCs could find applications beyond 4G communication system and become sufficiently adapted to the current 5G technology [19,20]. The 5G technology with increasing frequencies requires not only low loss but also low dielectric constant materials to reduce the delay of the signal [21,22].

Numbers of vanadate-related oxides were proposed as LTCC dielectrics. For instance, Mg₃(VO₄)₂, Ba₃(VO₄)₂, MgZn₂(VO₄)₂, and BaMg₂(VO₄)₂ ceramics all revealed a good combination of microwave dielectric properties with a sintering temperature ~960°C. BaV₂O₆ and Ba₃V₂O₇ belonging to the BaO-V₂O₅ family, were reported to be good candidates for ULTCC applications [23,24]. The R₂V₂O₇ (R = Ba and Sr) and SrMoO-V₂O₅ (M = Mg, Zn), and SrM₀.₇V₀.₃O₂ (M = Mg, Zn) families have also been found to offer good microwave dielectric properties at ultra-low sintering temperatures [25,26]. By using a small Zn substitution, (Mg₁₋ₓZnₓ)V₂O₆ ceramics (x ~ 9.3, Qxf ~ 15,300 GHz @15.5 GHz and τf ~ 3.4 ppm/°C) even can be sintered at 610°C [4]. In addition, the thermal and mechanical properties of some typical vanadate compositions such as BaV₂O₆ and BiMg₂V₂O₆ were investigated [23,27]. The coefficient temperature of thermal expansion (αT) of BaV₂O₆ is approximately 10 ppm/°C and BiMg₂V₂O₆ ceramics are mechanically stable and indicates that they are ductile materials. It can be expected that the αT of vanadate-related materials may be positive, considered as a stable material and have the potential to be an alternate material for LTCC applications. LiMWO₄ (M = Mg, Zn, Co, Ni) were investigated and found applications as a cathode material, humidity sensor, or a green phosphor [28–30]. Moreover, the LiMgVO₄ (τf ~ 9.1, Qxf ~ 33,730 GHz and τf ~ ~ 160
ppm/°C at 675°C) and LiZnVO₄ (εᵣ ~ 7.6, Qₓf ~ 22,000 GHz and τᵣ ~ 110 ppm/°C at 750°C) ceramics were reported to be a LTCC material [31,32]. However, microwave dielectric properties of LiCoVO₄ have yet been studied. In this work, the dielectric properties of LiCoVO₄ at microwave frequency were characterized and the effect of a minute substitution on the surface morphology, XRD patterns, structures, and microwave dielectric properties of LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) ceramics were systematically analyzed and the resulting ceramic of which featured an intrinsic ULTCC dielectric with a sintering temperature <660°C. Crystalline parameters were estimated from the X-ray profile refined by the GSAS program. Additionally, the compatibility of co-firing with an Al electrode was also reported.

2. Experimental procedure

LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) ceramics were prepared by solid state route using high purity (>99.9%) raw materials of Li₂O, V₂O₅, CoO, MgO, and ZnO, weighted, and ball milled in distilled water for 24 h, dried and calcined at 550°C for 2 h. The powders were then ground with PVA binder, pressed into pellets 11 mm in diameter under a uniaxial pressure of 1000 kg/cm² and sintered at 620–680°C for 4 h at a heating rate of 5°C/min. According to Thomas et al., the PVA binder is expected to burnout complete at sintering temperature of 600°C in air [33]. The crystalized phase was identified by using the X-ray diffraction method with Cu-Kα radiation. Rietveld refinement was also performed based on the XRD data using GSAS software. Raman spectrum was recorded using a 532 nm light source (Jobin Yvon/ Labram HR). Hitachi SU-8000 UHR-SEM with energy dispersion spectroscopy (EDS, Philips) was used to study the microstructures. The densities were measured by the Archimedes method. The dielectric constant and Q × f values of the samples were measured employing the Hakki–Coleman and Courtney methods [34,35] using a vector network analyzer (Agilent8364A, USA). Identical setup was also employed in measuring the τᵣ and can be expressed as

\[
\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}
\]

where f₁ and f₂ represent the resonant frequencies at 25°C (T₁) and 80°C (T₂), respectively.

3. Results and discussion

Table 1 demonstrates the dielectric properties of LiCo₀.₉₉Zn₀.₀₁VO₄ ceramic under sintering duration 2 h and 4 h at 650°C. Accordingly, a low relative density (93%) and Q × f value (32,000 GHz) were obtained for specimen at a 2-h sintering. Therefore, the specimen under a sintering duration of 4 h was suggested in the experiment.

Figure 1 shows the X-ray diffraction (XRD) patterns of as-sintered LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) ceramics recorded at room temperature. Accordingly,
all specimens composed of a cubic structure belonging to a space group of Fd-3 m (227) without any second phase and their XRD patterns are in agreement with the standard pattern of LiCoVO₄ (ICDD-PDF # 04-015-6750), which indicates the formation of a solid solution. In contrast to LiCoVO₄, there is no significant reflection peak shift observed for partially substituted specimens because the ionic radii of Mg³⁺ (0.72 Å, CN = 6), Zn²⁺ (0.74 Å, CN = 6) and Co³⁺ (0.745 Å, CN = 6) are similar. Also, there is no significant phase change or peak shift observed for a specimen with x = 0.01 at different sintering temperatures, which demonstrates that the temperature does not affect the crystal structure of the samples in the entire experimental range. Rietveld refinement was carried out on the XRD patterns of LiCoVO₄ using GSAS and the corresponding refined plot is illustrated in Figure 2. The refined lattice parameters were a = b = c = 8.27175 Å, cell volume = 565.97 Å³, and α = β = γ = 90°. A small Rwp of 8.704% and R² of 1.50 were also obtained which suggests that the structural model is valid along with reliable refinement results. The nonlinear variation of cell volume might be a result from the tilting or distortion of the specimen before reaching the optimal solid state in particularly for a minute substitution.

Microstructures of the LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) ceramics at different sintering temperatures are demonstrated in Figure 3. All the specimens revealed a dense microstructure. The hygroscopic nature of vanadium was not observed in the vanadate oxides in the experiment. The average grain size not only enlarged at high temperature but also increased with the increase of substitution content suggested that both Mg and Zn might play a role of sintering aid and have a positive effect on the sintering process of the specimens. Moreover, abnormal grain growth can be observed for specimen with x = 0.09 at 650°C, which may lead to a negative effect on its microwave dielectric properties. In addition, an inhomogeneous microstructure and rapid grain growth appeared at 680°C indicating an over-sintering temperature for the specimens.

Figure 4 illustrates the relative density of LiCo₁₋ₓAₓVO₄ (A = Mg, Zn; x = 0–0.09) ceramics at different sintering temperatures. A low relative density <90% was observed for specimens sintered at 620°C, which was mainly attributed to a relatively small grains as shown in Figure 3. The relative density of the specimens increased with increasing sintering temperature, reached a maximum value (97%) for the Zn-substituted one at 650°C, and then decreased thereafter. The decreased densification at higher sintering temperatures could be a result from oversintering as demonstrated in Figure 3. In addition to the sintering temperature, the relative density is also a function of the substitution. As shown in the inset of Figure 4, the highest density was obtained at x = 0.01 (Zn-substituted one) and there is a notch appeared at x = 0.03–0.05 corresponding to the cell volume variation as shown in Table 2. It suggested that both of the sintering temperature and the substitution content could control the density of the ceramics.

Sintering temperature and substitution-dependent εᵣ values of the specimens are demonstrated in Figure 5. The εᵣ value of the specimen exhibited a trend similar to that of relative density, which suggests that the dielectric constant of the specimen was dominated by the density and the composition. The maximum εᵣ of 13.2 (@12.2 GHz) was achieved, corresponding to the highest relative density of 97%, for a 0.01 mol% Zn-substituted specimen sintered at 650°C. The corrected dielectric constant (εᵣₑ) normally higher than the measured ones and had similar inclination, as the following equation [36]:

\[ εᵣ = εᵣₑ Ê \frac{1 - 3P(εᵣₑ - 1)}{2εᵣₑ + 1} \]  \hspace{1cm} (2)

where P is the porosity fraction. According to Clausius–Mosotti equation, εᵣ is directly proportional to the dielectric polarizability \( α₀ \) [37]:

\[ α₀ = \frac{V_m(εᵣₑ - 1)}{D(εᵣₑ + 2)} \]  \hspace{1cm} (3)

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**Figure 2.** Rietveld refinement and crystal structure of (a) LiCo₀.₉₉Mg₀.₀₁VO₄ (b) LiCo₀.₉₉Zn₀.₀₁VO₄ ceramic at 650°C.
where $V_m$ is the molecular volume, and a constant value $b = 4\pi/3$. Accordingly, the variation of $\varepsilon_{rc}$ is consistent with that of $\alpha D/V_m$ at small substitution as indicated in the inset of Figure 5.

Figure 6 shows the variation of $Q \times f$ value of LiCo$_{1-x}$A$_x$VO$_4$ ($A = \text{Mg, Zn}; x = 0–0.09$) ceramics as a function of the sintering temperature. With the increase of sintering temperature, the $Q \times f$ increased to a maximum at 650°C, corresponding to the highest relative density, and decreased thereafter. Variations of $Q \times f$ are consistent with that of relative density suggesting that the densification has a major effect on the $Q \times f$ of the specimens. Moreover, the decrease of $Q \times f$ at high temperatures was also a result from the oversintering along with a rapid grain growth and inhomogeneous microstructure as exposed in Figure 3. A $Q \times f$ of
Figure 4. The relative density of (a) LiCo$_{1-x}$MgxVO$_4$ and (b) LiCo$_{1-x}$ZnxVO$_4$ ($x = 0–0.09$) ceramics at different sintering temperatures and the inset represents the relative density versus the content of substitution.

Table 2. The refined lattice parameters, molecular volume, goodness of fit, reliability factors, relative density, dielectric constant, corrected dielectric constant, molecular volume, and ionic polarization of the (a) LiCo$_{0.99}$Mg$_{0.01}$VO$_4$ (b) LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ ceramics and (c) LiCo$_{1-x}$MgxVO$_4$ ($x = 0–0.09$) (d) LiCo$_{1-x}$ZnxVO$_4$ ($x = 0–0.09$) ceramics sintered at 650°C.

| (a)   | $T_s$ (°C) | 620 | 650 | 680 |
|-------|------------|-----|-----|-----|
| $a$  (Å) | 8.27513     | 8.27082 | 8.27447 |
| $\alpha$ = $\beta$ = $\gamma$ (%) | 90 | 90 | 90 |
| Cell Volume (Å$^3$) | 566.66 | 565.78 | 566.53 |
| $R_{pp}$ (%) | 2.082 | 4.502 | 5.665 |
| $V_c$ (Å$^3$) | 70.833 | 70.723 | 70.816 |
| $a_0$ (Å) | 13.732 | 13.801 | 13.655 |
| $a_0/V_m$ | 0.1939 | 0.1951 | 0.1928 |
| (b)   | $T_s$ (°C) | 620 | 650 | 680 |
| $a$  (Å) | 8.28240 | 8.26957 | 8.27575 |
| $\alpha$ = $\beta$ = $\gamma$ (%) | 90 | 90 | 90 |
| Cell Volume (Å$^3$) | 568.16 | 565.52 | 566.79 |
| $R_{pp}$ (%) | 2.851 | 3.839 | 12.437 |
| $\chi'$ | 0.63 | 0.76 | 1.86 |
| $\rho_c$ (Å$^3$) | 71.02 | 70.69 | 70.85 |
| $\rho_{cc}$ (Å$^3$) | 13.46 | 13.86 | 13.74 |
| $a_0$ (Å) | 13.732 | 13.801 | 13.655 |
| $a_0/V_m$ | 0.1921 | 0.1961 | 0.1939 |
| (c)   | $\chi$ content | x = 0 | x = 0.005 | x = 0.01 x = 0.03 | x = 0.05 | x = 0.07 | x = 0.09 |
| $a$  (Å) | 8.27175 | 8.27142 | 8.27082 | 8.27236 | 8.27200 | 8.27149 | 8.27353 |
| $\alpha$ = $\beta$ = $\gamma$ (%) | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Cell Volume (Å$^3$) | 565.97 | 565.78 | 566.09 | 566.02 | 565.91 | 566.33 |
| $R_{pp}$ (%) | 8.704 | 4.502 | 4.408 | 2.704 | 3.659 | 8.414 |
| $\chi'$ | 1.50 | 0.61 | 0.84 | 0.94 | 0.55 | 0.69 | 1.65 |
| $\rho_c$ (Å$^3$) | 94.5 | 96.3 | 96.5 | 92.2 | 95.1 | 95.7 | 91.6 |
| $\rho_{cc}$ (Å$^3$) | 12.52 | 12.86 | 13.05 | 13.26 | 12.65 | 12.75 | 12.31 |
| $V_c$ (Å$^3$) | 13.59 | 13.57 | 13.52 | 13.61 | 13.93 | 14.00 | 13.59 |
| $a_0$ (Å) | 13.746 | 13.738 | 13.723 | 13.761 | 13.753 | 13.739 | 13.791 |
| $a_0/V_m$ | 0.1928 | 0.1938 | 0.1951 | 0.1927 | 0.1928 | 0.1932 | 0.1926 |
| (d)   | $\chi$ content | x = 0 | x = 0.005 | x = 0.01 x = 0.03 | x = 0.05 | x = 0.07 | x = 0.09 |
| $a$  (Å) | 8.27175 | 8.27206 | 8.26557 | 8.27486 | 8.27583 | 8.27406 | 8.27835 |
| $\alpha$ = $\beta$ = $\gamma$ (%) | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Cell Volume (Å$^3$) | 565.97 | 565.78 | 566.09 | 566.02 | 565.91 | 566.33 |
| $R_{pp}$ (%) | 8.704 | 3.250 | 3.839 | 11.406 | 12.795 | 9.275 | 6.153 |
| $\chi'$ | 1.50 | 0.63 | 0.76 | 1.77 | 1.89 | 1.69 | 1.06 |
| $\rho_c$ (Å$^3$) | 94.5 | 96.3 | 96.9 | 95.7 | 95.1 | 95.7 | 94.8 |
| $\rho_{cc}$ (Å$^3$) | 12.52 | 12.96 | 13.06 | 12.87 | 12.83 | 12.93 | 12.80 |
| $V_c$ (Å$^3$) | 13.59 | 13.69 | 14.33 | 13.83 | 13.77 | 13.80 | 13.72 |
| $a_0$ (Å) | 13.746 | 13.738 | 13.723 | 13.761 | 13.753 | 13.739 | 13.791 |
| $a_0/V_m$ | 0.1928 | 0.1931 | 0.1961 | 0.1935 | 0.1932 | 0.1938 | 0.1930 |
>50,000 GHz (@12.2 GHz) can be achieved for specimens with $x = 0.01$ sintered at 650°C, which indicated a tremendous enhancement in comparison with that of pure LiCoVO$_4$. In addition, $Q \times f$ is known proportional to the packing fraction of the ceramics and can be expressed as

$$\text{Packing fraction(%) } = \frac{\text{volume of packed ions}}{\text{volume of unit cell}} \times Z \quad (4)$$

where $Z$ is the number of formula units per unit cell. Accordingly, the packing fraction is inversely proportional to the cell volume of the sample. As shown in the inset, the $Q \times f$ is proportional to the packing fraction indicating a consistent variation between the packing fraction and $Q \times f$, and the dependency was confirmed since high packing fraction limits the lattice vibration that leads to a low dielectric loss.

Figure 5. The $\varepsilon_r$ values of (a) LiCo$_{1-x}$Mg$_x$VO$_4$ and (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) ceramics at different sintering temperatures and the inset represents the $\varepsilon_r$ (black line) and $a_0/V_m$ (red line) versus the content of substitution.

Figure 6. The $Q \times f$ values of (a) LiCo$_{1-x}$Mg$_x$VO$_4$ and (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) ceramics at different sintering temperatures and the inset represents the $Q \times f$ (black line) and packing fraction (red line) versus the content of substitution.

Figure 7 illustrates $\tau_f$ values of the specimens as a function of sintering temperature and the corresponding TE$_{015}$ modes of each composition are list in Table 3. The $\tau_f$ slightly decreased with the increase of sintering temperature and ranged from $–53$ to $–85$ ppm/°C in the experiment. Additionally, the $\tau_f$ is also a function of $x$ value. Since there is no second phase in the specimen, the alternate compositions in the experiment may have an effect on the $\tau_f$ value. The $\tau_f$ of LiMgVO$_4$ and LiZnVO$_4$ are $–160$ ppm/°C and $–110$ ppm/°C, respectively. It suggested that the $\tau_f$ value of LiCo$_{1-x}$A$_x$VO$_4$ should move toward negative as the $x$ increased. However, a fluctuated variation of the $\tau_f$ was observed for specimens at $x = 0–0.09$. LiCoVO$_4$ possesses a cubic structure in which Li$^+$ and Co$^{3+}$ ions evenly reside in octahedral sites, and V$^{5+}$ ions occupy the tetrahedral sites. The Li-site bond valence of LiCo$_{1-x}$A$_x$VO$_4$ ($A = \text{Mg, Zn}; x = 0–0.09$) ceramics can be calculated by Equations (5) and (6) [38]:
Figure 7. The $T_f$ values of (a) LiCo$_{1-x}$Mg$_x$VO$_4$ and (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) ceramics at different sintering temperatures.

Table 3. The TE01D mode of (a) LiCo$_{1-x}$Mg$_x$VO$_4$ and (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) for temperature coefficient of resonant frequency measurement.

| (a) T$_s$ (°C) | $x$ content | $f_1$ | $T_1$ | $f_2$ | $T_2$ | $T_f = \frac{f_1 - f_2}{T_1 - T_2}$ |
|----------------|-------------|-------|-------|-------|-------|----------------------------------|
| 620            | 0           | 12.62 | 29.2  | 12.59 | 77.5  | -52.01                           |
|                | 0.005       | 12.57 | 29.7  | 12.52 | 81.5  | -65.58                           |
|                | 0.01        | 12.26 | 29.5  | 12.22 | 80.2  | -72.40                           |
|                | 0.03        | 12.33 | 28.9  | 12.29 | 80.1  | -71.28                           |
|                | 0.05        | 12.49 | 28.7  | 12.45 | 80.9  | -66.09                           |
|                | 0.07        | 12.35 | 30.0  | 12.30 | 80.5  | -67.78                           |
|                | 0.09        | 12.51 | 28.6  | 12.47 | 80.4  | -69.10                           |
| 650            | 0           | 12.36 | 29.9  | 12.58 | 77.8  | -56.42                           |
|                | 0.005       | 12.13 | 29.5  | 12.08 | 80.7  | -70.02                           |
|                | 0.01        | 12.08 | 29.9  | 12.04 | 80.7  | -74.86                           |
|                | 0.03        | 12.25 | 28.5  | 12.20 | 80.7  | -73.99                           |
|                | 0.05        | 12.20 | 28.1  | 12.15 | 80.7  | -71.63                           |
|                | 0.07        | 12.19 | 27.7  | 12.14 | 80.8  | -73.07                           |
|                | 0.09        | 12.22 | 29.2  | 12.17 | 80.9  | -72.76                           |
| 680            | 0           | 12.77 | 27.5  | 12.72 | 80.1  | -69.33                           |
|                | 0.005       | 12.46 | 30.3  | 12.42 | 80.7  | -77.07                           |
|                | 0.01        | 12.21 | 28.4  | 12.16 | 80.9  | -85.18                           |
|                | 0.03        | 12.37 | 29.7  | 12.32 | 80.8  | -84.08                           |
|                | 0.05        | 12.39 | 30.4  | 12.35 | 80.8  | -79.36                           |
|                | 0.07        | 12.28 | 29.7  | 12.22 | 81.9  | -81.55                           |
|                | 0.09        | 12.89 | 28.6  | 12.83 | 82.1  | -82.97                           |

| (b) T$_s$ (°C) | $x$ content | $f_1$ | $T_1$ | $f_2$ | $T_2$ | $T_f = \frac{f_1 - f_2}{T_1 - T_2}$ |
|----------------|-------------|-------|-------|-------|-------|----------------------------------|
| 620            | 0           | 12.62 | 29.2  | 12.59 | 77.5  | -52.01                           |
|                | 0.005       | 12.57 | 29.7  | 12.52 | 81.5  | -65.58                           |
|                | 0.01        | 12.26 | 29.5  | 12.22 | 80.2  | -72.40                           |
|                | 0.03        | 12.33 | 28.9  | 12.29 | 80.1  | -71.28                           |
|                | 0.05        | 12.49 | 28.7  | 12.45 | 80.9  | -66.09                           |
|                | 0.07        | 12.35 | 30.0  | 12.30 | 80.5  | -67.78                           |
|                | 0.09        | 12.51 | 28.6  | 12.47 | 80.4  | -69.10                           |
| 650            | 0           | 12.36 | 29.9  | 12.58 | 77.8  | -56.42                           |
|                | 0.005       | 12.13 | 29.5  | 12.08 | 80.7  | -70.02                           |
|                | 0.01        | 12.08 | 29.9  | 12.04 | 80.7  | -74.86                           |
|                | 0.03        | 12.25 | 28.5  | 12.20 | 80.7  | -73.99                           |
|                | 0.05        | 12.20 | 28.1  | 12.15 | 80.7  | -71.63                           |
|                | 0.07        | 12.19 | 27.7  | 12.14 | 80.8  | -73.07                           |
|                | 0.09        | 12.22 | 29.2  | 12.17 | 80.9  | -72.76                           |
| 680            | 0           | 12.77 | 27.5  | 12.72 | 80.1  | -69.33                           |
|                | 0.005       | 12.46 | 30.3  | 12.42 | 80.7  | -77.07                           |
|                | 0.01        | 12.21 | 28.4  | 12.16 | 80.9  | -85.18                           |
|                | 0.03        | 12.37 | 29.7  | 12.32 | 80.8  | -84.08                           |
|                | 0.05        | 12.39 | 30.4  | 12.35 | 80.8  | -79.36                           |
|                | 0.07        | 12.28 | 29.7  | 12.22 | 81.9  | -81.55                           |
|                | 0.09        | 12.89 | 28.6  | 12.83 | 82.1  | -82.97                           |
Table 4. Bond valence of (a) LiCo$_{1-x}$Mg$_x$VO$_4$ ($x = 0–0.09$) (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) ceramics sintered at 650°C.

| x value | $d_{i-O}$ | $R_{i-O}$ | $V_{i-A}$ | $d_{i-O}$ | $R_{i-O}$ | $V_{i-A}$ |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| 0       | 2.10670   | 1.7       | 0.33314   | 1.72672   | 1.803     | 1.22895   |
| 0.005   | 2.10713   | 1.699965  | 0.33309   | 1.72664   | 1.803     | 1.22922   |
| 0.01    | 2.10672   | 1.699930  | 0.33269   | 1.72629   | 1.803     | 1.23038   |
| 0.03    | 2.10694   | 1.699790  | 0.3327    | 1.72630   | 1.803     | 1.23053   |
| 0.05    | 2.10680   | 1.699650  | 0.33274   | 1.72637   | 1.803     | 1.23012   |
| 0.07    | 2.10723   | 1.699510  | 0.33283   | 1.72648   | 1.803     | 1.22975   |
| 0.09    | 2.10707   | 1.699370  | 0.33287   | 1.72587   | 1.803     | 1.22942   |

Figure 8. The corresponding relationships between the bond valence and $\tau_f$ values of the (a) LiCo$_{1-x}$Mg$_x$VO$_4$ and (b) LiCo$_{1-x}$Zn$_x$VO$_4$ ($x = 0–0.09$) ceramics at 650°C.

\[
V_i = \sum_j v_{ij} \tag{5}
\]

\[
v_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b'}\right) \tag{6}
\]

where $R_{ij}$ is the bond-valence parameter, $d_{ij}$ is the length of a bond between atoms $i$ and $j$, and $b'$ is a universal constant equal to 0.37 Å. The bond valences of the ceramics sintered at 650°C are demonstrated in Table 4, while Figure 8 illustrates the corresponding relationships between the bond valence and the $\tau_f$ of the specimens. The $\tau_f$ of complex pervoskite was investigated to vary consistently with the bond valence of the A-site due to the tilting of the oxygen octahedral [39]. A similar phenomenon was also reported with the tetragonal scheelite structure [40]. Moreover, B-site bond valence could be a function of the unit-cell volume and is inversely proportional to the $\tau_f$ value. According to Figure 8, the $\tau_f$ value also increases with the increase of bond valence in A-site; whereas, it decreases instead as the bond valence in B-site increases. The results would further confirm that the $\tau_f$ is highly related to the bond valence of the specimens in particular under a minute substitution.

Table 5 lists the comparison of the sintering temperature and microwave dielectric properties of some typical vanadite-related dielectrics for ULTCC applications. All dielectrics exhibit a large $\tau_f$ value lead to the restriction of applications. In contrast, the LiCo$_{0.99}$ Zn$_{0.01}$VO$_4$ reveals a high $Q \times f$ value and a relatively small $\tau_f$ value.

Table 5. Comparison of the sintering temperature and the microwave dielectric properties of some typical ceramics for ULTCC applications.

| Ceramics     | S.T. (°C) | $\varepsilon_r$ | $Q \times f$ (GHz) | $\tau_f$ (ppm/°C) | Ref |
|--------------|-----------|-----------------|-------------------|-------------------|-----|
| SrV$_2$O$_6$ | 630       | 9.66            | 23,200            | -205              | [41]|
| LiMnO$_2$    | 640       | 13.3            | 12,460            | +101              | [42]|
| LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ | 650 | 12.2           | 53,000           | -57.5            | This work|
| SrZnV$_4$O$_7$ | 660  | 10.2           | 31,900           | -76               | [26]|
| BaZnV$_2$O$_7$ | 660  | 10.8           | 46,400           | -78.1             | [43]|
profile revealed a sharp decrease at the interface, implying that there is no inter-diffusion occurred. Also, only a very low amount of compositions was detected in the Al electrode, which indicated no reaction occurred at the interface. Moreover, Figure 9(b) exhibits the cross-section of LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ co-fired with aluminum. It can be confirmed by the tighten interface between specimen and Al as excellent adhesion of aluminum to the material. Additionally, Figure 10 shows the XRD patterns of LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ co-fired with Al.

Figure 9. The corresponding (a) SEM image, EDS line scan and (b) the cross-section of LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ co-fired with Al at 650°C.

Figure 10. The XRD patterns of LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ co-fired with Al.
fired with Al. As observed, well-defined peaks of LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ and Al are clear further indicating that there is no chemical reaction occurred. The result revealed an excellent chemical compatibility between the LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ specimen and the Al electrode.

4. Conclusion

The effect of a minute substitution on the structure and microwave dielectric properties of LiCo$_{1-x}$A$_x$VO$_4$ (A = Mg, Zn) ceramics was investigated. A continuous solid solution with the cubic structure and a space group of was observed for specimens at $x = 0$–0.09. $Q \times f$ value is correlated to the packing fraction, the densification, and the surface morphology of the specimens. The highest $Q \times f$ of 53,000 GHz can be obtained for a specimen with 0.01 mol% Zn substitution at 650°C. The relative density and dielectric polarizability have significant impact on the $\varepsilon_r$ of the specimens, while $\tau_r$ was mainly controlled by the bond-valence of the samples in particular under a minute substitution. The $\tau_r$ is mainly controlled by the composition and the $\tau_r$ value. The LiCo$_{0.99}$Zn$_{0.01}$VO$_4$ specimen ($\varepsilon_r \sim 13.2$, $Q \times f \sim 53,000$ GHz, $\tau_r \sim 57.5$ ppm/°C) along with good Al-cofiring chemical compatibility can find ULTCC applications at high-frequency regions.

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Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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