Evolution of Phase Transformation on Microwave Dielectric Properties of BaSi$_{x}$O$_{1+2x}$ Ceramics and Their Temperature-Stable LTCC Materials

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Abstract: BaSi$_{1+x}$O$_{1+2x}$ $(1.61 \leq x \leq 1.90)$ and LiF-doped BaSi$_{1.63}$O$_{2.26}$ ceramics were prepared by using a traditional solid-state method at the optimal sintering temperatures. The evolution of phase compositions of BaSi$_{1+x}$O$_{1+2x}$ $(1.61 \leq x \leq 1.9)$ ceramics was revealed. The coexistence of Ba$_5$Si$_8$O$_{21}$ and Ba$_3$Si$_5$O$_{13}$ phases was obtained in BaSi$_{1.1+x}$O$_{1+2x}$ $(1.61 \leq x \leq 1.67)$ ceramics. The BaSi$_2$O$_5$ phase appeared in BaSi$_{1+x}$O$_{1+2x}$ $(1.68 \leq x \leq 1.90)$ ceramics. At $1.68 \leq x \leq 1.69$, only BaSi$_2$O$_5$ and Ba$_3$Si$_5$O$_{13}$ phases existed. With the further increase in $x$, the Ba$_5$Si$_8$O$_{21}$ phase appeared, and BaSi$_2$O$_5$, Ba$_5$Si$_8$O$_{21}$, and Ba$_3$Si$_5$O$_{13}$ phases coexisted in BaSi$_{1+x}$O$_{1+2x}$ $(1.70 \leq x \leq 1.90)$ ceramics. The phase compositions of BaSi$_{1+x}$O$_{1+2x}$ $(1.61 \leq x \leq 1.90)$ ceramics were controlled by the ratio of Ba:Si. The BaSi$_{1.1+x}$O$_{1+2x}$ $(x = 1.68)$ ceramics with 98.15 wt% Ba$_3$Si$_5$O$_{13}$ and 1.85 wt% BaSi$_2$O$_5$ phases exhibited a negative $\tau_f$ value ($-37.53$ ppm/°C), and the good microwave dielectric properties of $\varepsilon_r = 7.51$, $Q \times f = 13,038$ GHz and $\tau_f = +3.95$ ppm/°C were obtained for BaSi$_{1.63}$O$_{2.26}$ ceramics with 70.05 wt% Ba$_5$Si$_8$O$_{21}$ and 29.95 wt% Ba$_3$Si$_5$O$_{13}$ phases. The addition of LiF sintering aids were able to reduce the sintering temperatures of BaSi$_{1.63}$O$_{2.26}$ ceramics to 800 °C. The phase composition of BaSi$_{1.63}$O$_{2.26}$ ceramics was affected by the sintering temperature, and the coexistence of Ba$_5$Si$_8$O$_{21}$, Ba$_5$Si$_8$O$_{21}$, Ba$_3$Si$_5$O$_{13}$, and SiO$_2$ phases was achieved in BaSi$_{1.63}$O$_{2.26}$-3 wt% LiF ceramics. The BaSi$_{1.63}$O$_{2.26}$-3 wt% LiF ceramics sintered at 800 °C exhibited dense microstructures and excellent microwave dielectric properties ($\varepsilon_r = 7.10$, $Q \times f = 12,463$ GHz and $\tau_f = +5.75$ ppm/°C), and no chemical reaction occurred between BaSi$_{1.63}$O$_{2.26}$-3 wt% LiF ceramics and the Ag electrodes, which indicates their potential for low-temperature co-fired ceramic (LTCC) applications.

Keywords: barium silicate; phase composition; microwave dielectric property; low-temperature co-fired ceramic application

1. Introduction

The rapid development of telecommunication has promoted the high demand for multi-layer devices and microwave dielectric ceramics [1–5]. Barium silicates with excellent luminescence and dielectric properties are widely used in optical glasses and microwave dielectric ceramics [6–12]. The low cost and free of variable valence elements of barium silicates indicated their great application potential, especially in communication applications [13,14]. The Si–O bond was also strong because it is approximately 55% covalent and 45% ionic [15–17]. Barium silicates with high contents of SiO$_4$ tetrahedra and Si–O bonds...
demonstrated their low permittivity ($\varepsilon_r < 15$) and high-quality factor ($Q \times f$), which attracted considerable attention regarding microwave dielectric materials [18–22]. However, 13 crystalline phases were known in the BaO–SiO$_2$ system [23], which indicates that the complex phase compositions might exist in barium silicates. Ambiguous phase compositions might limit the application of barium silicates in microwave dielectric materials.

The microwave dielectric properties of barium silicates were first reported by Wen Lei et al. [9], and a BaSi$_2$O$_5$ ceramic with excellent microwave dielectric properties ($\varepsilon_r = 6.7$, $Q \times f = 59,500$ GHz and $\tau_f = -28.0$ ppm/°C) was synthesised through sintering at 1250 °C. Enzhu Li et al. pointed out that the synthesis temperature of a single-phase BaSi$_2$O$_5$ ceramic was more than 1100 °C, and the coexistence of BaSi$_2$O$_5$, Ba$_5$Si$_8$O$_{21}$ (BaSi$_{1.6}$O$_{4.2}$) and SiO$_2$ phases was identified in BaSi$_2$O$_5$ ceramics. The Ba$_5$Si$_8$O$_{21}$ phases existed in BaSi$_2$O$_5$-2 wt% Li$_2$O–B$_2$O$_3$–CaO–CuO glass ceramics when their sintering temperature was below 800 °C, which means that the Ba$_5$Si$_8$O$_{21}$ phase was easier to synthesise than the BaSi$_2$O$_5$ phase [10]. A single-phase BaSi$_2$O$_5$ ceramic sintered at 1225 °C was prepared by Yun Zhang [11]. The Ba$_5$Si$_8$O$_{21}$ ceramic with a stable phase composition and novel positive temperature coefficient of the resonance frequency ($\tau_f$) was used as a $\tau_f$ regulator to control the negative $\tau_f$ values of many low-$\varepsilon_r$ microwave dielectric ceramics [12]. The Ba$_5$Si$_8$O$_{21}$ ceramics always exhibited the Ba$_5$Si$_8$O$_{21}$ phase at a high sintering temperature (above 800 °C). However, the Ba$_5$Si$_3$O$_{13}$ (Ba$_{1.667}$Si$_{4.334}$O$_{12}$) ceramic, as an intermediate compound between Ba$_5$Si$_8$O$_{21}$ (BaSi$_{1.4}$O$_{4.2}$) and BaSi$_2$O$_5$, exhibited the highest structural and topological complexity in barium silicates [8]. The Ba$_5$Si$_3$O$_{13}$ (Ba$_{1.667}$Si$_{4.334}$O$_{12}$) ceramics sintering at different temperatures exhibited the opposite $\tau_f$ values (+37.0 ppm/°C sintering at 1200 °C and −36.0 ppm/°C sintering at 1250 °C) and different phase compositions (Ba$_5$Si$_8$O$_{21}$ and BaSi$_2$O$_5$ phases sintered at 1200 °C and Ba$_5$Si$_3$O$_{13}$ phase sintered at 1250 °C) [9]. Toshihiro Moriga et al. pointed out that Ba$_5$Si$_3$O$_{13}$ single-phase ceramics sintered at 1000 °C could be synthesised at stoichiometric ratios [7]. The small difference in the Ba:Si ratios of the Ba$_5$Si$_8$O$_{21}$, Ba$_5$Si$_3$O$_{13}$ and BaSi$_2$O$_5$ phases caused difficulty in synthesising Ba$_5$Si$_3$O$_{13}$ ceramics.

Considering the excellent application potential of barium silicate ceramics in LTCC technology, the variation in the phase compositions of Ba$_{1+2}$Si$_{1+2}$O$_{3}$ ceramics with stoichiometric ratios and sintering temperatures needs to be investigated. This study aimed to clarify the phase compositions of Ba$_{1+2}$Si$_{1+2}$O$_{3}$ (1.61 $\leq x \leq 1.9$) ceramics with different stoichiometric ratios and investigate the evolution of their phase compositions on microwave dielectric properties. Simultaneously, high-performance Ba$_{1+2}$Si$_{1+2}$O$_{3}$-based LTCC materials with LiF doped were prepared.

2. Materials and Methods

Ba$_{1+2}$Si$_{1+2}$O$_{3}$ (1.61 $\leq x \leq 1.9$)- and LiF-doped Ba$_{1+2}$Si$_{1+2}$O$_{3}$ ceramics were prepared using the solid reaction method. BaCO$_3$ (99.9%), SiO$_2$ (99.9%) and LiF (99.9%) were weighed according to the stoichiometric formulation of Ba$_{1+2}$Si$_{1+2}$O$_{3}$ (1.61 $\leq x \leq 1.9$) and ground in deionised water for 5 h. After drying, Ba$_{1+2}$Si$_{1+2}$O$_{3}$-prepared powders were calcined at 1050 °C for 5 h to obtain barium silicates. After being re-milled for 5 h and dryed, the as-prepared powders together with 8 wt% PVA were pressed into cylindrical samples. The Ba$_{1+2}$Si$_{1+2}$O$_{3}$ samples were then sintered at 1300–1325 °C for 5 h. The Ba$_{1+2}$Si$_{1+2}$O$_{3}$ calcined powders and LiF were weighed according to the mass percentage formulation of Ba$_{1+2}$Si$_{1+2}$O$_{3}$-y wt% LiF (1 $\leq y \leq 3$), which were sintered at 800–1025 °C for 3 h.

The sintered samples of Ba$_{1+2}$Si$_{1+2}$O$_{3}$ and Ba$_{1+2}$Si$_{1+2}$O$_{3}$-y wt% LiF (1 $\leq y \leq 3$) ceramics were broken up and ground into powders. The phase and crystal structure of powders were obtained using an X-ray diffractometer (X’Pert PRO). The Rietveld refinement of samples was conducted via Fullprof software [24]. The polished surfaces of samples were observed via scanning electron microscopy (SEM; Sirion 200) after thermal etching. The microwave dielectric properties of as-sintered Ba$_{1+2}$Si$_{1+2}$O$_{3}$ (1.61 $\leq x \leq 1.9$) and Ba$_{1+2}$Si$_{1+2}$O$_{3}$-y wt% LiF (1 $\leq y \leq 3$) ceramics were measured in the range of 10–14 GHz by employing the Hakki–Coleman methods with a network analyser (Keysight E5063A) [25].
3. Results

The Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics at the optimal sintering temperature ($T_{\text{sint}}$) were broken up and ground into powders for X-ray analysis. As shown in Figure 1a, the optimal sintering temperature of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.67) ceramics was between 1300 and 1325 °C. Only Ba$_{3}$Si$_{2}$O$_{7}$ phase seemed to exist in Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.62) ceramics, and the Ba$_{5}$Si$_{3}$O$_{13}$ (1.66 ≤ $x$ ≤ 1.67) ceramics exhibited the Ba$_{3}$Si$_{3}$O$_{13}$ single phase. The evident coexistence of Ba$_{3}$Si$_{3}$O$_{13}$ and Ba$_{3}$Si$_{3}$O$_{13}$ phases was observed in Ba$_{5}$Si$_{3}$O$_{13}$ (1.63 ≤ $x$ ≤ 1.65) ceramics. As illustrated in Figure 1c, the Ba$_{3}$Si$_{3}$O$_{13}$ single phase existed in the Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.68$) ceramics, and the obvious coexistence of Ba$_{3}$Si$_{3}$O$_{13}$ and Ba$_{3}$Si$_{2}$O$_{7}$ phases was observed in the Ba$_{5}$Si$_{3}$O$_{13}$ (1.69 ≤ $x$ ≤ 1.90) ceramics. However, the similar XRD patterns between Ba$_{3}$Si$_{3}$O$_{13}$ and Ba$_{3}$Si$_{3}$O$_{13}$ phases caused difficulty in distinguishing the phase compositions of Ba$_{5}$Si$_{3}$O$_{13}$ ceramics. The enlarged XRD patterns of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.9) ceramics at a 20°–30° scanning range can be seen in Figure 1b,d, along with the evolution of the main XRD peaks. The evident Ba$_{3}$Si$_{3}$O$_{13}$ second phase existed in Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.62$) ceramics, and the content of the Ba$_{3}$Si$_{3}$O$_{13}$ phase in Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.67) ceramics increased gradually with the rise in $x$. In the Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.67$) ceramics, the Ba$_{3}$Si$_{3}$O$_{21}$ second phase was present. The single-phase Ba$_{3}$Si$_{3}$O$_{13}$ ceramics might be seen in the Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.68$) ceramics (Figure 1d). With the further increase in $x$, the intensity of the XRD patterns of the Ba$_{3}$Si$_{3}$O$_{13}$ and Ba$_{3}$Si$_{3}$O$_{13}$ phases gradually rose and decreased, respectively. The evident Ba$_{3}$Si$_{3}$O$_{21}$ phase also existed in Ba$_{5}$Si$_{3}$O$_{13}$ (1.80 ≤ $x$ ≤ 1.85) ceramics, which indicates the complex evolution of the phase compositions of Ba$_{5}$Si$_{3}$O$_{13}$ (1.68 ≤ $x$ ≤ 1.90) ceramics. Moreover, the Ba$_{3}$Si$_{3}$O$_{13}$ ceramics were able to be synthesised via sintering at 1325 °C.

The Rietveld refinement of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics was conducted for quantitative analysis via phase composition. The results of the Rietveld refinement are shown in Table 1, and the calculated XRD patterns of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics matched the measured XRD patterns well (Figure 2). Therefore, the fitting content of phase compositions was accurate. As shown in Table 1, the Ba$_{3}$Si$_{3}$O$_{21}$ main phase and Ba$_{3}$Si$_{3}$O$_{13}$ second phase existed in Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.64) ceramics. The main phase in Ba$_{5}$Si$_{3}$O$_{13}$ (1.65 ≤ $x$ ≤ 1.67) ceramics changed from the Ba$_{3}$Si$_{3}$O$_{21}$ to Ba$_{3}$Si$_{3}$O$_{13}$ phase. Moreover, the Ba$_{3}$Si$_{3}$O$_{21}$ second phase changed to the Ba$_{3}$Si$_{2}$O$_{7}$ phase in the Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.68$) ceramics. The Ba$_{5}$Si$_{3}$O$_{13}$ ($x = 1.68$) ceramics with 98.5 wt% Ba$_{3}$Si$_{3}$O$_{13}$ and 1.85 wt% Ba$_{3}$Si$_{2}$O$_{7}$ was synthesised, and the Ba$_{3}$Si$_{2}$O$_{7}$-Ba$_{3}$Si$_{3}$O$_{13}$ system could be obtained in Ba$_{5}$Si$_{3}$O$_{13}$ (1.68 ≤ $x$ ≤ 1.69) ceramics. With the further increase in $x$, the other Ba$_{3}$Si$_{3}$O$_{21}$ second phase appeared in Ba$_{5}$Si$_{3}$O$_{13}$ (1.7 ≤ $x$ ≤ 1.90) ceramics, and the content of the Ba$_{3}$Si$_{2}$O$_{7}$ phase increased gradually. Lastly, the results of the Rietveld refinement indicated that the coexistence of the Ba$_{3}$Si$_{3}$O$_{21}$ and Ba$_{3}$Si$_{3}$O$_{13}$ phases were obtained in Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.67) ceramics (Ba$_{3}$Si$_{3}$O$_{21}$–Ba$_{3}$Si$_{3}$O$_{13}$ system), and the Ba$_{3}$Si$_{3}$O$_{13}$ single-phase ceramics could be synthesised in Ba$_{5}$Si$_{3}$O$_{13}$ (1.67 < $x$ < 1.68) ceramics. The phase compositions of the Ba$_{3}$Si$_{3}$O$_{13}$ ceramics were significantly affected by the ratio of Ba:Si.

As shown in Figure 3 and S1, the thermally etched SEM and EDS map scanning images of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics were obtained. The dense and smooth microstructures of Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics were observed. Only the grains of barium silicates were observed in Ba$_{5}$Si$_{3}$O$_{13}$ (1.61 ≤ $x$ ≤ 1.90) ceramics. However, the similar monoclinic structure and elemental composition caused difficulty in distinguishing the grains of Ba$_{3}$Si$_{3}$O$_{21}$ and Ba$_{3}$Si$_{3}$O$_{13}$ based on Figure 3 and S1. In Figure 3e, the EDS results of Spots A and B indicated that the strip-shaped (Spot B) and large (Spot A) grains were Ba$_{3}$Si$_{3}$O$_{13}$ and Ba$_{3}$Si$_{2}$O$_{7}$, respectively. The Ba$_{3}$Si$_{3}$O$_{13}$ second phase can be observed in Figure 3f. With the increase in $x$, the content of strip-shaped grains decreased gradually and the average grain sizes increased, which implies that the content of Ba$_{3}$Si$_{2}$O$_{7}$ rose gradually.
Figure 1. XRD patterns of BaSi$_x$O$_{1+2x}$ (1.61 ≤ $x$ ≤ 1.90) ceramics sintered at their densification temperature: (a) the XRD patterns of BaSi$_{1.61}$O$_{3.22}$ (1.61 ≤ $x$ ≤ 1.67) ceramics; (b) the enlarged XRD patterns of BaSi$_{1.61}$O$_{3.22}$ (1.61 ≤ $x$ ≤ 1.67) ceramics at 20°~30°; (c) the XRD patterns of BaSi$_{1.68}$O$_{3.36}$ (1.68 ≤ $x$ ≤ 1.90) ceramics; (d) the enlarged XRD patterns of BaSi$_{1.68}$O$_{3.36}$ (1.68 ≤ $x$ ≤ 1.90) ceramics at 20°~30°.

Figure 2. XRD patterns of BaSi$_x$O$_{1+2x}$ (1.61 ≤ $x$ ≤ 1.90) ceramics after whole XRD pattern fitting.

Figure 1. XRD patterns of BaSi$_x$O$_{1+2x}$ (1.61 ≤ $x$ ≤ 1.90) ceramics sintered at their densification temperature: (a) the XRD patterns of BaSi$_{1.61}$O$_{3.22}$ (1.61 ≤ $x$ ≤ 1.67) ceramics; (b) the enlarged XRD patterns of BaSi$_{1.61}$O$_{3.22}$ (1.61 ≤ $x$ ≤ 1.67) ceramics at 20°~30°; (c) the XRD patterns of BaSi$_{1.68}$O$_{3.36}$ (1.68 ≤ $x$ ≤ 1.90) ceramics; (d) the enlarged XRD patterns of BaSi$_{1.68}$O$_{3.36}$ (1.68 ≤ $x$ ≤ 1.90) ceramics at 20°~30°.

Figure 2. XRD patterns of BaSi$_x$O$_{1+2x}$ (1.61 ≤ $x$ ≤ 1.90) ceramics after whole XRD pattern fitting.
Table 1. The lattice parameters and Rietveld discrepancy factors of BaSi$_x$O$_{1+2x}$ (1.61 \(\leq x \leq 1.90\)) ceramics sintered at their densification temperatures.

<table>
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<tr>
<th>Compositions</th>
<th>Phase Compositions</th>
<th>Lattice Parameter of Main Phase</th>
<th>Rietveld Discrepancy Factors</th>
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<td></td>
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<td>Second Phase (wt%)</td>
<td>(a) (Å)</td>
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<td>Ba$_{5}$Si$<em>4$O$</em>{13}$ (42.79)</td>
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<td>(x = 1.67)</td>
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<td>Ba$_{5}$Si$<em>4$O$</em>{21}$ (8.73)</td>
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</table>

The microwave dielectric properties of the BaSi$_x$O$_{1+2x}$ (1.61 \(\leq x \leq 1.90\)) ceramics sintered at the optimal temperature were obtained, as shown in Table S1 (see Supplementary materials) and Figures 4 and 5. As shown in Figure 4a, the relative density (\(\rho_{rel}\)) and experimental relative permittivity (\(\varepsilon_{\text{r,exp}}\)) of BaSi$_x$O$_{1+2x}$ (1.61 \(\leq x \leq 1.90\)) ceramics fluctuated with the increase in \(x\), and all BaSi$_x$O$_{1+2x}$ (1.61 \(\leq x \leq 1.90\)) ceramics exhibited high \(\rho_{rel}\) (>95%) except th BaSi$_x$O$_{1+2x}$ (\(x = 1.75\)) ceramics. Therefore, \(\rho_{rel}\) might have little effect on the microwave dielectric properties of BaSi$_x$O$_{1+2x}$ ceramics. In the BaSi$_x$O$_{1+2x}$ (1.61 \(\leq x \leq 1.67\)) ceramics, the BaSi$_x$O$_{1+2x}$ (\(x = 1.67\)) ceramics with a 91.27 wt% Ba$_{5}$Si$_4$O$_{13}$ phase exhibited the largest
$\varepsilon_{\text{r-exp}}$ value, and a low $\varepsilon_{\text{r-exp}}$ (7.33) was obtained in BaSi$_x$O$_{1+2x}$ ($x = 1.61$) ceramics with a 95.87 wt% Ba$_5$Si$_8$O$_{21}$ phase, which was attributed to the low $\varepsilon_{\text{r-exp}}$ value (7.3) of Ba$_5$Si$_8$O$_{21}$ ceramics [9]. In BaSi$_x$O$_{1+2x}$ ($1.68 \leq x \leq 1.90$) ceramics, $\varepsilon_{\text{r-exp}}$ decreased from 7.49 to 6.94, and the BaSi$_x$O$_{1+2x}$ ($x = 1.90$) ceramics with a 71.12 wt% BaSi$_2$O$_5$ phase exhibited the lowest $\varepsilon_{\text{r-exp}}$ value. For multi-phase ceramics, $\varepsilon_{\text{r}}$ could be calculated using the Lichtenecker empirical rule [26–28].

$$ln \varepsilon_{\text{r-cal}} = V_1 ln \varepsilon_{\text{r-1}} + V_2 ln \varepsilon_{\text{r-2}} + V_3 ln \varepsilon_{\text{r-3}}$$  \hspace{1cm} (1)

where $\varepsilon_{\text{r-cal}}$ represents the calculated relative permittivity; $V_1$, $V_2$ and $V_3$ are the volume fraction of phases 1, 2 and 3; and $\varepsilon_{\text{r-1}}$, $\varepsilon_{\text{r-2}}$ and $\varepsilon_{\text{r-3}}$ are the $\varepsilon_{\text{r-exp}}$ values of Ba$_5$Si$_8$O$_{21}$, Ba$_3$Si$_5$O$_{13}$ and BaSi$_2$O$_5$ ceramics [9], respectively. The $\varepsilon_{\text{r-cal}}$ of BaSi$_x$O$_{1+2x}$ ($1.61 \leq x \leq 1.90$) ceramics increased initially and then decreased, and the variation tendency of the $\varepsilon_{\text{r-exp}}$ values was similar to $\varepsilon_{\text{r-cal}}$ with $x$ (Figure 4a). This finding implies that phase compositions significantly affected the $\varepsilon_{\text{r-exp}}$ values for BaSi$_x$O$_{1+2x}$ ($1.61 \leq x \leq 1.90$) ceramics. Moreover, the BaSi$_x$O$_{1+2x}$ ($x = 1.66$) ceramics exhibited lower $\varepsilon_{\text{r-exp}}$ (7.57) than BaSi$_x$O$_{1+2x}$ ($x = 1.64, 1.65, 1.67$) ceramics, which was attributed to their low $\rho_{\text{rel}}$. The BaSi$_x$O$_{1+2x}$ ($x = 1.80$) ceramics exhibited larger $\rho_{\text{rel}}$ and $\varepsilon_{\text{r-exp}}$ than BaSi$_x$O$_{1+2x}$ ($x = 1.75$) ceramics. Thus, the effect of $\rho_{\text{rel}}$ on the $\varepsilon_{\text{r-exp}}$ of BaSi$_x$O$_{1+2x}$ ($1.61 \leq x \leq 1.90$) ceramics cannot be neglected.

Figure 3. SEM and EDS images of thermally etched BaSi$_x$O$_{1+2x}$ ($1.61 \leq x \leq 1.90$) ceramics.
where $\tau_{\text{f-cal}}$ represents the calculated $\tau_f$; $V_1$, $V_2$ and $V_3$ are the volume fractions of phases 1, 2 and 3, respectively; and $\tau_{f1}$, $\tau_{f2}$ and $\tau_{f3}$ are the $\tau_f$ values of Ba$_5$Si$_8$O$_{21}$, Ba$_3$Si$_5$O$_{13}$ and Ba$_2$Si$_3$O$_5$ ceramics [9], respectively. $\tau_{\text{f-cal}}$ agreed well with the $\tau_{\text{f-exp}}$ in Ba$_{1+x}$O$_{1+2x}$ ceramics.
(1.61 ≤ x ≤ 1.90) ceramics, and τ_f-exp, τ_f-cal and content of BaSil8O21 phase of the BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics with x displayed a similar trend. Therefore, the content of the BaSil8O21 phase significantly affected the τ_f-exp of BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics. At 1.65 ≤ x ≤ 1.75, the BaSi1xO1+2x ceramics with the Ba3Si5O13 main phase exhibited negative τ_f-exp values. Therefore, the present study confirmed the negative τ_f value of Ba3Si5O13 ceramics, which was controversial in a previous work [9]. BaSil8O21, as a new τ_f compensator, successfully adjusted the negative τ_f-exp value of Ba3Si5O13 to near zero (+3.95 ppm/°C and −7.25 ppm/°C) in the BaSi1xO1+2x (x = 1.63, 1.64) ceramics.

In accordance with Formula (3) [29,30], the τ_f related to α_L and τ_e and α_L can be seen in Figure 5b.

\[
\tau_f = -\left(\alpha_L + \frac{1}{2} \tau_e\right)
\]

with the increase in measured temperature, the length of BaSi1xO1+2x (x = 1.63) ceramics increased gradually, and the average linear thermal expansion coefficient (CTE in Figure 5b) at 25–750 °C is 10.1 ppm/°C. The dependence of ε on temperature for BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics is shown in Figure 5, and the fitting τ_e values at 30–215 °C and 1 MHz were obtained. The negative τ_e values were obtained in BaSi1xO1+2x (1.61 ≤ x ≤ 1.64) ceramics, and BaSi1xO1+2x (1.66 ≤ x ≤ 1.90) ceramics exhibited positive τ_e values. At 1.61 ≤ x ≤ 1.64, the negative τ_e values increased gradually to near zero, and BaSi1xO1+2x (x = 1.64) ceramics exhibited a near-zero τ_e value (−2.9 ppm/°C). At 1.66 ≤ x ≤ 1.90, the small τ_e value was obtained in BaSi1xO1+2x (x = 1.80) ceramics. According to the τ_f–τ_e relationship, a similar variation in the τ_e and τ_f values of the BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics was observed as x increased, which indicates that the measured τ_f-exp values using the Hakki–Coleman method were exacted. The measured α_L (10.1 ppm/°C) and τ_e (−15.4 ppm/°C) values of BaSi1xO1+2x (x = 1.63) ceramics also confirmed their near-zero τ_f-exp value.

![Figure 6. Temperature and frequency dependences of relative permittivity for BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics.](image-url)

At high \( T_{\text{sint}} \) (≥1300 °C), the phase compositions of BaSi1xO1+2x (1.61 ≤ x ≤ 1.90) ceramics were revealed in this work. However, the phase compositions of barium silicates were sensitive to \( T_{\text{sint}} \), and the complex phase transformation of barium silicates existed...
with the change in $T_{\text{sint}}$, especially $\text{Ba}_5\text{Si}_8\text{O}_{21}$, $\text{Ba}_3\text{Si}_5\text{O}_{13}$ and $\text{BaSi}_2\text{O}_5$ ceramics [9,10]. Thus, the phase transformation of $\text{BaSi}_5\text{O}_{1+2x}$ ceramics with the change in $T_{\text{sint}}$ must be clarified. The $\text{BaSi}_5\text{O}_{1+2x}$ ($x = 1.63$) ceramics sintered at 1300 °C presented the coexistence of $\text{Ba}_5\text{Si}_8\text{O}_{21}$ and $\text{Ba}_3\text{Si}_5\text{O}_{13}$ phases and exhibited good microwave dielectric properties. As shown in Figure 7, the XRD patterns of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics were obtained. The coexistence of $\text{Ba}_5\text{Si}_8\text{O}_{21}$ and $\text{BaSi}_2\text{O}_5$ phases was obtained in $\text{BaSi}_{1.63}\text{O}_{4.26-1}$ wt% LiF ceramics sintered at 1025 °C, and the $\text{Ba}_3\text{Si}_5\text{O}_{13}$ second phase of $\text{BaSi}_{1.63}\text{O}_{4.26}$ ceramics sintered at 1300 °C was inhibited. However, the new $\text{Ba}_2\text{Si}_3\text{O}_8$ and $\text{SiO}_2$ second phases appeared in $\text{BaSi}_{1.63}\text{O}_{4.26-1}$ wt% LiF ceramics when $T_{\text{sint}} = 925$ °C, which implies that the $\text{Ba}_2\text{Si}_3\text{O}_8$ and $\text{SiO}_2$ phase can transform into $\text{BaSi}_2\text{O}_5$ phases at $T_{\text{sint}} = 1025$ °C. With the increase in the content of LiF, the $T_{\text{sint}}$ of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics decreased gradually. The coexistence of $\text{Ba}_5\text{Si}_8\text{O}_{21}$, $\text{Ba}_3\text{Si}_5\text{O}_{13}$ and $\text{BaSi}_2\text{O}_5$ and $\text{SiO}_2$ phases was observed in $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($y = 2, 3$) ceramics sintered at 925 and 800 °C.

![Figure 7. XRD patterns of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics at different sintering temperatures.](image)

Figure S2 and Table 2 show the results of Rietveld refinement. The calculated XRD patterns of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics matched the measured XRD patterns well (Figure S2). The phase compositions of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics were observed, as shown in Table 2. The $\text{BaSi}_{1.63}\text{O}_{4.26-1}$ wt% LiF ceramics with 74.39 wt% $\text{Ba}_5\text{Si}_8\text{O}_{21}$ and 25.61 wt% $\text{BaSi}_2\text{O}_5$ phases was obtained. The decrease in $T_{\text{sint}}$ induced the appearance of the $\text{Ba}_3\text{Si}_5\text{O}_{13}$ second phase, and 84.51 wt% and 68.69 wt% $\text{Ba}_5\text{Si}_8\text{O}_{21}$ phases were obtained in $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($y = 2, 3$) ceramics. The $\text{Ba}_3\text{Si}_5\text{O}_{13}$ phase could not be obtained in $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics with low $T_{\text{sint}}$ (≤1025 °C), which means that $\text{Ba}_3\text{Si}_5\text{O}_{13}$ phase can only be synthesised at high $T_{\text{sint}}$ (≥1300 °C). The $\text{Ba}_3\text{Si}_5\text{O}_{13}$, $\text{Ba}_5\text{Si}_8\text{O}_{21}$ and $\text{BaSi}_2\text{O}_5$ phases can be synthesised at low $T_{\text{sint}}$ (≤925 °C). In summary, the $\text{Ba}_5\text{Si}_8\text{O}_{21}$ phase was the most stable phase of barium silicates, and the phase compositions of $\text{BaSi}_{1.63}\text{O}_{4.26-y}$ wt% LiF ($1 \leq y \leq 3$) ceramics were related to $T_{\text{sint}}$. 
Table 2. The lattice parameters and Rietveld discrepancy factors of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF (1 \leq y \leq 3) ceramics sintered at their densification temperatures.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Phase Compositions</th>
<th>Lattice Parameter of Main Phase</th>
<th>Rietveld Discrepancy Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = 1</td>
<td>Ba_{5}Si_{8}O_{21}</td>
<td>a (Å) 32.687, b (Å) 4.694, c (Å) 13.877, β (°) 98.276, V (Å³) 2106.951, ( R_{exp} (%) ) 12.0, ( R_p (%) ) 9.1, ( \chi^2 ) 3.9</td>
<td></td>
</tr>
<tr>
<td>y = 2</td>
<td>Ba_{5}Si_{8}O_{21}</td>
<td>a (Å) 32.699, b (Å) 4.699, c (Å) 13.900, β (°) 98.155, V (Å³) 2114.038, ( R_{exp} (%) ) 18.3, ( R_p (%) ) 14.5, ( \chi^2 ) 7.6</td>
<td></td>
</tr>
<tr>
<td>y = 3</td>
<td>Ba_{5}Si_{8}O_{21}</td>
<td>a (Å) 32.697, b (Å) 4.697, c (Å) 13.898, β (°) 98.159, V (Å³) 2112.718, ( R_{exp} (%) ) 16.0, ( R_p (%) ) 12.6, ( \chi^2 ) 6.5</td>
<td></td>
</tr>
</tbody>
</table>

The thermally etched SEM images of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF and BaSi_{1.63}O_{4.26-\text{y}} wt% LiF-Ag electrode ceramics were obtained, as shown in Figure 8. Dense and smooth microstructures were observed in BaSi_{1.63}O_{4.26-\text{y}} wt% LiF ceramics. The evident small SiO_{2} second phase existed at the grain boundary, as shown in Figures 8 and S3. No LiF or liquid phases existed, and complex phase compositions could not be clarified via SEM images. As shown in Figure 8b, the surface of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF ceramics could be well combined with Ag electrodes, which indicates that it is well able to be co-fired with Ag electrodes at 800 °C.

Figure 8. SEM images of the thermally etched (a) BaSi_{1.63}O_{4.26-\text{y}} wt% LiF ceramics and (b) BaSi_{1.63}O_{4.26-\text{y}} wt% LiF-Ag electrode ceramics.

The evolution of the phase compositions and sintering characteristic of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF (1 \leq y \leq 3) ceramics on microwave dielectric properties was investigated. As shown in Table 3, with the addition of a LiF sintering aid, the optimal \( T_{sint} \) of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF (1 \leq y \leq 3) ceramics were able to be reduced to less than 1025 °C. At the optimal sintering temperatures, the \( \rho_{rel} \) of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF (1 \leq y \leq 3) ceramics decreased from 96.5% (y = 1) to 94.4% (y = 3), and the addition of a LiF sintering aid [31] and the decrease in sintering temperature caused a reduction in \( \rho_{rel} \). The \( \epsilon_{r-exp} \) and \( Q \times f \) values decreased gradually, and the \( \tau_{f-exp} \) values fluctuated with \( x \). The decrease in \( \epsilon_{r-exp} \) and \( Q \times f \) values was mainly attributed to the decline in \( \rho_{rel} \). According to Formula (2), the \( \tau_{f-cal} \) values of BaSi_{1.63}O_{4.26-\text{y}} wt% LiF (1 \leq y \leq 3) ceramics were calculated, and similar variations in \( \tau_{f-exp} \), \( \tau_{f-cal} \), and the content of the Ba_{5}Si_{8}O_{21} phase of the BaSi_{1.63}O_{4.26-\text{y}} wt%
LiF \((1 \leq y \leq 3)\) ceramics were observed as \(y\) increased. The \(\tau_{\text{f-exp}}\) values of BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((1 \leq y \leq 3)\) ceramics were significantly affected by the content of the BaSi\(_{8}\)O\(_{21}\) phase, and the near-zero \(\tau_{\text{f-exp}}\) value (+5.75 ppm/\(°C\)) was obtained in BaSi\(_{1.63}\)O\(_{4.26}\)-3 wt\% LiF ceramics with 68.69 wt\% BaSi\(_{8}\)O\(_{21}\), 15.55 wt\% Ba\(_{2}\)Si\(_{3}\)O\(_{8}\), 13.70 wt\% BaSi\(_{2}\)O\(_{5}\) and 2.06 wt\% SiO\(_{2}\) phases.

Table 3. The optimal sintering temperature, relative density and microwave dielectric properties of BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((1 \leq y \leq 3)\) ceramics.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>(T_{\text{sint}}) (°C)</th>
<th>(\rho_{\text{rel}}) (%)</th>
<th>(\varepsilon_{\text{r-exp}})</th>
<th>(Q \times f) (GHz)</th>
<th>(\tau_{\text{f}}) (ppm/°C)</th>
<th>(\tau_{\text{f-cal}}) (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(y = 1)</td>
<td>1025</td>
<td>96.5</td>
<td>7.42</td>
<td>14,252</td>
<td>+8.37</td>
<td>+11.00</td>
</tr>
<tr>
<td>(y = 2)</td>
<td>950</td>
<td>95.2</td>
<td>7.21</td>
<td>12,913</td>
<td>+11.90</td>
<td>+16.20</td>
</tr>
<tr>
<td>(y = 3)</td>
<td>800</td>
<td>94.4</td>
<td>7.10</td>
<td>12,463</td>
<td>+5.75</td>
<td>+6.12</td>
</tr>
</tbody>
</table>

4. Conclusions

BaSi\(_{1}O_{1+2x}\) \((1.61 \leq x \leq 1.90)\) and BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((1 \leq y \leq 3)\) ceramics were synthesised, and the evolution of their phase compositions was investigated. The two-phase system of BaSi\(_{8}\)O\(_{21}\) and Ba\(_{2}\)Si\(_{3}\)O\(_{8}\) was obtained at 1.61 \(\leq x \leq 1.67\), and no other second phase existed. At 1.67 \(\leq x \leq 1.69\), the content of BaSi\(_{8}\)O\(_{13}\) phase was more than 90 wt\%. The BaSi\(_{8}\)O\(_{21}\) second phase could be inhibited in BaSi\(_{1}O_{1+2x}\) \((1.68 \leq x \leq 1.69)\) ceramics, and the other Ba\(_{2}\)Si\(_{3}\)O\(_{8}\) phase was induced. At 1.70 \(\leq x \leq 1.90\), the excessive Si element content of BaSi\(_{1}O_{1+2x}\) ceramics caused the appearance of the BaSi\(_{8}\)O\(_{21}\) second phase, and the coexistence of BaSi\(_{2}\)O\(_{3}\), Ba\(_{2}\)Si\(_{3}\)O\(_{8}\), and Ba\(_{2}\)Si\(_{3}\)O\(_{13}\) phases was observed. Therefore, the phase compositions of BaSi\(_{1}O_{1+2x}\) \((1.61 \leq x \leq 1.90)\) ceramics sintered at high temperature \((\geq 1300 °C)\) were significantly controlled by the ratio of Ba/Si. The \(\varepsilon_{\text{r-exp}}\) and \(Q \times f\) values of BaSi\(_{1}O_{1+2x}\) \((1.61 \leq x \leq 1.90)\) ceramics were mainly affected by the phase compositions and \(\rho_{\text{rel}}\), and the \(\tau_{\text{f-exp}}\) values were controlled via the content of the BaSi\(_{8}\)O\(_{21}\) phase with a positive \(\tau_{f}\) value. The near-zero \(\tau_{\text{f-exp}}\) value (+3.95 ppm/°C) was obtained at \(x = 1.63\). Moreover, the LiF sintering aids were able to reduce the sintering temperature of BaSi\(_{1.63}\)O\(_{4.26}\) ceramics, and the low sintering temperature \((800 °C)\) was obtained in BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((y = 3)\) ceramics. When sintering temperature was less than 1025 °C, the BaSi\(_{8}\)O\(_{13}\) phase of BaSi\(_{1.63}\)O\(_{4.26}\) ceramics was inhibited and the Ba\(_{2}\)Si\(_{3}\)O\(_{8}\), BaSi\(_{2}\)O\(_{3}\) and SiO\(_{2}\) appeared. The content of phases could be affected by the sintering temperature, which shows that the phase compositions of BaSi\(_{1}O_{1+2x}\) ceramics were related to their sintering temperature. The development of microwave dielectric properties of BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((1 \leq y \leq 3)\) ceramics strongly relied on their phase compositions, and microwave dielectric properties \((\varepsilon_{r} = 7.10, Q \times f = 12,463\) GHz, and \(\tau_{f} = +5.75\) ppm/°C\) were obtained in BaSi\(_{1.63}\)O\(_{4.26}\)-3 wt\% LiF ceramics.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/cryst13060870/s1, Figure S1: EDS map scanning images of the thermally etched BaSi\(_{1}O_{1+2x}\) \((x = 1.67\) and 1.80) ceramics; Figure S2: XRD patterns of BaSi\(_{1.63}\)O\(_{4.26}\)-y wt\% LiF \((1 \leq y \leq 3)\) ceramics after whole XRD pattern fitting; Figure S3: EDS map scanning images of the thermally etched BaSi\(_{1.63}\)O\(_{4.26}\)-3 wt\% LiF ceramics; Table S1: Optimal sintered temperature \((T_{\text{sint}})\), relative density \((\rho_{\text{rel}})\) and microwave dielectric properties of BaSi\(_{1}O_{1+2x}\) \((1.61 \leq x \leq 1.90)\) ceramics.

Author Contributions: Conceptualization, T.W. and Y.L.; methodology, Z.Z.; software, X.L. (Xiaotian Liu); validation, X.L. (Xiaoxiao Li); formal analysis, T.W.; investigation, K.D.; resources, K.D.; data curation, T.W.; writing—original draft preparation, K.D.; writing—review and editing, K.D. and W.L.; visualization, Y.L.; supervision, C.Y.; project administration, Y.C.; funding acquisition, W.L. and S.W. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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