

Influence of Modified Solid-State Reaction Method on Sintering and Dielectric Properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ Ceramic

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Abstract

In this work, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic was prepared with the modified solid-state reaction method. The ceramic samples were calcined at 550 °C and then sintered at 680 °C for 4 h. After the ceramic samples had been thermally etched, their dense microstructure and straight grain boundary were observed by means of scanning electron microscopy, and a relative density of 95.1 % determined. The dielectric property of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic in this work was measured with a $Q \times f$ value of 28 000 GHz, a relative permittivity of 27.5 and a temperature coefficient of - 15 ppm/K. Compared with the measured result for the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic prepared with the traditional solid-state reaction method, the sintering temperature dropped from 720 °C to 680 °C and the $Q \times f$ value increased by 57 % from 17 500 GHz to 28 000 GHz. Ethanol and isostatic pressing technology can replace the polyvinyl ethanol and traditional press effectively and the modified solid-state reaction method is an excellent way to improve the sintering and dielectric properties of ceramic material.

Keywords: LTCC, modified solid-state reaction method, microwave dielectric ceramic

I. Introduction

With the rapid increase in applications in the growing microwave wireless communication and broadcasting industry, the demand for different ceramics with excellent sintering and dielectric properties is steadily rising¹. Meanwhile, electronic components combining multiple functions are becoming smaller in size while the interconnected wireless world is turning into reality. Thanks to the fast development of fifth-generation mobile communication technology, day-to-day electronic devices, such as smart phones, cameras and tablets, are now boasting new features. The signal delay has been reduced and the signal transmission speed in the antenna has been increased sharply. This enables connection of intelligent electronic and wearable devices by means of wireless equipment, which meets the requirements specific to each application. In industrial production, microwave dielectric ceramic is often co-fired with electrode material such as Ag and Al²⁻³. Then the ceramic is used to fabricate microwave components such as wave guides, oscillators and antennas based on multilayer co-fired ceramic technology. The requirements to be met by the dielectric ceramic for practical application differ. Ceramic with high permittivity is usually used to fabricate capacitors and realize the miniaturization of microwave components. Ceramic with low

permittivity is usually used to fabricate antennas for high signal transmission speed. The important characteristics for all applications are low sintering temperature, low dielectric loss or high $Q \times f$ value, near-zero temperature coefficient of the resonant frequency and good chemical compatibility with electrode materials. Lots of new ceramic dielectric materials are reported in the relevant literature every year. However, most of these ceramic materials require a high sintering temperature, which restricts their practical application. Reducing the sintering temperature cannot only reduce production costs in the industry but also enable co-firing of the ceramic with other low-melting-point electrode materials such as GaAs and polymer material. Moreover, the dielectric loss is also very important for the dielectric ceramic property. Owing to the continuous increase of the working frequency, more heat will be produced in the electronic devices, which affects the stability of the electronic component. Consequently, the new microwave communication ceramic materials must exhibit low dielectric loss. Meanwhile, high dielectric loss also impacts energy consumption. For 5G application, the dielectric ceramic material should not only require a low sintering temperature but also exhibit low dielectric loss⁴⁻⁵.

For the development of the wireless communication industry, the low-temperature co-fired ceramic (LTCC) technology has been well advanced recently. LTCC enables the use of dielectric ceramic green tape with a

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sintering temperature lower than the melting point of silver electrode (961 °C) for the fabrication of electric devices^{6–7}. Currently, numerous studies on finding new dielectric ceramic materials with a sintering temperature lower than 700 °C are under way and the number of papers on lowering ceramic firing temperature is increasing rapidly. Then the green ceramic tape is a promising candidate for co-firing with other low-melting-point electrode materials such as aluminium (660 °C) and polymer. However, ceramic materials with low dielectric loss always require a high firing temperature⁸. In the traditional ceramic preparation process, adding glasses with a low melting temperature is a common way to lower the ceramic sintering temperature. For example, MgO-B₂O₃-SiO₂, CaO-B₂O₃-SiO₂ and SrO-B₂O₃-SiO₂ glasses with a low melting temperature are commonly used as sintering additives in the ceramic sintering process^{9–10}. In the sintering process, the aids melt at low temperature and the liquid phase improves the mass transfer efficiency of the solid particles. As a result, the green ceramic body can be sintered at a lower temperature. However, it is difficult to burn out the glass in a green ceramic body during the sintering process, and the residual glass degrades the dielectric property of the ceramic sample, particularly its dielectric loss. Numerous experiments^{11–13} have shown that the solid solution method is also an effective way to modify the sintering property of ceramic. Owing to the change of ion type in the crystal, the lattice parameters change and the mass transfer efficiency improves at lower temperature. However, the solid solution method also degrades the dielectric property and commonly increases the dielectric loss. Consequently, adding glasses with a low melting point and the solid solution method are not suitable for the preparation of ceramic material with a low sintering temperature and low dielectric loss for the 5G communication industry. In our previous work¹⁴, the traditional ceramic preparation method was modified with ethanol and by means of isostatic pressing. Thanks to such improvements in the preparation process, the sintering temperature of K₂Mo₂O₇ ceramic decreases from 460 °C to 450 °C and the Q × f value increases by 68 % from 22 000 GHz to 37 000 GHz. Therefore, this modified traditional ceramic preparation method is a possibility for the preparation of ceramic material with excellent sintering and dielectric properties.

According to recently published papers, most ceramic materials with ultra-low sintering temperature are based on glasses, vanadates, molybdates and tellurates^{15–16}. However, the dielectric loss of glasses is always high. Vanadates and molybdates readily absorb moisture from the air, which causes a deterioration in the dielectric property of the ceramic sample and the stability of the electric components. Moreover, tellurates are usually poisonous. These characteristics limit their application in the area of telecommunications and mobile communication. Compared to these materials, tungstate ceramic materials usually have better stability and excellent dielectric property. Numerous tungstate-based ceramic materials have been reported recently^{17–18}. However, most of the reported tungstate ceramic materials have a high sintering temper-

ature. Improving the sintering and dielectric properties of tungstate ceramic is an effective way to aid the development of the communication industry. In our previous work¹⁹, Na₂WO₄ ceramic could be sintered at 565 °C and has a relative permittivity of 5.6, a Q × f value of 124 200 GHz and a TCF value of -63 ppm/K. In previous work^{20–21}, Hanuza and Klevtsov measured the cell parameters of the (Na_{0.5}Bi_{0.5})WO₄ ceramic and the result indicates the (Na_{0.5}Bi_{0.5})WO₄ ceramic belongs to scheelite structure. The structure parameters are $a = b = 5.282$ Å and $c = 11.50$ Å. Na⁺ and Bi³⁺ occupied A site with eight-fold coordination and W⁶⁺ occupied B site with four-fold coordination. Lots of studies²² have demonstrated that the (Na_{0.5}Bi_{0.5})WO₄ scheelite structure shows good stability.

According to the work of Pang *et al.*²³, (Na_{0.5}Bi_{0.5})WO₄ ceramic can be sintered at 720 °C and have a relative permittivity of 25.7, a low value of 17 500 GHz and a negative resonant frequency temperature coefficient of 18. Due to the ion substitution of Bi³⁺ on A site, the relative permittivity increases from 5.6 to 25.7, which is attributed to the increase in the total polarizability of the ceramic. However, because of the difference between the ionic radii of Bi³⁺ and Na⁺, the crystal structure of Na₂WO₄ ceramic is damaged. As a result, the dielectric loss increases considerably, which limits the application of (Na_{0.5}Bi_{0.5})WO₄ ceramic in the high-frequency communication industry. Given that, the modified traditional solid-state reaction method is used in this work to improve the sintering and dielectric property of (Na_{0.5}Bi_{0.5})WO₄ ceramic. Thanks to the improvement in the preparation process of the green ceramic body, the sintering temperature drops from 720 °C to 680 °C and the Q × f value increases by 57 % from 17 500 GHz to 28 000 GHz after sintering in a muffle furnace for 4 h. The (Na_{0.5}Bi_{0.5})WO₄ ceramic in this work possesses excellent sintering and dielectric properties, making it a potential candidate material for the manufacture of ultra-LTCC devices.

II. Experimental Procedure

The (Na_{0.5}Bi_{0.5})WO₄ ceramic is prepared with the modified solid-state reaction method, which has been described in detail in our previous work¹⁴. WO₃ (99.8 %, Shanghai Aladdin Biochemical Technology Component, Shanghai, China), Na₂CO₃ (99.8 %, Shanghai Aladdin Biochemical Technology Component, Shanghai, China) and Bi₂O₃ (99.9 %, Shanghai Aladdin Biochemical Technology Component, Shanghai, China) were used as starting materials in the preparation process. Before being mixed in the formula for (Na_{0.5}Bi_{0.5})WO₄, all the starting materials were placed in an oven at 120 °C for 24 h to remove any moisture. Subsequently, the mixed powders were ball-milled in the planetary mill for 4 h with ethanol as the medium. After being dried, the mixture was calcined at the temperature of 470–570 °C for 4 h in an air atmosphere. The powder was then milled again to reduce the particle size. The average particle size analyzed with a laser particle size analyzer is 430.7 nm. Subsequently, the suitable ethanol was sprayed onto the dried powder and stirred evenly in an agate mortar. Then, the powder was pressed

into cylindrical pellets measuring about 10 mm in diameter and 5 mm in thickness in a traditional press at the pressure of 100 MPa. Subsequently, all the cylinders were pressed again in an isostatic press (CIP AIP3-12-60C, American Isostatic Presses, Columbus, America) at the pressure of 200 MPa for 3 min. Before being sintered, the pellets were held in a sintering furnace at 120 °C for 2 h to remove the ethanol. Subsequently, the pellets were sintered in an air atmosphere and the sintering temperature was 660–700 °C for 4 h. Besides, all the green ceramic pellets were sintered embedded in $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ powder. In this way, the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ powder can closely envelop the ceramic body to prevent the Bi element from volatilizing during sintering process.

X-ray diffraction (XRD) was performed with Cu-K α radiation to identify the crystal structure. Scanning electron microscopy (SEM) was used to examine the polished and thermally etched surface of the ceramic samples. The linear intercept method was used to measure the average size of the grain (calculation based on 400 grains). The density of the ceramic sample was measured with the Archimedes method. The microwave dielectric property of the ceramic sample was obtained using a TE_{01δ} dielectric-shielded cavity in a 8720ES Network Analyzer and Delta 9023 temperature chamber. In order to calculate the relative permittivity, the dimension of the prepared ceramic disk was measured with the micrometer screw (Mitutoyo Co., Japan). The temperature coefficient of frequency TCF (τ_f) of the sample was obtained with the following formula:

$$\tau_f = (f_{85} - f_{25}) / (60 \times f_{25}) \times 10^6 (\text{ppm}/^\circ\text{C}) \quad (1)$$

in which f_{25} and f_{85} were the TE_{01δ} resonant frequencies at 25 °C and 85 °C respectively.

III. Results and Discussion

The XRD test result for the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic material calcined at different temperature for 4 h is shown in Fig. 1 and the tested range is 10° to 80°. In this work, the crystal structure of all the samples is measured with the X-ray powder method. Normally, XRD measurement can be divided into the powder method and block method. In the powder method, the ceramic sample is ground into tiny particles with an average particle size of 1 130.7 nm and then placed in a mould. Subsequently, the mould is placed in a SHIMADZU XRD-7000 and the crystal structure is measured. In the block method, the ceramic disk is pasted on the mould and then measured. Compared to the block method, the XRD result obtained with the powder method is more accurate. That is because the number of the tiny particles is large and the data is easier to collect. As shown in Fig. 1, the calcined samples contain many impurities when the temperature is lower than 550 °C according to the PDF card 87-1578. When the temperature is 550 °C, the characteristic peak of the impurity disappears, which indicates that the sample crystallizes in a tetragonal scheelite structure. This result indicates that the partial substitution of Bi for Na is achieved with the solid solution method. Besides, the intensity of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic characteristic peak increases with the increase in the calcining temperature.

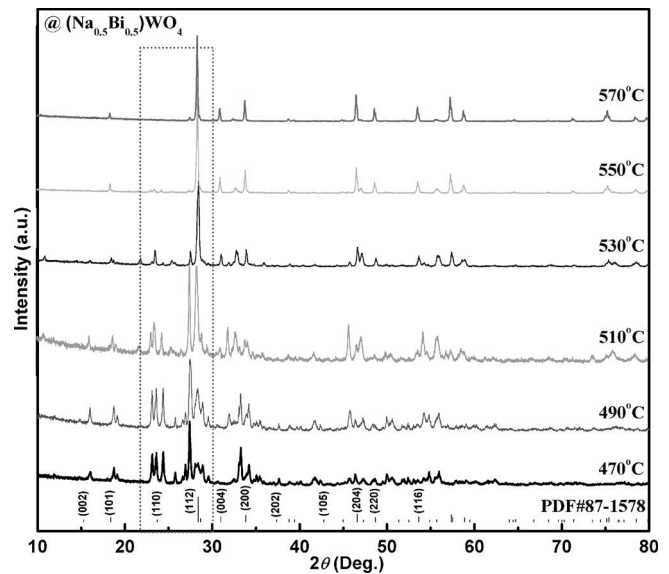


Fig. 1: XRD patterns of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic calcined at different temperature for 4 h.

In the solid phase preparation method for the ceramic, the calcining process is very important, with the mixed starting materials combining to form the required phase structure as a result of chemical reaction at appropriate temperature²⁴. If the temperature is low, the chemical reaction cannot occur adequately between the WO_3 , Na_2CO_3 and Bi_2O_3 powders. The residual starting materials remain in the pressed green ceramic sample and undergo chemical reaction in the following sintering process. Due to the chemical reaction between the starting materials, additional pores appear inside the sample and the produced CO_2 gas further decreases the mass transfer efficiency of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ powder in the sintering process. As a result, the sintering property and dielectric property of the prepared ceramic sample are poor. As a consequence, $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ powder should be synthesized as a result of chemical reaction at sufficient temperature. However, mass transfer may occur and the grains begin to grow in the calcining process when the calcining temperature is too high. The ceramic particle after growth is hard to grind in the following secondary ball milling process. Because the calcined ceramic particle size is large, the particles are difficult to compact during the pressing process. Finally, the gap between the particles in the pressed green ceramic sample is large, which will affect the sintering property of the prepared sample. Theoretically, a lower calcining temperature is beneficial for pressing of the green ceramic body and decreases the pore number in the ceramic sample. After several experiments, the XRD result shows that the characteristic peaks of impurities appear when the temperature is lower than 550 °C according to the standard $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ phase PDF card and the characteristic peaks of the impurities disappear when the temperature is above 550 °C. As a consequence, 550 °C has been chosen as the calcining temperature in this work.

Microstructures of the prepared $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic samples sintered at 680 °C for 4 h are presented in Fig. 2. Generally, the dielectric performance of the ceramic

material is influenced by many factors, which include extrinsic and intrinsic factors. According to Bloch's theorem, the electromagnetic wave travels in an ideal crystal and the velocity does not decrease. However, the phonon is produced by lattice vibration and the electromagnetic wave interacts with the phonon. As a result, the intrinsic dielectric loss is produced. Extrinsic factors, such as the porosity and the grain boundary, destroy the ideal structure of the crystal and affect the electromagnetic wave transmission, which increases the dielectric loss of the ceramic sample. Compared to intrinsic factors, many papers and research results^{25–27} have shown that the extrinsic factors usually have a major impact on the dielectric property of the sample, particularly its dielectric loss. Consequently, the grains are expected to grow sufficiently and the number of the grain boundary is small. Besides, the ceramic sample is also expected to have few pores inside. As shown in Fig. 2(A), it can be found that the grains on the surface of the ceramic sample are packed tightly and the shape is regular.

Although the embedding sintering method is applied in this work, the surroundings of the surface and inside structure of the ceramic sample are different in the sintering process. Thus, the SEM result on the surface does not perfectly represent the actual grain arrangement of the ceramic sample^{28–29}. In view of this, the prepared ceramic samples are polished with sandpaper of different specifications and then placed in an ultrasonic machine for 15 min. Subsequently, the polished samples are thermally etched at different temperatures for 2 h. If the temperature is too low, the powders in the grain gaps cannot be absorbed by the grain and the grain boundary cannot be presented clearly. However, the grains on the polished surface grow again and the actual grain arrangement cannot be observed when the thermally etched temperature is too high. After many experiments, the polished $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic sample can be thermally etched

effectively at 660 °C for 2 h. As presented in Fig. 2(B), a homogeneous and dense microstructure is observed. The grains inside the sample are in a tidy arrangement and the pores are fewer and smaller inside the prepared ceramic sample, which means the green $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic body has been well densified at 680 °C. Besides, it can be found that the grain size is between 4–10 μm as shown in Fig. 2(B). Considering the importance of the grain size, the average grain size of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic sample is measured with the linear intercept method, in which 400 grains are selected on each line. The measurement result shows that the average grain size is 6.02 μm for the prepared ceramic sample. Compared with the measured result of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic sample prepared by traditional means, the grain size in this work increases. This phenomenon has appeared in other studies^{30–31}. In essence, the sintering process is the process of grain growth. Because there is no liquid phase involved in this experiment, diffusion mass transfer is the main mass transfer mechanism in this work. According to the lattice dynamical theory, the large grain grows and the small one is absorbed gradually in the sintering process. And the grain boundary moves under the stress between the adjacent grains in the sintering process. Finally, the average grain size of the prepared ceramic sample increases and the grain boundary between the adjacent grains is straight. However, the gaps between the powders and the impurities in the green ceramic body hamper the movement of the grain boundary. As a result, growth of the grain is prevented. Compared with traditional method, the ethanol is distributed before the sintering process and there is no sintering aid in the modified solid-state reaction method. Consequently, in this work, the green ceramic body has a lower impurity content. Moreover, the isostatic pressing technology further decreases the gap between the powders. Consequently, the grains grow sufficiently and the average grain size increases in this work.

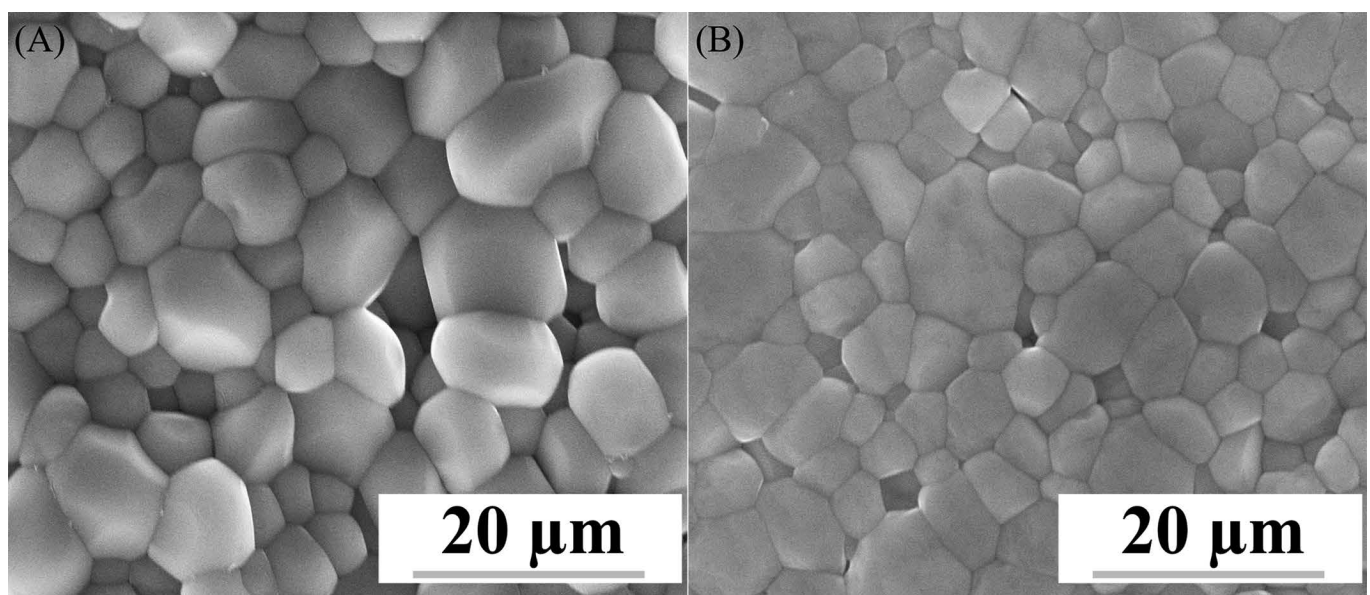


Fig. 2: SEM images of (A) at 680 °C and (B) thermally etched at 660 °C.

Fig. 3 presents the relative density of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic samples sintered at different temperature. Relative density is the most important index of sintering properties, and has a significant impact on the dielectric property of prepared ceramic samples³². As shown in Fig. 3, the relative density increases with the rise of the sintering temperature at the beginning. That is because the grain grows and the space between the grains continues to decrease in size. Then the volume of the sample shrinks, which results in the increase in the relative density. The relative density increases to the maximum value of 95.1 % (6.879 g/cm^3) when the sintering temperature is 680°C . The high relative density means the grain grows sufficiently at this temperature, which is consistent with the SEM result in Fig. 2. However, the relative density begins to decline as the sintering temperature continues to rise. Theoretically, secondary growth of the grain occurs when the sintering temperature is too high. Some grains begin to grow abnormally and the number of pores between the grains increases in this process. As a result, the volume of the prepared ceramic sample is enlarged and the relative density decreases. This phenomenon has also been reported in other literature^{33–34}. Thus, the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic has good sintering characteristics when the sintering temperature is 680°C .

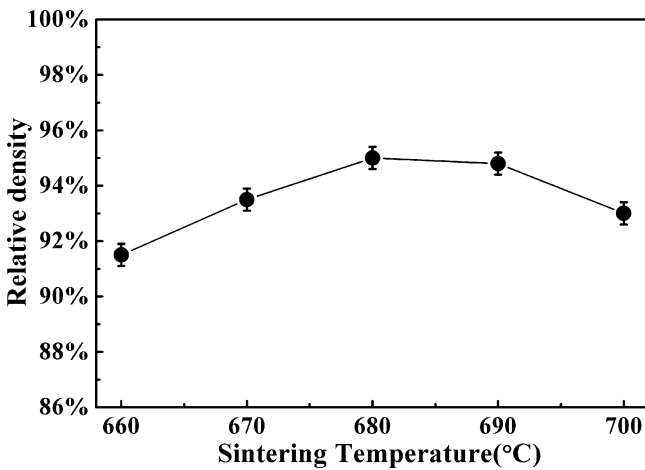


Fig. 3: Relative density of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ samples sintered at different temperature for 4 h.

The microwave dielectric property of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic samples as a function of the sintering temperature is presented in Fig. 4. As shown in Fig. 4, the dielectric loss continues to decrease with the increase in the sintering temperature, which is attributed to the growth of the grains and the increase in the relative density. It can be seen from Fig. 4 that the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic has a relative permittivity ~ 27.5 , a $Q \times f$ value $\sim 28\,000$ GHz and a TCF value ~ -15 ppm/K after being sintered at 680°C for 4 h. However, the $Q \times f$ value begins to decrease when the sintering temperature exceeds 680°C , which is consistent with the result in Fig. 2 and Fig. 3. Compared with the measurement result of the ceramic sample prepared with the traditional method, the dielectric property of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic is improved in this work, particularly the dielectric loss. The $Q \times f$ value increases by 57 % from 17 500 GHz to 28 000 GHz. Because of

the improvement to the preparation method, the grains grow further in the sintering process. Consequently, the number of grain boundaries decreases and the density of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic sample increases. As a result, the dielectric loss decreases when the electromagnetic wave passes through the ceramic sample. Moreover, the sintering temperature drops from 720°C to 680°C . As mentioned in the microstructure measurement result, the improvement to the preparation process increases the mass transfer efficiency in the sintering process and no residual sintering aid prevents the movement of the grain boundary^{35–36}. For this reason, the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic sample can be sintered effectively at lower temperature in this work.

In addition, the relative permittivity of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic increases from 25.7 to 27.5 as shown in Fig. 4. The relative permittivity is the main parameter referring to the polarization property of the dielectric material in an electrostatic field. The magnitude of the relative dielectric constant is closely related to the type of polarization inside the material. Theoretically, the relative permittivity can be explained according to Clausius-Mossotti equation³⁷:

$$(\epsilon_r - 1)/(\epsilon_r + 1) = (4\pi/3)(\alpha_D/V) \quad (2)$$

Then we can rearrange the equation and get

$$\begin{aligned} \epsilon_r &= (3V + 8\pi\alpha_D)/(3V - 4\pi\alpha_D) \\ &= 1 + 12\pi\alpha_D/(3V - 4\pi\alpha_D) \end{aligned} \quad (3)$$

in which V is the primary cell volume of the ceramic and α_D is the total polarizability of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic unit cell. V can be calculated based in the XRD result and the V of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic crystal structure is 79 \AA^3 in this work. According to Equation (3), α_D has a great influence on the relative permittivity. The relative permittivity increases with the total polarizability of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic unit cell. Based on Shannon's research findings³⁸, the total polarizability of a complex material crystal structure is the sum of all the ion polarizabilities in the unit cell. Using Shannon's additive rule³⁹, the α_D of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic is obtained as follows:

$$\alpha_D = 0.5 \times \alpha_{\text{Na}^+} + 0.5 \times \alpha_{\text{Bi}^{3+}} + \alpha_{\text{W}^{6+}} + 4 \times \alpha_{\text{O}^{2-}} \quad (4)$$

in which α_{Na^+} , $\alpha_{\text{Bi}^{3+}}$, $\alpha_{\text{W}^{6+}}$ and $\alpha_{\text{O}^{2-}}$ are the polarizability of Na^+ , Bi^{3+} , W^{6+} and O^{2-} respectively. According to the previous work²⁴, the W^{6+} is 4-coordinated in a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ scheelite structure, α_{Na^+} , $\alpha_{\text{Bi}^{3+}}$, $\alpha_{\text{W}^{6+}}$ and $\alpha_{\text{O}^{2-}}$ are 1.80 \AA^3 , 6.12 \AA^3 , 3.20 \AA^3 and 2.01 \AA^3 , respectively. Then the obtained theoretical relative permittivity is 28.1. Except for the intrinsic factors, the relative permittivity of the ceramic sample is also influenced by extrinsic factors^{40–41}, such as the grain boundaries and pores inside the ceramic sample. Considering the error of the ion polarizability and the influence of grain boundary and point defects inside the ceramic sample, the relative permittivity value of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic in this work is consistent with the theoretical value.

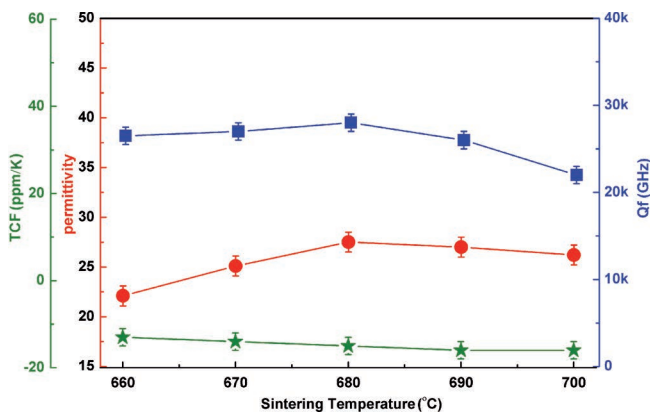


Fig. 4: Microwave dielectric properties (■: $Q \times f$ value, ●: permittivity, ★: TCF value) of $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic as a function of sintering temperature.

IV. Conclusions

With the rapid development of communication technology and the electronics industry, there is an urgent demand for new electro-ceramic material with a low dielectric loss and low sintering temperature. The developed ceramic material can be used in the high-frequency communication industry and co-fired with new electrode material or organic compound. In the semi-conductor preparation process, the electrode material is deposited on the dielectric ceramic layer and LTCC technology enables co-firing of semiconductor devices into the package. In recent years, many new ceramic materials with high $Q \times f$ value have been reported. However, these materials always have a high sintering temperature. Besides, ceramic materials with a low sintering temperature are always based on molybdates and vanadates, which are soluble in water. This means they are difficult to be apply in practical industrial production. In contrast, although the sintering temperature of the tungstates is always high, most tungstates exhibit good stability in air. Changing the process and reducing the sintering temperature is a feasible solution to optimize the performance of the tungstates. Compared with the addition of sintering aids and the solid solution method, improving the preparation process is an effective way to lower the sintering temperature of ceramic material.

In this work, the modified solid-state reaction method is applied to prepare $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic. Owing to the improvement in the preparation process, the ceramic samples can be sintered effectively at 680 °C for 4 h with a relative density of 95.1 %. The dielectric property of the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic in this work is measured with a $Q \times f$ value of 28 000 GHz, a relative permittivity of 27.5 and a temperature coefficient of -15 ppm/K. Compared with the measured result for the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ ceramic prepared with traditional solid-state reaction method, the sintering temperature dropped from 720 °C to 680 °C, and the $Q \times f$ value increased by 57 % from 17 500 GHz to 28 000 GHz. The experimental results indicate that the modified solid-state reaction method is an excellent way to improve the ceramic properties and the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{WO}_4$ system is a good candidate for the ULTCC technology.

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