Sintering behaviour, lattice energy and microwave dielectric properties of melilite-type BaCo₂Si₂O₇ ceramics

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Abstract

A novel melilite-type compound BaCo₂Si₂O₇ with monoclinic structure (C2/c) was prepared via solid-state reaction method. The correlations amongst microstructure, crystal structure, bond ionicity, lattice energy and microwave dielectric properties were systematically analyzed. The microwave dielectric properties of BaCo₂Si₂O₇ ceramics were determined by extrinsic (pores) and intrinsic (lattice energy) factors. The dielectric constant ($\varepsilon_r$), quality factor ($Q \times f$) and temperature coefficient of resonant frequency ($\tau_f$) were dominated by the relative density and the lattice energies of Si–O and Ba–O bonds. Optimum microwave dielectric properties for BaCo₂Si₂O₇ ceramics were obtained when sintered at 1060°C for 3 h: $\varepsilon_r = 9.26$, $Q \times f = 31,135$ GHz and $\tau_f = -92.05$ ppm C⁻¹.

1. Introduction

With the flourishment of 5G technology, millimeter-wave wireless communication has been leading the daily life of the general public [1]. High frequency is related to high transmission speed and short transmission distance; moreover, the number of devices, such as base station antennas, is considerably increased [2]. In addition to mobile communications, driverless cars have also generated rounds of discussion; meanwhile, vehicle radar is treated as the eye of the driverless cars, which also indicates the wide utilization of vehicle radar. The application of microwave dielectric ceramics for millimeter-wave devices, including dielectric antennae, resonators and filters, must be further studied [3].

In terms of traditional microwave wireless communication, microwave dielectric ceramics must present a high dielectric constant for devices miniaturization, a high quality factor to achieve excellent cross-coupling selectively and a near-zero temperature coefficient of resonant frequency to ensure the transmitted frequency [4, 5]. However, dielectric constant must be as small as possible for millimeter-wave wireless communication. The relationship between the dielectric constant and wavelength in dielectric and time delay are shown in equation (1):

$$\lambda = \lambda_0 / \varepsilon_r^{1/2}$$

(1)

$$T_{PD} = \varepsilon_r^{1/2} / c$$

(2)

where $\lambda_0$ is the wavelength in a vacuum, $\lambda$ is the wavelength in dielectric, $\varepsilon_r$ is the dielectric constant and $c$ is the speed of light in a vacuum. The wavelength in a vacuum ($\lambda_0$) has reached the millimeter level for millimeter-wave wireless communications; thus, high dielectric constant is not required for decreasing the wavelength ($\lambda$) in dielectric. Equation (2) reveals the significance of low dielectric constant on millimeter-wave wireless communications. High transmission speed (low time delay $T_{PD}$) plays a vital role in 5G communications. The velocity of light $c$ is a constant, therefore, low dielectric constant is expected for low time delay $T_{PD}$ [1, 6].

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Silicates generally present a low dielectric constant due to the [SiO₄] tetrahedra and the strong Si–O bond, which contains approximately half of the covalent bond [7, 8]. Many types of silicates, such as forsterite (Mg₂SiO₄), cordierite (Mg₂Al₂Si₅O₁₈), feldspar (BaAl₂Si₂O₈) and melilite (Ba₂ZnSi₂O₇), have been explored [9–12]. Previous work found that Ba₂ZnSi₂O₇ is also a ferroelectric, which renders us to attach more attention to the melilite-type silicates [13]. As shown in figure 1(a), two [SiO₄] tetrahedra connect with each other by corner sharing and form a [Si₂O₇]⁶⁻ group. Then, the [Si₂O₇]⁶⁻ group is connected by [ZnO₄]²⁻ tetrahedra. Both of the [SiO₄] tetrahedra and [ZnO₄]²⁻ tetrahedra connect each other in the a-c plane, hence Ba₂ZnSi₂O₇ shows a layered structure, and Ba²⁺ is located between the two layers. Except for Ba₂ZnSi₂O₇, BaCo₂Si₂O₇, which was firstly synthesized by Adams in 1996, also belongs to melilite-type silicates (figure 1(b)), the crystal structure and magnetic properties of BaCo₂Si₂O₇ were also investigated in the work [14]. Unlike Ba₂ZnSi₂O₇, the [SiO₄] tetrahedra in BaCo₂Si₂O₇ connect with each other by corner sharing in a-b plane and form a [Si₂O₇]⁶⁻ group [14]. [CoO₄]²⁻ tetrahedra then connect with each other in the a-c plane, and form a [CoO₄]²⁻ chain. The [CoO₄]²⁻ chain in a-c plane connects with the [Si₂O₇]⁶⁻ group in a-b plane and forms a skeleton structure. Finally, polyhedral gap is filled by Ba²⁺. At present, considerable attention has been provided to the dielectric properties of Ba₂ZnSi₂O₇ type mellilite, whilst studies on the dielectric properties of BaCo₂Si₂O₇ type melilite, especially the microwave dielectric properties, are unavailable. The rapid development of millimeter-wave communication motivated the exploration of new microwave dielectric ceramics with low dielectric constant. From the perspective of the relationship between crystal structure and dielectric properties, melilite-type BaCo₂Si₂O₇ ceramics may also have good microwave dielectric properties.

In this article, the BaCo₂Si₂O₇ ceramic was prepared through the solid-state reaction method. Bond ionicity and lattice energy were calculated based on the chemical bond theory. The relationships between microstructure, crystal structure, lattice energy and microwave dielectric properties were also systematically investigated for the first time.

### 2. Experimental procedure

BaCo₂Si₂O₇ ceramics were prepared by the conventional solid-state method using reagent grade BaCO₃ (99.8%), CoO (99.5%) and SiO₂ (99.5%) powders as raw materials [2]. Based on the chemical formula, the raw materials were weighed for ball milling in a polyethylene jar for 5 h using ZrO₂ balls with deionized water. After drying at 90 °C, the mixtures were calcined in air at 1000 °C for 3 h with a heating rate of 5 °C min⁻¹. The powders were then uniaxially pressed into samples with dimensions of 12 mm in diameter and approximately 6 mm in height under a pressure of 150 MPa. The samples were sintered at 1020 °C–1100 °C for 3 h at a heating rate of 5 °C min⁻¹, and then they were naturally cooled in the furnace. The pictorial representation of the experimental method is shown in figure 2.
The bulk density of the sintered samples was measured by Archimedes' method [12]. The relative density $\rho_{rel}$ was obtained by:

$$\rho_{rel} = \frac{\rho_{bul}}{\rho_{the}}$$

where $\rho_{bul}$ and $\rho_{the}$ are the bulk density and theoretical densities, respectively.

The XRD data were obtained via x-ray diffraction (XRD, XRD-7000, Shimadzu, Kyoto, Japan) using CuKα radiation. Phase analysis was performed by Rietveld refinement by utilizing GSAS and EXPGUI software [15–17]. The microstructure of the BaCo2Si2O7 samples was measured through the scanning electron microscope (SEM, Sirion 200, Netherlands). The $\varepsilon_r$ and the unloaded $Q \times f$ value was estimated at 12–14 GHz in the TE011 mode by Hakki and Coleman method [18] using a network analyzer (Agilent E8362B, Agilent Technologies, USA) and parallel silver boards. The $\tau_f$ value in the temperature range of 30 °C to 80 °C was calculated by equation (4):

$$\tau_f = \frac{1}{f(T_b)} \frac{f(T_1) - f(T_b)}{T_1 - T_b}$$

where $f(T_1)$ and $f(T_b)$ represent the resonant frequency at $T_1$ (80 °C) and $T_b$ (30 °C), respectively.

3. Results and discussion

Figure 3 shows the XRD patterns of BaCo2Si2O7 ceramics sintered at different temperatures. All diffraction peaks are indexed by monoclinic BaCo2Si2O7 (JCPDS#82-0184), and no second phase can be found. The relative intensity of the main diffraction peaks for BaCo2Si2O7 sintered at 1100 °C is lower than that of others. This finding indicates that this sintering temperature is detrimental to the crystallization of BaCo2Si2O7 ceramics. Table 1 and figure 4 show the results of the Rietveld refinement for BaCo2Si2O7 ceramics that belong to the C2/c (15) space group. The structure parameters and bond lengths are presented in table 1 and S1 is available online at stacks.iop.org/MRX/6/126322/mmedia.

Figures 5(a)–(e) show the scanning electron micrographs of fracture surface for BaCo2Si2O7 ceramics sintered at different temperatures. Figures 5(a) and (b) show that several interconnected pores exist on the fracture surface, but the interconnected pores evidently decrease at increased sintering temperature of 1020 °C to 1040 °C. The interconnected pores change into closed pores and become trapped in the grains when the sintering temperature increase to 1060 °C–1100 °C, which indicates that the range of the optimum sintering temperature is very narrow (approximately 60 °C). Figure 5(f) displays the bulk density of BaCo2Si2O7 ceramics
sintered at different temperatures. The bulk densities linearly increase and reach the maximum value at approximately 1080 °C. Despite few closed pores on the fracture surface (figure 5(e)), the bulk density starts to decrease after reaching the maximum value. This phenomenon may be due to the abnormal grain growth at substantially high sintering temperatures.

In order to reveal the relationships between crystal structure and microwave dielectric properties, the bond ionicity and lattice energy must be calculated based on Phillips-Van Vechten-Levine (P–V–L) theory, which was developed at the end of the 1960 s to 1973 s and finally generalized by Zhang in recent years[19–25]. According to the P–V–L theory[25], the complex crystals BaCo2Si2O7 could be decomposed into binary crystals, and the sub-chemical formula was written as follows:

\[
\text{BaCo}_2\text{Si}_2\text{O}_7 = \text{BaCo}(1)_{1/2}\text{Co}(2)_{1/2}\text{Co}(3)\text{Si}(1)\text{Si}(2)\text{O}(1)\text{O}(2)\text{O}(3)\text{O}(4)\text{O}(5)\text{O}(6)\text{O}(7)
\]

\[
= \text{Ba}_{1/8}\text{O}(2)_{1/4} + \text{Ba}_{1/8}\text{O}(2)_{1/4} + \text{Ba}_{1/8}\text{O}(3)_{1/4} + \text{Ba}_{1/8}\text{O}(4)_{1/4} + \text{Ba}_{1/8}\text{O}(5)_{1/4} + \text{Ba}_{1/8}\text{O}(6)_{1/4} + \text{Co}(1)_{1/4}\text{O}(1)_{1/4} + \text{Co}(1)_{1/4}\text{O}(2)_{1/4} + \text{Co}(1)_{1/4}\text{O}(3)_{1/4} + \text{Co}(1)_{1/4}\text{O}(4)_{1/4} + \text{Co}(1)_{1/4}\text{O}(5)_{1/4} + \text{Co}(1)_{1/4}\text{O}(6)_{1/4} + \text{Co}(1)_{1/4}\text{O}(7)_{1/4}
\]

The dielectric constant represents the polarization ability of materials under the electric field[26]. At microwave frequency, the polarization is dominated by electron displacement polarization and ionic displacement polarization. Thus, neglecting extrinsic factor, such as pores and the second phase, the dielectric constant can be determined by the ionic displacement polarization and calculated based on the P–V–L theory[27, 28].

Table 2 and S2 show the bond ionicity of BaCo2Si2O7. The average bond ionicity of Co–O and Si–O is approximately 0.45 and 0.60. However, the average bond ionicity of Ba–O is reaches approximately 0.84, which indicates that the Co–O and Si–O bonds are close to covalent bond, and Ba–O bond is a typical ionic bond. The weighted average bond ionicity of all bonds according to the chemical formula (A/f) is approximately 0.585. Therefore, the BaCo2Si2O7 ceramics will show a low dielectric constant.
Figure 6 shows the dielectric constant, relative density and weighted average bond ionicity of BaCo$_2$Si$_2$O$_7$ sintered at different temperatures. The weighted average bond ionicity of BaCo$_2$Si$_2$O$_7$ initially decreases and then linearly increases. However, these conditions do not show any relevance with dielectric constant. The dielectric constant and relative density increase to their maximum value at 1060°C–1080°C, maintaining the maximum value or demonstrating a slight decrease. The correlation between dielectric constant and relative density shows that the dielectric constant of BaCo$_2$Si$_2$O$_7$ ceramics sintered at the different temperatures is determined by the extrinsic factor (relative density). The low maximum relative density (approximately 96.6%) proves the poor sinterability of BaCo$_2$Si$_2$O$_7$ ceramics (figure 5).

Quality factor represents the dielectric loss of microwave dielectric ceramics, which can be affected by extrinsic and intrinsic losses. The extrinsic loss is affected by pores, the second phase, and grain boundary, whilst the intrinsic loss originates from anharmonic lattice vibration [29]. Numerous works confirmed that lattice energy largely affects quality factor [28, 30, 31].

Table 3 and S3 shows the lattice energy of BaCo$_2$Si$_2$O$_7$ ceramics sintered at the different temperatures. The total lattice energy of Si–O bonds ($\Sigma U$(Si–O)) is approximately 33 000 KJ mol$^{-1}$, which is around 76% of the lattice energy of BaCo$_2$Si$_2$O$_7$ ($U_{\text{cal}}$). Figure 7 shows the quality factor and the lattice energies of Si–O bonds and BaCo$_2$Si$_2$O$_7$ sintered at different temperatures. Quality factor and lattice energy increase to their maximum
value at 1060 °C and then decrease. The quality factor for the extrinsic part is mainly dominated by pores (relative density) for BaCo2Si2O7 ceramics, which can be proven from the microstructure evolution in figure 5 and the variation of relative density in figure 6. The quality factor for the intrinsic part is determined by the lattice energy of BaCo2Si2O7 (U_{cal}), particularly that of Si–O bonds. High bond energy indicates high bond strength, which stabilizes the structure and decreases the anharmonic lattice vibration \[32\]. Thus, the lattice energy of Si–O bonds plays a dominant role in the intrinsic dielectric loss. The variation of \(\Sigma U(Ba–O)\) presents an opposite trend with the quality factor, but the value of \(\Sigma U(Ba–O)\) is too low to have an apparent effect on quality factor when compared with that of the \(\Sigma U(Si–O)\).

Table 2. Average bond ionicity of BaCo2Si2O7 ceramics.

| fi   | 1020 °C | 1040 °C | 1060 °C | 1080 °C | 1100 °C |
|------|---------|---------|---------|---------|---------|
| fi(Ba–O) | 0.836 46 | 0.835 73 | 0.8359  | 0.836 39 | 0.836 66 |
| fi(Co1–O) | 0.447 46 | 0.445 69 | 0.445 31 | 0.446 63 | 0.447 37 |
| fi(Co2–O) | 0.452 56 | 0.451 78 | 0.451 69 | 0.451 67 | 0.451 64 |
| fi(Co3–O) | 0.448 86 | 0.447 58 | 0.447 92 | 0.449 08 | 0.450 66 |
| fi(Co–O) | 0.449 44 | 0.448 06 | 0.448 21 | 0.449 12 | 0.450 14 |
| fi(Si1–O) | 0.580 35 | 0.577 49 | 0.577 81 | 0.579 99 | 0.579 65 |
| fi(Si2–O) | 0.614 69 | 0.612 83 | 0.613 06 | 0.613 06 | 0.617 38 |
| fi(Si–O) | 0.597 52 | 0.595 16 | 0.595 43 | 0.597 57 | 0.598 52 |

\(fi(M–O)\) is the bond ionicity of M–O bond, and \(Af_i\) is the weighted average bond ionicity of all bond according to the chemical formula.

- Figure 5. SEM images of fracture surface for BaCo2Si2O7 ceramics sintered at different temperatures: (a) 1020 °C, (b) 1040 °C, (c) 1060 °C, (d) 1080 °C, (e) 1100 °C; and (f) bulk density of BaCo2Si2O7 ceramics.
Usually, the system with high lattice energy possesses a small $|\tau_f|$ value, but the variation of $\tau_f$ values present an opposite trend compared with that of the lattice energy of $\text{BaCo}_2\text{Si}_2\text{O}_7$ (figures 7 and 8). The $\tau_f$ is defined as follows [29]:
Grain growth emerges, and the bulk density decreases. The dielectric constant of BaCo$_2$Si$_2$O$_7$ ceramics increases.

Conclusions

where $\alpha_L$ is the linear thermal expansion coefficient, which is approximately 10 ppm C$^{-1}$ for oxide ceramics [33]. The first term $A$ mostly contributes to the temperature coefficient of dielectric constant ($\tau_f$), which represents the temperature dependence of the ionic polarizability [29]. The total ionic polarizability for Ba$^{2+}$, Co$^{3+}$ and Si$^{4+}$ in BaCo$_2$Si$_2$O$_7$ is 6.4, 3.3 and 1.74 Å$^3$, respectively [34]. Ba$^{2+}$ exhibits the largest ionic polarizability, which is larger than the sum of all Co$^{3+}$ and Si$^{4+}$. The lattice energy for BaCo$_2$Si$_2$O$_7$ ceramics is mainly attributed to Si–O bonds, but ionic polarizability is mainly contributed by Ba$^{2+}$. Therefore, Si–O bond largely influences quality factor, but slightly affects dielectric constant and temperature coefficient of resonant frequency. Unlike Si–O bond, the Ba–O bond largely influences dielectric constant and temperature coefficient of resonant frequency, but slightly affects quality factor due to the low lattice energy (ΣU(Ba–O)), high bond ionicity (Af$_f$(Ba–O)) and large ionic polarizability of Ba$^{2+}$. Figure 8 shows the variation of $\tau_f$ values and the lattice energy of Ba–O bond as a function of sintering temperatures. The $\tau_f$ values and ΣU(Ba–O) show good relevance. If the ΣU(Ba–O) decreases, then the bond strength of Ba–O bond decreases and the stability of [BaO$_6$] polyhedra also decreases. Thus, the ionic polarizability of Ba$^{2+}$ is susceptible to temperature, which increases the first term $A$ in equation (5), and then the $\tau_r$ decreases and $\tau_f$ increases. In summary, the $\tau_f$ value of BaCo$_2$Si$_2$O$_7$ ceramics sintered at the different temperatures is highly dependent on the lattice energy of Ba–O bond.

4. Conclusions

BaCo$_2$Si$_2$O$_7$ microwave dielectric ceramics with low dielectric constant have been prepared by the solid state-reaction method. At increasing the sintering temperature from 1020°C to 1060°C, the interconnected pores change into closed pores and are trapped in the grains. At sintering temperatures higher than 1080°C, abnormal grain growth emerges, and the bulk density decreases. The dielectric constant of BaCo$_2$Si$_2$O$_7$ ceramics increases with relative densities, but the weighted average bond ionicity of BaCo$_2$Si$_2$O$_7$ does not show any relevance with the dielectric constant. This finding indicates that the extrinsic factor plays a dominant role in dielectric constant. Quality factor is affected by both extrinsic and intrinsic factors. For the extrinsic part, the quality factor is mainly dominated by pores (relative density) of BaCo$_2$Si$_2$O$_7$ ceramics. For intrinsic part, the quality factor is determined by the lattice energy, especially that Si–O bonds. The quality factor, lattice energy ($U_{cal}$) and lattice energy of Si–O bonds $\Sigma U$(Si–O) are initially increased and linearly decreased. The $\tau_f$ values show an evident correlation with ΣU(Ba–O), and both initially decrease and then increase. Ba$^{2+}$ largely affects $\tau_f$ values due to low lattice energy (ΣU(Ba–O)), high bond ionicity (Af$_f$(Ba–O)) of Ba–O bond and large ionic polarizability. The optimum microwave dielectric properties with $\varepsilon_r = 9.26$, $Q \times f = 31$ 135 GHz and $\tau_f = -92.05$ ppm/°C were obtained at 1060°C for 3 h.
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