

Short Communication

Effects of B_2O_3 - V_2O_5 on Sinterability and Microwave Dielectric Properties of $(Mg_{1-x}Cu_x)_2SiO_4$ Ceramics

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Abstract

The crystal structure, microstructure, and microwave dielectric properties of B_2O_3 - V_2O_5 co-doped $(Mg_{1-x}Cu_x)_2SiO_4$ ($x=0.05-0.20$) ceramics were investigated. The sintering temperature was successfully reduced to about 1250 °C/4 h for the B_2O_3 - V_2O_5 co-doped $(Mg_{1-x}Cu_x)_2SiO_4$ specimens. The $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 -6 wt% V_2O_5 ceramics sintered at 1250 °C for 4 h achieved excellent microwave dielectric properties of $\epsilon_r = 6.55$, $Q \cdot f = 37\,500$ GHz and a τ_f of -35.65 ppm/K.

Keywords: Microwave dielectric properties, B_2O_3 - V_2O_5 co-doped, $(Mg_{0.95}Cu_{0.05})_2SiO_4$, microwave ceramics

I. Introduction

A significant amount of interest has been observed in low-permittivity microwave dielectric materials with a high quality factor ($Q \cdot f$) because of the expanding frequency ranges of microwave wireless communications. Low permittivity can minimize cross-coupling with conductors and shorten the time for the electronic signal transition, and the high quality factor can increase selectivity and simplify the heat-dispersing structure¹⁻³. Forsterite Mg_2SiO_4 ceramics with high performance have been particularly considered because of their low-cost, easily processable, and lightweight characteristics. Recently, the modification of the microwave dielectric properties of forsterite ceramics has been reported with the addition of additives or formation of solid solutions⁴.

Compared to Mg^{2+} , Cation ($M = Cu^{2+}$, Co^{2+} , and Fe^{2+}) can be expected to tailor the τ_f value of the forsterite ceramic owing to its relatively small ionic radius. Cu^{2+} doping affects the dielectric properties (especially the temperature coefficient τ_ϵ of the dielectric constant ϵ_r) and thermal expansion coefficient (α_L) by altering the microstructure, phase composition, and lattice vibration modes of the ceramics, ultimately achieving the regulation of the temperature coefficient of the resonant frequency (τ_f). To our knowledge, the literature on the microwave dielectric properties and the structure of the copper-doped Mg_2SiO_4 system is sparse. Furthermore, the optimum sintering temperature of $(Mg_{1-x}Cu_x)_2SiO_4$ is remarkably high in the current reports on microwave dielectric ceramics. Therefore, 6 wt% B_2O_3 and 6 wt% V_2O_5 were used as sintering aids, to decrease its sintering temperature down to a medium temperature or even a low range. In the present work, we have reported on the fabri-

cation of $(Mg_{1-x}Cu_x)_2SiO_4$ ceramics based on a sol-gel method. The impacts of additive B_2O_3 - V_2O_5 on the phase compositions, microstructure and microwave dielectric properties have been investigated for the first time.

II. Experimental Procedure

All chemicals were analytical-grade reagents and used as received without further purification. All experiments were conducted in air. $(Mg_{1-x}Cu_x)_2SiO_4$ powders were synthesized using the sol-gel method. For this purpose, $Mg(NO_3)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ were dissolved individually in 100 ml ethanol and 10 ml distilled water and then added into the mixture under magnetic stirring, marked as A. Tetraethyl orthosilicate (TEOS) and $CuSO_4$ were used as received. The starting sol was prepared by hydrolysis of TEOS under magnetic stirring in the presence of 100 ml alcohol solution in 40 °C water for 30 min, marked as B. Subsequently, the B solution was added to A by means of continuous magnetic vigorous stirring for 3 h at 40 °C water and then kept at 60 °C overnight to allow gel formation. Finally, the obtained products were dried and calcined at 900 °C for 4 h to obtain $(Mg_{1-x}Cu_x)_2SiO_4$ powders. The prepared powders were divided into two groups. The first group was not doped, while the second group was doped with B_2O_3 - V_2O_5 . Both groups of powders were pressed individually with a polyvinyl alcohol water solution into cylindrical compacts with the diameter of 11.5 mm under a uniaxial pressure of 120 MPa. The undoped compacts were placed in an alumina crucible and heated to sintering temperatures varying from room temperature to 1350 °C at a rate of 5 K/min. After being sintered for 4 h in air atmosphere, the compacts were freely cooled down to room temperature inside the furnace. The B_2O_3 - V_2O_5

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doped $(\text{Mg}_{1-x}\text{Cu}_x)_2\text{SiO}_4$ ceramics were sintered at 1 000–1 350 °C for 4 h.

The XRD patterns obtained on a D/max-2550V/PC X-ray diffractometer (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation at a scan rate $2\theta = 0.02 \text{ s}^{-1}$ were used to identify the crystalline phases. The morphology of the prepared samples was characterized by means of high-resolution transmission electron microscopy (JEM-2100, Japan) and scanning electron microscopy (SEM, FEI-quanta200, USA). The X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an AXIS ULTRA spectrometer (Kratos Analytical Ltd, Japan) with a monochromatic Al.

The bulk densities of the sintered pellets were measured with the Archimedes method using distilled water as the medium. The phase evolution of the $(\text{Mg}_{1-x}\text{Cu}_x)_2\text{SiO}_4$ ceramics was analyzed by means of XRD. The microstructures were observed on the as-sintered ceramic surfaces of samples by means of scanning electron microscopy (SEM, FEI-quanta 200, USA). Cylindrical samples with a diameter of about 10 mm and thickness of about 5 mm were used for evaluation of the microwave dielectric properties. Dielectric behaviors at microwave frequency were measured with the $\text{TE}_{01\delta}$ shielded cavity method by means of a vector network analyzer (ZVB20, Rohde & Schwarz, Germany). The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \cdot (80 - 25)} \quad (1)$$

where f_{80} and f_{25} were the $\text{TE}_{01\delta}$ resonant frequency measured at 80 °C and 25 °C, respectively.

III. Results and Discussion

Fig. 1(a) shows the XRD patterns of $(\text{Mg}_{1-x}\text{Cu}_x)_2\text{SiO}_4$ ($x=0.05-0.20$) ceramics sintered at 1 350 °C for 4 h. It can be seen that all the main diffraction peaks can be well indexed to the standard patterns of Mg_2SiO_4 (PDF#72-0296), indicating that the forsteritic-olivine solid solution was formed as a single phase. Very little protoenstatite Mg_2SiO_3 secondary phase appeared along with the main phase Mg_2SiO_4 in all compositions, which is similar to the results reported by J. Li *et al.*¹⁰. A possible reason might be that the amount of MgO is sufficient so that it could not react with MgSiO_3 secondary phase to form Mg_2SiO_4 . Moreover, as shown in the Fig. 1(b), with an increase in the Cu content (x), the main peak of Mg_2SiO_4 shifts slightly toward lower angles, indicating an increase of the unit-cell volume (Fig. 1(c)), these results are similar to those obtained in our previous work¹⁰.

B_2O_3 and V_2O_5 are both known glass formers with relatively low melting points. The literature suggests that the B_2O_3 - V_2O_5 system can form low-temperature eutectics, which we hypothesized would effectively promote liquid-phase sintering at a reduced temperature for the magnesium silicate system. But excessive B_2O_3 and V_2O_5 lead to the formation of unfavorable secondary phases $\text{Mg}_2\text{B}_2\text{O}_5$ or MgV_2O_6 and excessive glass phases, leading to a deterioration in the microwave dielectric properties of the ceramics¹¹⁻¹².

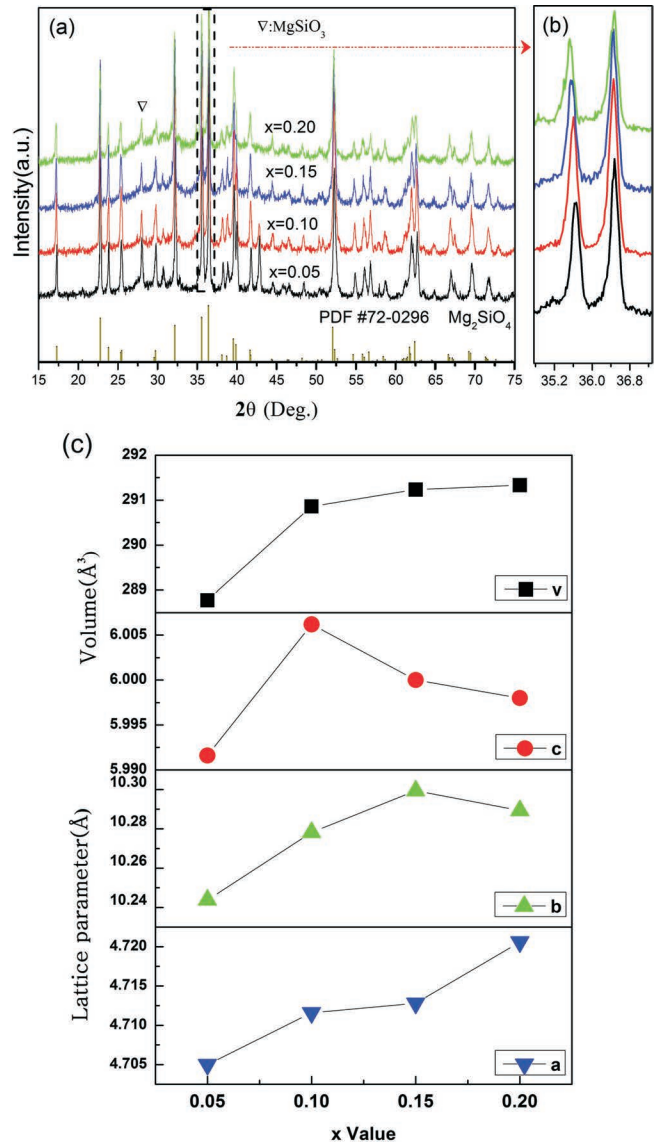


Fig. 1: XRD patterns of $(\text{Mg}_{1-x}\text{Cu}_x)_2\text{SiO}_4$ ($x = 0.05-0.20$) ceramics sintered at 1 350 °C for 4 h.

Fig. 2 shows the variation in the bulk density (ρ) of the $(\text{Mg}_{0.95}\text{Cu}_{0.05})_2\text{SiO}_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 ceramics as a function of sintering temperature. The ρ values increased with rising sintering temperature and reached a maximum value of about 3.20 g/cm³ (relative density corresponding to 97%) at 1 250 °C, before it decreased with a further increase in the temperature. As shown in the inset images in Fig. 2, the variation in microstructure agreed with the change in the bulk density of the specimens. $(\text{Mg}_{0.95}\text{Cu}_{0.05})_2\text{SiO}_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 composite ceramic sintered at 1 150 °C exhibited a porous microstructure with a grain size in a range of 90 ~ 400 nm. With increasing sintering temperature, the grain boundary extended and the sample became more compact. The pores were almost eliminated for the sample sintered at 1 200 °C. However, as the sintering temperature increased further, more and more pores formed owing to overheating, which induced the decrease in the bulk density and led to a deterioration in the microwave dielectric properties of the ceramics.

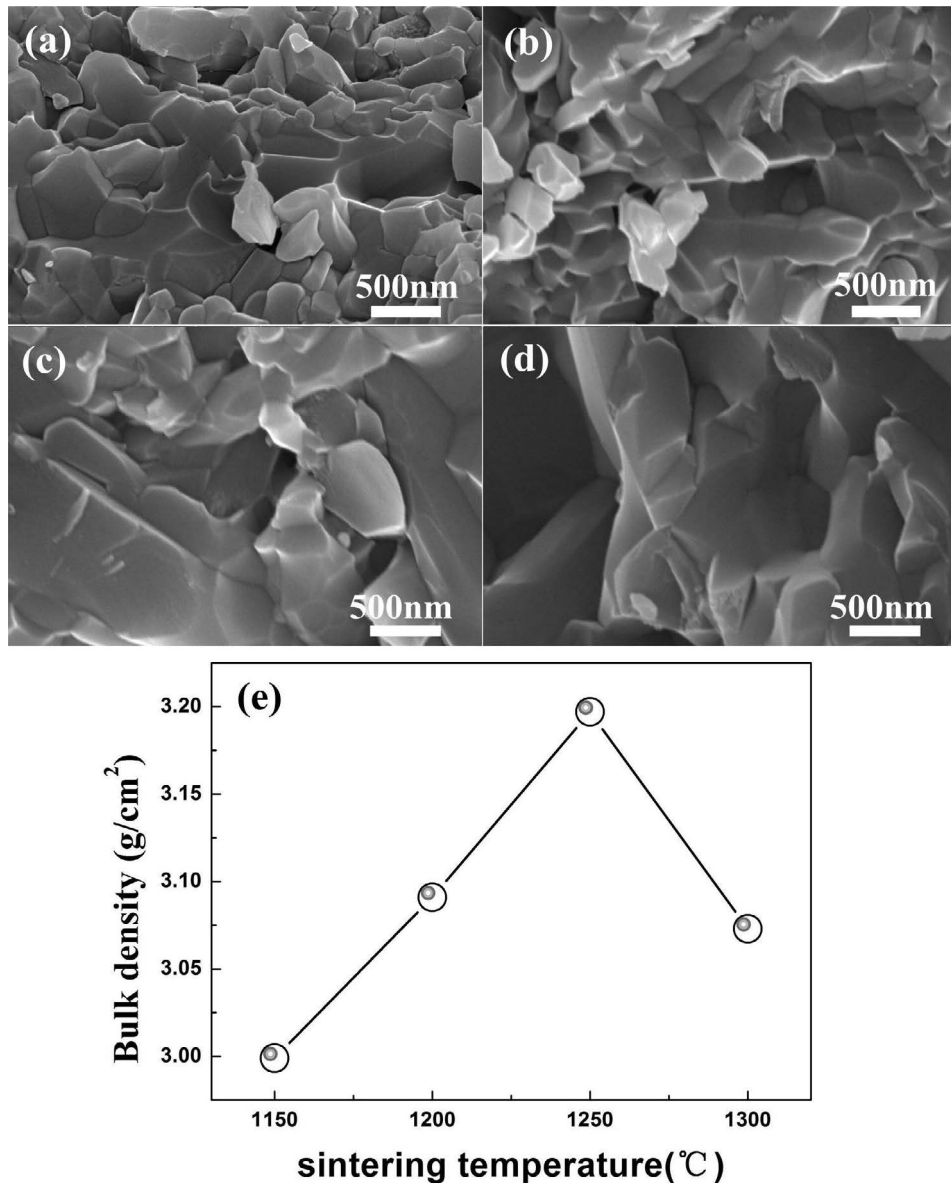


Fig. 2: SEM images of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 sintered at (a) 1150 °C, (b) 1200 °C, (c) 1250 °C, and (d) 1300 °C; (e) Variation of the bulk density of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 sintered at different temperatures.

Fig. 3 shows the XRD patterns of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 ceramics sintered at varying temperature ranging from 1150 to 1300 °C for 4 h. The main phase Mg_2SiO_4 (PDF#72-0296) was detected in all ceramics samples sintered at different temperatures with different secondary phase. The minor secondary phase MgO was found in the samples sintered at 1150, 1200 and 1250 °C and the increasing intensity of its diffraction peak indicates that the MgO content increased with rising sintering temperature, reaching the maximum at 1250 °C. The XRD pattern of the sample sintered at 1250 °C showed coexistence of MgO (PDF 45-0946) and Mg_2SiO_4 (PDF 34-0189). It is well known that these magnesium oxides are beneficial in improving the microwave properties of ceramics. The XRD pattern of the sample sintered at 1300 °C showed a slight amorphous phase and a few impurity phases ($Mg_2B_2O_5$ and MgV_2O_6), which damages the microwave properties of the ceramics.

Fig. 4 shows that the ϵ_r and $Q \cdot f$ values increased with a rise in the sintering temperature up to 1250 °C and then slightly decreased with the further rise in the sintering temperature. The optimized $Q \cdot f$ value 37500 GHz was obtained at 1250 °C, while a further increase in sintering temperature remarkably led to a decrease in the $Q \cdot f$ values. It is well known that ϵ_r is dependent on the density, polarizabilities, phase composition, and structural characteristics, while the $Q \cdot f$ values are affected not only by these factors but also by the crystal vibration mode, secondary phase, densification and crystal defect⁶⁻⁹. In this work, the observed change trend in ϵ_r and $Q \cdot f$ values of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 is attributed primarily to variations in bulk density (see Fig. 3).

The ionic radius of Cu^{2+} (0.73 Å) is remarkably close to that of Mg^{2+} (0.72 Å). This proximity allows Cu^{2+} to readily intercalate into the magnesium olivine (Mg_2SiO_4) lattice, displacing Mg^{2+} from its octahedral positions. Although the radii are close, Cu^{2+} is a Jahn-Teller ion

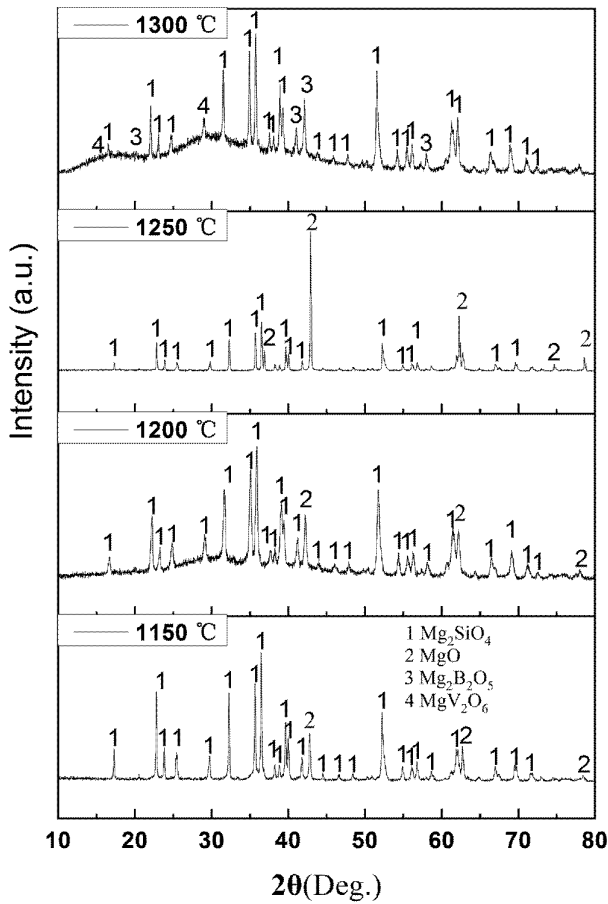


Fig. 3: XRD patterns of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 – 6 wt% V_2O_5 ceramics sintered at varying temperature ranging from 1150 to 1300 °C.

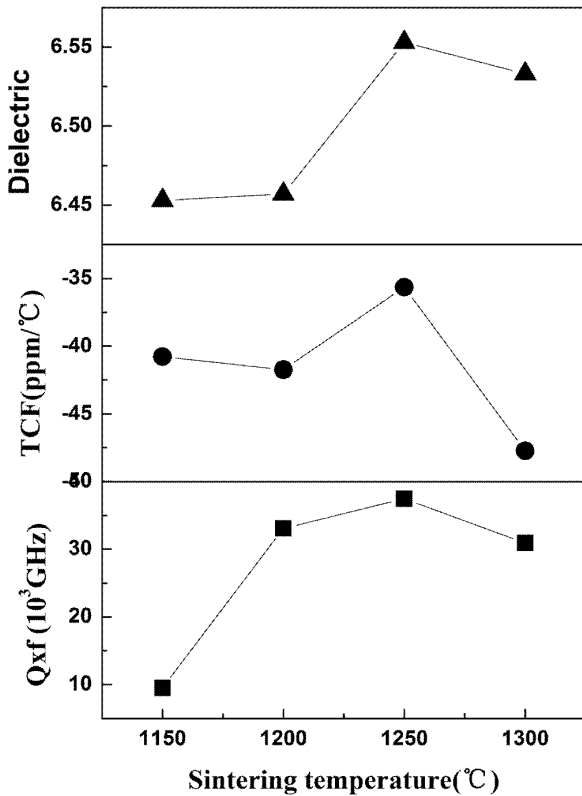


Fig. 4: Dielectric constant ϵ_r , quality factor $Q \times f$, and temperature coefficient of resonant frequency τ_f of $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 – 6 wt% V_2O_5 as a function of sintering temperature.

that tends to distort the surrounding oxygen octahedrons (stretching or flattening them). This distortion changes the overall stiffness of the lattice. Dielectric responses at microwave frequencies are closely related to lattice vibrations (optical phonons).

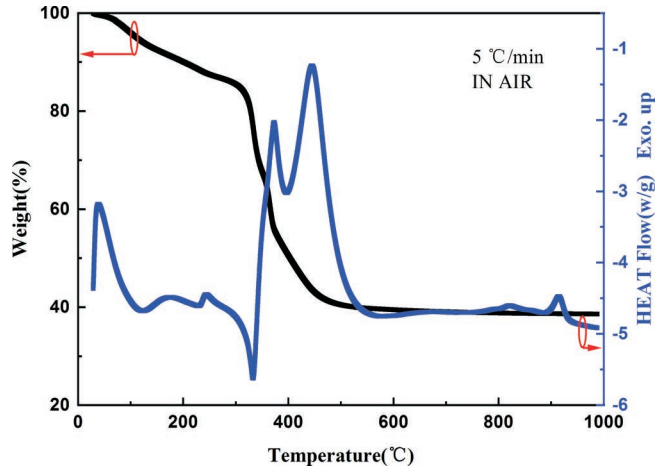


Fig. S1: The DTA/TG curves of $(Mg_{1-x}Cu_x)_2SiO_4$ gel under an air atmosphere with a heating rate of 5 K/min.

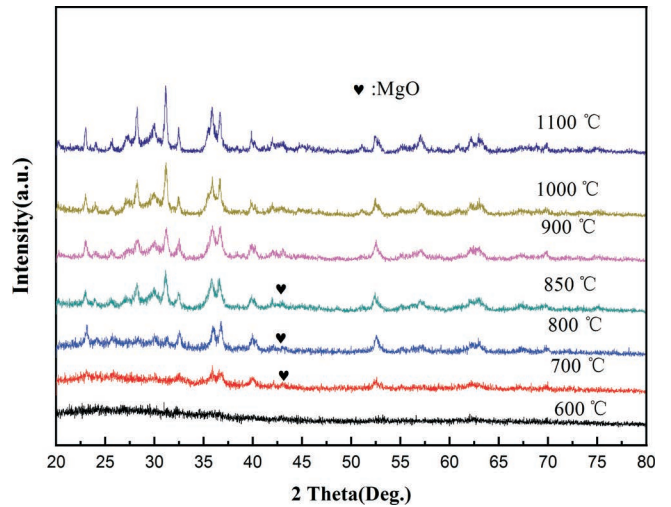


Fig. S2: XRD patterns of $(Mg_{1-x}Cu_x)_2SiO_4$ gel under at different temperatures.

Lattice distortion alters the vibration frequencies and modes of these phonons, thereby directly affecting the temperature coefficient of dielectric constants (τ_ϵ). τ_ϵ fundamentally reflects the sensitivity of the lattice polarization rate to temperature changes, which is directly linked to lattice vibrations. By changing the lattice vibration characteristics, Cu doping can directly calibrate the value τ_ϵ so that it moves in a direction more favorable to $\tau_f \approx -(\frac{1}{2}\tau_\epsilon + \alpha_L) = 0$

The τ_f values of the ceramics, on the other hand, appeared to be a small change (from -45 ~ -35 ppm/K) to sintering temperature, as shown in Fig. 4(c).

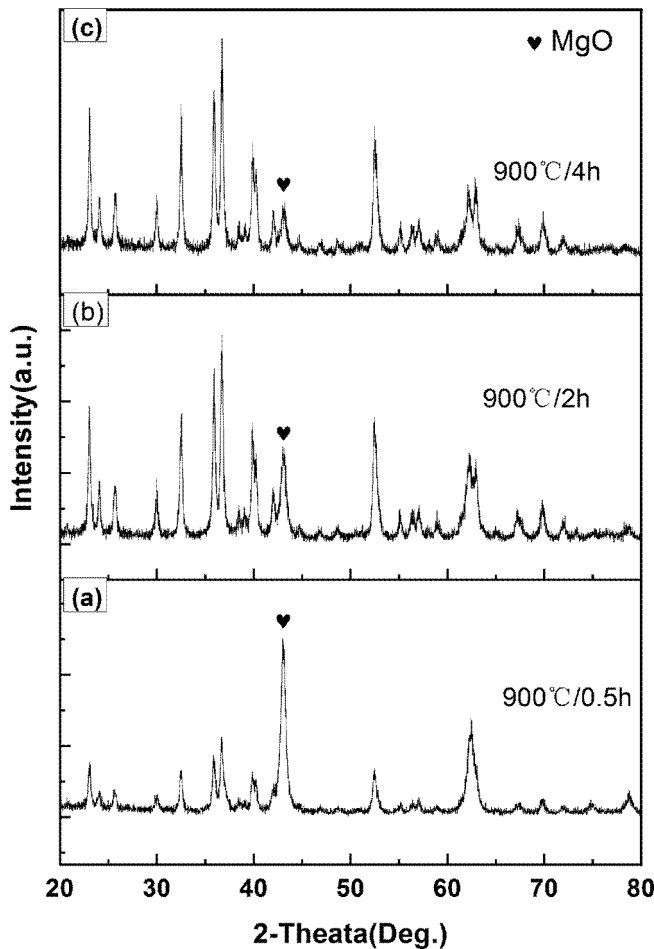


Fig. S3: XRD patterns of $(Mg_{1-x}Cu_x)_2SiO_4$ gel calcined at 900 °C with different duration times.

IV. Conclusions

The microwave dielectric properties of $(Mg_{1-x}Cu_x)_2SiO_4$ ($x = 0.05 - 0.20$) ceramics were investigated in terms of their structural characteristics, microstructure, as well as the sintering behavior. The results demonstrate that the Cu substitution not only significantly boosts the sintering behavior but also improves the microwave dielectric properties of the ceramics. The $(Mg_{0.95}Cu_{0.05})_2SiO_4$ with 6 wt% B_2O_3 - 6 wt% V_2O_5 ceramics sintered at 1250 °C for 4 h achieved excellent microwave dielectric properties of $\epsilon_r = 6.55$, $Q \cdot f = 37\,500$ GHz and a τ_f of -35.65 ppm/K and are proposed as a suitable material for millimeter-wave devices.

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