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Phase Composition, Crystal Structure, and Microwave Dielectric Properties of 4BaO-4SiO$_2$-V$_2$O$_5$ Composite Ceramic

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4BaO-4SiO$_2$-V$_2$O$_5$ composite ceramic has been prepared by a solid-state reaction method and its phase composition, microstructure, and microwave dielectric properties investigated. The 4BaO-4SiO$_2$-V$_2$O$_5$ composite ceramic was made up of BaSi$_2$O$_5$, Ba$_3$(VO$_4$)$_2$, and SiO$_2$. The presence of BaSi$_2$O$_5$ and SiO$_2$ would decrease the relative permittivity (ε_r) and $Q \times f$ value and optimize the temperature coefficient of resonant frequency (τ_f). The fired density, $Q \times f$, ε_r, and τ_f values of the ceramic showed similar trends with increasing sintering temperature. The ceramic sintered at 1050°C exhibited the best microwave dielectric properties with $Q \times f$ of 24,300 GHz, ε_r of 8.3, and τ_f of 29.6 ppm/°C.

Key words: Composite ceramic, microwave dielectric properties, phase structure

INTRODUCTION

With the rapid development of electronic circuits for integration and high-frequency applications, microwave components must offer good stability, low price, and high potential for integration,[1–4] requiring that microwave dielectric materials have high quality factor ($Q \times f$), low permittivity (ε_r), and near-zero temperature coefficient of resonant frequency (τ_f).[5,6] Many ceramics show good microwave dielectric properties, including Mg$_2$SiO$_4$,[7] MgTiO$_3$,[8] and Ba(Zn$_{1/3}$Nb$_{2/3}$)O$_3$.[9] However, their high sintering temperatures (above 1200°C) result in high production costs. To reduce the sintering temperature of ceramics, three methods are usually adopted, i.e., use of sintering aids, superfine powders, and raw materials with low melting point.[10–12] Addition of sintering aids seriously degrades the microwave dielectric properties of the material. Synthesis of superfine powders makes the preparation process more complicated, resulting in high cost. Therefore, many studies have focused on the search for materials with low sintering temperature and good microwave dielectric properties.

Recently, Zhuang et al.[13] reported that Ba$_3$(VO$_4$)$_2$ ceramic sintered at 1100°C showed excellent microwave dielectric properties with $Q \times f$ value of 42,200 GHz, ε_r of 14.2, and τ_f of 52.3 ppm/°C. Fang et al.[14] reported that SiO$_2$ exhibited good microwave dielectric properties with $Q \times f$ value of 80,400 GHz, ε_r of 3.8, and τ_f of −16.1 ppm/°C. It can be expected that a microwave dielectric material with high $Q \times f$ value, low ε_r, and near-zero τ_f value could be obtained by combining Ba$_3$(VO$_4$)$_2$ with BaSi$_2$O$_5$ and SiO$_2$. In the present work, the 4BaO-4SiO$_2$-V$_2$O$_5$ composite ceramic was designed and prepared by solid-state reaction method and its phase composition, surface morphology, sintering behavior, and microwave dielectric properties investigated.

EXPERIMENTAL PROCEDURES

4BaO-4SiO$_2$-V$_2$O$_5$ ceramic was prepared by the solid-state reaction method. High-purity raw powders of BaCO$_3$ (≥99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), V$_2$O$_5$ (≥99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and SiO$_2$ (quartz, ≥99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, quartz) were stoichiometrically weighed and ball milled with zirconia ball in alcohol (ethanol) medium for 4 h. The mixture was calcined at 800°C in air for 2 h after drying. The calcined powders were ball-milled for 4 h again. After drying, the powders were granulated with 5 wt.% polyvinyl alcohol (PVA) and pressed into disks with 12 mm diameter and 6 mm thickness under uniaxial pressure of ∼200 MPa. The disks were heated to 550°C in air for 4 h with heating rate of 1°C/min, and sintered at 1000°C to 1100°C in air for 2 h. At the same time, BaSi$_2$O$_5$ ceramic was prepared by the above process. The calcination and sintering conditions for the ceramics were 1150°C and 1175°C to 1275°C in air for 2 h, respectively.

The crystalline structure of the sintered samples was investigated by x-ray diffraction (XRD) analysis using Cu K$_\alpha$ radiation generated at 40 kV and 40 mA (X'Pert PRO, PANalytical, Almelo, The Netherlands), collecting XRD data over 1 h in the 2θ range from 10° to 80°. The surface morphology of the ceramics was studied by scanning electron microscopy (SEM, JSM6380-LV, JEOL, Tokyo, Japan), and their constituents were analyzed by energy-dispersive spectrometry (EDS). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Scientific) was used to investigate the chemical state of elements. Thermogravimetric analysis of the calcined powders was carried out using a Netzsch STAR449F3 analyzer. The powders were heated in an alumina crucible under nitrogen protective gas from 500°C to 1100°C at rate of 10°C/min. The fired density of the ceramics was determined by the weight–volume method. Their dielectric behavior at microwave frequencies was measured using the TE$_{01\delta}$ shielded cavity method with a network analyzer (N5230A, Agilent Co., CA, 10 MHz to 40 GHz). The temperature coefficient of resonant frequency (τ_f) was measured by the open cavity method using an Invar cavity in a temperature chamber (DELTA 9039, Delta Design, USA) in T$_{011}$ mode. The τ_f values were calculated using the formula

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)}, \tag{1}$$

where f_T and f_0 are the resonant frequencies at temperature of T (85°C) and T_0 (25°C), respectively.

RESULTS AND DISCUSSION

The XRD patterns of the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures are shown in Fig. 1a. All ceramics showed presence of Ba$_3$(VO$_4$)$_2$ (PDF: 00-029-0211), BaSi$_2$O$_5$ (PDF: 01-072-0171), and SiO$_2$ (PDF: 00-039-1425), with Ba$_3$(VO$_4$)$_2$ as main phase. The crystalline properties of the ceramic changed with increasing sintering temperature. The TG curve of the calcined 4BaO-4SiO$_2$-V$_2$O$_5$ powders in the measured temperature range of 500°C to 1100°C is illustrated in Fig. 1b, indicating evaporation of V^{5+}, which can deteriorate the crystallinity of the ceramic. For sintering temperature below 1050°C, the effect of temperature on the crystallinity is greater than that of V^{5+} evaporation, and the crystalline properties of the ceramics improved with increasing sintering temperature. Melting of Ba$_3$(VO$_4$)$_2$ phase could be observed when the sintering temperature was about 1050°C. A small amount of liquid phase could promote the sintering behavior of the ceramic, so the crystalline properties continued to improve. However, due to massive melting of Ba$_3$(VO$_4$)$_2$, the crystalline properties of the ceramic deteriorated with further increase of the sintering temperature. The whole-pattern fitting method was used to calculate the relative content of each phase, and the results are presented in Table I. The relative content of each phase changed with increasing sintering temperature, due to grain melting, changing the intensity of each diffraction peak.

Figure 2 shows SEM images of the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures. All samples showed strip, square, and granular grains. The grains gradually grew with increasing sintering temperature from 1000°C to 1025°C. For sintering temperature of 1050°C, the grain size of the ceramic was larger than for the sample sintered at 1025°C, but some strip grains began to melt. The sintering temperature of pure Ba$_3$(VO$_4$)$_2$ is ∼1100°C.[13] However, Ba$_3$(VO$_4$)$_2$ could act as a low-temperature sintering additive, and melting of Ba$_3$(VO$_4$)$_2$ was observed at 950°C in the Li$_2$Zn$_3$Ti$_4$O$_{12}$-Ba$_3$(VO$_4$)$_2$ system, indicating that the second phase has an effect on the melting point of Ba$_3$(VO$_4$)$_2$.[15] As a result, Ba$_3$(VO$_4$)$_2$ melted below 1100°C in the 4BaO-4SiO$_2$-V$_2$O$_5$ multiphase system. The phenomenon of strip grain melting became more obvious for sintering temperature of 1075°C. Figure 3 shows a backscattered electron image and EDS analysis of the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at 1050°C for 2 h. From the backscattered electron image, it can be seen that there are three kinds of crystal structures, including square, strip, and granular crystals, marked as "I," "II," and "III," respectively. Grain I contained Si, Ba, and O elements, with atomic number ratio of Si and Ba elements of 2:1. Grain II was composed of V, Ba, and O elements, with atomic number ratio of V and Ba elements close to 2:3. Grain III comprised V, Ba, Si, and O elements. Due to the small grain size and the influence of Ba$_3$(VO$_4$)$_2$ grains, grain III contained Ba and V. After eliminating these influential factors, we concluded that grain III was SiO$_2$. These
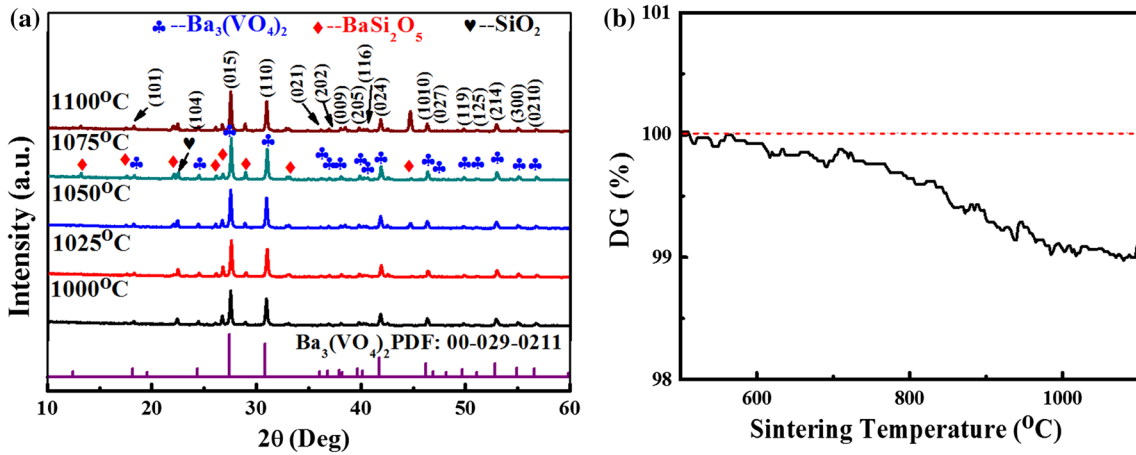
Fig. 1. (a) XRD patterns of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures. (b) TG curve of calcined 4BaO-4SiO$_2$-V$_2$O$_5$ powder in the measured temperature range of 500 to 1100°C.

Table I. Relative content of each phase in 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures

Condition	Phase	PDF code	wt.%	Parameters
4BaO-4SiO$_2$-V$_2$O$_5$ (1000°C)	Ba$_3$(VO$_4$)$_2$	00-029-0211	68	R_{WP} = 8.1%
	BaSi$_2$O$_5$	01-072-0171	15	R_P = 4.8%
	SiO$_2$	00-039-1425	17	R_B = 3.7%
4BaO-4SiO$_2$-V$_2$O$_5$ (1025°C)	Ba$_3$(VO$_4$)$_2$	00-029-0211	66	R_{WP} = 8.5%
	BaSi$_2$O$_5$	01-072-0171	18	R_P = 5.6%
	SiO$_2$	00-039-1425	16	R_B = 2.8%
4BaO-4SiO$_2$-V$_2$O$_5$ (1050°C)	Ba$_3$(VO$_4$)$_2$	00-029-0211	62	R_{WP} = 6.8%
	BaSi$_2$O$_5$	01-072-0171	24	R_P = 4.3%
	SiO$_2$	00-039-1425	14	R_B = 2.5%
4BaO-4SiO$_2$-V$_2$O$_5$ (1075°C)	Ba$_3$(VO$_4$)$_2$	00-029-0211	58	R_{WP} = 7.9%
	BaSi$_2$O$_5$	01-072-0171	26	R_P = 5.1%
	SiO$_2$	00-039-1425	16	R_B = 3.4%
4BaO-4SiO$_2$-V$_2$O$_5$ (1100°C)	Ba$_3$(VO$_4$)$_2$	00-029-0211	55	R_{WP} = 7.2%
	BaSi$_2$O$_5$	01-072-0171	27	R_P = 4.5%
	SiO$_2$	00-039-1425	18	R_B = 3.0%

results confirm that the samples contained BaSi$_2$O$_5$, Ba$_3$(VO$_4$)$_2$, and SiO$_2$ crystals.

Vanadium exists in a variety of valences including V(II), V(III), V(IV), and V(V), among which V(IV) and V(V) are relatively stable. X-ray photoelectron spectroscopy was used to determine the valences of V. Figure 4 shows the photoelectron spectra of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at 1050°C for 2 h. All peaks are based on the standard of C 1s peak at 284.8 eV. The binding energies of V 2$p_{3/2}$ and V 2$p_{1/2}$ for 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic were found at 517.08 eV and 524.42 eV, respectively, in good agreement with that of V$_2$O$_5$ (V 2$p_{3/2}$ and V 2$p_{1/2}$ at 517.20 eV and 524.50 eV, respectively).[16] Compared with the photoelectron spectrum of V, the valence of V for the 4BaO-4SiO$_2$-V$_2$O$_5$ samples was V(V).

Figure 5 shows the fired density, relative permittivity, $Q \times f$, and τ_f values of the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic as functions of sintering temperature. On the one hand, melting of Ba$_3$(VO$_4$)$_2$ phase and

evaporation of V^{5+} from the bulk of the pellet could cause a decrease in the fired density. On the other hand, the fired density was also affected by the porosity. Due to the decrease of the porosity, the fired density of the samples gradually increased from 3.77 g/cm^3 to 3.83 g/cm^3 with increasing sintering temperature from 1000°C to 1025°C. Although some Ba$_3$(VO$_4$)$_2$ grains began to melt, the densification degree of the ceramic sintered at 1050°C was higher than that of the ceramic sintered at 1025°C. So, the fired density of the ceramics reached a maximum value of 3.98 g/cm^3 at 1050°C. With further increase of the sintering temperature, the phenomenon of Ba$_3$(VO$_4$)$_2$ grain melting became more obvious, and the fired density of the samples began to decline.

The microwave losses of a dielectric material include intrinsic and extrinsic loss. Intrinsic loss is contributed by internal vibrations of atoms, ions, or electrons in the material, whereas extrinsic loss is caused by porosity, crystal defects, phase
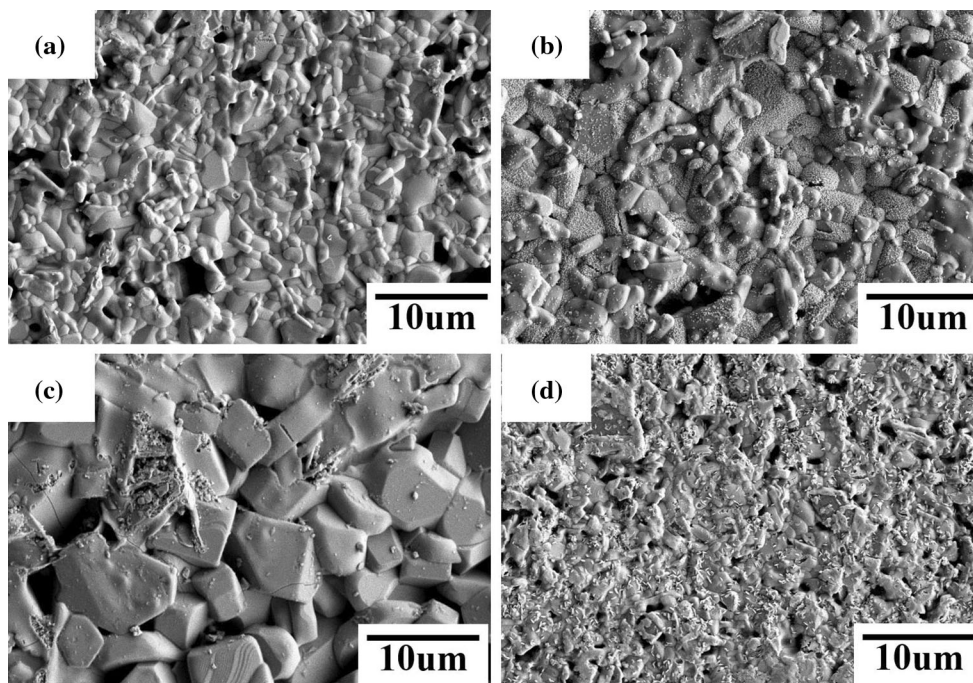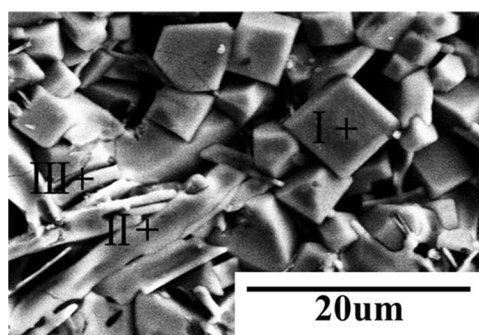
Fig. 2. SEM images of 4BaO-4SiO₂-V₂O₅ ceramic sintered at: (a) 1000°C, (b) 1025°C, (c) 1050°C, and (d) 1075°C.

Grains	Element Atomic (%)			
	Ba	Si	V	O
I	11.54	24.57	-	63.89
II	30.82	-	18.29	50.98
III	29.74	3.71	16.46	50.09

Fig. 3. Backscattered electron image and EDS of 4BaO-4SiO₂-V₂O₅ ceramic sintered at 1050°C for 2 h.
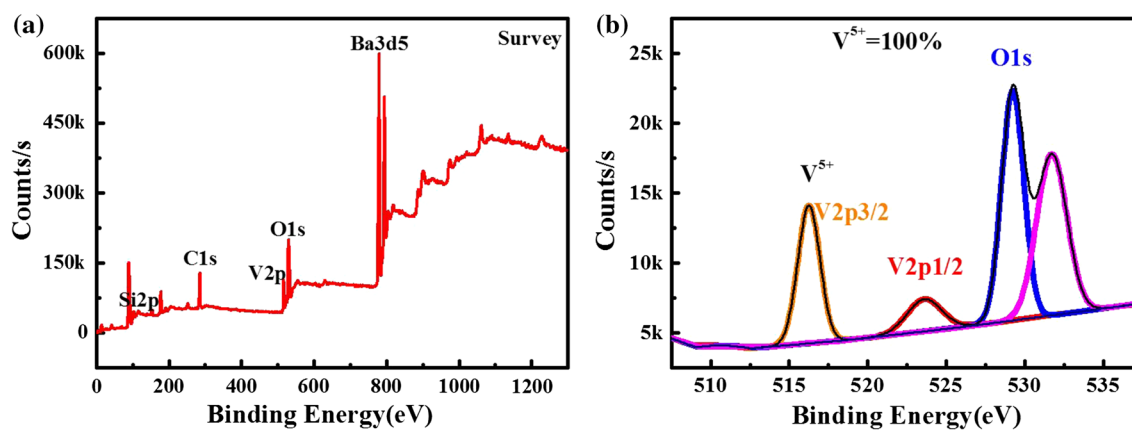

Fig. 4. Survey spectrum (a) and high-resolution XPS of V 2p (b) for 4BaO-4SiO₂-V₂O₅ ceramic sintered at 1050°C for 2 h.
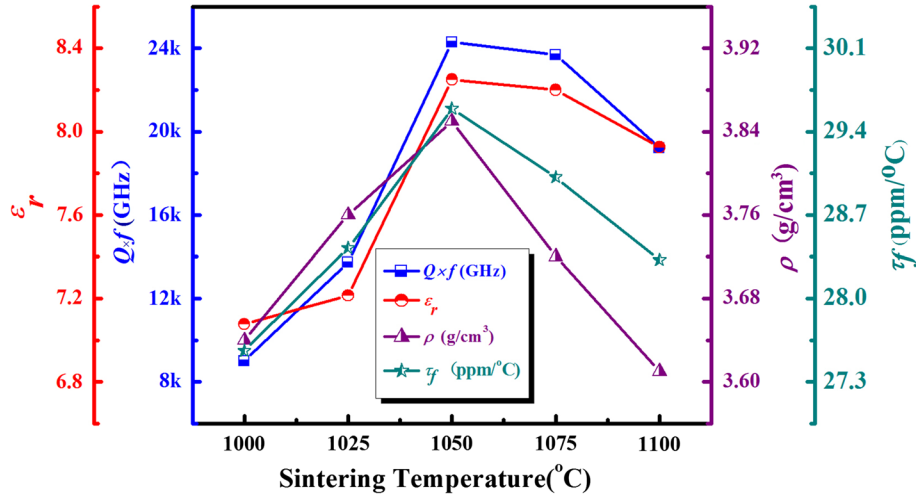
Fig. 5. Fired density, relative permittivity, $Q \times f$, and τ_f values of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic as functions of sintering temperature.

Table II. Microwave dielectric properties of BaSi$_2$O$_5$ ceramic

Sintering temperature (°C)	Fired density (g/cm³)	Relative permittivity	$Q \times f$ (GHz)	τ_f (ppm/°C)
1175	3.47	5.9	11,516	–
1200	3.54	6.8	12,047	–
1225	3.64	7.1	15,040	−57.8
1250	3.62	7.0	12,208	–
1275	3.59	7.0	10,092	–

composition, grain size, and phase transition in ceramics.[17,18] The $Q \times f$ values of ceramics are mainly affected by the density, grain size, and phase composition.[19,20] As shown in Fig. 5, the $Q \times f$ value and fired density of the ceramics presented similar trends. For sintering temperature of 1000°C to 1050°C, the fired density of the ceramics was enhanced with increasing sintering temperature, so the $Q \times f$ value increased from 9005 GHz to 24,300 GHz. The $Q \times f$ values decreased with further increase of the sintering temperature from 1050°C to 1100°C. This phenomenon was caused by the following reasons: Firstly, the fired density of the ceramics began to decline, leading to the decrease of the $Q \times f$ value. Secondly, with increasing sintering temperature, the increasing amount of BaSi$_2$O$_5$ phase with low $Q \times f$ value would increase the dielectric loss of the ceramics (as seen in Table II).

Microwave dielectric ceramics are mainly composed of grains, grain boundaries, and pores. Increase of the average grain size and decrease of the pore per unit volume will improve the relative permittivity.[21] The phase composition also has a great effect on the relative permittivity of ceramics.[22] The relative permittivity and fired density showed the same tendency with increasing sintering temperature. Due to the change of the porosity,

grain size, and relative content of each phase, the permittivity increased from 7.1 to 8.3 then decreased to 7.9, with increasing sintering temperature.

In general, the temperature coefficient of resonant frequency (τ_f) for a multiphase composite system follows the law of mixtures. As presented in Table III, the temperature coefficient of resonant frequency for Ba$_3$(VO$_4$)$_2$, BaSi$_2$O$_5$, and SiO$_2$ ceramics is 52.3 ppm/°C, −57.8 ppm/°C, and −16.1 ppm/°C, respectively.[23] Therefore, the temperature coefficient of resonant frequency for the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic should range from −57.8 ppm/°C to 52.3 ppm/°C. τ_f is usually defined as

$$\tau_f = -\alpha - 1/2\tau_\varepsilon, \qquad (2)$$

where α is the thermal expansion coefficient and τ_ε is the temperature coefficient of permittivity. Table III presents the calculated and measured τ_f values for the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures (assuming α is 10 ppm/°C). With increasing sintering temperature, the measured τ_f value exhibits a similar trend to the calculated τ_f value. There is a small difference between the measured and calculated τ_f value for each sintering temperature. As shown in Fig. 5, the change trend of the τ_f values for the ceramic was similar to that exhibited by the fired density: the τ_f

Table III. Calculated and measured τ_f values of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic sintered at different temperatures

Sintering temperature (°C)	Calculated value (ppm/°C)	Measured value (ppm/°C)
1000	20.6	27.6
1025	21.2	28.4
1050	25.4	29.6
1075	24.6	29.0
1100	21.6	28.3

Table IV. Comparison of microwave dielectric properties of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic versus other systems

Ceramic composition	Sintering temperature (°C)	Relative permittivity	$Q \times f$ (GHz)	τ_f (ppm/°C)	Refs.
Ba$_3$(VO$_4$)$_2$	1100	14.2	42,200	52.3	13
ZnAl$_2$O$_4$	1425	8.5	60,000	−79	23
Ca$_3$Si$_2$O$_7$	1300	7.8	28,400	10	24
SiO$_2$	1650	3.8	80,400	−16.1	14
BaSi$_2$O$_5$	1225	7.1	15,040	−57.8	Our work
4BaO-4SiO$_2$-V$_2$O$_5$	1050	8.3	24,300	29.6	Our work

values increased to a maximum of 29.6 ppm/°C then decreased with increasing sintering temperature.

Table IV compares the microwave dielectric properties of the 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic with those of other systems. ZnAl$_2$O$_4$[24] and Ca$_3$Si$_2$O$_7$ ceramics[25] demonstrate good microwave dielectric properties with low permittivity and high $Q \times f$ value. However, high sintering temperature restricts their further application. By contrast, 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic has a relatively low sintering temperature of 1050°C with good microwave dielectric properties of $Q \times f$ = 24,300 GHz, ε_r = 8.3, and τ_f = 29.6 ppm/°C, indicating that this material has potential for application in microwave devices with low cost.

CONCLUSIONS

The phase evolution, sintering behavior, and microwave dielectric properties of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic were investigated. The ceramic contained mixed phases BaSi$_2$O$_5$, Ba$_3$(VO$_4$)$_2$, and SiO$_2$. The presence of BaSi$_2$O$_5$ and SiO$_2$ would decrease the relative permittivity, $Q \times f$, and τ_f values. The fired density, relative permittivity, $Q \times f$, and τ_f values increased to a maximum then decreased with increasing sintering temperature from 1000°C to 1100°C. The best properties of ρ = 3.98 g/cm^3, $Q \times f$ = 24,300 GHz, ε_r = 8.3, and τ_f = 29.6 ppm/°C were obtained for the ceramic sintered at 1050°C for 2 h. The low fired density, high $Q \times f$ value, small ε_r value, and low sintering temperature of 4BaO-4SiO$_2$-V$_2$O$_5$ ceramic could meet the requirements of light weight, high frequency, stability, and low cost of microwave dielectric materials. However, the mixed phases raise issues regarding the stability and reproducibility of such ceramics, hindering their application.

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