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Cu\textsuperscript{2+}-Ion-Substitution-Driven Microstructure and Microwave Dielectric Properties of Mg\textsubscript{1−x}Cu\textsubscript{x}Al\textsubscript{2}O\textsubscript{4} Ceramics

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Abstract: In this work, Cu-substituted MgAl\textsubscript{2}O\textsubscript{4} ceramics were prepared via solid-state reaction. The crystal structure, cation distribution, and microwave dielectric properties of Mg\textsubscript{1−x}Cu\textsubscript{x}Al\textsubscript{2}O\textsubscript{4} ceramics were investigated. Cu\textsuperscript{2+} entered the MgAl\textsubscript{2}O\textsubscript{4} lattice and formed a spinel structure. The substitution of Cu\textsuperscript{2+} ions for Mg\textsuperscript{2+} ions contributed to Al\textsuperscript{3+} ions preferential occupation of the octahedron and changed the degree of inversion. The quality factor (Qf) value, which is correlated with the degree of inversion, increased to a maximum value at \( x = 0.04 \) and then decreased. Ionic polarizability and relative density affected the dielectric constant (\( \varepsilon_r \)) value. The temperature coefficient of the resonant frequency (\( \tau_f \)) value, which was dominated by the total bond energy, generally shifted to the positive direction. Satisfactory microwave dielectric properties were achieved in \( x = 0.04 \) and sintered at 1550 °C: \( \varepsilon_r = 8.28 \), Qf = 72,800 GHz, and \( \tau_f = -59 \) ppm/°C. The Mg\textsubscript{1−x}Cu\textsubscript{x}Al\textsubscript{2}O\textsubscript{4} solid solution, possessing good performance, has potential for application in the field of modern telecommunication technology.

Keywords: microwave dielectric properties; MgAl\textsubscript{2}O\textsubscript{4} ceramics; solid solution; lattice energy; bond energy

1. Introduction

The microwave dielectric ceramics have been extensively applied in various fields, including fifth-generation wireless systems, intelligent transmission systems, and ultrahigh-speed wireless local area networks [1–3]. In the application of millimeter waves, there is an urgent requirement for microwave dielectric ceramics with excellent performance in the following areas: a high quality factor (Qf) to enable microwave frequency selectivity, a low dielectric constant (\( \varepsilon_r \)) to shorten the delay time of signal propagation, and a near-zero temperature coefficient of resonant frequency (\( \tau_f \)) to ensure the stability of frequency against temperature changes [4,5]. However, few single-phase materials can meet these requirements simultaneously due to the mutual restrictions of the three parameters. In general, ideal \( \varepsilon_r \) and Qf values can be obtained by selecting material systems, whereas the near-zero \( \tau_f \) value is tailored through two materials with opposite \( \tau_f \) values [6–9]. However, this approach tends to deteriorate the \( \varepsilon_r \) and Qf values.

Previous studies have found that the \( \tau_f \) value is related to octahedral distortion in some ceramic crystals [10,11]. Microwave dielectric ceramics with superior \( \tau_f \) values can be obtained by adjusting the distortion of the octahedron without deteriorating the \( \varepsilon_r \) and Qf values [4]. Therefore, it is important to improve the microwave dielectric properties utilizing the crystal structure. In general, the spinel structural degrees of freedom, such
as the cell parameters, the oxygen fractional coordinates, and degrees of inversion, can be tailored via substitution [12]. MgAl$_2$O$_4$ is known to have a typical cubic spinel belonging to symmetry group Fd-3m (227); the molecular formula is [Mg$_{1-x}$Al$_x$]$_4$[Al$_2$$_4$Mg$_x$]$_6$O$_{12}$, where $\lambda$ value, which is related to the degree of inversion [13,14], represents the occupation of Al$^{3+}$ cations at tetrahedral site.

MgAl$_2$O$_4$ ceramic, which generally exhibits a Qf value of ~68,900 GHz (the highest Qf value is over 200,000 [15]) and a low $\varepsilon_r$ value (~8.75), is one of the candidate material for a millimeter-wave communication substrate [16]. However, it has a large negative $\tau_f$ value (~−75 ppm/°C). It has been reported that MgAl$_2$O$_4$-based composite dielectric ceramics, such as MgAl$_2$O$_4$-TiO$_2$ and MgAl$_2$O$_4$-(Ca$_{0.5}$Sr$_{0.2}$)TiO$_3$, have near-zero $\tau_f$ values [6,7]. However, the $\varepsilon_r$ and Qf values are also deteriorated in this system. It is worth mentioning that the $\tau_f$ value in MgAl$_2$O$_4$ can be improved through the crystal structure [17,18]. Previously, in MgAl$_2$O$_4$ ceramics, it has been shown that the enhancement in Qf value corresponds to the cation distribution [19]. Moreover, the degree of inversion in MgAl$_2$O$_4$ ceramics, prepared by the solid-state reaction or molten-salt reaction routes, has also been investigated [15]. A high degree of inversion represents a high Qf value, and the preferential occupation of Al$^{3+}$ could enhance the covalency of M-O bonds in a [MO$_4$] tetrahedron of MgAl$_2$O$_4$ (M = Mg and Al). Consequently, the cation distribution of Al$^{3+}$ in MgAl$_2$O$_4$ can be discussed to ameliorate the microwave dielectric properties.

In general, the ionic radius of Cu$^{2+}$ ion is close to that of Mg$^{2+}$ ions [4,20,21], which is beneficial for forming Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ solid solutions. Additionally, a significant Jahn–Teller effect can be observed when Cu$^{2+}$ ions occupy the octahedral site in a spinel structure [22]. This can contribute to the regulation of the microstructure of MgAl$_2$O$_4$. In addition, CuO can also reduce the sintering temperature of ceramics [4,21]. Therefore, in this work, the Cu$^{2+}$ ion was considered as a substitution of the Mg$^{2+}$ ion in MgAl$_2$O$_4$. Mg$_{1−x}$Cu$_x$Al$_2$O$_4$ ceramics were synthesized through a solid-state route. The phase composition, microstructure, and microwave dielectric properties were investigated in detail.

2. Experimental Procedure

Mg$_{1−x}$Cu$_x$Al$_2$O$_4$ (x = 0, 0.04, 0.08, 0.12, 0.16, and 0.20) ceramics were synthesized via the conventional solid-state route. Analytic-grade purity MgO, CuO, and Al$_2$O$_3$ powders (Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) with the range of particle size at 45–80 µm were used as starting materials, which were weighed and wet-mixed in deionized water using zirconia balls in a plastic container at 300 rpm for 4 h. The obtained slurries were dried and calcined in alumina crucibles at 1450 °C in a nitrogen atmosphere with a step of 45–80 °C, using Cu Kα radiation ($\lambda$ = 1.54 Å) at room temperature, was measured in the 2θ angle range between 10° and 120° with a step of 0.01°, and counting time for 5 s per step. Based on the XRD results, the crystal structure was analyzed using the Rietveld refinement method using FullProf software (FullProf Suite May2021 64b, The FullProf Team, Grenoble, France) [23]. The microstructures and morphologies of the samples were analyzed by a scanning electron microscope (SEM, JSM-6490; JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV. The Al$^{3+}$ ion distributions of Mg$_{1−x}$Cu$_x$Al$_2$O$_4$ were investigated through $^{27}$Al solid-state magic-angle spinning nuclear magnetic resonance (MAS-NMR) with a spinning frequency of 12 kHz (Avance II 600 MHz, Bruker, Fällanden, Switzerland).

Microwave dielectric properties ($\varepsilon_r$, Qf, and $\tau_f$) of these samples were measured by the Hakki–Coleman dielectric resonator with a vector network analyzer (N5230A, Agilent Technologies, Santa Clara, CA, USA). The $\tau_f$ value was calculated based on the resonant frequencies at 25 and 85 °C:
where \( f_t \) represents the resonant frequency at \( t \) °C.

### 3. Results and Discussion

Figure 1 shows the microwave dielectric properties of \( \text{Mg}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4 \) ceramics sintered at 1450–1600 °C. Good microwave dielectric properties were obtained at \( x = 0.04 \) with sintering at 1550 °C: \( \varepsilon_r = 8.28 \), \( Q_f = 72,800 \) GHz, and \( \tau_f = -59 \) ppm/°C. With the sintering temperature at 1550 °C, the \( \tau_f \) value experienced a significant increase in the negative direction to about \(-59 \) ppm/°C at \( 0 \leq x \leq 0.04 \); then, the rapid fall was witnessed and a steady rise was observed at \( 0.08 \leq x \leq 0.20 \). Figure 1b shows the \( \varepsilon_r \) value, which increased first up to \( x = 0.12 \) and then presented a modest downward trend when the sintering temperatures were 1450 and 1500 °C, whereas it remained virtually unchanged at 1550 and 1600 °C. In addition, it is well known that Qf values are determined by both intrinsic and extrinsic factors. Intrinsic factor is mainly caused by lattice vibration, while extrinsic factor is dominated by grain boundary, secondary phase, and densification [24,25].

With the increase in the \( x \) value, the Qf values of the samples with different sintering temperatures increased initially and then showed a steady drop. The maximum Qf value was acquired at \( x = 0.04 \) with sintering at 1550 and 1600 °C. Compared with previous studies (see Table 1) [6,15,17,18,26–33], the sintering temperature and \( \tau_f \) value of this work can be improved. However, Qf is lower than the best reported value [15], one of the reasons may be the different experimental conditions, such as preparation method, sintering temperature and ball milling time, etc. To understand the microstructure and microwave dielectric properties of \( \text{Mg}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4 \) ceramics, the phase composition, relative density, and cation distribution were investigated in this study.

Figure 1. The microwave dielectric properties of \( \text{Mg}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4 \) (\( x = 0–0.2 \)) ceramics sintered at 1450–1600 °C: (a) Qf value, (b) \( \varepsilon_r \) value, and (c) \( \tau_f \) value.

### Table 1. Microwave dielectric properties and preparation condition of MgAl2O4-based and ZnAl2O4 ceramics.

| Sample                     | \( \tau_f \) (ppm/°C) | Qf (GHz)   | \( \varepsilon_r \) | \( T_s \) (°C) | Milling Time (h) | Preparation Method           | Ref.        |
|----------------------------|------------------------|------------|---------------------|---------------|------------------|-------------------------------|------------|
| \( \text{Mg}_{0.96}\text{Cu}_{0.04}\text{Al}_2\text{O}_4 \) | −59                    | 72,800     | 8.28                | 1550          | 4                | solid state reaction          | This work  |
| \( \text{MgAl}_2\text{O}_4 \)   | N/A                    | 82,000     | 7.9                 | 1550–1700     | 24               | solid state reaction          | [26]       |
| \( \text{ZnAl}_2\text{O}_4 \)  | N/A                    | 106,000    | 8.6                 | 1550–1700     | 24               | solid state reaction          | [26]       |
| \( \text{Mg}(\text{Al}_{1-x}\text{Ga}_{x})_2\text{O}_4 \) | −16                   | 107,000    | 8.87                | 1265–1535     | 6                | solid state reaction          | [27]       |
| \( \text{MgAl}_{1.94}(\text{Mg}_{0.5}\text{Ti}_{0.5})_{0.06}\text{O}_4 \) | −61.36                | 98,000     | 9.1                 | 1425          | 6                | solid state reaction          | [28]       |
| \( \text{Mg}_{62.4}\text{Zn}_{37.6}\text{Al}_2\text{O}_4 \) | −60                   | 222,600    | 8.40                | 1600          | 24               | solid state reaction          | [29]       |
| \( 0.75\text{MgAl}_2\text{O}_4\cdot0.25\text{Ti}_2\text{O}_3 \) | −12                   | 105,400    | 11.04               | 1400–1460     | 24               | solid state reaction          | [6]        |
| \( \text{Mg}_{62.4}\text{Ni}_{37.6}\text{Al}_2\text{O}_4 \) | −53.5                 | 130,000    | 8.21                | 1480–1600     | 24               | solid state reaction          | [17]       |
| \( \text{Mg}_{62.4}\text{Zn}_{37.6}\text{Al}_2\text{O}_4 \) | −64–70                | 156,000    | 8.1                 | 1480–1600     | 12               | solid state reaction          | [20]       |
| \( \text{ZnAl}_{2}\text{O}_4 \)   | −66                   | 202,468    | 8.2                 | 1500–1600     | 24               | molten salt method            | [31]       |
| \( \text{MgAl}_2\text{O}_4 \)   | −62.4                 | 201,690    | 7.8                 | 1600          | 24               | molten salt method            | [15]       |
| \( \text{Mg}_{62.4}\text{Al}_2\text{O}_4 \) | −60                   | 201,111    | 7.7                 | 1600          | 24               | molten salt method            | [32]       |
| \( \text{Mg}_{62.4}\text{Al}_2\text{O}_4 \) | −60                   | 232,301    | 7.5                 | 1600          | 24               | molten salt method            | [32]       |
| \( \text{Mg}_{62.4}\text{Cu}_{0.2}\text{Al}_2\text{O}_4 \) | −60                   | 49,300     | 8.46                | 1475–1500     | 12               | reaction-sintering process    | [18]       |
| Transparent \( \text{MgAl}_2\text{O}_4 \) | N/A                   | 52,640     | 8.20                | 1350          | N/A              | spark plasma sintering        | [33]       |

Note: N/A is not applicable.
XRD analysis is often carried out to identify phases. The XRD patterns of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C are illustrated in Figure 2. All the diffraction peaks can be assigned to those for the standard MgAl$_2$O$_4$ (PDF # 21-1125) pattern with a space group Fd-3m (227). Meanwhile, there is no apparent peak corresponding to any additional secondary phase containing Cu or structural phase transitions observed from Figure 2, indicating the successful formation of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ solid solutions [34].

![Figure 2](image)

**Figure 2.** The XRD patterns of the Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics.

Figure 3 displays the Rietveld refinement of the XRD patterns for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics, and the refinement results are presented in Table 2. Both the Bragg positions models are well within the standard indexed peaks, indicating that the refinement result is acceptable. According to the refinement, the Cu$^{2+}$ ions occupied the tetrahedral site, with the exception of a small amount of the octahedral site. Figure 4 shows the schematic diagram of a crystal structure from MgAl$_2$O$_4$ to Mg$_{1-x}$Cu$_x$Al$_2$O$_4$. The Mg$^{2+}$ and Cu$^{2+}$ ions significantly occupy the 8a Wyckoff position, and the Al$^{3+}$ ions mainly occupy the 16d Wyckoff position. They form a [Mg(T)/Cu(T)O$_4$] tetrahedron and an [Al(M)O$_6$] octahedron, respectively. In general, Al$^{3+}$ ions preferentially occupy tetrahedra, which can effectively improve the Qf value (~232,301 GHz) [19,26]. However, Al$^{3+}$ ions mainly occupy the octahedron, which is consistent with low Qf values (~72,800 GHz) of the Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ system. The cell parameters showed a nonlinear trend with an increase in Cu$^{2+}$ ions content; that is, they first increased, then decreased, and finally increased. On the one hand, the radius of a Cu$^{2+}$ ion ($r = 0.73$ Å) is slightly larger than that of a Mg$^{2+}$ ion ($r = 0.72$ Å) [20], which may have led to the increase in cell parameters. On the other hand, the Cu$^{2+}$ ions’ octahedral coordination has a significant Jahn–Teller effect. The Jahn–Teller distortion can enhance the polarizing effect of Cu$^{2+}$ ions [22]. Therefore, the hybridization of Cu$^{2+}$ ions is responsible for a decrease in average cell parameters [22]. Consequently, the two mechanisms were in competition with each other, resulting in a nonlinear variation trend of cell parameters. The cation distribution, which is a significant variation, had no obvious effect on the microwave dielectric properties.
Figure 3. The XRD with Rietveld refinements: (a) \( x = 0 \), (b) \( x = 0.04 \), (c) \( x = 0.08 \), (d) \( x = 0.12 \), (e) \( x = 0.16 \), and (f) \( x = 0.20 \).

Table 2. The cell parameters, density, and reliable factors were obtained based on the Rietveld refinements of XRD.

| \( x \) | \( a = b = c \) (Å) | \( V \) (Å³) | \( R_p \) (%) | \( R_w \) (%) | \( R_{exp} \) (%) | \( \chi^2 \) | \( \rho_m \) (g cm⁻³) | \( \rho_t \) (g cm⁻³) | \( \rho_r \) (%) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 8.0849 | 528.467 | 6.35 | 8.54 | 4.72 | 3.27 | 3.379 | 3.577 | 94.49 |
| 0.04 | 8.0864 | 528.775 | 6.51 | 8.88 | 4.60 | 3.73 | 3.454 | 3.614 | 95.59 |
| 0.08 | 8.0869 | 528.857 | 5.41 | 7.19 | 4.29 | 2.81 | 3.465 | 3.652 | 94.90 |
| 0.12 | 8.0838 | 528.259 | 4.76 | 6.10 | 3.94 | 2.40 | 3.491 | 3.696 | 94.49 |
| 0.16 | 8.0817 | 527.841 | 4.35 | 5.63 | 3.70 | 2.32 | 3.484 | 3.738 | 92.79 |
| 0.20 | 8.0828 | 528.060 | 3.99 | 5.17 | 3.56 | 2.10 | 3.503 | 3.776 | 92.79 |

Note: The \( \rho_m \), \( \rho_t \), and \( \rho_r \) are the measured density, the measured density, and the relative density, respectively.
For further analysis of the effects of the introduction of Cu\(^{2+}\) ions on microwave dielectric properties, the variations in the cation distribution in Al\(^{3+}\) were measured via the \(^{27}\)Al solid-state MAS-NMR measurement, which was used to evaluate the Al\(^{3+}\) sites in Mg\(_{1-x}\)Cu\(_x\)Al\(_2\)O\(_4\) ceramics. Figure 5a shows the \(^{27}\)Al NMR spectra of Mg\(_{1-x}\)Cu\(_x\)Al\(_2\)O\(_4\) ceramics sintered at 1550 °C. The spectra indicate three signals with chemical shifts at ca. 10, 17, and 71 ppm. They correspond to octahedrally coordinated aluminum (AlO\(_6\)), pentahedrally coordinated aluminum (AlO\(_5\)), and tetrahedrally coordinated aluminum (AlO\(_4\)), respectively [35,36]. For the emergence of AlO\(_5\), a dynamic disorder occurred between the twisted tetrahedral structure and octahedral structure and froze some Al ions stuck in the pentahedral structure at high temperatures [37]. In Figure 5a, the peak intensities of AlO\(_4\) at 71 ppm gradually weakened, whereas the peaks of AlO\(_5\) at 10 ppm and AlO\(_6\) at 17 ppm first increased and then decreased with the increase in Cu\(^{2+}\) content. This result indicated that the redistribution of Al\(^{3+}\) ions in the lattice occurred by the substitution of Cu\(^{2+}\) for Mg\(^{2+}\). Moreover, the peaks transferred to low chemical shifts on account of the second-order quadrupolar-order shifts with the increase in Cu\(^{2+}\) content [31,38]. On the whole, the peak intensity of AlO\(_6\) is significantly larger than that of AlO\(_4\), which indicates that Al\(^{3+}\) ions mainly occupied octahedral sites. This was in accordance with the XRD results. The different peaks indicated the existence of an intermediate spinel structure in the system. The intermediate spinel structure can be described as [Mg\(_{1-\lambda}\)Al\(_{\lambda}\)]\(^{\text{IV}}\)[Al\(_{2}\)Mg\(_{3}\)]\(^{\text{VI}}\)O\(_4\), where \(\lambda\) is the degree of the inversion of spinel structure, corresponding to the fraction of Al\(^{3+}\) ions in the tetrahedral site. The value of \(\lambda\) ranges from 0 (normal spinel: (Mg\(^{2+}\))\(^{\text{IV}}\)(Al\(^{3+}\))\(^{\text{VI}}\)O\(_4\)) to 1 (inverse spinel: (Al\(^{3+}\))\(^{\text{IV}}\)(Mg\(^{2+}\))\(^{\text{VI}}\)O\(_4\)) [13,14]. It is known that the microwave dielectric properties are related to \(\lambda\) [14,15,39]. The value of \(\lambda\) can be calculated with the following formula [40]:

\[
\lambda = \frac{2I(\text{AlO}_4)}{I(\text{AlO}_4) + I(\text{AlO}_6)}
\]

where \(I(\text{AlO}_4)\) and \(I(\text{AlO}_6)\) are the intensities of tetrahedral and octahedral resonances, respectively. The \(\lambda\) values are displayed in Figure 5b. Considering the trend of \(\lambda\) in Figure 5b, the Al\(^{3+}\) cations preferentially occupied the octahedral sites. It has been reported that the preferential tetrahedron site occupation of Al\(^{3+}\) could enhance the Qf value of the system [19,26]. Consequently, when 0.04 < \(x\) < 0.16, the Qf values reduce with the decrease in the \(\lambda\) value in Mg\(_{1-x}\)Cu\(_x\)Al\(_2\)O\(_4\) ceramics (see Figure 5b). In addition, the entry of Cu\(^{2+}\) ions into the MgAl\(_2\)O\(_4\) lattice can lead to disordered charge distribution, which can cause a decrease in Qf value at high Cu\(^{2+}\) ions content [41].

![Figure 5.](image_url)

**Figure 5.** (a) \(^{27}\)Al NMR spectra of Mg\(_{1-x}\)Cu\(_x\)Al\(_2\)O\(_4\) ceramics sintered at 1550 °C; (b) the effects of the degree of inversion on Qf value at 1550 °C.

The relative density can be calculated according to measured and theoretical density. The theoretical density can be derived from XRD refinements. The results are presented in Table 2. The relative density first increased and then gradually decreased, and the maximum value, which was obtained at \(x = 0.04\), was 95.59%. The SEM shows that the
densification was consistent with the relative density (see Figure S1). It also indicates that the moderate amount of CuO can promote the sintering of MgAl2O4 ceramics, which is beneficial for obtaining uniform and dense microstructures (see Figure S1). The relationship between the $\varepsilon_r$ value and the relative density is presented in Figure 6, which shows that the $\varepsilon_r$ value and relative density showed the same trend when $x \leq 0.12$. With the increase in Cu$^{2+}$ at $x > 0.12$, the pores in ceramics also played an important role for the $\varepsilon_r$ value. To further investigate the effect of porosity on the $\varepsilon_r$ value, the porosity-corrected dielectric constant ($\varepsilon_{rc}$) can be calculated by a spherical-pore model [42]:

$$
\varepsilon_r = \varepsilon_{rc}\left(1 - \frac{3P(\varepsilon_{rc} - 1)}{2\varepsilon_{rc} + 1}\right)
$$

(3)

where $\varepsilon_r$ and $P$ (1 - $\rho_{relative}$) are the measured $\varepsilon_r$ and the porosity, respectively. The calculated results are listed in Table 3. The $\varepsilon_{rc}$ value was higher than the $\varepsilon_r$ value, which indicated that the air trapped in the pores contributed to the decrease in the dielectric constant [43]. It is worth mentioning that, with the increase in Cu$^{2+}$ at $x > 0.12$, the relative density maintained a declining trend, while the $\varepsilon_r$ value had a slight growth. In response to this difference, apart from the relative density and pores, the variation in the $\varepsilon_r$ value can be evaluated by the Clausius–Mosotti equation [44]:

$$
\varepsilon_{theo} = \frac{3V_m + 8\pi a_{theo}}{3V_m - 4\pi a_{theo}}
$$

(4)

where $V_m$ and $a_{theo}$ represent the molecular volume and theoretical ionic polarizabilities, respectively. $a_{theo}$ can be calculated as follows [45,46]:

$$
a_{theo} = (1 - x)a_{Mg^{2+}} + xa_{Cu^{2+}} + 2a_{Al^{3+}} + 4a_{O^{2-}}
$$

(5)

where the $a_i$ value corresponds to the individual ionic dielectric polarizabilities. The results are listed in Table 3. The theoretical ionic polarizabilities of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics, which increased linearly from 10.94 to 11.10, are shown in Figure 6. In general, the increase in polarizabilities led to the increase in the $\varepsilon_r$ value, and the expected variation only occurred at $x \geq 0.12$ [47]. This indicates that the ionic polarizabilities have a more significant impact on the $\varepsilon_r$ value than that of the relative density at $x > 0.12$.

![Figure 6](image-url)  
**Figure 6.** The variation between $\varepsilon_r$ value at 1550 °C and theoretical ionic polarizabilities; the relative density.
Table 3. Measured dielectric constant ($\varepsilon_r$) and porosity-corrected dielectric constant ($\varepsilon_{rc}$) of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C.

| $x$ Value | $x = 0$ | $x = 0.04$ | $x = 0.08$ | $x = 0.12$ | $x = 0.16$ | $x = 0.2$ |
|-----------|---------|------------|------------|------------|------------|-----------|
| $P$       | 0.055   | 0.044      | 0.051      | 0.055      | 0.068      | 0.072     |
| $\varepsilon_r$ | 8.14    | 8.28       | 8.23       | 8.22       | 8.26       | 8.29      |
| $\varepsilon_{rc}$ | 8.75    | 8.76       | 8.80       | 8.83       | 9.04       | 9.12      |
| $\varepsilon_{theo}$ | 7.79    | 7.92       | 8.05       | 8.23       | 8.40       | 8.54      |

In order to clarify the correlation between the chemical bonds and the microwave dielectric properties of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics at 1550 °C, the complex chemical bond theory analysis was carried out, which was contributed by Phillips, Van Vecten, and Levine (P-V-L) [48–52]. The detailed process of the P-V-L theory analysis is presented in the Supplementary Materials. The bond length, lattice energy, and bond energy, which are calculated through P-V-L theory, are shown in Tables S1–S4, respectively. The $\tau_f$ value is the combined result of the bonding strength and the crystal structure. In general, the binding force between the ions in the unit cell was stronger, the restoring force that affected the tilt of the oxygen octahedron was higher, the unit cell was less affected at high temperatures, and the $\tau_f$ value was closer to zero [21,53]. Figure 7 shows the $\tau_f$ value and the total bond energy as a function of the $x$ value. When $x \leq 0.04$ and $x \geq 0.08$, the $\tau_f$ value shifted to zero with the increase in total bond energy, indicating that the system tended to be stable.

Figure 7. The $\tau_f$ value and the total bond energy of Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C.

4. Conclusions

A single-phase Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramic with a spinel structure was formulated and analyzed. The Cu$^{2+}$ ions occupied the tetrahedral site, whereas the Al$^{3+}$ ions preferentially occupied octahedral site, resulting in a low the $Q_f$ value. In addition, the entry of Cu$^{2+}$ ions into the MgAl$_2$O$_4$ lattice lead to disordered charge distribution, which can cause a decrease in $Q_f$ value at high Cu$^{2+}$ ions content. The Cu substitution had the high bond energy, which contributed to the temperature stability of the samples at $x \leq 0.04$ and $x \geq 0.08$. Then, the $\tau_f$ value moved toward the positive direction. Good microwave dielectric properties were achieved at $x = 0.04$, sintered at 1550 °C: $\varepsilon_r = 8.28$, $Q_f = 72,800$ GHz, and $\tau_f = -59$ ppm/°C. Therefore, the $Q_f$ and $\tau_f$ values of the Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ solid solution were improved, maintaining a low $\varepsilon_r$ value. This study suggests that Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ is a promising candidate ceramic, possessing a high $Q_f$ value and a low dielectric constant, for use in modern communication systems.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/nano12193332/s1. Figure S1: SEM micrograph for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics: (a) $x = 0$, 1550 °C; (b) $x = 0.04$, 1550 °C; (c) $x = 0.12$, 1550 °C; (d) $x = 0.04$, 1450 °C; (e) $x = 0.04$, 1350 °C.
1500 °C; and (f) $x = 0.04$, 1600 °C. Table S1: Bond length $d$ (Å) for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C. Table S2: Parameters of lattice energy for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C. Table S3: Lattice energy $U_C$ (kJ mol$^{-1}$) for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C. Table S4: Bond energy $E$ (kJ mol$^{-1}$) for Mg$_{1-x}$Cu$_x$Al$_2$O$_4$ ceramics sintered at 1550 °C. References [21,51,54–63] were cited in the Supplementary Materials.

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