Microwave dielectric characteristics of MCAS glass addition Ba$_2$Ti$_9$O$_{20}$ Ceramics

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Abstract

Trying to lower the sintering temperatures of Ba$_2$Ti$_9$O$_{20}$ ceramics MgO-CaO-SiO$_2$Al$_2$O$_3$ (MCAS) composite glass powder was used as the low melting glass addition to lower the sintering temperatures of Ba$_2$Ti$_9$O$_{20}$ ceramics. The mainly crystal phases of MCAS glass were cordierite and anorthite, but the crystal phases of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics were Ba$_2$Ti$_9$O$_{20}$ and cordierite. The temperatures needed to densify the MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics was decreased as the content of MCAS glass increased. The bulk densities of densified MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics decreased with the increase of MCAS glass content. The logarithmic Maxwell’s relationship: $V \log D = \Sigma V_i \log D_i$ could be used to predict the theoretical bulk densities of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics. In this study, the microwave dielectric characteristics of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics were also developed as a function of sintering temperatures and MCAS glass content.

Keywords: Ba$_2$Ti$_9$O$_{20}$, MgO-CaO-SiO$_2$Al$_2$O$_3$ glass, logarithmic Maxwell's relationship

1. Introduction

Ba$_2$Ti$_9$O$_{20}$ was the one most common high-Q dielectric materials used in the microwave range. Ba$_2$Ti$_9$O$_{20}$ was first reported by Jonker [1] and investigated as microwave materials by O’Bryan and Plourde et al [2-5]. The dielectric properties of Ba$_2$Ti$_9$O$_{20}$ ceramics with several different additives had also been investigated in the microwave region. For the preparation of monophasic samples of Ba$_2$Ti$_9$O$_{20}$ ceramics from BaCO$_3$ and TiO$_2$ by conventional solid-state reaction, the stoichiometry could be precisely controlled. Since there were various thermodynamically stable compounds in the vicinity of the desired composition of TiO$_2$-system, including BaTi$_3$O$_7$, BaTi$_5$O$_{12}$, BaTi$_7$O$_{16}$, and Ba$_4$Ti$_9$O$_{20}$. Lu et al. Reported that the BaO:TiO$_2 = 2:9$ powder, obtained by sol-gel method, could be calcined at 1200°C for 10h to produce Ba$_2$Ti$_9$O$_{20}$ sole phase. In this research, the solid-state reaction processes of BaCO$_3$ and TiO$_2$ to form Ba$_2$Ti$_9$O$_{20}$ phase at different temperatures and times were developed, and our finding on the Ba$_2$Ti$_9$O$_{20}$ compounds had shown some degree of difference from those in the literature [2-6].

A high sintering temperature of 1400°C was required to achieve densification of Ba$_2$Ti$_9$O$_{20}$ ceramics in order to avoid the compositional fluctuation [2-5]. Low melting glass addition, chemical processing, and smaller particle sizes of starting materials were three of the methods used to reduce the sintering temperatures of dielectrics [7]. However, there were few references in the literature reporting the influence of glass addition on the microwave dielectric of Ba$_2$Ti$_9$O$_{20}$ ceramics. In this study, calcined 2BaCO$_3 + 9$TiO$_2$ composition at 1200°C for 10h did not form Ba$_2$Ti$_9$O$_{20}$ phase completely. And the 1200°C-calcined Ba$_2$Ti$_9$O$_{20}$ composite was used as the precursor. The MgO-CaO-SiO$_2$-Al$_2$O$_3$ (MCAS) composite glass, which was fabricated by sol-gel method [8], was used as the low melting glass addition to lower the sintering of Ba$_2$Ti$_9$O$_{20}$ ceramics. It was found that the addition of MCAS glass did not inhibit the residual satellite to form Ba$_2$Ti$_9$O$_{20}$ phase. The purpose of this study was to gain insight into properties and microstructure variations of Ba$_2$Ti$_9$O$_{20}$ ceramics from the addition of MCAS glass. We discussed the sintering behavior and microwave dielectric properties of commercial Ba$_2$Ti$_9$O$_{20}$ ceramics with the addition of MCAS glass. Relationships among the sintering temperature, microstructure evolution, phase formation, and the microwave dielectric properties of MCAS-fluxed Ba$_2$Ti$_9$O$_{20}$ dielectric was developed.

2. Experimental Procedures

In the present investigation, a homogeneous glass of composition containing (in wt%) 5% MgO, 19% CaO, 26% Al$_2$O$_3$, and 50% SiO$_2$ (approximate stoichiometry MgO : CaO : Al$_2$O$_3$ : SiO$_2$ =6.5 : 14.5 : 27.5 : 51.5, abbreviated as MCAS) was prepared by the sol-gel method. In a typical laboratory scale synthesis using the nitrates, 40% colloidal silica was dispersed in 600 ml of deionized water, and concentrated nitric acid was also added into the solution. To this acidic suspension we added magnesium nitrate hexahydrate, calcium nitrate hexahydrate, and aluminum nitrate hexahydrate. The
The subsequent addition of ammonium hydroxide resulted in the quantitative precipitation of magnesium, calcium, and aluminum hydroxides. The glass powder was formed in the solided format. The solids were collected by filtration and calcined at 300°C for 1hr. The calcination step was desirable to convert any ammonium nitrate present to oxides of nitrogen and water. The resulting material was a white, free-flowing powder, and it was the MCAS glass precursor. High purity (>99.5%) BaCO$_3$ and TiO$_2$ powders were used as the starting materials of Ba$_2$Ti$_9$O$_{20}$, and they were mixed and ball-milled in deionized water in accordance with the composition of Ba$_2$Ti$_9$O$_{20}$. After drying, the reagent powder was calcined at different temperatures with different times. The crystal structures of calcined powders were examined by using an X-ray diffractometer.

The 1200°C-10h-calcined Ba$_2$Ti$_9$O$_{20}$ powder was mixed with 0, 5, and 10wt% MCAS glass by agate mortar and pestle with deionized water for 1h. After drying, the powder was pressed into pellets uniaxially in a steel die. Typical dimensions of the pellets were 15mm in diameter and 1.5mm in thickness. Sintering of these pellets was carried out at a temperature between 1180°C and 1340°C under ambient conditions for a duration of 4h. Crystallization of the sintered MCAS-Ba$_2$Ti$_9$O$_{20}$ was investigated using X-ray diffraction patterns. X-ray diffraction patterns were taken at 2θ=4° per minute using CuKα radiation. The bulk densities of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics as a function of sintering temperatures were measured using the Archimedes method. The microstructural observations and analyses of the MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics were directly performed with the SEM (scanning electronic micrograph). Microwave dielectric characteristics were measured by Hakki and Coleman’s dielectric resonator method [9], which was improved by Courtney [10]. An HP8720B network analyzer was used for the microwave characteristic measurements. The dielectric constants could be accurately determined by measuring the resonant frequency of the Te$_{011}$ mode and verified by the Te$_{011}$ resonant modes. The temperature coefficient of the resonant frequency (τr) was defined as follows:

$$\tau_r = \frac{f_0 - f_9}{f_9} \times 65$$

(1)

Where $f_20$ and $f_9$ were the resonant frequency at 20°C and 85°C, respectively.

3. Results and discussion

It is well known that in the BaO-TiO$_2$ system numberous satellite phases, e.g. Ba$_2$Ti$_9$O$_{20}$, BaTi$_9$O$_{20}$, Ba$_2$Ti$_5$O$_{20}$, and Ba$_2$Ti$_6$O$_{20}$ exist. Furthermore, various phases are also observed in BaO-TiO$_2$ rare earth oxide system. The conventional solid-state reaction process for synthesizing Ba$_2$Ti$_9$O$_{20}$ compounds were based on the following:

$$\text{2BaCO}_3 + 9\text{TiO}_2 \rightarrow \text{Ba}_2\text{Ti}_9\text{O}_{20} + 2\text{CO}_2$$

(2)

However, the real solid reaction processes are usually more complex. From the X-ray diffraction patterns, as shown in Table 1, even calcining at 1150°C for 2h is not enough to form Ba$_2$Ti$_9$O$_{20}$ phase, only the TiO$_2$, Ba$_2$Ti$_5$O$_{20}$, and Ba$_2$Ti$_6$O$_{20}$ phases are detected in the calcined powders. Proceeding calcination at 1150°C for 10h is not enough to form Ba$_2$Ti$_9$O$_{20}$ phase, and the source material TiO$_2$, BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$ phases are residual. Further increasing the calcining temperature to 1200°C, and 2h and 10h are used as the calcining times, the BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$ phases are still residual. It is found 1200°C and 70h is the needed calcining condition to form Ba$_2$Ti$_9$O$_{20}$ phase only. This result suggests that forming Ba$_2$Ti$_9$O$_{20}$ using the solid-state reaction method, high calcining temperature and long calcining time are needed.

The X-ray diffraction patterns from the as-sintered surface of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics as a function of sintering temperatures and MCAS content are shown in Table 2. It was reported that the sintered MCAS glass existed the anorthite and cordierite as two mainly crystal structures, and the Ba$_2$Ti$_9$O$_{20}$precursor contained the satellite phases of BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$. Therefore, phase control is expected to be extremely difficult in such a system. As 0wt%-MCAS-added Ba$_2$Ti$_9$O$_{20}$ ceramics are sintered at 1260°C, the major phase is the Ba$_2$Ti$_9$O$_{20}$ and the the satellite phases of BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$, are still residual, but the the satellite phases of BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$ are not residual as 5wt% and 10wt% MCAS glass are added as sintering aid. This result suggests that the MCAS glass will improve the the satellite phases of BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$ to from Ba$_2$Ti$_9$O$_{20}$. For 0wt%-MCAS-added Ba$_2$Ti$_9$O$_{20}$ ceramics to consume the satellite phases of BaTi$_9$O$_{20}$ and BaTi$_6$O$_{20}$, sintered at 1340°C is needed. For 5wt%- and 10wt%-MCAS as the fluxedcontent, the Ba$_2$Ti$_9$O$_{20}$ ceramics will melt at 1340°C.

The variations of the bulk densities of Ba$_2$Ti$_9$O$_{20}$ ceramics against the sintering temperatures and glass content are shown in Fig.1. The logarithmic Maxwell's relationship: $V \log D = \Sigma V_i \log D_i$ could be used to predict the theoretical densities of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics, where $V$ is the volume of each component and D is the density of each component. The estimated theoretical bulk densities of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics are measured from the values of MCAS (2.58g/cm$^3$) and Ba$_2$Ti$_9$O$_{20}$ ceramics (4.58g/cm$^3$). The estimated theoretical bulk densities of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics are 4.417g/cm$^3$ and 4.278g/cm$^3$ for 5wt%- and 10wt%-MCAS glass fluxed Ba$_2$Ti$_9$O$_{20}$ ceramics, respectively. The density curves of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics show that the densities increase with the increase of sintering temperatures, independent of MCAS glass content. The temperatures needed to densify the Ba$_2$Ti$_9$O$_{20}$ ceramics decrease with the increase of MCAS glass content. The temperatures for 0, 5, and 10wt%-MCAS-added Ba$_2$Ti$_9$O$_{20}$ ceramics needed to reach > 97% theoretical densities are 1300, 1260, and 1220°C, respectively.

The dielectric constants (εr values) of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics are shown in Fig.3, the sintering temperatures are changed from 1180°C to 1340°C. The εr values of MCAS-Ba$_2$Ti$_9$O$_{20}$ ceramics increase with the increase of sintering temperatures independent of MCAS content. The εr values saturate at 1340, 1260, and 1220°C for 0wt%-5wt%-, and 10wt%-MCAS fluxed ceramics, respectively. The saturated εr values of 5wt%- and 10wt%-MCAS-fluxed Ba$_2$Ti$_9$O$_{20}$ ceramics are lower than those of Ba$_2$Ti$_9$O$_{20}$ ceramics reported, that the εr values of MCAS glass has the lower saturated than Ba$_2$Ti$_9$O$_{20}$ ceramics does will lead to this result.
The quality values (Qxf) of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics are investigated as a function of sintering temperatures and MCAS content, and the results are shown in Fig.3. For 0wt%-MCAS fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics, as the sintering temperatures increase from 1220$^\circ$C to 1300$^\circ$C, the Qxf values increase apparently. For 5wt%- and 10wt%-MCAS fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics, as the sintering temperatures increase from 1180$^\circ$C to 1260$^\circ$C, the Qxf values increase apparently. The decrease of pores and increase in grain growth will cause this result. The saturated Qxf values decrease with the increase of MCAS content, and the saturated Qxf values are 38500, 29500, and 26500, respectively. Even the addition of MCAS will lower down the sintering temperatures of Ba$_2$Ti$_3$O$_{20}$ ceramics, the shortcoming is the decrease of Qxf values.

The $\tau_f$ values of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics are shown in Fig.4. As the Fig.4 shows, the sintering temperatures and MCAS content have large effect on the $\tau_f$ values of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics. As the sintering temperatures increase, the $\tau_f$ values for 0wt%-MCAS fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics linearly change from +0.2ppm/$^\circ$C (sintered at 1220$^\circ$C) to +4.5 ppm/$^\circ$C (1340$^\circ$C). The $\tau_f$ values for 5wt%-MCAS fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics linearly change from -11.5ppm/$^\circ$C (1180$^\circ$C) to -3.2 ppm/$^\circ$C (1300$^\circ$C). The $\tau_f$ values for 10wt%-MCAS fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics linearly change from -16.5ppm/$^\circ$C (1180$^\circ$C) to -9.7 ppm/$^\circ$C (1300$^\circ$C).

4. Conclusions

The reaction process of Ba$_2$O:TiO$_2$=2:9 powder and the sintering and the microwave dielectric characteristics of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics have been developed in this study, and several conclusions are deduced as follows:

1. Calcining the Ba$_2$O:TiO$_2$=2:9 powder at 1200$^\circ$C for 10h, the Ba$_2$Ti$_3$O$_{20}$ are not formed completely, and the satellite phases are residual. The addition of MCAS glass does not inhibit the residual satellite phases to transform into Ba$_2$Ti$_3$O$_{20}$ phase.

2. The densities, the dielectric constants, and the quality values of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics increase with the increase of sintering temperature. The needed temperatures to reveal the saturation values of the densities, the dielectric constants, and the quality values are shifted to lower values as the amount of MCAS content increases.

3. As the MCAS glass content increase from 0wt% to 10wt%, the saturated $\tau_f$ values change from positive values to negative ones.

References


Table. 1 The X-ray patterns analysis of Ba$_2$Ti$_3$O$_{20}$ calcined powders. (O: exist, X: not exist)

<table>
<thead>
<tr>
<th>Calcining condition</th>
<th>BaTi$_2$O$_7$</th>
<th>TiO$_2$</th>
<th>BaTi$<em>3$O$</em>{11}$</th>
<th>Ba$_2$Ti$<em>2$O$</em>{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150$^\circ$C/2h</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>1150$^\circ$C/10h</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
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<tr>
<td>1200$^\circ$C/2h</td>
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<td>X</td>
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<td>O</td>
<td>X</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>1200$^\circ$C/70h</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

Table. 2 The X-ray patterns analysis of MCAS-Ba$_2$Ti$_3$O$_{20}$ ceramics. (O: exist, X: not exist, ST: sintering temperature)

<table>
<thead>
<tr>
<th>ST/MCAS content(wt%)</th>
<th>BaTi$_2$O$_7$</th>
<th>BaTi$<em>3$O$</em>{11}$</th>
<th>cordierite</th>
<th>Ba$_2$Ti$<em>2$O$</em>{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1260$^\circ$C/0wt</td>
<td>O</td>
<td>O</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>1260$^\circ$C/5wt</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>1260$^\circ$C/10wt</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>1340$^\circ$C/0wt</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>O</td>
</tr>
</tbody>
</table>

Fig.1 The bulk densities of MCAS-fluxed Ba$_2$Ti$_3$O$_{20}$ ceramics, as a function of sintering temperatures and MCAS content.
Fig. 2 The microwave dielectric constants of MCAS-fluxed Ba$_2$Ti$_9$O$_{20}$ ceramics, as a function of sintering temperatures and MCAS content.

Fig. 3 The quality values of MCAS-fluxed Ba$_2$Ti$_9$O$_{20}$ ceramics, as a function of sintering temperatures and MCAS content.

Fig. 4 The temperature coefficients of resonant frequency of MCAS-fluxed Ba$_2$Ti$_9$O$_{20}$ ceramics, as a function of sintering temperatures and MCAS content.