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# High quality factor of $(Zn_{0.6}Mg_{0.4})_{1.918}GeO_{3.918}$ microwave dielectrics

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## Abstract

The dependence of the microwave dielectric properties on the structural characteristics of $(Zn_{1-x}Mg_x)_{1.918}GeO_{3.918}$ $(0.2 \le x \le 0.6)$ was investigated. With increasing $Mg^{2+}$ substitution up to $x=0.4$, the single-phase rhombohedral structure was detected, however, the secondary phase of $Mg_2GeO_4$ with orthorhombic structure was observed for further substitution of $Mg^{2+}$. The quality factor (*Qf*) was dependent on the structural symmetry, in particular the tetrahedral distortion. $(Zn_{0.6}Mg_{0.4})_{1.918}GeO_{3.918}$ showed the highest *Qf* value throughout the entire compositional range, which could be attributed to the high symmetry of the crystal structure with equilateral hexagonal rings composed of $GeO_4$ and $(Zn,Mg)GeO_4$ tetrahedra. The dielectric constant (*K*) and the temperature coefficient of resonant frequency (*TCF*) of the specimens changed only slightly up to $x=0.4$, while at $x=0.5$ and 0.6, they changed remarkably due to the formation of the secondary phase of $Mg_2GeO_4$.

*Keywords:* Quality factor; Structural symmetry; Tetrahedral distortion; Microwave dielectrics

## 1. Introduction

Various types of dielectric materials have been investigated to meet the requirements for the components and devices working at microwave and millimeter-wave frequencies due to the remarkable progress in wireless communications. For these applications, dielectric materials should have a low dielectric constant (*K*) to minimize cross-coupling with conductors, a high quality factor (*Qf*) to increase the selectivity, and a near-zero temperature coefficient of resonant frequency (*TCF*) to ensure stability of the frequency against temperature changes [1].

Several dielectric ceramics with low *K* and high *Qf* value, such as $Al_2O_3$ [2], $Mg_4Nb_2O_9$ [3], $Ca_3Sn_2SiO_9$ [4], $Mg_2SiO_4$ [5], and $Zn_2SiO_4$ [6] have received attention with respect to applications as ceramic substrate materials of microwave integrated circuits (MIC) to minimize the cross-coupling with conductors and to shorten the time for electronic signal transmission.

Recently, $Zn_2SiO_4$ (willemite)-based ceramics [6–9] were widely investigated because of their high *Qf* values, as shown in Table 1. However, the data exhibit a lack of reproducibility and low *Qf* values of $Zn_2SiO_4$ were also reported, which could be improved by $Mg^{2+}$ substitution (see Table 1). According to Li et al. [7], the *Qf* value of $Zn_2SiO_4$ ceramic can be improved by the substitution of 0.4 mol of $Mg^{2+}$ for $Zn^{2+}$ owing to the suppression of secondary-phase formation. However, Song et al. [8] reported that $(Zn_{0.6}Mg_{0.4})_2SiO_4$ ceramics with single, pure rhombohedral phase showed high *Qf* values, even though these ceramics were prepared by the same solid-state reaction method. This result indicated that the reason for the high *Qf* value of $Mg^{2+}$ substituted willemite ceramics cannot be explained by only extrinsic factors, such as the relative density, grain size, and percentage of the secondary phase, but that intrinsic factors, such as the structural characteristics, degree of crystal structural ordering, and lattice distortions have to be included [10–12]. However, the relationships between the *Qf* value and the intrinsic factors based on crystal structural characteristics were not reported yet for willemite-type ceramics.

It has been reported [13] that $Zn_2SiO_4$ has a rhombohedral structure belonging to space group *R*-3, and $Mg_2SiO_4$ has an orthorhombic structure belonging to space group *Pmnb*. The unit cell of $Zn_2SiO_4$ consist of two $ZnO_4$ tetrahedra and one $SiO_4$ tetrahedron connected by a shared vertex, and $Mg_2SiO_4$

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Table 1
Microwave dielectric properties of $(Zn,Mg)_2SiO_4$ prepared by solid-state reaction.

| Composition | K | Qf (GHz) | TCF (ppm/°C) | Ref. |
|---|---|---|---|---|
| $Zn_2SiO_4$ | 6.6 | 219,000 | −61 | [6] |
| $Zn_2SiO_4$ | 6.5 | 34,700 | −52 | [7] |
| $(Zn_{0.6}Mg_{0.4})_2SiO_4$ | 6.1 | 148,740 | −54 | |
| $Zn_2SiO_4$ | 6.7 | 35,330 | −58 | [8] |
| $(Zn_{0.6}Mg_{0.4})_2SiO_4$ | 6.6 | 95,650 | −60 | |
| $Zn_{1.8}SiO_{3.8}$ | 6.6 | 147,000 | −22 | [9] |

is composed of two $MgO_4$ octahedra connected to one $SiO_4$ tetrahedron by a shared vertex and edge. Similarly, $Zn_2GeO_4$ and $Mg_2GeO_4$ also have same crystal structures like the silicates $Zn_2SiO_4$, $Mg_2SiO_4$. With the substitution of $Mg^{2+}$ for $Zn^{2+}$ in $Zn_2GeO_4$, the coexistence of the rhombohedral and orthorhombic phase was reported at the 0.5 mol of $Mg^{2+}$ in $Zn_2GeO_4$ [14,15]. From these structural considerations, it could be expected that the *Qf* value of $Zn_2GeO_4$ would be improved by the substitution of $Mg^{2+}$ for $Zn^{2+}$. Therefore, the investigation of the relationships between *Qf* value and crystal structural characteristics of $Mg^{2+}$ substituted $Zn_2GeO_4$ may clarify the reason for the high *Qf* value of these substitutional oxides, as well as promote the development of new willemite-type ceramics with high *Qf* value.

In this study, the effects of $Mg^{2+}$ substitution on the microwave dielectric properties of $(Zn_{1-x}Mg_x)_{1.918}GeO_{3.918}$ $(0.2 \leq x \leq 0.6)$ were investigated, based on crystal structural characteristics by means of Rietveld refinements of X-ray diffraction data and analysis of Raman spectra.

## 2. Experimental procedure

$(Zn_{0.6}Mg_{0.4})_2GeO_4$ and $(Zn_{1-x}Mg_x)_{1.918}GeO_{3.918}$ $(0.2 \leq x \leq 0.6)$ were synthesized by the solid-state reaction method. High purity oxide powders of ZnO (99%), MgO (99.9%), and $GeO_2$ (99.9%) were mixed in stoichiometric ratios and the mixed powders were milled with $ZrO_2$ balls for 24 h in ethanol. The powders were calcined at 1000 °C for 3 h and the calcined powders were re-milled for 24 h, dried, and then sieved through 250 meshes. Finally, the powders were isostatically pressed into pellets under a pressure of 1500 kg/cm$^2$. These pellets were sintered at 1300 °C for 4 h in air.

The density of the sintered specimens was measured by the Archimedes method. Scanning electron microscopy (BSEM, JSM-7500F, JEOL, Japan), energy dispersive X-ray spectrometry (EDS, JSM-7500F, JEOL, Japan), high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL, Japan) and X-ray powder diffraction analysis (XRD, D/Max-2500V/PC, RIGAKU, Japan) were used to evaluate the crystalline phases and microstructures of the sintered specimens.

The crystal structural characteristics of the specimens were determined by Rietveld refinements of the XRD patterns using the FullProf program [16]. Raman spectra of $(Zn_{1-x}Mg_x)_{1.918}GeO_{3.918}$ were obtained with a Micro-Raman spectrometer (Dispersive Raman, SENTERRA Raman, Bruker Corporation, Germany) using a He–Ne laser (633 nm, 10 mW).

The microwave dielectric properties (*K*, *Qf*) were measured by the Hakki and Colema method [17] with the $TE_{011}$ mode at 12 GHz, and the *TCF* was measured by the cavity method [18] in a chamber over a temperature range from 25 °C to 80 °C.

## 3. Results and discussion

### 3.1. Preparation of single phase $(Zn_{0.6}Mg_{0.4})_2GeO_4$ with rhombohedral structure

$(Zn_{0.6}Mg_{0.4})_2GeO_4$ was prepared by conventional solid-state reaction and their XRD patterns are given in Fig. 1. For $(Zn_{0.6}Mg_{0.4})_2GeO_4$, the ZnO secondary phase was detected, as well as $Zn_2GeO_4$ (JCPDS no. 80-0580) with rhombohedral structure as the main phase. According to Nguyen et al. [9], the complete interaction between $SiO_2$ and ZnO in $Zn_2SiO_4$ is difficult because of the stable crystal structure of crystalline $SiO_2$, which induces the formation of ZnO as secondary phase in $Zn_2SiO_4$, along with a degenerated *Qf* value. Similarly, $GeO_2$ also has the same crystal structure like $SiO_2$ and is non-reactive toward other oxide [19], which caused the formation of ZnO as secondary phase in $(Zn_{0.6}Mg_{0.4})_2GeO_4$ sintered at 1300 °C for 4 h.

In order to remove the secondary ZnO phase, the A-site mole fraction of $(Zn_{0.6}Mg_{0.4})_2GeO_4$ was reduced from 2 to 1.918. It was reported that the quality factor (*Qf*) of willemite ceramics could be improved by the elimination of the secondary ZnO phase in $Zn_2SiO_4$ [9]. As shown in Fig. 1, the secondary phase of ZnO was clearly removed and single phase rhombohedral zinc germanate (JCPDS no. 80-0580) was confirmed for $(Zn_{0.6}Mg_{0.4})_{1.918}GeO_{3.918}$ sintered at 1300 °C for 4 h. Furthermore, the rhombohedral structure could be observed by high-resolution TEM (HRTEM) and a spot pattern of the selected-area electron diffraction (SAED) is shown in Fig. 2. HRTEM images showed the rhombohedral crystal structure along the *c*-axis and the corresponding (001) lattice planes exhibited smaller spacing of 0.69 nm than that reported for $Zn_2GeO_4$ (0.724 nm) [19] due to the smaller ionic size of

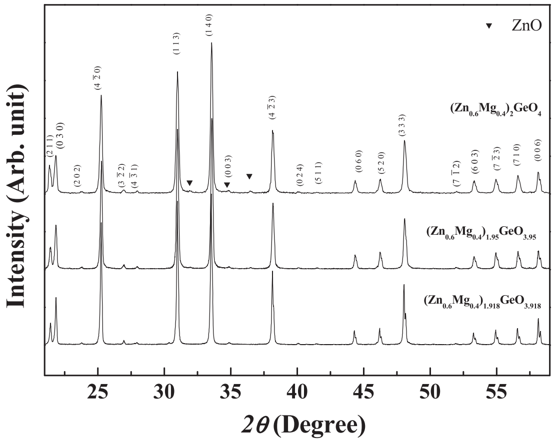

Fig. 1. XRD patterns of $(Zn_{0.6}Mg_{0.4})_2GeO_4$, $(Zn_{0.6}Mg_{0.4})_{1.95}GeO_{3.95}$, and $(Zn_{0.6}Mg_{0.4})_{1.918}GeO_{3.918}$ sintered at 1300 °C for 4 h.