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Microwave dielectric materials based on the $MgO–SiO_2–TiO_2$ system

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Abstract

Ceramics in the system $MgO–SiO_2–TiO_2$ were prepared by standard mixed oxide route. By adding $ZnO–B_2O_3$ to the starting mixtures, the firing temperature of the ceramics could be reduced to 1160 °C. Small additions of $MnCO_3$ and $CaTiO_3$ improve microwave dielectric properties leading to an increase in insulation resistance and a decrease in temperature coefficient of capacitance. By adding Co_2O_3 grain growth can be inhibited and the dielectric *Qf* value greatly increased. The resultant ceramic material exhibited low dielectric constant and low dielectric loss: relative permittivity (ε_r): 20±2; temperature coefficient of capacitance (τ_c): 0±30 ppm/°C; *Qf*: 100,000 (at 10 GHz); insulation resistance: 10^{13} Ω cm:

Keywords: Additives; Dielectric properties; Firing; Grain growth; $MgO–SiO_2–TiO_2$ system

1. Introduction

With the recent advances in microwave telecommunication and satellite broadcasting, a variety of microwave devices have been developed using dielectric resonator as the frequency determining components. A dielectric resonator (DR) provides significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of high frequency devices. The important characteristics required for a DF are high quality factor and low temperature variation of resonant frequency for stability.

Amongst the many kinds of dielectric materials used for microwave applications,[1–3] the dielectric ceramic materials with low permittivity and small dielectric losses are employed in dielectric filters. $MgO–SiO_2–TiO_2$-based ceramics have improved microwave dielectric properties.[4] They have excellent microwave properties with low dielectric constant, high *Q* value and low temperature coefficient of capacitance. The addition of $ZnO–B_2O_3$ to the system enables the use of lower firing temperatures and use cheaper internal metallic conductors.

In the $MgO–SiO_2–TiO_2$ system, Mg_2TiO_4 and Mg_2SiO_4 can be synthesized by solid-state reactions with MgO, TiO_2 and SiO_2, respectively. The Mg_2TiO_4 has a low dielectric constant and dielectric loss; its temperature coefficient of capacitance (TCC) has a small positive value. If mixed with materials having negative TCC, ceramic materials with adjustable TCC can be obtained. However, it is difficult to control the firing temperature of Mg_2TiO_4 because the firing temperature is high, up to 1400C. During processing, if optimum firing temperatures are exceeded, the dielectric properties will be degraded due to the increase of pores and abnormal grain growth. Mg_2SiO_4 is anther kind of high frequency ceramic material with simple processing and stable dielectric properties. The TCC of materials can be adjusted by selecting Mg_2SiO_4. Mg_2TiO_4 and Mg_2SiO_4 are selected as the principal composition of the system. In addition, small amount of additives and flux can be added to reduce the firing temperature and improve the dielectric properties.

2. Experimental procedure

2.1. Sample preparation

Calculated amounts of reagent-grade chemicals of MgO, SiO_2 and TiO_2 were weighed, with 0.45 wt.%–0.52% $MnCO_3$ ~0.01 wt.%–0.04 wt.%MnO_2, 0.40 wt.%–2.40 wt.%Co_2O_3, 0.40 wt.%–0.80 wt.% $CaTiO_3$ and appropriate quantities of flux of $ZnO–B_2O_3$. The mixtures were milled for 8 h using zirconia balls and

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deionized water as milling media, dried and added with binder, and then moulded into disks 20 mm in diameter and 2 mm in thickness under a pressure of 4 MPa. The disks were sintered in air at 1160 °C.

2.2. Characterization

The capacitance and dielectric loss were measured using HP4291B. The insulation resistance was measured by ZC36 microampere meter. MC-710P (GZ-ESPEC Co.), YY2815 Precision Analyzer and HM27002 were used to measure the TCC. The measurement frequency was 1 GHz. The dielectric constant and unloaded quality factor were measured at 10 GHz by HP8720ES Network Analyzer using TE_{011} resonatant mode and Hakki and Coleman method. A cylindrically shaped dielectric resonator was positioned between two brass plates.

X-ray diffraction (XRD) was used to determine the main phases and the lattice parameters. The microstructures of the samples were examined by scanning electron microscopy (SEM).

3. Results and discussion

3.1. The effect of sintering aid on dielectric properties

In order to reduce the firing temperature of the ceramics, low melting glass addition was used in the present study. $ZnO–B_2O_3$ was selected to act as flux due to its low melting point about 1100 °C.[5] The melting points of the compounds of $3ZnO·B_2O_3$:$ZnO·B_2O_3$ and $ZnO·3B_2O_3$ are 1125 °C, 1025 °C and 900 °C, respectively (the ratio of the additive content $ZnO:B_2O_3$ were 3:1,1:1,1:3 respectively). As long as the ratio of $ZnO:B_2O_3$ was properly adjusted, sintering aids with different low melting points can be obtained. The optimum addition of $ZnO–B_2O_3$ was determined from experiments. The results are shown in Table 1. The optimum addition of sintering aid is 15 wt.%. In this case, the material had optimum dielectric properties and firing temperature can be reduced to 1160 °C.

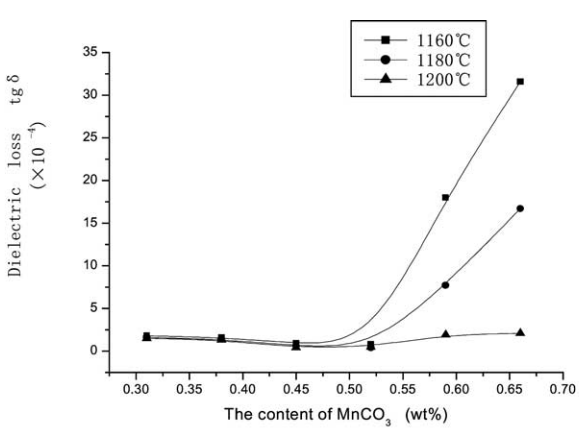

Fig. 1. Dielectric loss as a function of $MnCO_3$ content (the samples fired at 1160 °C, 1180 °C and 1200 °C).

3.2. The effect of additives on microwave dielectric properties

In order to improve the dielectric properties of the ceramics, selective additives were added to the systems. The effects of additives of $MnCO_3·CaTiO_3$ and Co_2O_3 were studied.

3.2.1. The addition of $MnCO_3$

$MnCO_3$ was chosen for the following reasons. First MnO, which can be obtained from $MnCO_3$ by heating encourages grain growth. Secondly $MnCO_3$ can be considered as a kind of oxidizer. It can make the reaction $Oo^{\times} = Vo^{\cdot\cdot} + 2e^{\blacksquare} + 1/2O_2$ process reversible. As a result, the number of free electron could diminish so that the dielectric loss decrease accordingly.[6] However excessive $MnCO_3$ may damage the dielectric properties due to defects and porosity. The results from experiments are shown in Fig. 1 and Table 2. In this system, the $MnCO_3$ content should be controlled to be in the range of 0.45–0.53 wt.%.

3.2.2. The addition of $CaTiO_3$

The temperature coefficient of capacitance of $CaTiO_3$ is −1500 ppm/°C. It can compensate materials with positive temperature coefficient of capacitance to make τ_c approximately equal to zero. The results are shown in Fig. 2. It can be confirmed from Fig. 3 that $CaTiO_3$

Table 1
The dielectric properties of the samples prepared with different amount of sintering aid

Content (wt.%)[a]	ST (°C)	tg δ ($\times10^{-4}$) (1 GHz)	I_R (Ω cm)	ε (1GHz)
10	1200	1.5	1.1×10^{13}	20.929
15	1160	1.2	1.0×10^{14}	20.192
20	1220	9.6	2.2×10^{13}	20.63
25	1230	42.1	1.1×10^{11}	20.097

[a] The ratio of $ZnO:B_2O_3$ was 2:1.

Table 2
The dielectric properties of the samples prepared with different amounts of $MnCO_3$

Content (wt.%)	τ_c ($\times10^{-6}$/°C)	tg δ ($\times10^{-4}$) (1 GHz)	I_R (Ω cm)	ε (1 GHz)
0.31	102.5	1.8	1.3×10^{14}	12.1
0.38	96.9	1.6	6.5×10^{13}	12.5
0.45	116.5	0.6	1.5×10^{14}	12.6
0.52	109.2	0.4	6.0×10^{14}	13.4
0.66	108.6	31.6	1.5×10^{11}	12.9

exists in the system. In addition, the appropriate content of $CaTiO_3$ can also reduce dielectric loss and improve insulation resistance of the ceramic materials. The results can be seen in Figs. 4 and 5.

From Figs. 2, 4 and 5, the optimum content of $CaTiO_3$ is determined to be 0.6 wt.%. The results were verified by many experimental data, but the mechanisms of its effects on dielectric loss and insulation resistance were need to be investigated further.

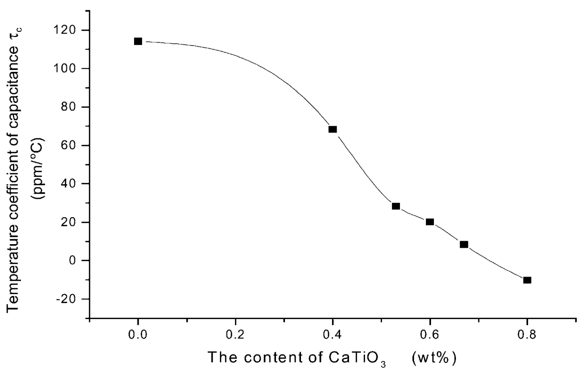

Fig. 2. TCC as a function of $CaTiO_3$ content.

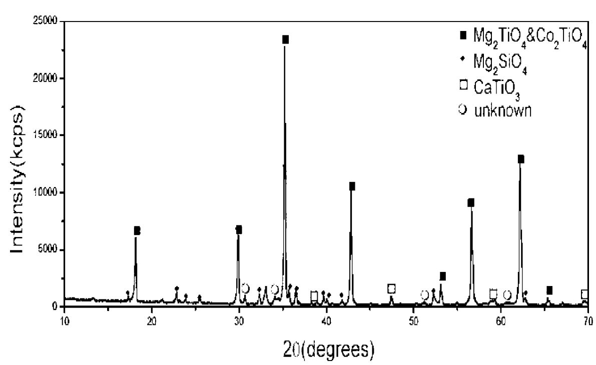

Fig. 3. XRD pattern of $MgO–SiO_2–TiO_2$ calcined powder addition of 0.6 wt.% $CaTiO_3$.

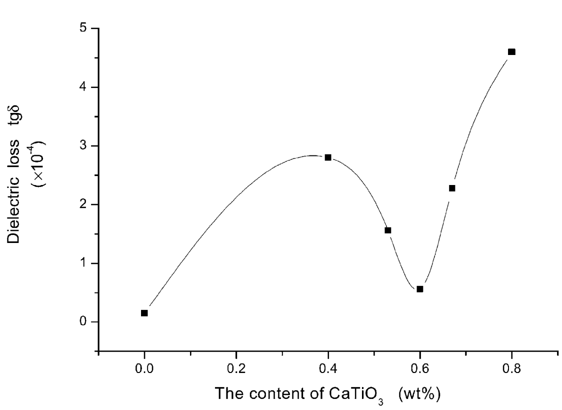

Fig. 4. Dielectric loss tg δ as a function of $CaTiO_3$ content.

3.2.3. *The addition of Co_2O_3*

Co_2O_3 is a kind of mineralizer which can reduce free oxides to improve the bulk densities of the sintered bodies. Furthermore, it can act as a grain inhibitor to improve the Q value of the system greatly.[7] Fig. 6 shows

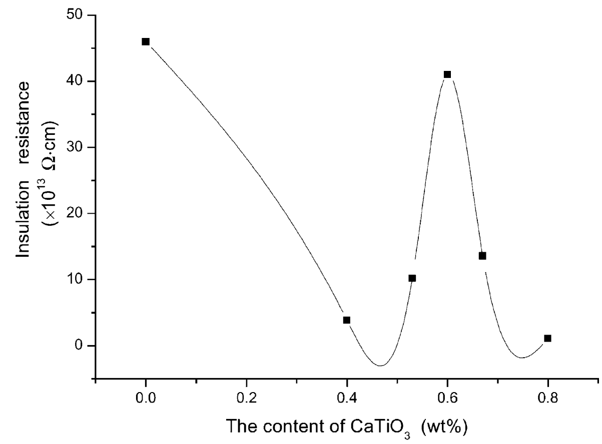

Fig. 5. Insulation resistance as a function of $CaTiO_3$ content.

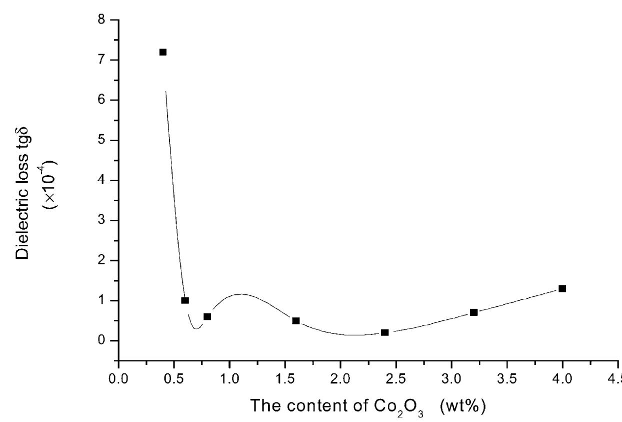

Fig. 6. Dielectric loss as function of Co_2O_3 content.

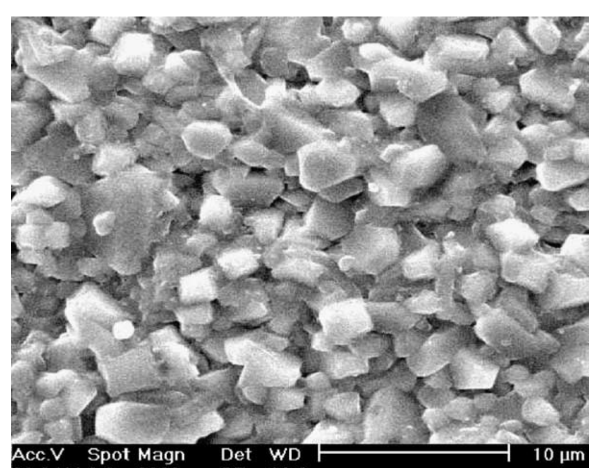

Fig. 7. SEM micrograph of $MgO–SiO_2–TiO_2$ ceramic added with 2.4 wt.% Co_2O_3.

that the optimum content of Co_2O_3 is about 2.4 wt.%. The typical microstructure of the as-sintered surface of $MgO–SiO_2–TiO_2$ ceramic prepared with 2.4 wt.% Co_2O_3 is shown in Fig. 7.

After adding $MnCO_3$, $CaTiO_3$ and Co_2O_3, the losses of ceramics in the system $MgO–SiO_2–TiO_2$ were reduced greatly; accordingly, high quality (Q) values were obtained.

4. Conclusion

1. $Mg_2TiO_4–Mg_2SiO_4$ yielded high frequency ceramic materials with low dielectric constant.
2. $ZnO–B_2O_3$ acts as sintering aid to reduce the firing temperature to 1160 °C.
3. Addition of $MnCO_3$ should be controlled in the range 0.45–0.53 wt.%. At this level it can decrease the dielectric loss.
4. The optimum content of $CaTiO_3$ is about 0.6 wt.%. It can reduce the temperature coefficient of capacitance to be within 0 ± 30 ppm/°C.
5. Addition of 2.4 wt.% Co_2O_3 can also improve the dielectric properties remarkably.
6. The dielectric properties of the resultant ceramic material are: Dielectric constant ε: 20 ± 2, temperature coefficient of capacitance τ_c: 0 ± 30 ppm/°C, Qf (at 10 GHz): 100,000 (at 10 GHz), Insulation resistance: 10^{13} Ω cm.

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