

Article

Fabrication of Temperature-Stable Low-Temperature Co-Fired Ceramics via Reaction Between $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4

Du-Won Kim ¹, Hye-Won Jeong ² and Kyoung-Ho Lee ^{2,*}

¹ Department of Advanced Materials Engineering, Soonchunhyang University, 22, Soonchunhyang-ro, Asan-si 31538, Chungnam, Republic of Korea; kdo3546@hanyang.ac.kr

² Department of Electronic Materials, Devices and Equipment Engineering, Soonchunhyang University, 22, Soonchunhyang-ro, Asan-si 31538, Chungnam, Republic of Korea; hwjeong@sch.ac.kr

* Correspondence: khlee@sch.ac.kr

Abstract

New glass-free low-temperature co-fired microwave dielectric composites with compositions $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2-x\text{BaWO}_4-(2x/3)\text{Li}_3\text{VO}_4$ ($x = 0.3-0.7$) were fabricated by reactive liquid-phase sintering of $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ mixtures at 850 °C. During sintering, Li_2WO_4 is fully consumed by reacting with $\text{Ba}_3(\text{VO}_4)_2$ to form BaWO_4 and Li_3VO_4 while providing a transient liquid phase that promotes densification. As a result, the sintered ceramics achieve high relative densities of $\approx 94-98\%$ at 850 °C. The relative fractions of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 can be systematically tailored by adjusting the initial Li_2WO_4 content, enabling effective control of the temperature coefficient of the resonant frequency (τ_f) and the quality factor ($Q \times f$). With increasing Li_2WO_4 content, the τ_f values shift from +23.97 to −45.48 ppm/°C, owing to the increasing contributions of the negative τ_f phases BaWO_4 and Li_3VO_4 , while the $Q \times f$ values increase moderately from 44,300 to 47,300 GHz. The optimal microwave dielectric properties are obtained for $x = 0.5$, meaning $\epsilon_r = 9.19$, $Q \times f = 45,900$ GHz, and $\tau_f = -1.15$ ppm/°C when sintering at 850 °C for 1 h. Chemical compatibility tests confirmed that the composites exhibit no detectable reaction with Ag electrodes, indicating that the $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 system is a promising glass-free dielectric for LTCC applications requiring low firing temperature, near-zero thermal drift, and reliable electrode compatibility.

Keywords: low-temperature co-fired ceramics (LTCC); reactive liquid-phase sintering; microwave dielectric properties; temperature coefficient of resonant frequency; $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 composites; Li_2WO_4 additive



Academic Editor: Dinesh Agrawal

Received: 23 January 2026

Revised: 15 February 2026

Accepted: 25 February 2026

Published: 27 February 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

The development of the latest wireless communication systems, such as 5G communication systems or portable mobile phones, has created an increased demand for new dielectric substrate materials to fulfill the requirements of increased signal transmission speed, enhanced miniaturization, and improved integration of passive elements [1–4]. The key material requirements for such applications include a low dielectric permittivity (ϵ_r) to minimize signal propagation delay, a high quality factor ($Q \times f$) to ensure frequency selectivity and reduce power consumption, a low temperature coefficient of resonant frequency (τ_f) to guarantee temperature-stable operation, and a sufficiently low sintering temperature to enable multilayer low temperature co-fired ceramics (LTCC) processing [5–8].

However, many commercial dielectric materials used in high-frequency devices require relatively high sintering temperatures and are therefore not well matched to LTCC

processes. To lower the sintering temperature of dielectric ceramics, glasses are generally added to promote densification via liquid phase sintering. Unfortunately, the presence of a glassy phase can increase dielectric loss, as many glass-forming oxides exhibit higher dielectric loss than the crystalline phases used in microwave dielectrics [9–11]. The use of sintering aids is thus a cost-effective and simple way to reduce the firing temperature, but it tends to compromise the intrinsic microwave dielectric properties. For this reason, the exploration of glass-free, low-melting compounds suitable for LTCC applications has attracted considerable attention. Several low-temperature-melting ceramic systems, particularly those based on bismuth- or tellurium-containing compounds, have been investigated as glass-free LTCC materials [12–15]. Although these materials can be fired at relatively low temperatures, they often show limited chemical compatibility with Ag electrodes, which limits their use in multilayer devices.

Li_2WO_4 has attracted considerable attention as a low-melting additive because it exhibits reasonably good intrinsic microwave dielectric properties ($\epsilon_r \approx 5.5$, $Q \times f \approx 62,000$ GHz, $\tau_f \approx -145$ ppm/°C) and has a relatively low melting temperature (~ 741 °C) [16]. These characteristics enable Li_2WO_4 to effectively reduce the sintering temperature of various microwave dielectric ceramics via liquid-assisted sintering [17–21]. Furthermore, owing to its large negative τ_f , Li_2WO_4 has also been employed in temperature-compensated systems, for example, in the Li_2TiO_3 – Li_2WO_4 system [18]. However, it has also been reported that Li_2WO_4 reacts with Ag electrodes, raising potential limitations in its direct use as a sintering aid in LTCC systems containing internal Ag conductors [18].

In our laboratory, we found that Li_2WO_4 reacts with Ba-containing compounds such as $\text{Ba}_3(\text{VO}_4)_2$, BaV_2O_6 , or $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ to produce BaWO_4 and Li-containing vanadates or niobates such as Li_3VO_4 , LiVO_3 , and LiNbO_3 . In particular, when Li_2WO_4 reacts with $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 and Li_3VO_4 phases are formed and Li_2WO_4 eventually disappears, while a certain amount of $\text{Ba}_3(\text{VO}_4)_2$ can remain as a residual phase depending on the initial Li_2WO_4 content. Unlike conventional glass additives that primarily act as inert fluxes, Li_2WO_4 functions as a reactive liquid-phase sintering additive that forms a low-temperature incipient liquid and chemically interacts with $\text{Ba}_3(\text{VO}_4)_2$ during sintering. Through this reaction pathway, crystalline BaWO_4 and Li_3VO_4 phases are generated in situ instead of forming an amorphous glass. This reactive liquid-phase sintering mechanism enables efficient densification at 850 °C while maintaining a fully glass-free microstructure, which is highly advantageous for LTCC processing. From the dielectric perspective, the in situ formation of BaWO_4 and Li_3VO_4 is particularly important because both phases possess negative τ_f values and lower intrinsic permittivities relative to $\text{Ba}_3(\text{VO}_4)_2$. Consequently, the overall dielectric response can be systematically tuned by controlling the initial Li_2WO_4 content, which directly determines the final phase fractions through the stoichiometric reaction pathway.

$\text{Ba}_3(\text{VO}_4)_2$ sintered at 1600 °C exhibits $\epsilon_r \approx 11$, $Q \times f \approx 40,000$ GHz, and $\tau_f \approx +60$ ppm/°C [6]. BaWO_4 sintered at 1100 °C shows $\epsilon_r \approx 8$, $Q \times f \approx 57,500$ GHz, and $\tau_f \approx -78$ ppm/°C [7]. The Li_3VO_4 phase, which was characterized in our laboratory, exhibits $\epsilon_r \approx 8$, $Q \times f \approx 22,000$ GHz, and $\tau_f \approx -38$ ppm/°C when sintered at 900 °C. Although each individual phase shows a relatively large $|\tau_f|$ and requires a relatively high sintering temperature, an appropriate combination of the positive τ_f ($\text{Ba}_3(\text{VO}_4)_2$) and the negative τ_f (BaWO_4 and Li_3VO_4) phases suggests that a composite with near-zero τ_f can be achieved.

For LTCC applications, most microwave dielectric composites reported so far have been designed by physically mixing crystalline phases with opposite τ_f values (a positive τ_f component and a negative τ_f component), together with a small amount of a low-melting glass or oxide, such as V_2O_5 , $\text{CuO-V}_2\text{O}_5$, or LiF , to reduce the sintering temperature [22–24].

In such systems, the glassy or liquid additive acts essentially as an inert sintering aid, while the overall τ_f is tuned by adjusting the volume ratio between the positive and negative τ_f phases. Although this approach is effective in lowering the firing temperature, the incorporation of low-melting additives can adversely affect the microwave dielectric properties because the liquid phase introduced during sintering may increase dielectric loss or disrupt the intrinsic performance of the crystalline phases.

In contrast, the present work adopts a different strategy. Instead of using an inert glassy sintering aid, we introduce Li_2WO_4 as a low-melting, reactive liquid-phase sintering additive into a $\text{Ba}_3(\text{VO}_4)_2$ matrix with positive τ_f . During low-temperature sintering, Li_2WO_4 reacts in situ with $\text{Ba}_3(\text{VO}_4)_2$ to form BaWO_4 and Li_3VO_4 , both of which possess negative τ_f values, while simultaneously providing a transient liquid phase that promotes densification. Consequently, the overall τ_f of the resulting $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 composite can be tuned by controlling the initial Li_2WO_4 content, without introducing any glassy phase. To the best of our knowledge, this reactive liquid-phase sintering route—in which a low-temperature sintering additive is intentionally used to generate in situ negative τ_f phases and achieve τ_f compensation in a glass-free LTCC-compatible composite—represents a novel and distinct strategy for LTCC-compatible microwave dielectric design and has not been explicitly reported. This work therefore focuses specifically on the Li_2WO_4 – $\text{Ba}_3(\text{VO}_4)_2$ reaction, which represents a complete reactive pathway leading to BaWO_4 and Li_3VO_4 and enables τ_f tuning via a fully glass-free approach. Through this approach, a glass-free LTCC-compatible composite strategy is established in which a stoichiometrically constrained reactive liquid-phase pathway is intentionally employed to achieve systematic τ_f compensation. Accordingly, in this study, we demonstrate this concept by preparing $(1-x)\text{Ba}_3(\text{VO}_4)_2$ – $x\text{Li}_2\text{WO}_4$ mixtures ($x = 0.3$ – 0.7), clarifying the reaction pathway between $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 , and systematically investigating the densification behavior, microstructure, phase assemblage, and microwave dielectric properties of the resulting $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 ceramics.

2. Materials and Methods

The starting materials used were high-purity (99.9%) powders of BaCO_3 , V_2O_5 , Li_2CO_3 , and WO_3 (Sigma Aldrich, St. Louis, MO, USA). $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 powders were separately synthesized via a conventional mixed-oxide route by calcining mixtures of BaCO_3 – V_2O_5 and Li_2CO_3 – WO_3 of stoichiometric compositions at 800 and 550 °C, respectively, for 5 h with a heating rate of 10 °C/min. These calcination temperatures were selected with reference to previously reported synthesis conditions [6,20] and were slightly adjusted to ensure complete phase formation for the precursors used in this study. Phase purity of both calcined powders was confirmed by XRD. Prior to calcination, oxide/carbonate mixtures (25 g total) were wet-milled in 100 mL of ethanol for 12 h at 20 rpm using a Teflon jar containing zirconia balls of two sizes (10 mm, 400 g; and 6 mm, 200 g), corresponding to a ball-to-powder ratio of 24:1, to achieve homogeneous mixing. After calcination, the resulting $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 powders were lightly milled and passed through a 150-mesh sieve.

The $(1-x)\text{Ba}_3(\text{VO}_4)_2$ – $x\text{Li}_2\text{WO}_4$ mixtures ($x = 0.3$ – 0.7) were prepared by mixing the synthesized $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 powders with desired molar ratios. The composition range ($x = 0.3$ – 0.7) was selected to ensure complete reaction between $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 , effective low-temperature densification via reaction-assisted liquid-phase sintering, and stable three-phase formation without excessive dominance of either the residual $\text{Ba}_3(\text{VO}_4)_2$ phase or the reaction-derived BaWO_4 – Li_3VO_4 phase assemblage. Compositions with lower Li_2WO_4 contents resulted in insufficient densification at 850 °C, whereas excessively high Li_2WO_4 contents led to phase assemblages dominated by BaWO_4 and Li_3VO_4 , which are

less favorable for temperature-stable LTCC applications. The mixtures were then ball-milled under the same conditions as described above. For granulation, the milled powder was mixed with 1 wt.% polyvinyl alcohol (PVA) as a binder in a 3-roll mill (EXAKT 50I, EXAKT, Norderstedt, Germany); the resulting granules were then dried at 90 °C and sieved through a 60-mesh sieve.

The granulated powders were uniaxially pressed into cylindrical pellets with a height of 5 mm and a diameter of 10 mm under a pressure of 150 MPa for the measurement of density, microstructure, and microwave dielectric properties. Rectangular bars with dimensions of 5 mm (width) × 3 mm (thickness) × 10 mm (length) were also prepared for shrinkage-curve measurements. Linear shrinkage ($\Delta L/L_0$) as a function of temperature was monitored using a dilatometer (DIL 402PC, Netzsch-Gerätebau GmbH, Selb, Germany) at a heating rate of 10 °C/min. The onset temperature of net shrinkage, T_{onset} , was defined as the intersection point of the linear extrapolations of the thermal expansion region and the subsequent shrinkage region in the shrinkage curve. The maximum shrinkage rate temperature, T_{peak} , was taken as the temperature at which the shrinkage rate curve $d(\Delta L/L_0)/dT$ reached its most negative, corresponding to the peak shrinkage rate (R_{peak}).

For sintering, the green pellets were first heated to 600 °C at a rate of 2 °C/min and held for 4 h to burn out the organic binder. Subsequently, the temperature was raised to 850 °C at a heating rate of 10 °C/min, and the pellets were sintered at 850 °C for 1 h in air, followed by furnace cooling at 10 °C/min. The dwell time and sintering temperature were selected based on the dilatometric shrinkage behavior. To evaluate chemical compatibility with Ag, mixed powders containing 20 wt.% Ag were cofired at 850 °C for 1 h under the same conditions.

The crystalline phases formed in the sintered samples were identified by X-ray diffraction (XRD) using an Empyrean diffractometer (PANalytical, Almelo, The Netherlands), with Cu K_α radiation over a 2θ range of 10–70°. For phase identification, diffraction patterns were collected with a step size of 0.02° (2θ) and a counting time of 1 s per step. For Rietveld refinement, high-statistics scans were recorded with a reduced step size of 0.01° (2θ) and a counting time of 4 s per step to ensure reliable quantitative analysis. A representative sample ($x = 0.6$) was selected for Rietveld refinement, which was performed using the FullProf Suite (May 2021 release, Institut Laue–Langevin, Grenoble, France). The bulk densities (ρ_{bulk}) of the sintered specimens were measured by Archimedes' method, and the relative densities were calculated from the bulk densities and the theoretical densities (ρ_{th}). The theoretical density (ρ_{th}) of the composites was calculated using Equation (1) [18]:

$$\rho_{\text{th}} = \frac{\omega_1 + \omega_2 + \omega_3}{\omega_1/\rho_1 + \omega_2/\rho_2 + \omega_3/\rho_3} \quad (1)$$

where ρ_1 , ρ_2 , and ρ_3 are the theoretical densities of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 (5.18, 6.38, and 2.64 g/cm³, respectively), and ω_1 , ω_2 , and ω_3 are the corresponding mass fractions of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 in the composite. The mass fractions were calculated based on the molar amounts predicted by the stoichiometric reaction pathway described in Equation (3), using the molar masses and theoretical densities of the individual phases.

The microstructures of the polished and thermally etched (800 °C for 10 min) surfaces were observed using a scanning electron microscope (SEM, Coxem SNE-3000M, Daejeon, Republic of Korea). Energy-dispersive X-ray spectroscopy (EDS) was employed to qualitatively analyze the local chemical compositions of grains with different contrast. Grain sizes were quantitatively evaluated from thermally etched SEM micrographs using ImageJ image-analysis software (version 1.54g, NIH, Bethesda, MD, USA). For grain size measurement, SEM micrographs were acquired from multiple randomly selected

areas for each composition to ensure statistical representativeness. Grain size was defined as the maximum grain length measured along a fixed in-plane reference direction (x-direction) from two-dimensional SEM images. This fixed-direction intercept length was used consistently for all samples, and the grains did not exhibit pronounced in-plane anisotropy, making this metric appropriate for compositional comparison. For each composition, more than 200 grains were analyzed to obtain statistically reliable grain size distributions.

Microwave dielectric properties were measured in the frequency range of approximately 7–11 GHz using a vector network analyzer (HP 8720ES, Agilent Technologies, Santa Clara, CA, USA). The ϵ_r was determined according to the Hakki–Coleman resonator method using the TE₀₁₁ resonant mode at ~11 GHz, while the unloaded $Q \times f$ was measured by the cavity method using the TE_{01 δ} resonant mode at ~7 GHz [25,26]. The temperature coefficient of resonant frequency (τ_f) was calculated using Equation (2) by measuring the resonant frequencies f_1 and f_2 at $T_1 = 25$ °C and $T_2 = 85$ °C, respectively [27]:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (2)$$

This temperature interval (25–85 °C) follows a standard range commonly adopted for τ_f evaluation in microwave dielectric measurements.

The detailed experimental procedure is schematically summarized in Figure S1 of the Supplementary Materials.

3. Results and Discussion

3.1. Phase Formation and Reaction Pathway in the Ba₃(VO₄)₂–Li₂WO₄ System

X-ray diffraction (XRD) patterns of the (1–x)Ba₃(VO₄)₂–xLi₂WO₄ ceramics (x = 0.3–0.7) sintered at 850 °C for 1 h are presented in Figure 1. The rationale for selecting the sintering temperature (850 °C) and dwell time (1 h), based on the dilatometric shrinkage behavior, is described in detail in Section 3.2. All compositions exhibit three crystalline phases—Ba₃(VO₄)₂ (rhombohedral, R $\bar{3}$ m), BaWO₄ (tetragonal, I₄/a), and Li₃VO₄ (orthorhombic, Pmn2₁)—and no residual Li₂WO₄ (rhombohedral, R $\bar{3}$) is detectable within the XRD detection limit. With increasing Li₂WO₄ content, the intensities of BaWO₄ (+) and Li₃VO₄ (↓) peaks increase systematically, whereas those of Ba₃(VO₄)₂ (○) decrease, indicating progressive consumption of the Ba₃(VO₄)₂ phase.

In addition, SEM–EDS analysis reveals V–O-rich grains without detectable Ba or W, which is consistent with the formation of Li₃VO₄ inferred from XRD. These complementary structural and microchemical observations consistently indicate that sintering proceeds through a well-defined reaction pathway leading to a Ba₃(VO₄)₂–BaWO₄–Li₃VO₄ three-phase assemblage. Although the precise reaction pathway cannot be conclusively determined from the present data, the shrinkage behavior suggests that Li₂WO₄ undergoes partial and localized melting as the temperature approaches its melting point. The resulting transient liquid enhances cation mobility at the Ba₃(VO₄)₂/Li₂WO₄ interfaces. Such liquid-assisted reactions may proceed either through partial dissolution of Ba₃(VO₄)₂ followed by precipitation of BaWO₄ and Li₃VO₄, or through liquid infiltration into Ba₃(VO₄)₂ grains, which facilitates cation exchange and structural rearrangement. Increasing the Li₂WO₄ content likely increases the extent of such localized liquid formation, consistent with the earlier shrinkage onset (T_{onset}) and higher maximum shrinkage rates (R_{peak}) observed in the shrinkage analysis.

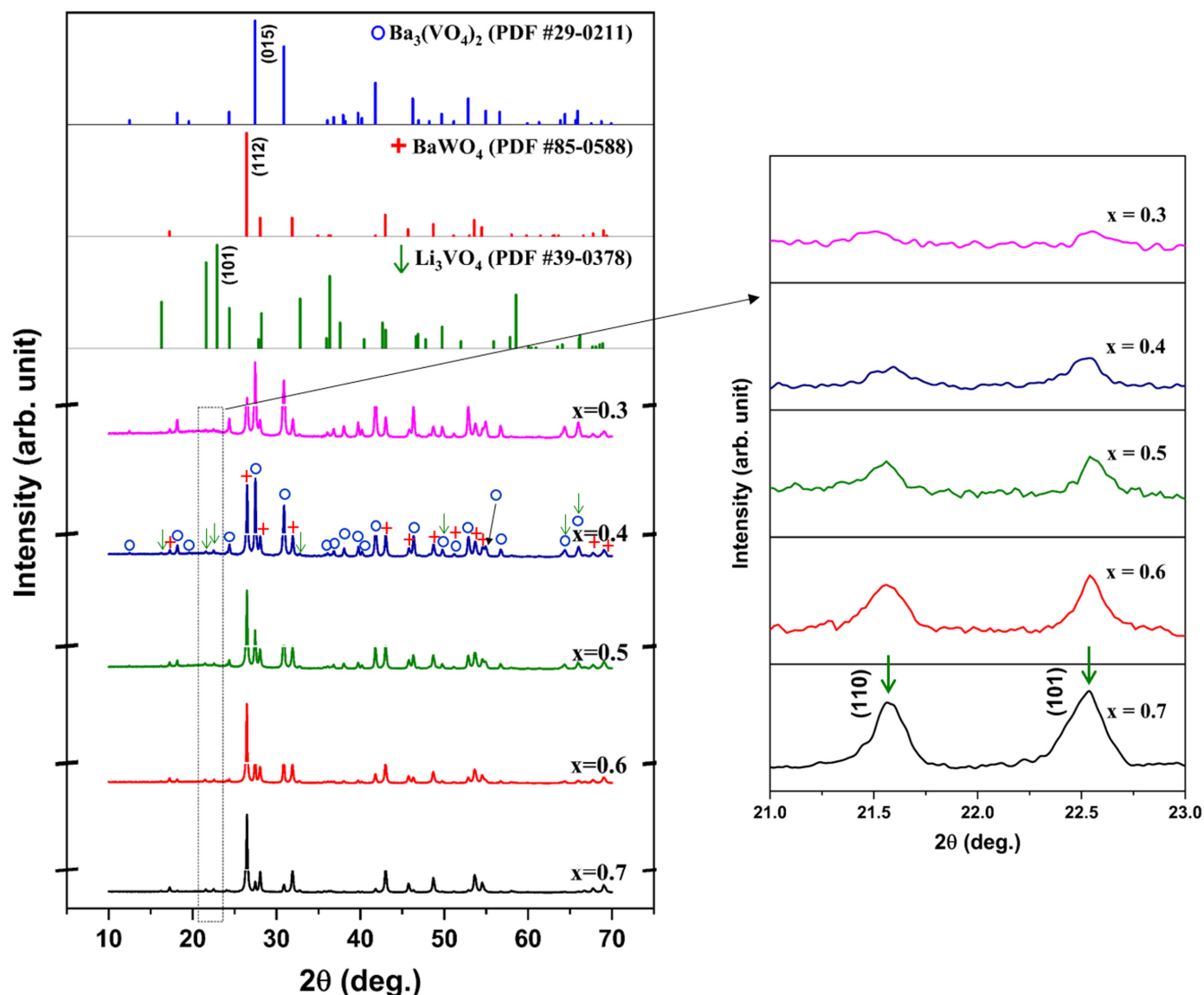
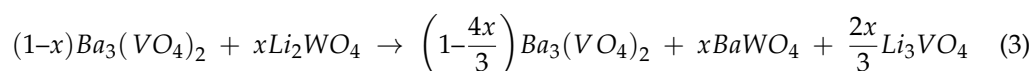


Figure 1. X-ray diffraction (XRD) patterns of ceramics obtained by sintering $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ mixtures ($x = 0.3\text{--}0.7$) at 850°C for 1 h. Reference patterns of $\text{Ba}_3(\text{VO}_4)_2$ (○, PDF #29-0211), BaWO_4 (+, PDF #85-0588), and Li_3VO_4 (↓, PDF #39-0378) are included for phase identification. For the representative composition ($x = 0.4$), all diffraction peaks are fully indexed and labeled with the corresponding symbols. The enlarged patterns in the 2θ range of $21\text{--}23^\circ$ highlight the characteristic Li_3VO_4 reflections.

Based on these considerations and XRD evidence, Li_2WO_4 is found to be fully consumed during sintering, forming BaWO_4 and Li_3VO_4 as reaction products. Accordingly, the overall mass-balanced reaction for the $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ mixtures can be expressed as:



Because this reaction pathway is uniquely constrained by stoichiometry, the final phase fractions are determined solely by the initial Li_2WO_4 content. To experimentally validate Equation (3), Rietveld quantitative phase analysis was performed for a representative composition ($x = 0.6$), and a typical refined pattern is shown in Figure 2. The composition $x = 0.6$ was selected because the reaction produces $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 in well-

balanced proportions, avoiding cases in which one phase becomes excessively dominant or too minor for reliable refinement. Such a balanced phase assemblage provides the most stable conditions for quantitative analysis and therefore offers the most appropriate basis for validating the stoichiometric reaction in Equation (3). The refined weight fractions of the three phases show excellent agreement with the theoretical values predicted by Equation (3), with deviations below 2% in mean absolute percentage error (MAPE). The refinement quality indicators ($R_{wp} = 9.67\%$, Bragg R -factors of approximately 7–8%, and RF-factors of approximately 6–7%) further support the stability of the refinement and the reliability of the phase-fraction estimates. Collectively, these results provide strong experimental evidence supporting the validity of the proposed reaction pathway. Accordingly, in the subsequent analyses, quantities such as the theoretical density and the phase volume fractions were calculated using the phase amounts derived directly from the stoichiometric reaction pathway described in Equation (3).

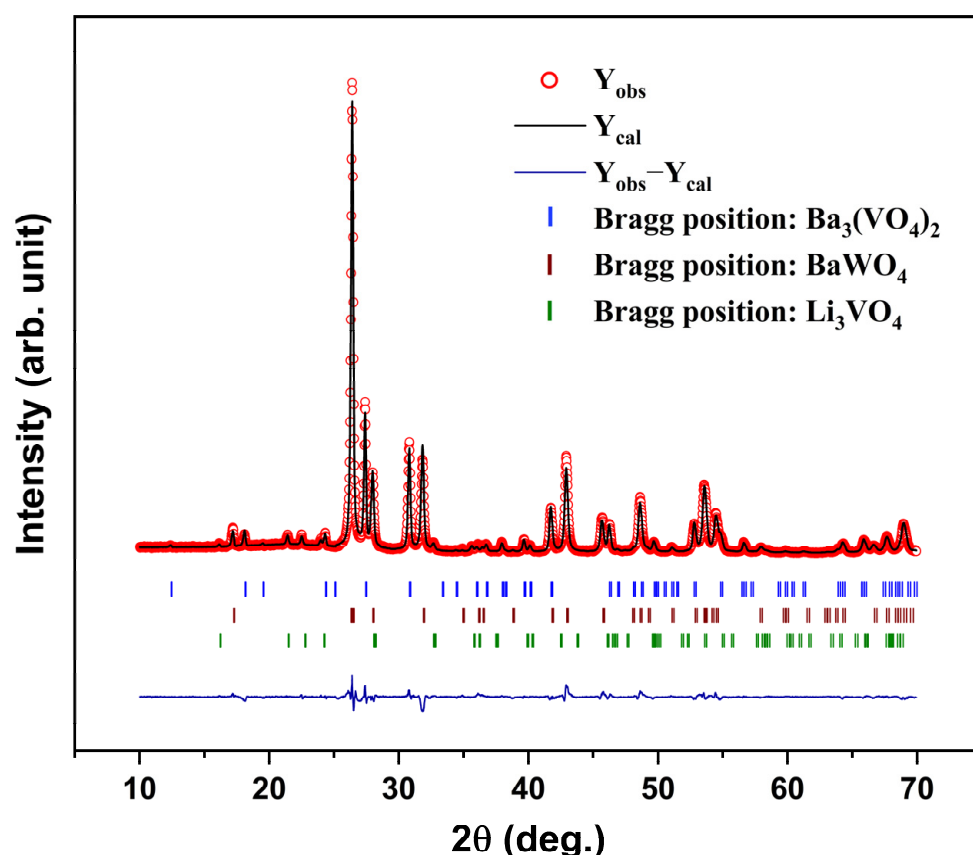


Figure 2. Rietveld-refined X-ray diffraction pattern of the ceramic corresponding to the reaction product of the $0.4\text{Ba}_3(\text{VO}_4)_2\text{--}0.6\text{Li}_2\text{WO}_4$ mixture ($x = 0.6$) sintered at 850°C for 1 h, yielding a final phase assemblage of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 (nominal ratio 0.2:0.6:0.4).

3.2. Sintering Behavior and Microstructural Evolution of the $\text{Ba}_3(\text{VO}_4)_2\text{--}\text{BaWO}_4\text{--}\text{Li}_3\text{VO}_4$ Composites

To clarify how Li_2WO_4 influences the densification of the $(1-x)\text{Ba}_3(\text{VO}_4)_2\text{--}x\text{Li}_2\text{WO}_4$ ceramics, dilatometric shrinkage measurements were carried out as a function of Li_2WO_4 content. Figure 3 shows the shrinkage ($\Delta L/L_0$) and shrinkage rate [$d(\Delta L/L_0)/dT$] curves for the $(1-x)\text{Ba}_3(\text{VO}_4)_2\text{--}x\text{Li}_2\text{WO}_4$ compacts ($x = 0.3\text{--}0.7$), together with those of the pure $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , Li_3VO_4 , and Li_2WO_4 ceramics for comparison.

All $(1-x)\text{Ba}_3(\text{VO}_4)_2\text{--}x\text{Li}_2\text{WO}_4$ compositions exhibit a similar shrinkage onset temperature, T_{onset} , of approximately 690°C . However, the magnitude and rate of shrinkage change systematically with x . As the Li_2WO_4 content increases from $x = 0.3$ to 0.7 , the maximum

shrinkage rate (R_{peak}) increases from ~ 0.083 to $\sim 0.207\%/^{\circ}\text{C}$, while the temperature of the maximum shrinkage rate (T_{peak}) shifts from $\sim 773^{\circ}\text{C}$ down to $\sim 740^{\circ}\text{C}$. This quantitative trend indicates that higher Li_2WO_4 contents promote earlier and more rapid densification through reaction-assisted transient liquid-phase formation. In contrast, compositions with lower Li_2WO_4 contents retain a larger fraction of $\text{Ba}_3(\text{VO}_4)_2$, which exhibits relatively poor sinterability and therefore requires higher temperatures for effective densification. These results demonstrate that both the sintering behavior and the resulting phase assemblage can be optimized by controlling the initial Li_2WO_4 content.

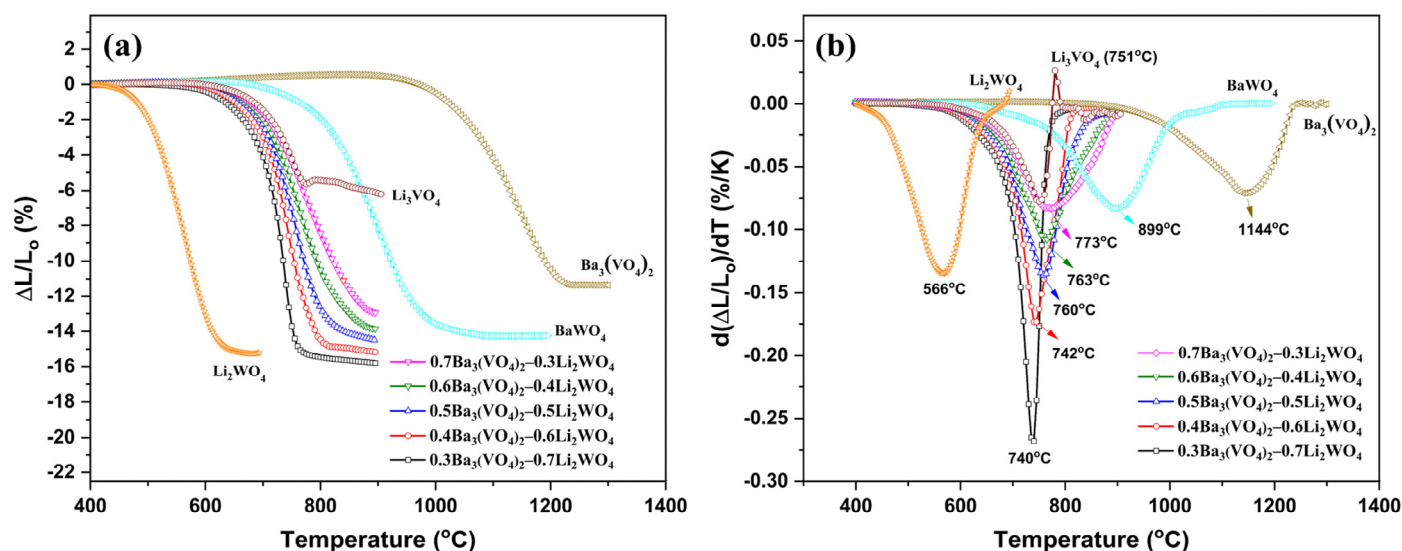


Figure 3. (a) Linear shrinkage ($\Delta L/L_0$) curves of $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ compacts ($x = 0.3-0.7$) measured at $10^{\circ}\text{C}/\text{min}$; (b) shrinkage rate $[d(\Delta L/L_0)/dT]$ curves of the same compacts. The shrinkage behaviors of pure $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , Li_3VO_4 , and Li_2WO_4 are also included for comparison.

These variations in T_{onset} , R_{peak} , and T_{peak} cannot be reproduced solely by a linear combination of the shrinkage behaviors of the individual end-member phases $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 . This behavior indicates that Li_2WO_4 is not a passive component but actively participates in the densification process of the $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ ceramics before it is completely consumed according to Equation (3).

To further examine the role of Li_2WO_4 , two different specimens were prepared with the same final overall composition, namely $0.3\text{Ba}_3(\text{VO}_4)_2-0.7\text{Li}_2\text{WO}_4$ and $0.067\text{Ba}_3(\text{VO}_4)_2-0.7\text{BaWO}_4-0.47\text{Li}_3\text{VO}_4$, according to the reaction in Equation (3), and their shrinkage behaviors are compared in Figure 4. Although both compositions are expected to yield the same $\text{Ba}_3(\text{VO}_4)_2-\text{BaWO}_4-\text{Li}_3\text{VO}_4$ phase assemblage after complete reaction, the two compacts exhibit markedly different densification behaviors. The $0.067\text{Ba}_3(\text{VO}_4)_2-0.7\text{BaWO}_4-0.47\text{Li}_3\text{VO}_4$ compact, in which Li_2WO_4 is absent from the beginning, shows a higher shrinkage onset temperature ($T_{\text{onset}} \approx 786^{\circ}\text{C}$), a higher temperature of the maximum shrinkage rate ($T_{\text{peak}} \approx 831^{\circ}\text{C}$), and a smaller maximum shrinkage rate ($R_{\text{peak}} \approx 0.129\%/^{\circ}\text{C}$) than the $0.3\text{Ba}_3(\text{VO}_4)_2-0.7\text{Li}_2\text{WO}_4$ compact ($T_{\text{onset}} \approx 698^{\circ}\text{C}$, $T_{\text{peak}} \approx 740^{\circ}\text{C}$, $R_{\text{peak}} \approx 0.207\%/^{\circ}\text{C}$). In other words, when the mixture is pre-reacted so that $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 are present before shrinkage starts, densification becomes slower and requires a higher temperature, suggesting that efficient densification is difficult to achieve without Li_2WO_4 during the early sintering stage.

The melting temperature of Li_2WO_4 ($\sim 741^{\circ}\text{C}$) is higher than the shrinkage onset temperature of the $0.3\text{Ba}_3(\text{VO}_4)_2-0.7\text{Li}_2\text{WO}_4$ compact, so the enhanced densification cannot be attributed to simple bulk melting of Li_2WO_4 . Instead, these results suggest that a transient liquid—likely eutectic or reactive in nature—forms at the interfaces between

Li_2WO_4 and $\text{Ba}_3(\text{VO}_4)_2$ at relatively low temperatures, promotes particle rearrangement and rapid densification, and then disappears as Li_2WO_4 is fully consumed by the reaction in Equation (3). Thus, Li_2WO_4 acts as a temporary but very effective liquid-phase sintering aid that plays its role before vanishing from the final microstructure. Taken together, the earlier-than-expected shrinkage onset, complete consumption of Li_2WO_4 , and concurrent formation of BaWO_4 and Li_3VO_4 provide consistent indirect evidence for reaction-assisted liquid-phase sintering in the present system.

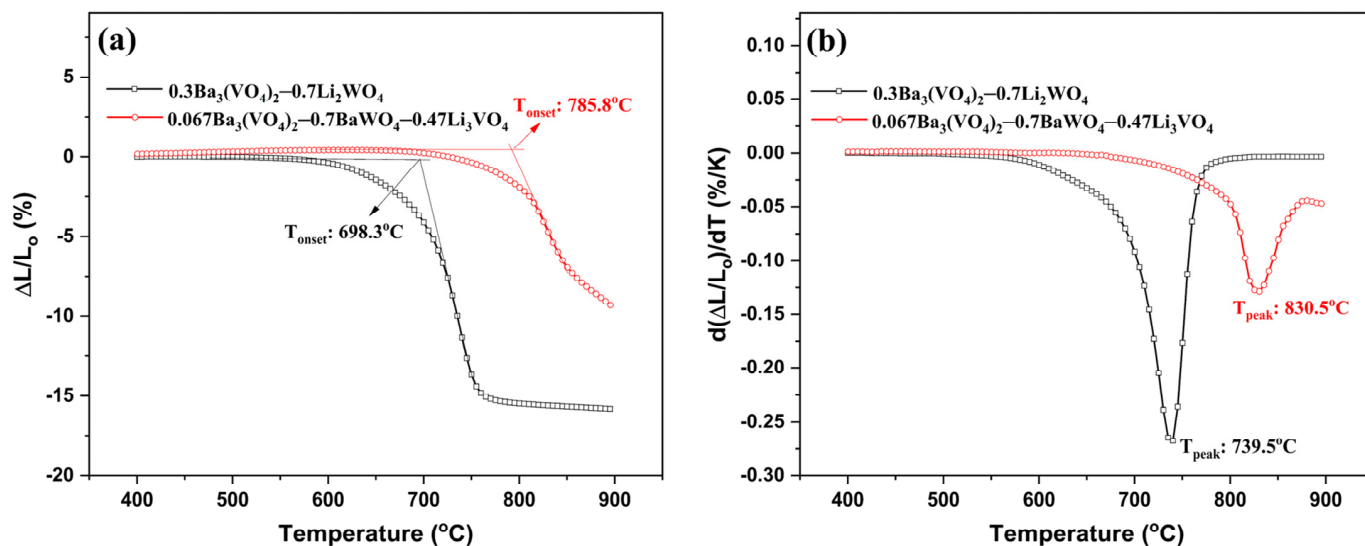


Figure 4. Comparison of (a) linear shrinkage ($\Delta L/L_0$) curves; (b) shrinkage rate [$d(\Delta L/L_0)/dT$] curves of two compacts with the same nominal composition measured at $10^\circ\text{C}/\text{min}$: $0.3\text{Ba}_3(\text{VO}_4)_2-0.7\text{Li}_2\text{WO}_4$ (reactive mixture) and $0.067\text{Ba}_3(\text{VO}_4)_2-0.7\text{BaWO}_4-0.47\text{Li}_3\text{VO}_4$ (pre-reacted mixture).

When developing new dielectric materials for LTCC applications, reactions with conductive electrodes must be carefully considered. To minimize interdiffusion between the dielectric and the Ag electrode, the sintering temperature should generally not exceed 850°C . As shown in Figure 3, the linear shrinkage of the composites, particularly for compositions with low initial Li_2WO_4 contents ($x = 0.3-0.4$), is approximately 11.6–13% at 850°C . To assess whether this level of shrinkage is sufficient to achieve practical densification under LTCC-compatible conditions, the final density can be roughly estimated from the green density assuming isotropic shrinkage using the following relation [28]:

$$\rho_{\text{cal}} = \frac{\rho_{\text{press}}}{\left(1 - \frac{\Delta L}{L_0}\right)^3} \quad (4)$$

where ρ_{cal} and ρ_{press} are the calculated and pressed (green) densities, respectively, and $\Delta L/L_0$ is the shrinkage value at 850°C . The green density (ρ_{press}) was determined from the measured mass of the pellet and its geometrically calculated volume. Using a green density of approximately 58.2% of the theoretical density, Equation (4) indicates that the estimated density remains below full densification, suggesting that additional holding time at 850°C is necessary to achieve sufficient densification.

The effect of Li_2WO_4 content and dwelling time on the densification behavior is further illustrated in Figure 5. The relative density values shown in Figure 5 were determined from the ratio of the bulk density (ρ_{bulk}), measured by the Archimedes' method, to the theoretical density (ρ_{th}) calculated using Equation (1). As shown in Figure 5a, the relative density of the $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2-x\text{BaWO}_4-(2x/3)\text{Li}_3\text{VO}_4$ ceramics obtained from the $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ mixtures at 850°C varies with both the Li_2WO_4 content and the sintering time.

Compositions with higher initial Li_2WO_4 contents ($x \geq 0.5$) exhibit rapid densification during the first 20–40 min, which is consistent with the formation of a transient liquid phase, which promotes particle rearrangement and mass transport. In contrast, the $x = 0.3$ and 0.4 samples show comparatively slower densification because they contain a larger fraction of $\text{Ba}_3(\text{VO}_4)_2$, which shrinks at higher temperatures and with a lower shrinkage rate than BaWO_4 and Li_3VO_4 (see Figure 3), consistent with its relatively poor sinterability [6]. Even so, all compositions eventually reach high relative densities. As summarized in Figure 5b, the relative density increases monotonically with x , and all samples achieve ≈ 94 –98% of the theoretical density after sintering at 850 °C for 1 h. These results demonstrate the important role of Li_2WO_4 prior to its complete reaction with $\text{Ba}_3(\text{VO}_4)_2$ in enhancing the densification of the $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 composite system.

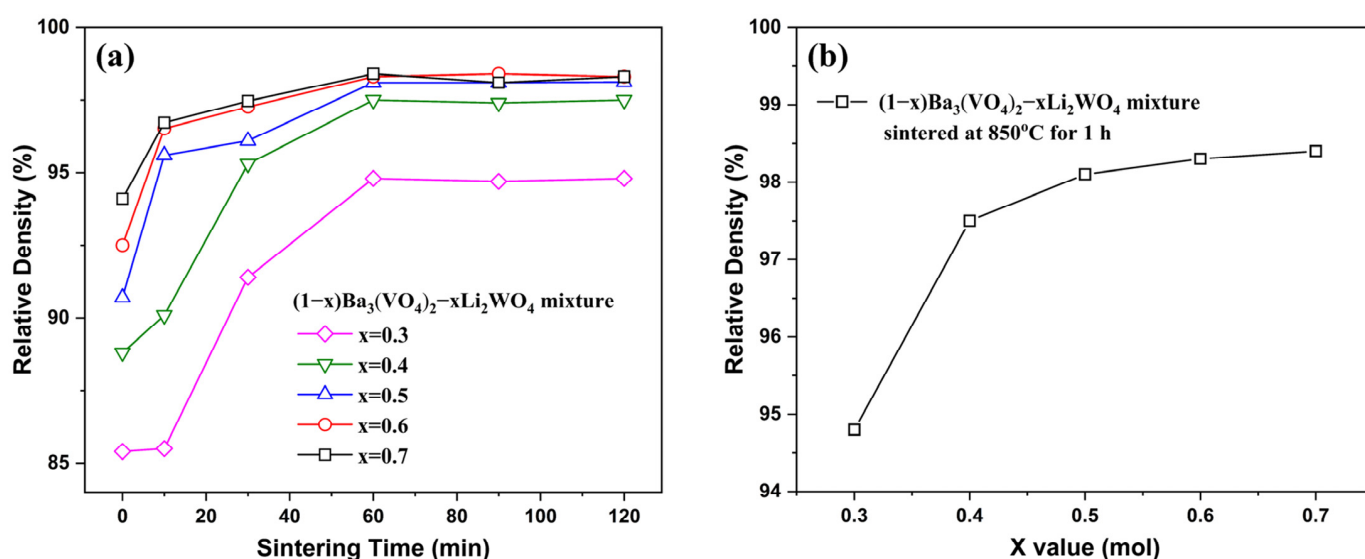


Figure 5. (a) Relative densities of the $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2$ – $x\text{BaWO}_4$ – $(2x/3)\text{Li}_3\text{VO}_4$ ceramics obtained by sintering the $(1-x)\text{Ba}_3(\text{VO}_4)_2$ – $x\text{Li}_2\text{WO}_4$ mixtures at 850 °C as a function of sintering time; (b) relative density as a function of x for samples sintered at 850 °C for 1 h.

The microstructural evolution of the $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 composites was investigated using SEM observation, quantitative grain size analysis, and EDS characterization, as summarized in Figures 6–8.

Representative SEM micrographs of the polished and thermally etched samples are shown in Figure 6. Three distinct grain types can be observed: small bright grains corresponding to the $\text{Ba}_3(\text{VO}_4)_2$ phase, larger bright grains corresponding to the BaWO_4 phase, and darker grains corresponding to the Li_3VO_4 phase. These phase assignments are consistent with the XRD results and with the EDS observations (Figure 8), in which V–O-rich grains without detectable Ba or W are observed, consistent with the Li_3VO_4 phase identified by XRD. As the initial Li_2WO_4 content increases, the microstructure evolves from one dominated by fine $\text{Ba}_3(\text{VO}_4)_2$ grains to one containing an increasing fraction of larger BaWO_4 and Li_3VO_4 grains. This trend reflects the progressive consumption of $\text{Ba}_3(\text{VO}_4)_2$ and the concurrent formation of BaWO_4 and Li_3VO_4 as predicted by the reaction pathway in Equation (3). In addition, pronounced grain growth is observed for the BaWO_4 and Li_3VO_4 phases at higher x values, whereas the $\text{Ba}_3(\text{VO}_4)_2$ grains remain relatively small, which is consistent with the much higher optimum sintering temperature and relatively poorer sinterability of $\text{Ba}_3(\text{VO}_4)_2$ [6].

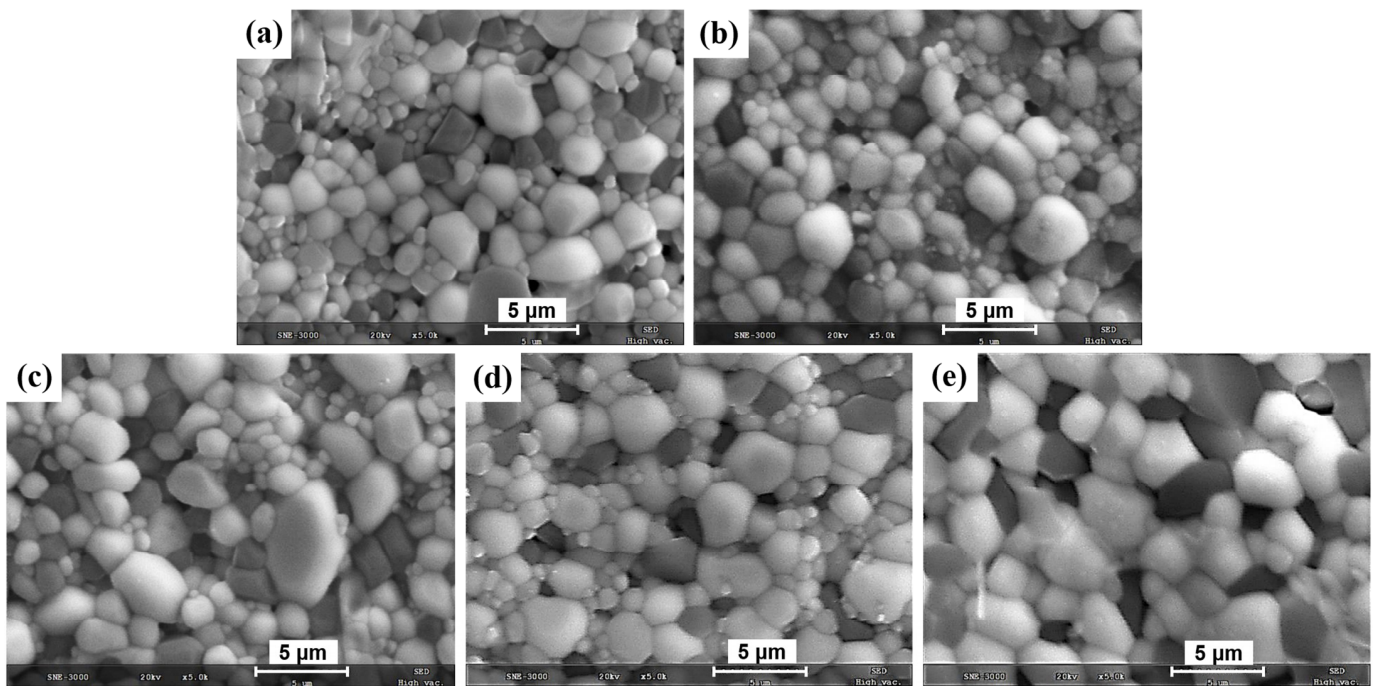


Figure 6. SEM micrographs of the $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ -derived $\text{Ba}_3(\text{VO}_4)_2\text{-BaWO}_4\text{-Li}_3\text{VO}_4$ ceramics sintered at 850°C for 1 h: (a) $x = 0.3$; (b) $x = 0.4$; (c) $x = 0.5$; (d) $x = 0.6$; (e) $x = 0.7$.

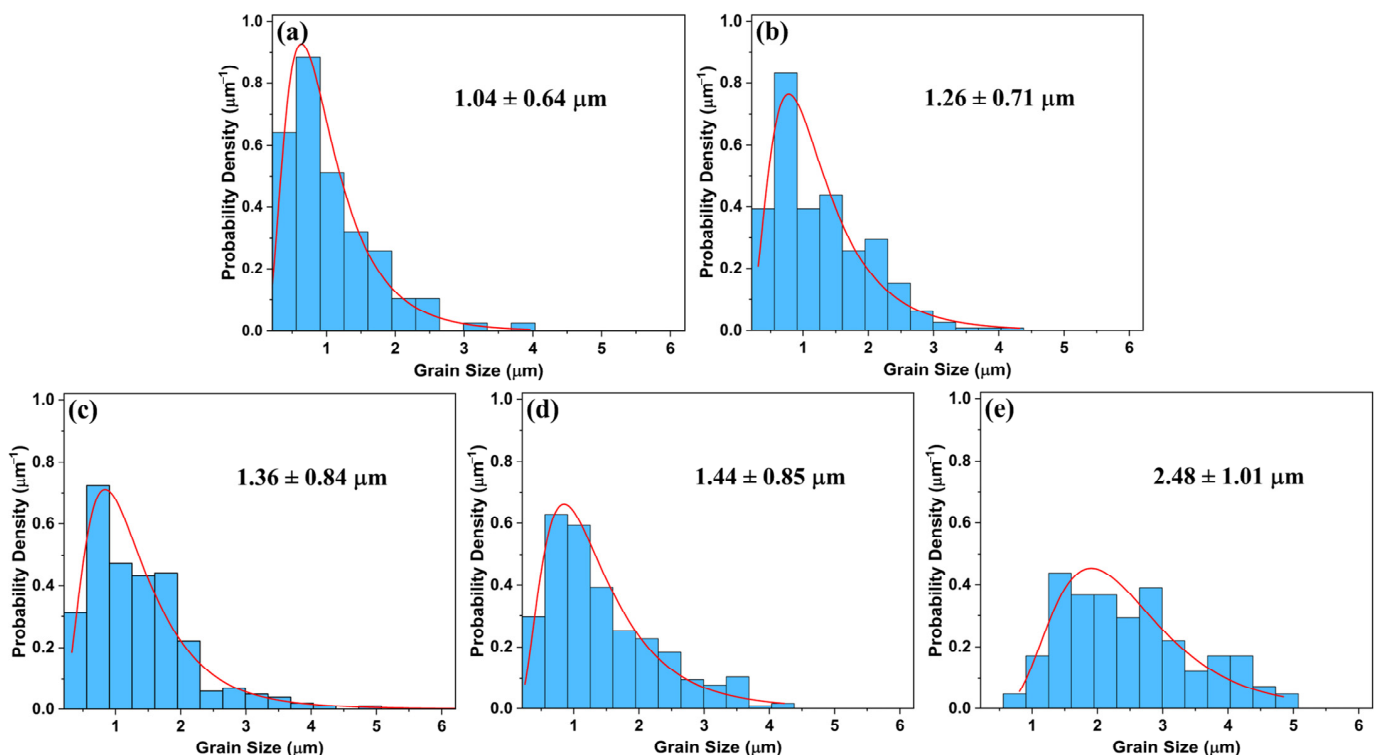


Figure 7. Grain size distributions of the $\text{Ba}_3(\text{VO}_4)_2\text{-BaWO}_4\text{-Li}_3\text{VO}_4$ ceramics derived from the $(1-x)\text{Ba}_3(\text{VO}_4)_2-x\text{Li}_2\text{WO}_4$ mixtures ($x = 0.3\text{--}0.7$), obtained from thermally etched SEM micrographs: (a) $x = 0.3$; (b) $x = 0.4$; (c) $x = 0.5$; (d) $x = 0.6$; (e) $x = 0.7$. The histograms are normalized such that the total area under each distribution equals unity. The probability density (μm^{-1}) represents the number fraction of grains per unit grain-size interval. The solid lines represent log-normal fits to the experimental data.

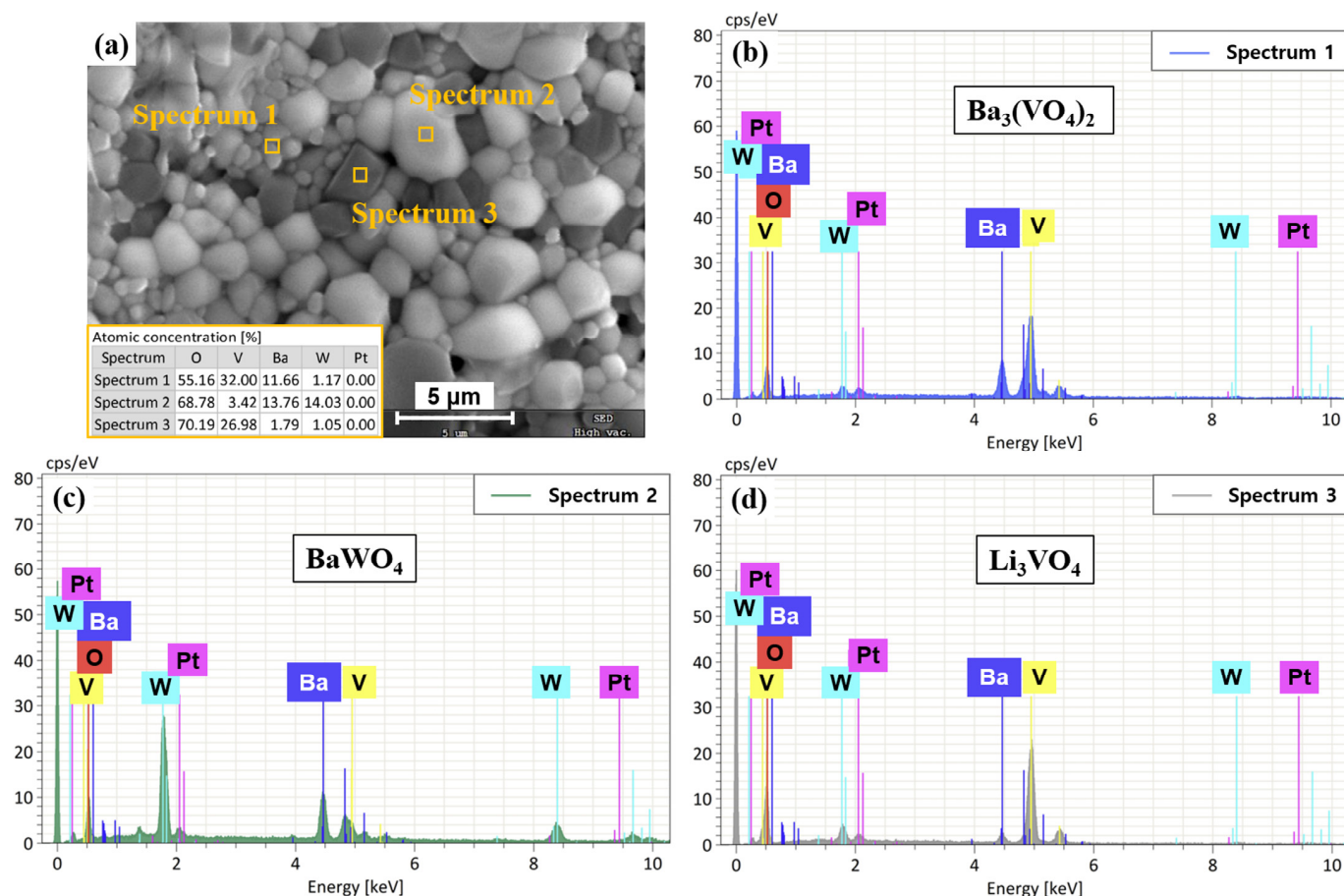


Figure 8. (a) SEM micrograph with locations selected for EDS analysis; (b) EDS spectrum from a $\text{Ba}_3(\text{VO}_4)_2$ grain; (c) EDS spectrum from a BaWO_4 grain; and (d) EDS spectrum from a V-O-rich grain corresponding to Li_3VO_4 .

Quantitative grain size analysis was carried out based on the thermally etched SEM micrographs, and the resulting grain size distributions are presented in Figure 7. The average grain size increases markedly with increasing x , from approximately $1.04 \mu\text{m}$ at $x = 0.3$ to $2.48 \mu\text{m}$ at $x = 0.7$, indicating systematic grain growth as the Li_2WO_4 content increases. This quantitative trend provides a strong indication for enhanced mass transport and particle rearrangement at higher Li_2WO_4 contents, which is consistent with reaction-assisted transient liquid-phase sintering inferred from the dilatometric shrinkage behavior.

Figure 8 presents representative EDS spectra acquired from grains with different contrast in the SEM micrographs. Grains assigned to the $\text{Ba}_3(\text{VO}_4)_2$ phase exhibit dominant Ba and V signals, whereas BaWO_4 grains are characterized by strong Ba and W peaks. In contrast, V-O-rich grains without significant Ba or W are observed, consistent with the formation of the Li_3VO_4 phase identified by XRD.

BaWO_4 , $\text{Ba}_3(\text{VO}_4)_2$, and Li_3VO_4 possess distinct crystal structures, which prevent the formation of solid solutions among them. BaWO_4 crystallizes in the scheelite-type tetragonal structure ($\text{I4}_1/\text{a}$), in which W^{6+} is tetrahedrally coordinated, and the $[\text{WO}_4]$ units are linked through eight-fold coordinated Ba^{2+} ions [29]. $\text{Ba}_3(\text{VO}_4)_2$ adopts a rhombohedral structure ($\text{R}\bar{3}\text{m}$), where V^{5+} occupies tetrahedral $[\text{VO}_4]$ sites connected through six- and ten-fold coordinated Ba^{2+} ions [30]. Li_3VO_4 crystallizes in the orthorhombic $\text{Pmn}2_1$ structure, which can be regarded as an ordered wurtzite derivative, with both V^{5+} and Li^+ in tetrahedral coordination. The $[\text{VO}_4]$ tetrahedra remain close to the ideal geometry (107.6 – 111.2°), whereas the $[\text{LiO}_4]$ tetrahedra deviate more significantly (105.5 – 121.9°) [31].

Because these three phases differ substantially in both cation coordination environments and in the connectivity of their tetrahedral units, the formation of $\text{BaWO}_4\text{--Ba}_3(\text{VO}_4)_2\text{--Li}_3\text{VO}_4$ solid solutions is not favored due to their distinct crystal chemistries. As a result, the three phases coexist in the sintered ceramics without forming additional reaction products, in full agreement with the XRD patterns shown in Figure 1.

3.3. Microwave Dielectric Properties of the $\text{Ba}_3(\text{VO}_4)_2\text{--BaWO}_4\text{--Li}_3\text{VO}_4$ Composites

The microwave dielectric properties of the $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2\text{--}x\text{BaWO}_4\text{--}(2x/3)\text{Li}_3\text{VO}_4$ ceramics with maximal densities are shown in Figure 9. The dielectric properties of the end-member phases obtained in this study— $\epsilon_r = 10.82$, $Q \times f = 43,200$ GHz, and $\tau_f = +63.34$ ppm/°C for $\text{Ba}_3(\text{VO}_4)_2$ and $\epsilon_r = 8.25$, $Q \times f = 58,900$ GHz, and $\tau_f = -76.82$ ppm/°C for BaWO_4 —are in good agreement with previously reported values [6,7]. The Li_3VO_4 synthesized in this study exhibited $\epsilon_r = 7.62$, $\tau_f = -37.59$ ppm/°C, and $Q \times f = 22,300$ GHz under the present synthesis conditions. Because the dielectric properties of Li_3VO_4 are known to be highly sensitive to synthesis conditions and microstructural features, the values reported in the literature vary widely [32,33]. In this study, the dielectric behavior of the composite ceramics was analyzed using the dielectric properties of the constituent phases synthesized and characterized in this work. The composition-dependent trends in ϵ_r , $Q \times f$, and τ_f are presented in Figure 9 and are discussed in detail below.

As x increased from 0.3 to 0.7, the ϵ_r values decreased from 9.95 to 8.23, whereas the τ_f values shifted from +23.97 to −45.48 ppm/°C. In contrast, the $Q \times f$ values increased from 44,300 to 47,400 GHz over the same composition range, as shown in Figure 9.

As shown in Figure 9a, this monotonic decrease in ϵ_r with increasing x is primarily attributed to the increasing volume fractions of BaWO_4 ($\epsilon_r = 8.25$) and Li_3VO_4 ($\epsilon_r = 7.62$), both of which possess significantly lower intrinsic permittivities than $\text{Ba}_3(\text{VO}_4)_2$ ($\epsilon_r = 10.82$). It should also be noted that, for compositions with $x = 0.3\text{--}0.4$, the measured ϵ_r values are noticeably lower than the corresponding porosity-corrected values, which is consistent with the relatively higher porosity observed for these compositions, as shown in Figure 5b.

The corrected dielectric permittivity ϵ_r^{cor} , eliminating the influence of porosity, was calculated using the empirical relation [34,35]:

$$\epsilon_r^{\text{cor}} = \epsilon_r^{\text{mea}} / \left[1 - \left\{ \frac{3P(\epsilon_r^{\text{mea}} - 1)}{2\epsilon_r^{\text{mea}} + 1} \right\} \right] \quad (5)$$

where P is the porosity and ϵ_r^{mea} is the measured permittivity. Here, the porosity P was determined from the bulk density measurements presented in Section 3.2 (Figure 5b), where $P = 1 - \rho_{\text{bulk}}/\rho_{\text{th}}$. In the following discussion, ϵ_r refers to the porosity corrected value ϵ_r^{cor} .

To provide a quantitative description of the compositional dependence of ϵ_r based on the phase assemblage, an empirical multiphase mixing model was employed [36]. The effective permittivity ϵ_r was simulated using the generalized mixing law:

$$\epsilon_r^\alpha = V_1\epsilon_{r1}^\alpha + V_2\epsilon_{r2}^\alpha + V_3\epsilon_{r3}^\alpha \quad (6)$$

where V_1 , V_2 , and V_3 are the volume fractions of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 and Li_3VO_4 , respectively, and ϵ_{r1} , ϵ_{r2} , and ϵ_{r3} are their intrinsic permittivities. The phase volume fractions ($V_1\text{--}V_3$) were calculated from the reaction stoichiometry given in Equation (3), based on the predicted molar amounts of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 , and Li_3VO_4 for a given composition x , and then converted to pore-free volume fractions using the theoretical densities of the individual phases. The phase volumes were normalized such that $V_1 + V_2 + V_3 = 1$, excluding porosity. The parameter α determines the mixing behavior: $\alpha = 1$, -1 , and 0 correspond to

the parallel, series, and logarithmic (Lichtenecker) models, respectively. The case $\alpha = 0$ does not represent a simple mathematical exponent of zero. Instead, the logarithmic mixing rule is obtained as the limiting form of Equation (6) as $\alpha \rightarrow 0$, yielding the Lichtenecker relation [37]:

$$\ln \varepsilon_r = V_1 \ln \varepsilon_{r1} + V_2 \ln \varepsilon_{r2} + V_3 \ln \varepsilon_{r3} \quad (7)$$

In Figure 9a, the $\alpha = 0$ logarithmic mixing model provides a reasonable description of the composition-dependent variation of the corrected permittivity ε_r in the present system. This logarithmic model is commonly used for randomly intermixed multiphase microstructures [37,38]. The smooth, composition-dependent variation of ε_r further indicates good interfacial compatibility between the $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 and Li_3VO_4 phases and suggests negligible Maxwell–Wagner interfacial polarization within the measured microwave frequency range [39].

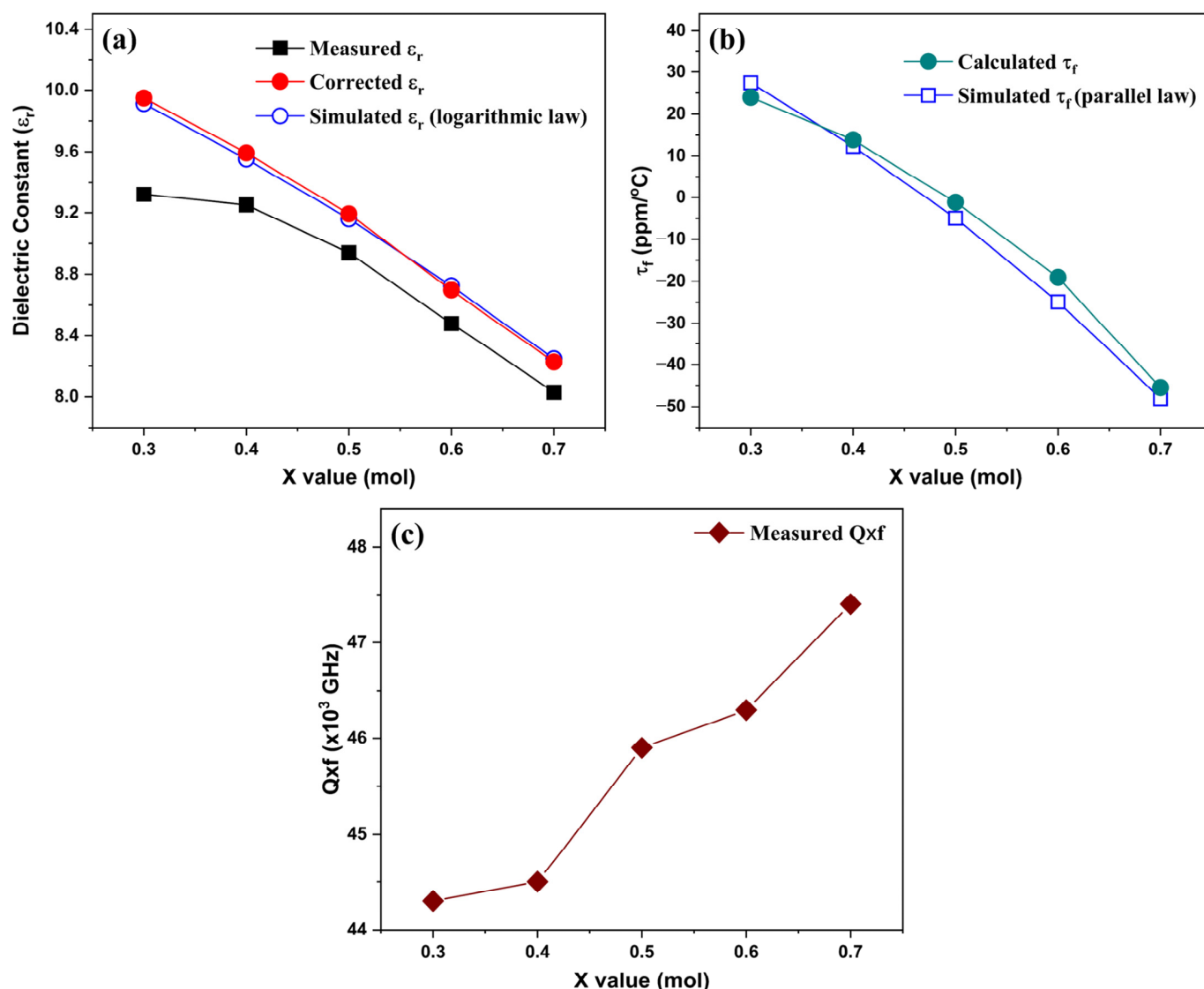


Figure 9. The microwave dielectric properties of the $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 ceramics derived from the $(1-x)\text{Ba}_3(\text{VO}_4)_2$ – $x\text{Li}_2\text{WO}_4$ mixtures ($x = 0.3$ – 0.7) and sintered at 850°C for 1 h as a function of x (a) relative permittivity (ε_r), including measured, porosity-corrected, and simulated values based on the logarithmic mixing model; (b) temperature coefficient of the resonant frequency (τ_f), compared with simulated values using the linear mixing rule; (c) quality factor ($Q \times f$) values.

The τ_f was simulated using the linear volume-fraction-weighted rule:

$$\tau_f = V_1\tau_{f1} + V_2\tau_{f2} + V_3\tau_{f3} \quad (8)$$

where τ_{f1} , τ_{f2} , and τ_{f3} are the τ_f values of $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 and Li_3VO_4 , respectively. Here, V_1 – V_3 denote the pore-free phase volume fractions, consistent with those used in the permittivity analysis. The linear relationship can be derived by substituting the permittivity-mixing relation (Equation (9)) into the general identity for τ_f (Equation (10)):

$$\tau_{\varepsilon,\text{mix}} = \frac{1}{\varepsilon_{r,\text{mix}}} \frac{(d\varepsilon_{r,\text{mix}})}{dT} = \frac{d(\ln\varepsilon_{r,\text{mix}})}{dT} = V_1\tau_{\varepsilon1} + V_2\tau_{\varepsilon2} + V_3\tau_{\varepsilon3} \quad (9)$$

$$\tau_{f,\text{mix}} = -\left(\frac{1}{2} \tau_{\varepsilon,\text{mix}} + \alpha_{L,\text{mix}}\right) \quad (10)$$

where τ_{ε} denotes the temperature coefficients of permittivity; subscripts 1, 2, and 3 refer to the $\text{Ba}_3(\text{VO}_4)_2$, BaWO_4 and Li_3VO_4 phases; and $\alpha_{L,\text{mix}}$ is the effective linear thermal-expansion coefficient of the composite, approximated by a volume-fraction average ($\alpha_{L,\text{mix}} = V_1\alpha_{L1} + V_2\alpha_{L2} + V_3\alpha_{L3}$). It should be emphasized that the linear volume-fraction-weighted relation for τ_f is a direct consequence of the logarithmic mixing behavior of ε_r and the thermodynamic definition of τ_f as the temperature derivative of $\ln\varepsilon_r$, together with the thermal-expansion contribution. Therefore, the use of different apparent mixing rules for ε_r and τ_f is mathematically consistent and does not imply an incoherent modeling framework.

Figure 9b shows that Equation (8) captures the compositional trend of τ_f , which shifts from positive to negative with increasing x due to the increasing contributions of the negative τ_f phases BaWO_4 and Li_3VO_4 . A straight line computed from Equation (8) using the τ_f values of end-member phases reproduces the overall slope, although the experimental data points are slightly offset. This modest, composition-independent offset is expected, since residual porosity and microstructural features—such as closed pores and boundary cavities, or thin intergranular films—can still influence the temperature dependence of permittivity, $\tau_{\varepsilon} = (1/\varepsilon_r)(d\varepsilon_r/dT) = d(\ln\varepsilon_r)/dT$, even after standard porosity correction, and consequently cause a small shift in τ_f [34,35]. In addition, Equation (10) indicates that the thermal-expansion term can contribute a constant offset: minor variations in the effective linear expansion coefficient (α_L)—arising from CTE mismatch, mechanical constraint between the phases, or residual thermal-expansion stresses at their interfaces—may further shift τ_f .

Figure 9c shows the $Q \times f$ values of the $(1-4x/3) \text{Ba}_3(\text{VO}_4)_2-x\text{BaWO}_4-(2x/3)\text{Li}_3\text{VO}_4$ ceramics as a function of x . Although both $Q \times f$ and density increase with x , the difference in their compositional trends indicates that porosity alone is insufficient to account for the observed evolution of $Q \times f$. At first glance, the increase in $Q \times f$ with increasing x appears to follow the same trend as the increase in relative density, as shown in Figure 5b. The influence of porosity on microwave dielectric loss has been widely reported [34,35]. However, although both density and $Q \times f$ increase with x in the present system, the differences in relative density (94–98%) are too small to account for the full variation in $Q \times f$. Thus, porosity alone cannot explain the observed $Q \times f$ evolution.

According to Tamura, lattice anharmonicity and defect-related scattering—particularly those associated with disordered charge distributions—play an important role in determining the intrinsic microwave loss of dielectric ceramics rather than porosity alone [40]. Therefore, changes in defect concentration and lattice dynamics with composition may also contribute to the $Q \times f$ behavior. Nevertheless, in the present composite system, the main factor governing the $Q \times f$ values is the intrinsic loss behavior of the constituent phases

and their relative fractions determined by the reaction in Equation (3). BaWO₄ possesses a significantly higher intrinsic $Q \times f$ (~58,900 GHz) than Ba₃(VO₄)₂ (~40,000–43,000 GHz) and Li₃VO₄ (~22,300 GHz). As x increases, the progressive formation and accumulation of BaWO₄ enhance the overall $Q \times f$ of the composite. At the same time, the increasing fraction of Li₃VO₄—which has the lowest intrinsic $Q \times f$ among the three phases—partially offsets this beneficial effect. This competition between the enhancement driven by BaWO₄ and the reduction associated with Li₃VO₄ results in the moderate, nearly linear increase in the $Q \times f$ values observed in Figure 9c. Consequently, the evolution of $Q \times f$ in the $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2-x\text{BaWO}_4-(2x/3)\text{Li}_3\text{VO}_4$ composites is controlled primarily by the intrinsic $Q \times f$ values and volume fractions of Ba₃(VO₄)₂, BaWO₄, and Li₃VO₄, rather than by small differences in porosity among samples. This behavior reflects the significant influence of intrinsic lattice vibrational characteristics on microwave dielectric loss in heterogeneous composite systems. It should be noted that, in the present composition series, grain size and phase fractions change simultaneously with the initial Li₂WO₄ content; therefore, the isolated effect of grain size on the dielectric properties cannot be rigorously separated. Moreover, because the intrinsic dielectric properties (ϵ_r , $Q \times f$, and τ_f) of Ba₃(VO₄)₂, BaWO₄, and Li₃VO₄ differ far more significantly than any grain-size-related contributions, the observed dielectric trends are dominated by phase-fraction effects, with grain-size effects considered secondary.

At $x = 0.5$, the composite exhibits $\epsilon_r = 9.19$, $Q \times f = 45,900$ GHz, and $\tau_f = -1.15$ ppm/°C, representing a temperature-stable, low-permittivity LTCC material obtained via the reactive sintering of 0.5Ba₃(VO₄)₂–0.5Li₂WO₄ at 850 °C/1 h.

3.4. Chemical Compatibility with Ag Electrodes

To assess the suitability of the $(1-4x/3)\text{Ba}_3(\text{VO}_4)_2-x\text{BaWO}_4-(2x/3)\text{Li}_3\text{VO}_4$ composites for LTCC applications, their chemical compatibility with Ag electrodes was examined. The composition 0.5Ba₃(VO₄)₂–0.5Li₂WO₄ was selected for this test because it exhibited the most favorable microwave dielectric properties among the investigated compositions. Figure 10 shows the XRD pattern of a mixture of 0.5 Ba₃(VO₄)₂–0.5Li₂WO₄ powders containing 20 wt.% Ag ($D_{50} \approx 5 \mu\text{m}$) that was cofired at 850 °C for 1 h. After cofiring, only the peaks corresponding to Ba₃(VO₄)₂, BaWO₄, Li₃VO₄, and metallic Ag are observed, and no detectable reaction phases are detected. This result indicates that the reaction between Ba₃(VO₄)₂ and Li₂WO₄ proceeds normally in the presence of Ag and that no reaction products are detectable within the XRD detection limit between the dielectric phases and Ag during the cofiring process. Therefore, the present composite system is chemically compatible with Ag under the present cofiring conditions.

It is worth placing these results in the context of previously reported LTCC-related microwave dielectrics. Many low-temperature sintering systems, such as Bi₂W₂O₉-, BiNbO₄-, and Zn₂Te₃O₈-based materials, can be densified below 900 °C but often require glass additives or exhibit poor compatibility with Ag electrodes, which limits their applicability in multilayer structures. In contrast, the present Ba₃(VO₄)₂–BaWO₄–Li₃VO₄ composites achieve densification at 850 °C without any glassy phase and show good compatibility with Ag. The dielectric properties obtained for $x = 0.5$ ($\epsilon_r = 9.19$, $Q \times f = 45,900$ GHz, and $\tau_f = -1.15$ ppm/°C) lie within a practically useful regime for LTCC substrates, offering a balanced combination of low relative permittivity, reasonably high $Q \times f$ values, and near-zero thermal drift.

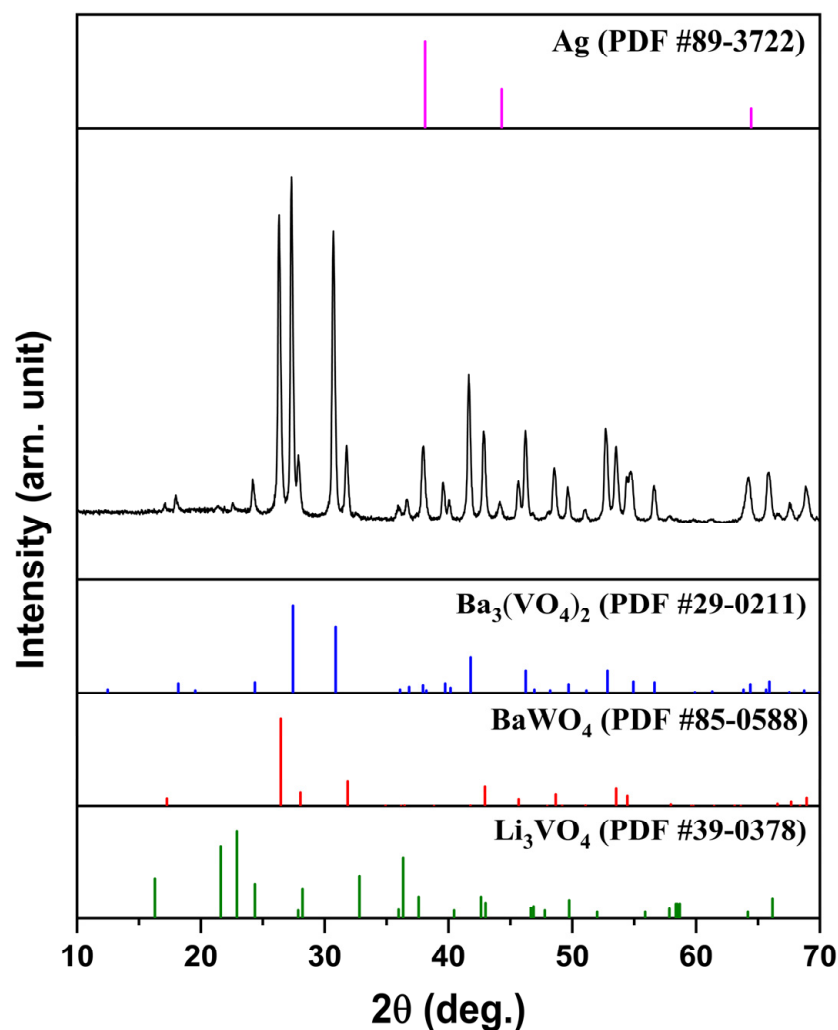


Figure 10. XRD pattern of the $0.5\text{Ba}_3(\text{VO}_4)_2$ – $0.5\text{Li}_2\text{WO}_4$ mixture containing 20 wt.% Ag after cofiring at $850\text{ }^\circ\text{C}$ for 1 h in air.

This performance is achieved through a reactive liquid-phase sintering mechanism, in which Li_2WO_4 simultaneously promotes densification and generates in situ negative τ_f phases (BaWO_4 and Li_3VO_4). The dual function of Li_2WO_4 distinguishes the present approach from many conventional LTCC strategies that rely on inert glass additives and physical mixing of positive and negative τ_f phases. Therefore, the proposed method provides an alternative route to obtaining temperature-stable, glass-free LTCC dielectrics with controllable thermal behavior and reliable electrode compatibility.

4. Conclusions

Ceramic composites with the $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 phase assemblage were successfully obtained by reactive sintering of $\text{Ba}_3(\text{VO}_4)_2$ and Li_2WO_4 mixtures at $850\text{ }^\circ\text{C}$ for 1 h. During sintering, Li_2WO_4 reacts completely with $\text{Ba}_3(\text{VO}_4)_2$ to form BaWO_4 and Li_3VO_4 while providing a transient liquid phase that promotes densification. The onset and peak temperatures of shrinkage for the composite consisting only of $\text{Ba}_3(\text{VO}_4)_2$ – BaWO_4 – Li_3VO_4 ($T_{\text{onset}} = 785.8\text{ }^\circ\text{C}$, $T_{\text{peak}} = 830.5\text{ }^\circ\text{C}$) occur at significantly higher temperatures than those of the corresponding $\text{Ba}_3(\text{VO}_4)_2$ – Li_2WO_4 mixture ($T_{\text{onset}} = 698.3\text{ }^\circ\text{C}$, $T_{\text{peak}} = 739.5\text{ }^\circ\text{C}$), confirming that Li_2WO_4 acts as an effective reactive liquid-phase sintering aid.

Among the compositions studied, the $0.33\text{Ba}_3(\text{VO}_4)_2$ – 0.5BaWO_4 – $0.33\text{Li}_3\text{VO}_4$ ceramic obtained by sintering the $0.5\text{Ba}_3(\text{VO}_4)_2$ – $0.5\text{Li}_2\text{WO}_4$ mixture at $850\text{ }^\circ\text{C}$ for 1 h exhibits

attractive microwave dielectric properties, with $\epsilon_r = 9.19$, $Q \times f = 45,900$ GHz, and $\tau_f = -1.15$ ppm/°C, together with a high relative density of approximately 97% of the theoretical value. Chemical compatibility tests further demonstrated that this ceramic is stable in contact with Ag electrodes during cofiring at 850 °C. The present approach demonstrates that reactive liquid-phase sintering can be effectively used in this system not only to lower the sintering temperature but also to generate in situ functional phases for precise control of microwave dielectric properties.

In summary, sintering the 0.5Ba₃(VO₄)₂–0.5Li₂WO₄ mixture at 850 °C for 1 h provides a practical processing window that meets the key dielectric requirements for LTCC applications, such as sub-900 °C firing, low ϵ_r , reasonably high $Q \times f$, near-zero τ_f , and good compatibility with Ag electrodes. These results establish the Ba₃(VO₄)₂–BaWO₄–Li₃VO₄ composites developed in this work as promising glass-free, temperature-stable, low-loss LTCC materials for advanced microwave applications, including 5G-advanced and future 6G systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma19050889/s1>, Supplementary Figure S1. Schematic flow chart of the experimental procedure.

Author Contributions: Conceptualization, K.-H.L.; methodology, D.-W.K. and K.-H.L.; validation, K.-H.L. and D.-W.K.; formal analysis, D.-W.K., H.-W.J. and K.-H.L.; investigation, D.-W.K., H.-W.J. and K.-H.L.; resources, K.-H.L.; data curation, D.-W.K. and H.-W.J.; writing—original draft preparation, D.-W.K.; writing—review and editing, K.-H.L. and D.-W.K.; visualization, D.-W.K. and H.-W.J.; supervision, K.-H.L.; project administration, K.-H.L.; funding acquisition, K.-H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially supported by the Soonchunhyang University Research Fund and was also supported by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (RS-2025-02263458, HRD Program for Industrial Innovation).

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Hill, M.D.; Cruickshank, D.B.; MacFarlane, I.A. Perspective on ceramic materials for 5G wireless communication systems. *Appl. Phys. Lett.* **2021**, *118*, 120501. [CrossRef]
- Lou, W.C.; Mao, M.M.; Song, K.X.; Xu, K.W.; Liu, B.; Li, W.J.; Yang, B.; Qi, Z.M.; Zhao, J.W.; Sun, S.K.; et al. Low permittivity cordierite-based microwave dielectric ceramics for 5G/6G telecommunications. *J. Eur. Ceram. Soc.* **2022**, *42*, 2820–2826. [CrossRef]
- Tian, H.R.; Zhang, X.H.; Zhang, Z.D.; Liu, Y.; Wu, H.T. Low-permittivity LiLn(PO₃)₄ (Ln = La, Sm, Eu) dielectric ceramics for microwave/millimeter-wave communication. *J. Adv. Ceram.* **2024**, *13*, 602–620. [CrossRef]
- Tian, H.R.; Zhang, Y.Y.; Wang, R.H.; Wu, H.T.; Shan, L.W. Effect of Ge⁴⁺-substituted on the structure characteristics and microwave/terahertz dielectric properties of ultra-low ϵ_r , high Q-f cordierite ceramics. *J. Mater. Sci. Technol.* **2025**, *216*, 165–177. [CrossRef]
- Wang, D.W.; Li, L.H.; Jiang, J.; Lu, Z.L.; Wang, G.; Song, K.X.; Zhou, D.; Reaney, I.M. Cold sintering of microwave dielectric ceramics and devices. *J. Mater. Res.* **2021**, *36*, 333–349. [CrossRef]
- Umamura, R.; Ogawa, H.; Yokoi, A.; Ohsato, H.; Kan, A. Low-temperature sintering-microwave dielectric property relations in Ba₃(VO₄)₂ ceramic. *J. Alloys Compd.* **2006**, *424*, 388–393. [CrossRef]
- Yoon, S.H.; Kim, D.W.; Cho, S.Y.; Hong, K.S. Investigation of the relations between structure and microwave dielectric properties of divalent metal tungstate compounds. *J. Eur. Ceram. Soc.* **2006**, *26*, 2051–2054. [CrossRef]
- Xia, J.J.; Ma, X.H.; Zhang, Z.L.; Nahm, S.; Zhang, S.L.; Ma, X.Y.; Guo, F. Low-temperature sintering and microwave dielectric properties of ZnGa_{2–x}O_{4–1.5x} ceramics with added B₂O₃. *J. Mater. Sci. Mater. Electron.* **2023**, *34*, 1941. [CrossRef]
- Pan, C.L.; Shen, C.H.; Lin, W.C.; Lin, S.H. Effect of B₂O₃ glass on the sintering and microwave dielectric properties of MgTiO₃–CaTiO₃. *Appl. Mech. Mater.* **2014**, *666*, 27–30. [CrossRef]

10. Lin, W.C.; Lin, S.H. Effects of ZnO addition and sintering temperature on dielectric properties of MgTiO₃ ceramic. *Key Eng. Mater.* **2014**, *616*, 145–152. [[CrossRef](#)]
11. Sayyadi-Shahraki, A.; Taheri-Nassaj, E.; Hassanzadeh-Tabrizi, S.A.; Barzegar-Bafrooei, H. Low temperature cofirable Li₂Zn₃Ti₄O₁₂ microwave dielectric ceramic with Li₂O–ZnO–B₂O₃ glass additive. *J. Mater. Sci. Mater. Electron.* **2014**, *25*, 355–360. [[CrossRef](#)]
12. Feteira, A.; Sinclair, D.C. Microwave dielectric properties of low firing temperature Bi₂W₂O₉ ceramics. *J. Am. Ceram. Soc.* **2008**, *91*, 1338–1341. [[CrossRef](#)]
13. Zhou, D.; Wang, H.; Yao, X. Microwave dielectric properties and co-firing of BiNbO₄ ceramic with CuO substitution. *Mater. Chem. Phys.* **2007**, *104*, 397–402. [[CrossRef](#)]
14. Kwon, D.; Lanagan, D.; Shrout, T.R. Microwave dielectric properties and low-temperature cofiring of BaTe₄O₉ with aluminum metal electrode. *J. Am. Ceram. Soc.* **2005**, *88*, 3419–3422. [[CrossRef](#)]
15. Subodh, G.; Sebastian, M.T. Glass-free Zn₂Te₃O₈ microwave ceramic for LTCC applications. *J. Am. Ceram. Soc.* **2007**, *90*, 2266–2268. [[CrossRef](#)]
16. Zhou, D.; Randall, C.A.; Pang, L.X.; Wang, H.; Guo, J.; Zhang, G.Q.; Wu, X.G.; Shui, L.; Yao, X. Microwave dielectric properties of Li₂WO₄ ceramic with ultra-low sintering temperature. *J. Am. Ceram. Soc.* **2011**, *94*, 348–350. [[CrossRef](#)]
17. Kim, S.J.; Kim, E.S. Microwave dielectric properties of 0.85CaWO₄–0.15SmNbO₄ ceramics with sintering additives. *Ceram. Int.* **2009**, *35*, 137–141. [[CrossRef](#)]
18. Zhen, W.; Li, S.; Bian, J. Low temperature sintering and microwave dielectric properties of Li₂TiO₃–Li₂WO₄. *Ceram. Int.* **2013**, *39*, 9767–9772. [[CrossRef](#)]
19. Zhang, Z.; Su, H.; Tang, X.; Zhang, H.; Zhou, T.; Jing, Y. Glass-free low-temperature sintering and microwave dielectric properties of CaWO₄–Li₂WO₄ ceramics. *Ceram. Int.* **2014**, *40*, 1613–1617. [[CrossRef](#)]
20. Qian, Y.; Zhang, Q.; Tang, X.; Huang, F.; Li, Y. Sintering characteristics and microwave dielectric properties of low-temperature-fired (1–x)Li₃Mg₂NbO₆–xLi₂WO₄ ceramics. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 22450–22458. [[CrossRef](#)]
21. Huang, B.; Chen, G.; Xia, T.; Shang, F. Microwave dielectric properties of Li₂WO₄-added SrWO₄ ceramics for LTCC applications. *J. Mater. Sci. Mater. Electron.* **2022**, *33*, 21925–21934. [[CrossRef](#)]
22. Zhu, J.; Liu, J.; Lu, S.; Zeng, Y. Effects of V₂O₅ addition on microwave dielectric properties of Li₂ZnTi₃O₈ ceramics for LTCC applications. *New J. Glass Ceram.* **2019**, *9*, 25–32. [[CrossRef](#)]
23. Lee, H.R.; Yoon, K.H.; Kim, E.S.; Choi, J.W.; Boucher, R. Microwave dielectric properties of BiNbO₄ ceramics with CuO–V₂O₅ addition. *Ceram. Int.* **2012**, *38*, S177–S181. [[CrossRef](#)]
24. Tong, J.X.; Zhang, Q.L.; Yang, H.; Zou, J.L. Low-temperature firing and microwave dielectric properties of Ca[(Li_{0.33}Nb_{0.67})_{0.9}Ti_{0.1}O_{3–δ}] ceramics with LiF addition. *Mater. Lett.* **2005**, *59*, 3252–3255. [[CrossRef](#)]
25. Hakki, B.W.; Coleman, P.D. A dielectric resonator method of measuring inductive capacities in the millimeter range. *IEEE Trans. Microw. Theory Tech.* **1960**, *8*, 402–410. [[CrossRef](#)]
26. Courtney, W.E. Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators. *IEEE Trans. Microw. Theory Tech.* **1970**, *18*, 476–485. [[CrossRef](#)]
27. Sebastian, M.T. *Dielectric Materials for Wireless Communication*; Elsevier: Amsterdam, The Netherlands, 2008.
28. German, R.M. *Sintering Theory and Practice*; John Wiley and Sons: New York, NY, USA, 1996.
29. Chang, L.L.Y.; Scroger, M.G.; Phillips, B. Alkaline-earth tungstates: Equilibrium and stability in the M–W–O systems. *J. Am. Ceram. Soc.* **1966**, *49*, 385–390. [[CrossRef](#)]
30. Whitmore, M.H. Electron-paramagnetic-resonance spectroscopy of manganese-doped Ba₃(VO₄)₂: Identification of tetrahedral Mn⁵⁺ and Mn⁴⁺ centers. *Phys. Rev. B* **1993**, *47*, 11479–11482. [[CrossRef](#)] [[PubMed](#)]
31. Shannon, R.D.; Calvo, C. Refinement of the crystal structure of low temperature Li₃VO₄ and analysis of mean bond lengths in phosphates, arsenates, and vanadates. *J. Solid State Chem.* **1973**, *6*, 538–549. [[CrossRef](#)]
32. Fang, L.; Deng, J.; Tang, J. Microwave Dielectric Ceramic Li₃VO₄ and Preparation Method Thereof. CN Patent CN103145419A, 12 June 2013.
33. Tseng, C.-F.; Chang, W.-H.; Huang, B.-Z.; Han, C.-H. Microwave dielectric properties and chemical bond characteristics of low temperature firing Li₃VO₄ ceramics with low permittivity. *Ceram. Int.* **2023**, *49*, 36299–36307. [[CrossRef](#)]
34. Luo, W.; Guo, J.; Randall, C.; Lanagan, M. Effect of porosity and microstructure on the microwave dielectric properties of rutile. *Mater. Lett.* **2017**, *200*, 101–104. [[CrossRef](#)]
35. Penn, S.J.; Alford, N.M.; Templeton, A.; Wang, X.; Xu, M.; Reece, M.; Schrapel, K. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. *J. Am. Ceram. Soc.* **1997**, *80*, 1885–1888. [[CrossRef](#)]
36. Paladino, A.E. Temperature-compensated MgTi₂O₅–TiO₂ dielectrics. *J. Am. Ceram. Soc.* **1971**, *54*, 168–169. [[CrossRef](#)]
37. Lichtenecker, K.; Rother, K. Die Herleitung des logarithmischen Mischungs-gesetzes aus allgemeinen Prinzipien der stationären Strömung. *Phys. Z.* **1931**, *32*, 255–260.
38. Sihvola, A. *Electromagnetic Mixing Formulas and Applications*; The Institution of Engineering and Technology: Stevenage, UK, 1999; pp. 1–296. [[CrossRef](#)]

39. Vu, T.T.N.; Teyssedre, G.; Le Roy, S.; Laurent, C. Maxwell–Wagner effect in multi-layered dielectrics: Interfacial charge measurement and modelling. *Technologies* **2017**, *5*, 27. [[CrossRef](#)]
40. Tamura, H. Temperature coefficient of resonant frequency and dielectric loss of microwave dielectrics. *J. Eur. Ceram. Soc.* **2006**, *26*, 1775–1780. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.