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Controllable τ_f value of barium silicate microwave dielectric ceramics with different Ba/Si ratios

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Abstract

$Ba_{1+1/M}[Si_2O_{5+1/M}]$ low-permittivity microwave dielectric ceramics are prepared using the conventional solid-state method. Pure phases are obtained in barium silicates with M=1, 3, 4, 5, and ∞, except for M=7, in which two phases, $Ba_5Si_8O_{21}$ and $BaSi_2O_5$, are observed. As the complexity of the crystal structure described by the Shannon information per reduced unit cell increases, the τ_f value tends to change from a negative to a positive value, except for M=5, which has the highest complexity. A single $Ba_5Si_8O_{21}$ phase with ε_r anomaly peak at −180 °C exhibits a rare positive τ_f value (+25 ppm/°C), which is a novel temperature compensator.

Keywords: Silicates; Electroceramics; Dielectric properties

1. Introduction

Low-permittivity ($\varepsilon_r < 15$) silicate microwave dielectric ceramics such as M_2SiO_4 (M=Ba, Zn, Mg, Co, and Ni),[1,2] $(Sr_{1-x}A_x)_2(Zn_{1-x}B_x)Si_2O_7$ (A=Ca, Ba and B=Co, Mg, Mn, Ni),[3-6] $MAl_2Si_2O_8$ (M=Ba, Sr, and Ca),[7,8] $Mg_2Al_4Si_5O_{18}$,[9] $Sr_2Al_2SiO_7$,[10] and $LiRe_9(SiO_4)_6O_2$ (Re=rare earth elements),[11] have attracted considerable scientific attention because they can be used for various applications, such as high-frequency substrates, wave-transparent windows, dielectric antennas, high-accuracy capacitors, and millimeter-wave components. Low-permittivity can reduce reflection at the interface between air and dielectrics, minimize cross-coupling with conductors, and shorten the time for electronic signal transition.[12] Moreover, high quality factor ($Q\times f$) is required to increase the selectivity and near-zero temperature coefficient of the resonant frequency (τ_f) to ensure the stability of the frequency against temperature changes.

However, low-permittivity microwave dielectric ceramics exhibit generally high-magnitude negative τ_f values according to the ε_r - τ_f relationship.[13-15] In general, temperature compensated dopants with a large positive τ_f value, such as TiO_2, $CaTiO_3$, and $SrTiO_3$, are used in conventional processes in air to control the τ_f value of low-permittivity microwave dielectric ceramics.[16] Occasionally, this measure encounters difficulties, including (1) the reaction between dopants and matrix, such as TiO_2 and Co_2TiO_4, to form $CoTiO_3$ with a negative τ_f value,[17] and (2) the reduction of Ti^{4+} ions at high temperature or reducing atmosphere, which drastically deteriorates the quality factor.[18]

Single-phase $Ba_5Si_8O_{21}$ low-permittivity microwave dielectric ceramic with abnormally positive τ_f value has been discovered. The ceramic will provide another option to achieve stable frequency or permittivity characteristics against temperature. In barium silicates, the microwave dielectric properties of Ba_2SiO_4 (ε_r = 13.1, $Q\times f$ = 17,900 GHz, τ_f = −17 ppm/°C)[19] and $BaSi_2O_5$ (ε_r = 7.1, $Q\times f$ = 15,040 GHz, τ_f = −57.8 ppm/°C)[20] have been reported. Other barium silicates with different Ba/Si ratios from 1:1 to 1:2 also exhibit low-permittivity microwave dielectric properties. The τ_f values of these silicates are closely related to the crystal structure and structural complexity.

The concept of structural complexity is popular in mineral or crystal fields. However, a quantitative definition of crystal structure complexity, which is described by the Shannon information per reduced unit cell (${}^{str}I_{G,\ total}$), as shown in Eq. (1), was not established until recently:[21, 22]

$$ {}^{str}I_{G,total} = -v\sum_{i=1}^{k}\frac{m_i}{v}\log_2\left(\frac{m_i}{v}\right) \qquad (1)$$

$$ v = \sum_{i=1}^{k} m_i \qquad (2)$$

where m_i and v are the multiplicity of the ith crystallographic orbit and the number of atoms in the reduced unit cell, respectively; and k is the number of crystallographic orbits in the structure.

All the lattice structures in barium silicates include [SiO4] tetrahedrons and form a tetrahedral chain or 1-D structure for $BaSiO_3$, $Ba_2Si_3O_8$, $Ba_5Si_8O_{21}$, and $Ba_3Si_5O_{13}$ and a layered or 2-D structure for $BaSi_2O_5$.[22] For the 1-D and 2-D structures, the tetrahedral chains are *zweier*, which have two [SiO4] tetrahedrons in their repeat units. Therefore, $Ba_{1+1/M}[Si_2O_{5+1/M}]$ can be adopted to describe the barium silicate according to the multiplicity (or number) of single silicate chain (M).[22] The layered structure of the $BaSi_2O_5$ consists of an infinite number of single chain, that is, $M = \infty$.

The phase compositions, lattice structures, and microwave dielectric properties of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics were investigated in this study. A relation between the structural complexity and the τ_f value of the ceramics with a single-phase structure was also established.

2. Experimental procedure

The $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=1, 3, 4, 5, 7, and ∞) ceramics were prepared by conventional solid-state method using reagent grade $BaCO_3$ (99.8%, Shandong Boshan Chemical Reagent Co., Ltd, China) and SiO_2 (99.0%, Shanghai Hengxin Chemical Reagent Co., Ltd, China) powder as raw materials. According to desired stoichiometry, the raw materials were weighed to ball milled in a polyethylene jar for 5 h using ZrO_2 balls with deionized water. After drying at 85 °C, the mixtures were calcined in air at 1100 °C for 3 h with a heat rate of 5 °C/min. And then the powders were uniaxially pressed into samples with dimensions of 12 mm in diameter and approximately 6 mm in height under a pressure of 150 MPa. After sintered at densification temperature of 1200-1300 °C for 3 h at a heating rate of 5 °C/min, these samples were cooled at a rate of 2 °C/min down to 600 °C and then naturally cooled in the furnace.

The XRD data were obtained using X-ray diffraction (XRD, XRD-7000, Shimadzu, Kyoto, Japan) using CuKα radiation. The ε_r-T curve was tested at the temperature from −250 to 200 °C using an Agilent 4294A impedance analyzer (Aglient Technologies, Santa Clara, USA) and VDMS-2000 measuring system (Partulab, Wuhan, China). The ε_r and the unloaded $Q\times f$ value were measured at about 12.5 GHz in the TE_{011} mode by Hakki and Coleman method[23] using a network analyzer (Agilent E8362B, Agilent Technologies, Santa Clara, USA) and parallel silver boards. The τ_f value in the temperature range of 25 °C - 80 °C was calculated by Eq. (3):

$$\tau_{\mathrm{f}} = \frac{1}{f(T_0)} \frac{[f(T_1) - f(T_0)]}{T_1 - T_0} \qquad (3)$$

where $f(T_1)$ and $f(T_0)$ represent the resonant frequency at T_1 (80 °C) and T_0 (25 °C), respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics sintered at densification temperature for 3 h in air. A single phase can be obtained in the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics for M=1, 3, 4, 5, and ∞, corresponding to orthorhombic $BaSiO_3$ (Fig. 1(a)), monoclinic $Ba_2Si_3O_8$ (Fig. 1(b)), monoclinic $Ba_5Si_8O_{21}$ (Fig. 1(c)), monoclinic $Ba_3Si_5O_{13}$ (Fig. 1(d)), and orthorhombic $BaSi_2O_5$ (Fig. 1(f)), respectively. By contrast, mixture phases, including $Ba_5Si_8O_{21}$ and $BaSi_2O_5$, are observed in the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramic for M=7, as shown in Fig. 1(e).

Table 1 shows the structural complexity, phase compositions, and microwave dielectric properties of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics sintered at densification temperature for 3 h in air. All the barium silicates can be sintered well at 1200 °C -1300 °C and reach high relative density (ρ_r) above 92.0%. All the average linear coefficients of the thermal expansion (α_L) are approximately 10 ppm/°C. The ε_r and $Q\times f$ values of the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=1) ceramic are vastly different from the values of other compositions. The ε_r value of the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=1) (ε_r=11.1) is significantly higher, and its $Q\times f$ value ($Q\times f$=6,600 GHz) is significantly lower (Table 1), which results from the weak ferroelectric effect in $BaSiO_3$ ceramic.[5] The ε_r value slightly decreases from 8.2 (M=3) and 6.7 (M=∞) for the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ($M > 1$) ceramics. Meanwhile, the $Q\times f$ value reduces initially from 29,800 GHz at M = 3 to 12,500 GHz at M = 5 (single phase) and then increases gradually to 59,500 GHz at M = ∞. The τ_f value likewise changes from a negative to a positive value and reaches the maximum value of +37 ppm/°C at M = 5 (mixture phases), and then decreases to −28 ppm/°C at M = ∞. The phase composition and τ_f value for M=5 are sensitive to the sintering temperature. When sintering temperature increases from 1200 °C to 1250 °C, a pure monoclinic $Ba_3Si_5O_{13}$ phase is achieved and τ_f value varies from +37 ppm/°C to −36 ppm/°C. However, density does not change. This phenomenon will be explained later.

The positive τ_f value is very rare for low-permittivity microwave dielectric ceramics with a single-phase structure, especially for those with ε_r <10. To date, only a single-phase $CaSnSiO_5$ ceramic with a low ε_r value of 9.08 has exhibited a rare positive τ_f value (+35 ppm/°C).[24] For low-permittivity microwave dielectric ceramics, ionic displacement polarization plays a dominant role in controlling the ε_r value and increases along with the increase in temperature. Therefore, the temperature coefficient of the dielectric constant (τ_ε) is a typical positive value, and the τ_f value subsequently takes on a negative value, as shown in Eqs. (4) and (5):

$$\tau_f = -(\alpha_L + 0.5\tau_\varepsilon) \qquad (4)$$

$$\tau_\varepsilon = \frac{1}{\varepsilon(T_0)} \frac{[\varepsilon(T_1) - \varepsilon(T_0)]}{T_1 - T_0} \qquad (5)$$

where α_L is the linear thermal expansion coefficient of approximately 10 ppm/°C, and $\varepsilon(T_1)$ and $\varepsilon(T_0)$ are the relative permittivity at T_1 and T_0, respectively.

In this study, only one $Ba_5Si_8O_{21}$ phase can be confirmed directly to have a positive τ_f value (+25 ppm/°C). However, the nominal $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M = 5 and 7) ceramics with mixture phases, namely, $Ba_5Si_8O_{21}$ and $BaSi_2O_5$, also exhibit a rare positive τ_f value (Table 1). For the $Ba_5Si_8O_{21}$-$BaSi_2O_5$ two-phase system, $Ba_3Si_5O_{13}$ and $Ba_4Si_7O_{18}$ can be described theoretically through Eqs. (6) and (7), respectively, and their τ_f values can be calculated using the mixing rule shown in Eq. (8).

$$Ba_3Si_5O_{13}=0.5Ba_5Si_8O_{21}+0.5BaSi_2O_5 \qquad (6)$$

$$Ba_4Si_7O_{18}=0.5Ba_5Si_8O_{21}+1.5BaSi_2O_5 \qquad (7)$$

$$\tau_f = \sum_{i=1}^{k} v_i \tau_{fi} \qquad (8)$$

where v_i and τ_{fi} are the volume fraction and temperature coefficient of the resonant frequency of the *i*th phase, respectively. The molar mass of $Ba_5Si_8O_{21}$ (1247 g/mol) is much higher than that of $BaSi_2O_5$ (273 g/mol), while the theoretical density of $Ba_5Si_8O_{21}$ (3.92 g/cm^3) is close to that of $BaSi_2O_5$ (3.70 g/cm^3). Thus, the volume fraction of the $BaSi_2O_5$ phase can be neglected in the $Ba_3Si_5O_{13}$ ceramic with equal mole $Ba_5Si_8O_{21}$ and $BaSi_2O_5$ system. However, the molar amount of the $BaSi_2O_5$ phase is three times that of the $Ba_5Si_8O_{21}$ phase in the $Ba_4Si_7O_{18}$ ceramic with $Ba_5Si_8O_{21}$ and $BaSi_2O_5$ phases. Hence, the $BaSi_2O_5$ phase can effectively adjust the τ_f value to near zero. The calculated τ_f value of $Ba_4Si_7O_{18}$ ceramic is approximately +3 ppm/°C, which agrees well with the measured value of +2 ppm/°C. However, the calculated τ_f value of $Ba_3Si_5O_{13}$ ceramic is lower than the measured value, which could be attributed to other reasons that will be identified later.

A special lattice structure and a reduction in polarization with temperature for low-permittivity microwave dielectric ceramics with abnormal τ_f value are expected to occur in $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics with positive τ_f value. Therefore, the dependence of ε_r and tanδ on temperature was measured for the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=4 and 5) ceramics sintered at different densification temperatures. The results are shown in Fig. 2.

An ε_r anomaly peak appears along with an increase in dielectric loss at −180 °C in the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=4) ceramic (see Fig. 2(a)). The ε_r value at room temperature and 100 kHz is close to the value of the microwave frequency (approximately 12.5 GHz) (Table 1). This outcome indicates that the total polarization is nearly independent from the frequency range of 100 kHz - 12.5 GHz because of the dominant ion polarization in the $Ba_5Si_8O_{21}$ phase. When the temperature reaches −180 °C, the ε_r value increases sharply to 29.8 (see Fig. 2(a)), which is approximately fourfold of the ε_r value at room temperature. The ε_r anomaly peak could correspond to a paraelectric-ferroelectric phase transition. However, exhibiting a low relative permittivity at low temperature for the ferroelectric phase is rare. Therefore, further investigations should be performed to understand this phenomenon.

The larger negative τ_ε value at the measured temperature scale from 25 °C to 80 °C was observed in the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=5) ceramic sintered at 1200 °C with $Ba_5Si_8O_{21}$ and $BaSi_2O_5$ phases compared with that in the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=4) ceramic with pure $Ba_5Si_8O_{21}$ phase, as shown in Fig. 2(b). The increase in slope of the ε_r-T curve could have resulted from the right shift of the permittivity anomaly peak because of the increasing tilting and distortion of [SiO4] tetrahedrons in the $Ba_5Si_8O_{21}$ lattice structure induced by the $BaSi_2O_5$ phase.[25] Therefore, the $Ba_5Si_8O_{21}$ phase in the nominal $Ba_3Si_5O_{13}$ ceramic with two phases exhibits a higher τ_f value than the single-phase $Ba_5Si_8O_{21}$ ceramic (see Table 1). Eq. (4) can be used to qualitatively explain the opposite variation trend of τ_f and τ_ε values. However, the relations between τ_f and τ_ε values cannot absolutely follow Eq. (4) because of the different measured frequencies of τ_f (at about 12.5 GHz) and τ_ε (at 100 kHz and 1 MHz) and the strong nonlinear α_L curve (not shown). When the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ (M=5) ceramic sintered at 1250 °C forms a single $Ba_3Si_5O_{13}$ phase with monoclinic structure, its ε_r-T curve clearly changes and shows a positive slope. This result suggests that the single-phase $Ba_3Si_5O_{13}$ ceramic possesses a negative τ_f value according to Eq. (4).

A close relation between structural complexity described by the ${}^{str}I_{G,\ total}$ and the τ_f value of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics is also observed, as shown in Table 1. As the crystal structure complexity increases, the τ_f value tends to change from a negative to a positive value, except for M=5, which has a single monoclinic structure of the highest crystal structure complexity. The outcome indicates that the τ_f value could be related to other factors, such as the tilting and distortion of [SiO4] tetrahedrons. [25]

4. Conclusions

$Ba_{1+1/M}[Si_2O_{5+1/M}]$ in barium silicates sintered at 1200 °C -1300 °C for 3 h in air can be adopted to describe silicates according to the multiplicity (or number) of single silicate chain (M). A single phase can be obtained in the ceramics for M=1, 3, 4, 5, and ∞, corresponding to orthorhombic $BaSiO_3$, monoclinic $Ba_2Si_3O_8$, monoclinic $Ba_5Si_8O_{21}$, monoclinic $Ba_3Si_5O_{13}$, and orthorhombic $BaSi_2O_5$ phase, respectively. By contrast, mixture phases, including $Ba_5Si_8O_{21}$ and $BaSi_2O_5$, are observed in the ceramic for M=7. The ε_r value of the $BaSiO_3$ (ε_r=11.1) is considerably higher than that of other compositions and its $Q\times f$ value ($Q\times f$=6,600 GHz) is considerably lower, which results from the weak ferroelectric effect in $BaSiO_3$ ceramic. The ε_r value slightly decreases from 8.2 (M=3) and 6.7 (M=∞) for the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ($M > 1$) ceramics, and the $Q\times f$ value decreases initially from 29,800 GHz at M = 3 to 12,500 GHz at M = 5, and then increases gradually to 59,500 GHz at M = ∞. As the complexity of the crystal structure increases, the τ_f value tends to change from a negative to a positive value, except for M=5, which has a single phase of the highest crystal structure complexity. A single $Ba_5Si_8O_{21}$ phase with ε_r anomaly peak at −180 °C exhibits a rare positive τ_f value (+25 ppm/°C), which is a novel temperature compensator. Especially for M=5, the phase compositions and τ_f value are sensitive to sintering temperature. When the sintering temperature increases from 1200 °C to 1250 °C, a pure monoclinic $Ba_3Si_5O_{13}$ phase is achieved and the τ_f value varies from +37 ppm/°C to −36 ppm/°C. Therefore, the τ_f value of the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics is closely related to the complexity of the crystal structure, the phase compositions, and the tilting and distortion of [SiO4] tetrahedrons.

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Figure Captions

FIG. 1. XRD patterns of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics sintered at densification temperature for 3 h in air: (a) M=1, 1200 °C; (b) M=3, 1300 °C; (c) M=4, 1200 °C; (d) M=5, 1250 °C; (e) M=7, 1200 °C; (f) M=∞, 1250 °C.

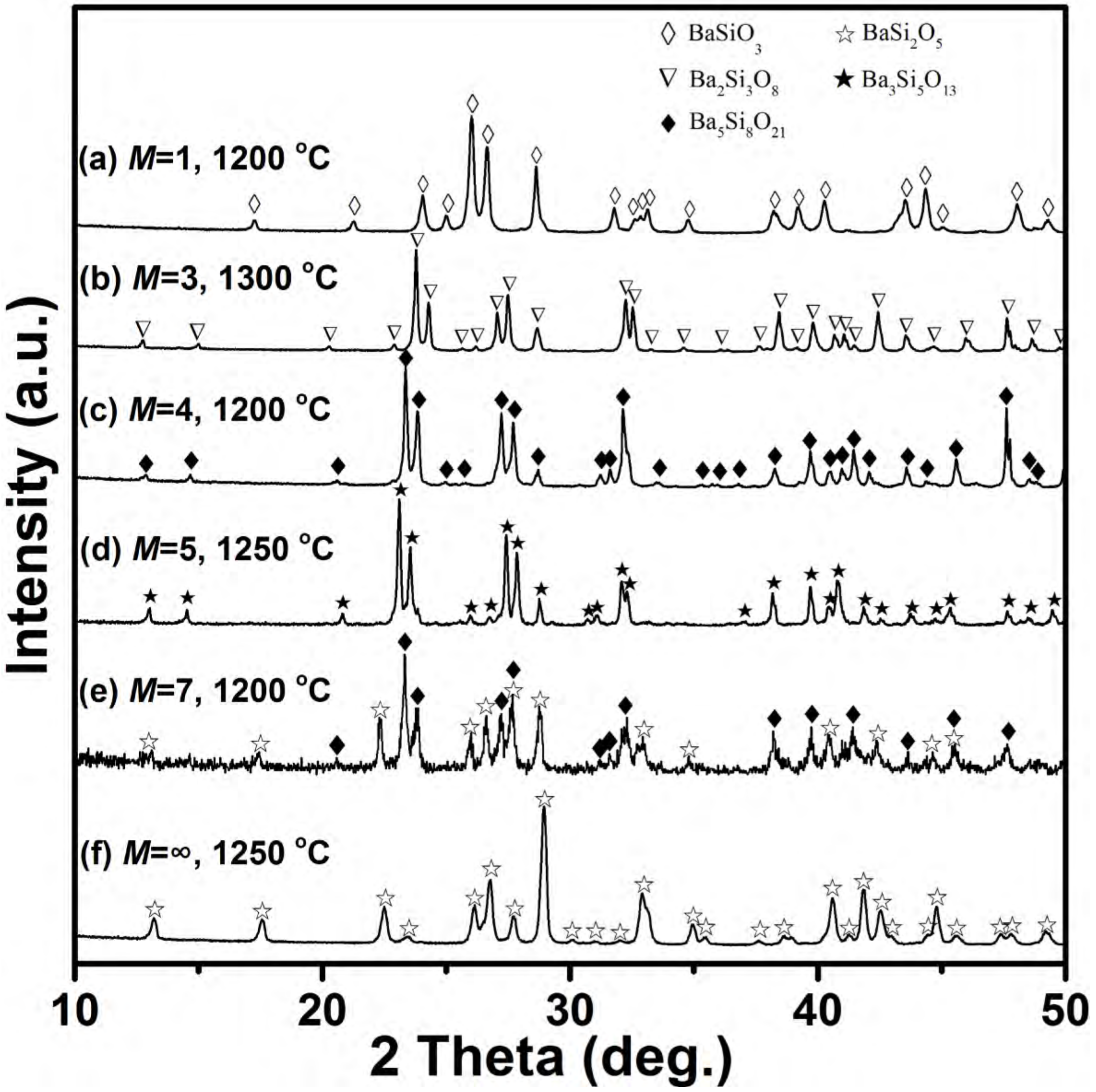
FIG. 2. The dependence of ε_r and tanδ on temperature for the $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics: (a) M=4, sintered at 1200 °C; (b) M=5, sintered at 1200 °C and 1250 °C.

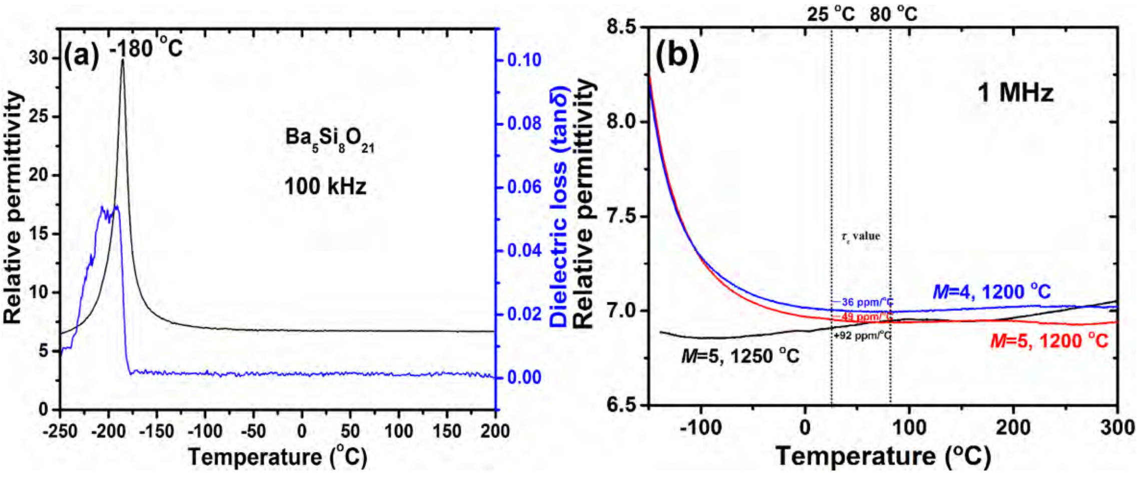
Table Captions

Table 1 Structural complexity, phase compositions, and microwave dielectric properties of $Ba_{1+1/M}[Si_2O_{5+1/M}]$ ceramics sintered at densification temperature for 3 h in air.

M value	T_{sint} (°C)	Structural complexity[22] (bits/cell)	Phase compositions	ρ_a (g/cm^3)	ρ_r (%)	α_L (ppm/°C)	f_r (GHz)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
M=1	1200	46.439	orthorhombic $BaSiO_3$	4.10	92.4	9.82	11.7	11.1	6,600	−35
M=3	1300	192.423	monoclinic $Ba_2Si_3O_8$	3.91	98.6	11.7	13.1	8.2	29,800	−37
M=4	1200	281.947	monoclinic $Ba_5Si_8O_{21}$	3.63	92.6	10.6	12.4	7.3	16,700	+25
M=5	1200	—	$Ba_5Si_8O_{21}$ and $BaSi_2O_5$	3.46	—	—	12.6	7.1	14,800	+37
	1250	368.955	monoclinic $Ba_3Si_5O_{13}$	3.46	93.5	11.8	12.7	6.9	12,500	−36
M=7	1200	—	$Ba_5Si_8O_{21}$ and $BaSi_2O_5$	3.61	—	10.6	12.7	7.1	20,400	+2
M=∞	1250	72.000	orthorhombic $BaSi_2O_5$	3.40	92.0	11.5	12.6	6.7	59,500	−28

T_{sint}: densification temperature, ρ_a: absolute density, ρ_r: relative density, α_L: average linear coefficient of thermal expansion, and f_r: resonant frequency.


◇ BaSiO$_3$
☆ BaSi$_2$O$_5$
▽ Ba$_2$Si$_3$O$_8$
★ Ba$_3$Si$_5$O$_{13}$
◆ Ba$_5$Si$_8$O$_{21}$
(a) M=1, 1200 °C
(b) M=3, 1300 °C
(c) M=4, 1200 °C
(d) M=5, 1250 °C
(e) M=7, 1200 °C
(f) M=∞, 1250 °C
Intensity (a.u.)
10
20
30
40
50
2 Theta (deg.)


(a)
-180 °C
Ba$_5$Si$_8$O$_{21}$
100 kHz
Relative permittivity
Dielectric loss (tanδ)
30
25
20
15
10
5
0
0.10
0.08
0.06
0.04
0.02
0.00
-250
-200
-150
-100
-50
0
50
100
150
200
Temperature (°C)
(b)
25 °C
80 °C
1 MHz
τ$_ε$ value
-36 ppm/°C
-49 ppm/°C
+92 ppm/°C
M=4, 1200 °C
M=5, 1200 °C
M=5, 1250 °C
Relative permittivity
8.5
8.0
7.5
7.0
6.5
-100
0
100
200
300
Temperature (°C)