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Sintering Behaviour and Dielectric Properties of $MnCO_3$-doped MgO-based Ceramics

WANG Zhixiang[1,2,3], CHEN Ying[2,3,4], PANG Qingyang[2,3], LI Xin[2], WANG Genshui[1,2,3,4]

(1. School of Chemistry and Materials Science, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China; 2. Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 3. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; 4. The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China)

Abstract: Ceramic dielectric materials with high dielectric strength and mechanisms of their internal factors affecting dielectric strength are significantly valuable for industrial application, especially for selection of suitable dielectric materials for high-power microwave transmission devices and reliable power transmission. Pure magnesium oxide (MgO), a kind of ceramic dielectric material, possesses great application potential in high-power microwave transmission devices due to its high theoretical dielectric strength, low dielectric constant, and low dielectric loss properties, but its application is limited by high sintering temperature during preparation. This work presented the preparation of a new type of multiphase ceramics based on MgO, which was MgO-1%ZrO_2-1%$CaCO_3$-x%$MnCO_3$ ($MZCM_x$, x = 0, 0.25, 0.50, 1.00, 1.50, in molar), and their phase structures, morphological features, and dielectric properties were investigated. It was found that inclusion of ZrO_2 and $CaCO_3$ effectively inhibited excessive growth of MgO grains by formation of second phase, while addition of $MnCO_3$ promoted the grain boundary diffusion process during the sintering process and reduced activation energy for the grain growth, resulting in a lower ceramic sintering temperature. Excellent performance, including high dielectric strength (E_b = 92.3 kV/mm) and quality factor ($Q \times f$= 216642 GHz), simultaneously accompanying low dielectric loss (< 0.03%), low temperature coefficient of dielectric constant (20.3×10^{-6} ℃$^{-1}$, 85 ℃) and resonance frequency (-12.54×10^{-6} ℃$^{-1}$), was achieved in $MZCM_{1.00}$ ceramics under a relatively low sintering temperature of 1350 ℃. This work offers an effective solution for selecting dielectric materials for high-power microwave transmission devices.

Key words: MgO ceramic; dielectric strength; sintering temperature; growth activation energy

The trend towards high integration, density, and power in electronic circuits has led to more stringent requirements for the dielectric strength, mechanical strength, and thermal conductivity of dielectric materials. The research for dielectric materials with high and reliable dielectric strength and properties is of great significance for engineering applications in various fields such as dielectric capacitors[1-2], high-power microwave device components[3-4] and substrates[5]. In the past decade, great efforts have been made to study the dielectric strength of different materials. Polymers usually have low dielectric constants, dense microstructure, and amorphous state, which are the best choices for high dielectric strength[6-7]. While ceramic materials have become a research hotspot due to their excellent temperature stability, aging stability, and extended service life[8-9]. However, characteristics like high dielectric constant, porous and coarse grain structure make ceramics easier to breakdown at low electric field, which are usually lower than one-tenth of that of polymers[10]. Therefore, searching for ceramics with high dielectric strengths is of great importance. At present,

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Biography: WANG Zhixiang (1999–), male, Master candidate. E-mail: wangzhixiang21@mails.ucas.ac.cn
王智祥(1999–), 男, 硕士研究生. E-mail: wangzhixiang21@mails.ucas.ac.cn
Corresponding author: WANG Genshui, professor. E-mail: genshuiwang@mail.sic.ac.cn;
CHEN Ying, associated professor. E-mail: chenying@mail.sic.ac.cn
王根水, 研究员. E-mail: genshuiwang@mail.sic.ac.cn; 陈 莹, 副研究员. E-mail: chenying@mail.sic.ac.cn

chemical composition regulation, including ion doping to modify phase structure, construct defects, or regulate microstructure, has been extensively studied and proven to be simpler and more feasible[11-12].

For MgO ceramics, lower dielectric constant (~10), higher bandgap (nearly 7.77 eV) and simple rock salt crystal structure contribute to high dielectric strength as 232 kV/mm[13-14]. However, the actual value is usually much lower than the theoretical one, which requires the regulation of the non-intrinsic factors, such as the ceramic microstructure. Former studies have shown that the addition of 1%–1.5% (in molar) ZrO_2 and $CaCO_3$ is proved effective to inhibit abnormal grain growth of MgO and promote pore discharge, leading to high density and mechanical strength, which are beneficial to enhance the dielectric strength[15-16]. Therefore, ZrO_2 reinforced MgO ceramics possess great potential in high-voltage microwave dielectric application. However, sintering temperature of the above-mentioned MgO-based ceramics is higher than 1500 ℃, which limits their application in microwave capacitors and insulators. Fortunately, previous researches have indicated that $MnCO_3$ is effective in lowering the sintering temperature of ceramics and enhancing the density[17-19]. Hence, $MnCO_3$ is utilized here to reduce the sintering temperature of MgO-based ceramics, and their relevant application potential substrate materials are worth exploring.

In this work, MgO-1%ZrO_2-1%$CaCO_3$-x%$MnCO_3$ ($MZCM_x$, x = 0, 0.25, 0.50, 1.00, 1.50, in molar) ceramics were prepared, and ZrO_2 and $MnCO_3$ are used as reinforcing phase and sintering additive, respectively. The microstructure evolution and dielectric properties were studied and discussed in detail. The results show that the doping of $MnCO_3$ significantly reduces the sintering temperature of MgO by ion substitution to activate the lattice and reduce the sintering activation energy, which affects and changes the sintering behaviour and dielectric properties of MgO.

1 Experimental

1.1 Material preparation

Light magnesium oxide (MgO, 99.650%), ZrO_2 (99.980%), $CaCO_3$ (99.657%) and $MnCO_3$ (99.916%) were mixed and ball milled for 6 h with ethanol by a planetary ball mill, then the dried powders were pressed into ϕ13 mm × 2 mm pellets and ϕ13 mm × 10 mm cylinders at a pressure of 200 MPa. Finally, these pellets and cylinders were sintered at 1520 ℃ (for pure MgO ceramics), 1540 ℃ (for $MZCM_0$ ceramics), 1400 ℃ (for $MZCM_{0.25}$ and $MZCM_{0.50}$ ceramics), and 1350 ℃ (for $MZCM_{1.00}$ and $MZCM_{1.50}$ ceramics) for 2 h, respectively. The sintered pellets were machined into ϕ10.0 mm × 0.5 mm and coated with silver electrode (ϕ8.0 mm) for capacitance and dielectric strength measurement. The cylinders were machined into ϕ10.0 mm × 5.5 mm samples by plane and outer edge processing for microwave performance test.

1.2 Material characterization

The chemical composition of ceramic powders was measured by an X-ray fluorescence spectrometer (Axios, PANalytical, Netherlands). The density of the sintered ceramic samples was tested by Archimedes method, and the crystal structure of the materials was analyzed by an X-ray diffractometer (XRD, PANalytical 9430070 99991 series). The morphology and chemical composition of the ceramic samples were characterized by a field emission scanning electron microscope (SEM, Magellan400, FEI, USA). The dielectric strength of the samples (at least 8 pieces for each composition) at room temperature was tested using high-voltage source (WISMAN, DL120P600, 0–120 kV). The temperature and frequency dependence of the dielectric constant and dielectric loss were evaluated *via* a broadband dielectric Novocontrol Alpha spectrometer (Novocontrol Technologies, Germany). Vector network analyzer (Agilent E8362B) and temperature chamber were used to measure the microwave dielectric properties of the samples. The quality factor ($Q \times f$) of samples was estimated by the TE01δ mode dielectric resonator method. The resonant frequency temperature coefficient τ_f was calculated by the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times \Delta T} \quad (1)$$

where f_{85} and f_{25} represent the resonant frequencies at 85 and 25 ℃, respectively. ΔT represents the temperature difference, 60 ℃. The capacitance temperature coefficient τ_c could be calculated using a similar equation:

$$\tau_c = \frac{C_2 - C_1}{C_1 \times (T_2 - 25)} \quad (2)$$

where C_2 and C_1 represent the capacitances at T_2 and 25 ℃, respectively.

2 Results and discussion

Fig. 1 shows the dependence of densities of $MZCM_x$ (x = 0, 0.25, 0.50, 1.00, 1.50) ceramics *versus* x and sintering temperature. According to the changing trend of density, the optimal sintering temperature for sample densification can be obtained, which is 1520 ℃ for pure MgO, 1540 ℃ for x = 0, 1400 ℃ for x = 0.25, 0.50, and 1350 ℃ for x = 1.00, 1.50, respectively. The optimal

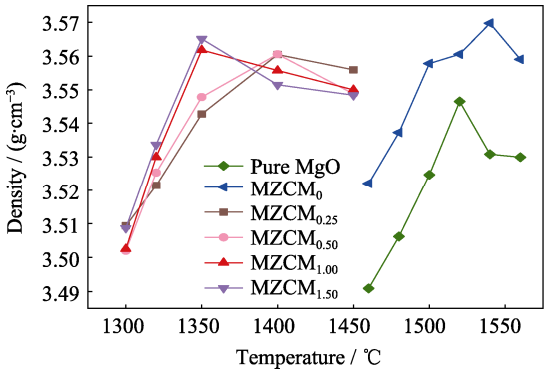

Fig. 1　Densities of the pure MgO and $MZCM_x$ (x = 0, 0.25, 0.50, 1.00, 1.50) ceramics at different sintering temperatures (1300–1560 ℃, 2 h)

sintering temperature decreases with the increase of x.

The sintering theory of ceramics points out that the growth process of grains conforms to the kinetic equation:

$$G_t^n - G_0^n = k_0 t \cdot \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

where G_0 and G_t represent the initial grain size as well as the grain size after sintering for t time at T temperature, R is the ideal gas constant, n and Q represent the grain growth index and the grain growth activation energy, respectively. To solve these two key parameters, the above equation can be deformed:

$$\ln G = \frac{1}{n}\ln t + \frac{1}{n}\left(\ln k_0 - \frac{Q}{RT}\right) \tag{4}$$

$$\ln\frac{G^n}{t} = -\frac{Q}{RT} + \ln k_0 \tag{5}$$

where G is the average grain size of the ceramic, and k_0 is the constant. The grain growth index n can be solved using the graphical method by controlling the sintering temperature and sintering time of the ceramics to make the logarithmic fitting curves of the average grain size to the sintering time and temperature, respectively[20].

The calculation results of pure MgO ceramics show that the grain growth index n = 3 of pure MgO ceramics corresponds to the volume diffusion process, and the grain growth activation energy Q is about 556.9 kJ/mol[20]. Fig. 2 is the solution of grain growth index and grain growth activation energy of $MZCM_{1.00}$ ceramics. The grain growth index n of $MZCM_{1.00}$ ceramics sintered at 1300 ℃ is 1.97 (≈ 2). Among them, the size of n represents different diffusion mechanisms in the sintering process of ceramics. n = 2 corresponds to the grain boundary diffusion process, while the grain boundary diffusion mode can be regarded as a fast channel for material diffusion. Therefore, $MZCM_{1.00}$ ceramic grain growth gradually changes from the grain boundary diffusion mode to the intrinsic bulk diffusion mode of MgO with the increase of temperature, implying that the introduction of Mn significantly promotes the grain growth process during the initial stage of ceramic sintering. Meanwhile, due to the change of grain growth index during the sintering process of ceramics, n = 2.5 is taken to further solve the grain growth activation energy. The average grain growth activation energy is about 301.56 kJ/mol, which is much lower than that of pure MgO ceramics, further proving the promotion effect of Mn on the sintering process of MgO ceramics.

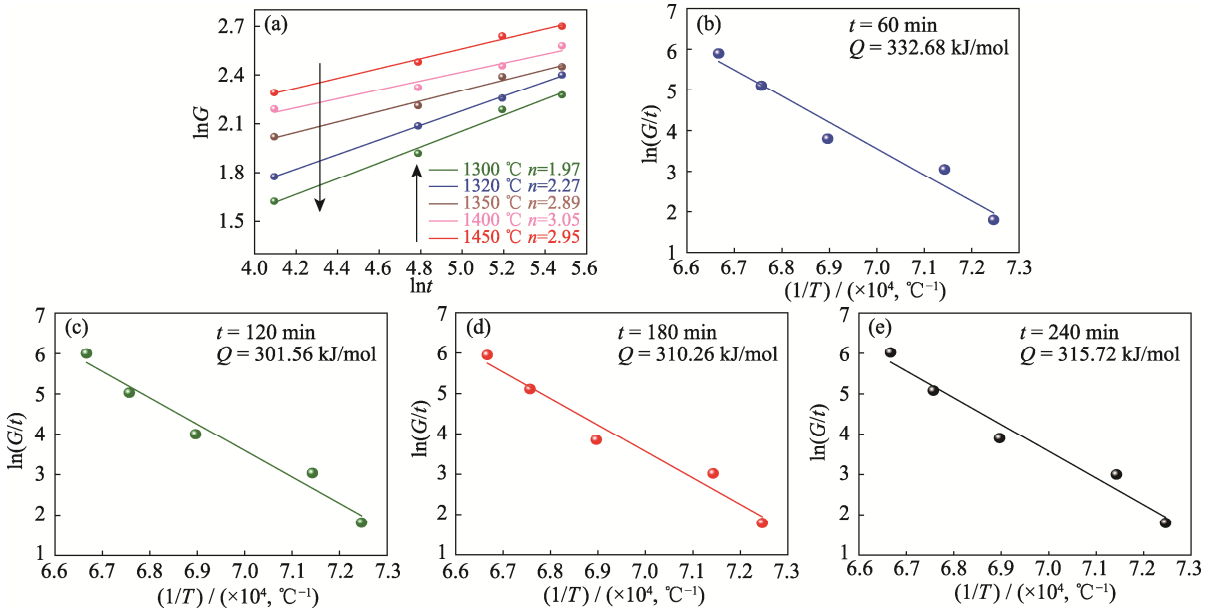

Fig. 2　Kinetic curves of grain growth in $MZCM_{1.00}$ ceramics

(a) Grain growth index n at different sintering temperatures; (b-e) Activation energy of grain growth with different sintering time

Fig. 3 shows the XRD patterns of $MZCM_x$ ceramics. A composite structure composed of cubic-MgO (PDF#45-0946), cubic-ZrO_2 (PDF#49-1642) and glass phase can be clearly observed while the diffraction peaks of cubic-ZrO_2 weaken with the increase of $MnCO_3$ content, which means the decrease of cubic-ZrO_2 content. Firstly, Ca^{2+} solid dissolves into MgO lattice completely, and then the introduction of $MnCO_3$ results in the replacement of Ca^{2+} and the formation of glass phase.

Fig. 4 reveals the morphological evolution and the grain size distribution of different thermal etched $MZCM_x$ samples. Initially, the average grain size of pure

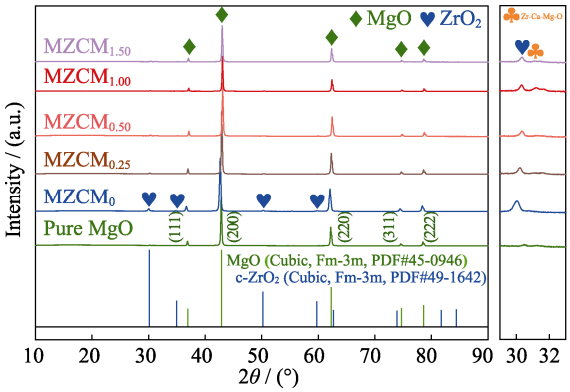

Fig. 3 XRD patterns of pure MgO and $MZCM_x$ (x = 0, 0.25, 0.50, 1.00, 1.50) ceramics

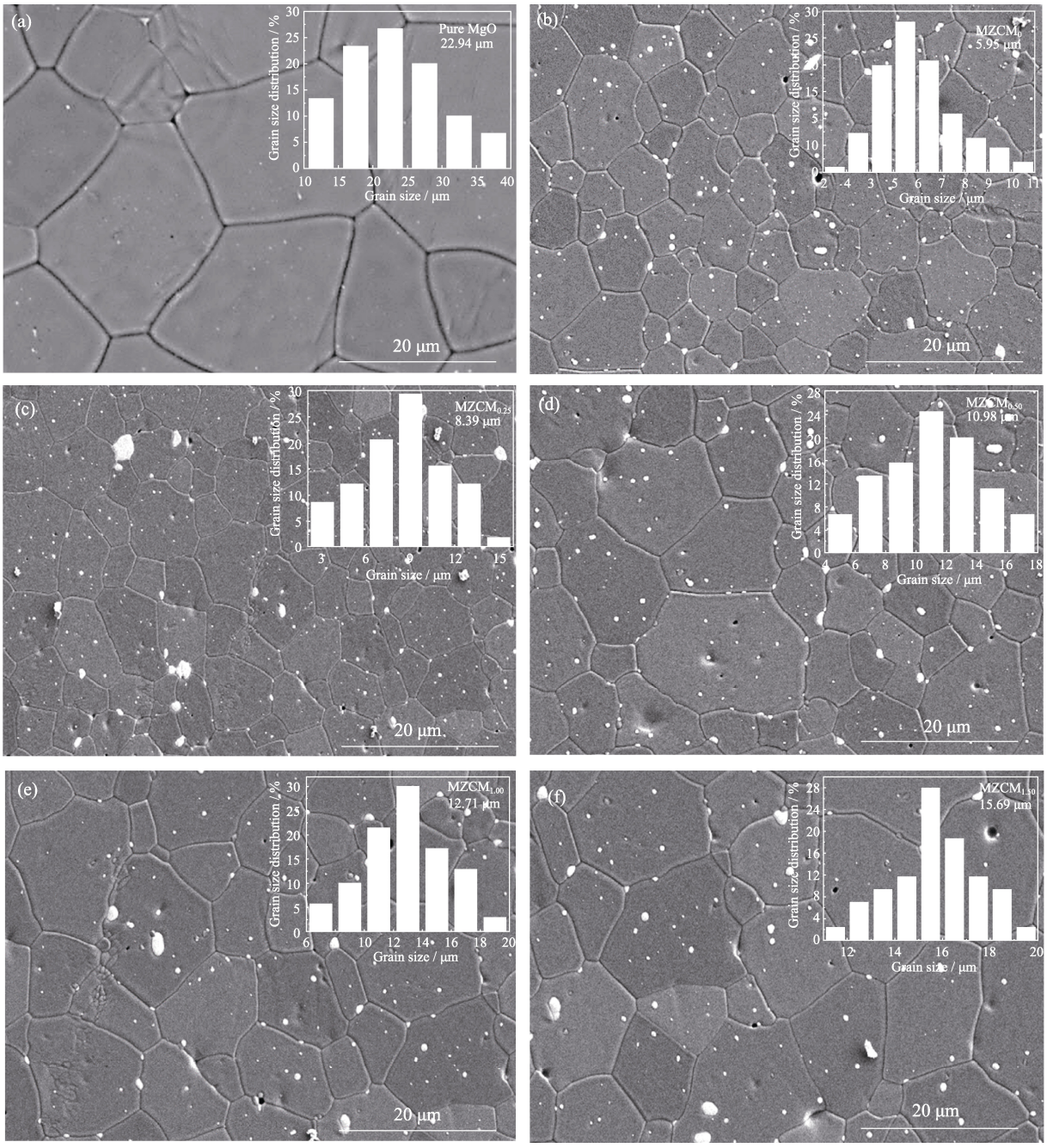

Fig. 4 FESEM images of thermal etched surface morphologies of ceramics with insets showing grain size distribution of ceramics
(a) Pure MgO; (b-f) $MZCM_x$ (x = 0, 0.25, 0.50, 1.00, 1.50) ceramics

MgO ceramics is high up to 22.94 μm, and the addition of ZrO_2 and $CaCO_3$ forms the nano-sized second phase at the grain boundaries of MgO, leading to the grain size decreasing to 5.95 μm. After that, with the doping of $MnCO_3$, the content of the second phase decreases, resulting in an increase for grain size, but the overall size is still smaller than that of pure MgO. The ion vacancy concentration significantly affects the grain growth and sintering process. Similar condition happens to Cooper *et al.*[21], who found that increasing the concentration of U^{4+} vacancies could significantly promote the growth of UO_2 grains. The sintering process of MgO is dominated by anion diffusion, and the doping of $MnCO_3$ further reduces the oxygen vacancy concentration and inhibits the mass transfer process during the later stages of sintering, resulting in an increase in grain size.

X-ray photoelectron spectroscopy (XPS) is used to characterize the changes in oxygen vacancy concentration, and $MZCM_{1.00}$ and $MZCM_{1.50}$ ceramic samples are selected to test due to the limited doping concentration of $MnCO_3$. The samples were subjected to argon ion etching to eliminate adsorbed oxygen on the sample surfaces prior to testing for the oxygen element, and the results of the fitted analyses are shown in Fig. 5. Oxygen in the samples mainly exists in the forms of lattice oxygen (LO) and oxygen vacancy (OV), and doping of Mn ions leads to a reduction of the ratio of the vacancy oxygen peak area to the lattice oxygen peak area, implying that the concentration of oxygen vacancies decreases in the systems. It is worth noting that the oxygen vacancies in the ceramic systems prepared in this work originate from intrinsic oxygen vacancies due to the susceptibility of MgO to Schottky defect reactions[22].

The Weibull distribution is widely used to describe the dielectric strength[12]. In this model, the probability of dielectric breakdown is defined as follows:

$$P_i = 1 - \exp\left(-\left(\frac{E_i}{E_\mathrm{b}}\right)^{\beta}\right) \tag{6}$$

where E_i, E_b and β are specific breakdown strength of single sample, characteristic breakdown strength and shape parameter that indicates the width of distribution, respectively. Fig. 6(a) illustrates the Weibull distribution of the dielectric strength for $MZCM_x$ ceramics, in which X_i and Y_i are two parameters which can be described as follows:

$$X_i = \ln E_i \tag{7}$$

$$Y_i = \ln(-\ln(1 - i/(n+1))) \tag{8}$$

where i and n are sample sequence in specific order and total amount of samples for each composition. The fitting

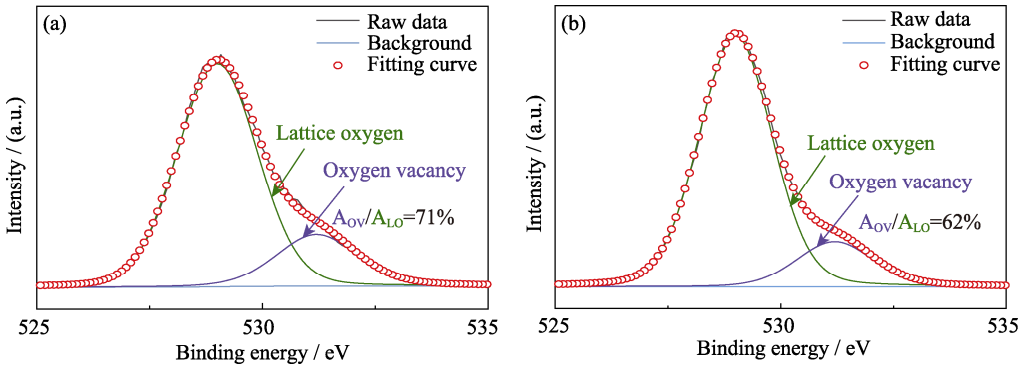

Fig. 5　XPS spectra of O1s of ceramics

(a) $MZCM_{1.00}$; (b) $MZCM_{1.50}$. Colorful figures are available on website

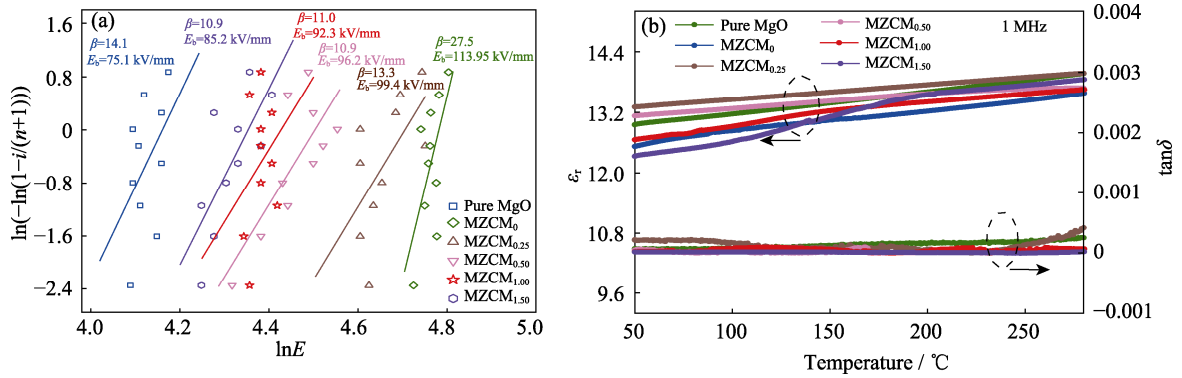

Fig. 6　Dieletric properties of pure MgO and $MZCM_x$ (x = 0, 0.25, 0.50, 1.00, 1.50) ceramics

(a) Linear fitting for dielectric strength of Weibull distribution; (b) Temperature dependence of the dielectric constant and loss in 1 MHz. Colorful figures are available on website

Table 1 Microwave dielectric properties of pure MgO and $MZCM_x$ ceramics

Sample	τ_c/(×10^{-6}, ℃$^{-1}$, –25 ℃)	τ_c/(×10^{-6}, ℃$^{-1}$, 85 ℃)	($Q \times f$)/GHz	τ_f/(×10^{-6},℃$^{-1}$)
Pure MgO	79.6	85.1	138240	–35.62
$MZCM_0$	63.9	74.4	124623	–32.36
$MZCM_{0.25}$	28.6	34.4	130330	–20.64
$MZCM_{0.50}$	20.1	46.1	156196	–18.36
$MZCM_{1.00}$	4.91	20.3	216642	–12.54
$MZCM_{1.50}$	16.06	78.4	123216	–14.60

dielectric strengths of $MZCM_x$ are 113.95, 99.4, 96.2, 92.3, and 85.2 kV/mm for x = 0, 0.25, 0.50, 1.00, and 1.50, respectively. The fine grain and dense structure of $MZCM_0$ ceramics allow for a significant increase in dielectric strength. And doping of $MnCO_3$ results in reduction in dielectric strength due to the weakened second phase and intergranular bonding strength[23]. Fig. 6(b) shows the temperature dependence of the dielectric constant and dielectric loss of MgO-based dielectric ceramics at 1 MHz, respectively. The dielectric losses of all samples are less than 0.1% in the tested temperature range, presenting a low loss characteristic. In addition, the dielectric properties of all samples maintain good stability in the temperature range of 50–300 ℃, which is beneficial to their application as core materials in extreme environments.

The dielectric properties of MgO-based ceramics are characterized in this work, which are shown in Table 1. $MZCM_{1.00}$ ceramics exhibit low τ_c in the temperature range of –25–85 ℃, which further proves the good temperature stability. The microwave dielectric properties of the samples were measured at a resonant frequency range of 10.2–10.5 GHz. In particular, $MZCM_{1.00}$ ceramics have a $Q \times f$ of up to 216642 GHz, and τ_f is relatively close to zero (–12.54×10^{-6} ℃$^{-1}$), which is conducive to the integration and miniaturization of electronic circuits[24]. The addition of $MnCO_3$ reduces oxygen vacancies, resulting in the creation of free electrons. Therefore, the overabundant $MnCO_3$ causes excessive electrons, increasing dielectric loss and decreasing $Q \times f$[25].

3 Conclusions

In summary, $MnCO_3$ doped MgO-ZrO_2-$CaCO_3$ high-voltage dielectric ceramics are designed and prepared. The ultrahigh dielectric strength of 92.3 kV/mm was achieved in $MZCM_{1.00}$ ceramics, and the sintering temperature is significantly reduced to 1350 ℃. The remarkable improvement of dielectric strength is mainly due to two main factors. Firstly, MgO has the potential to achieve high dielectric strength. Secondly, the introduction of ZrO_2 and $CaCO_3$ modifies the microstructure, eliminates external factors, and fully utilizes its dielectric properties. At the same time, $MnCO_3$ can reduce the sintering temperature of MgO ceramics by accelerating mass transfer caused by ionic vacancies. The series of ceramics with high dielectric strength and medium sintering temperature also show high $Q \times f$, which makes the MgO-based ceramic a candidate material for microwave applications. This MgO-based ceramic also has the advantages of simple components and preparation process, displaying the great potential for the application in dielectric materials of high-power microwave transmission devices.

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碳酸锰掺杂氧化镁基陶瓷的烧结行为和介电性能

王智祥[1,2,3], 陈　莹[2,3,4], 逄清阳[2,3], 李　鑫[2], 王根水[1,2,3,4]

(1. 国科大杭州高等研究院 化学与材料科学学院, 杭州 310024; 2. 中国科学院 上海硅酸盐研究所, 无机功能材料与器件重点实验室, 上海 200050; 3. 中国科学院大学 材料科学与光电工程中心, 北京 100049; 4. 中国科学院上海硅酸盐研究所, 高性能陶瓷与超微结构国家重点实验室, 上海 200050)

摘　要: 追求具有高介电强度的陶瓷介质材料, 探究影响介电强度的内在因素, 对选择合适的高功率微波传输器件介质窗材料、保证功率传输的可靠性具有重大的科学研究和工程应用价值。氧化镁(MgO)陶瓷具有高理论介电强度和低介电损耗的介电性能, 在高功率微波传输器件应用方面潜力巨大, 但其烧结温度过高, 阻碍了设计与应用。本工作通过传统固相反应法制备了 MgO-1%ZrO_2-1%$CaCO_3$-x%$MnCO_3$(MZCM$_x$, x = 0、0.25、0.50、1.00、1.50, 摩尔比)系列陶瓷, 并对其相结构、形貌特征和介电性能等进行表征分析。研究发现: 引入 ZrO_2 和 $CaCO_3$ 形成了第二相, 显著抑制了 MgO 晶粒的过分长大; 添加 $MnCO_3$ 促进了陶瓷烧结初期的晶界扩散过程, 降低了陶瓷的晶粒生长激活能, 从而有效降低了陶瓷烧结温度。最终在 1350 ℃下烧结制备的 $MZCM_{1.00}$ 陶瓷获得了高介电强度和品质因数(E_b = 92.3 kV/mm, $Q \times f$ = 216642 GHz), 同时具有低介电损耗(<0.03%)、低电容温度系数(20.3×10^{-6} ℃$^{-1}$, 85 ℃)和相对接近于零的谐振频率温度系数(-12.54×10^{-6} ℃$^{-1}$)。本研究为高功率微波传输器件选择介质窗材料以及提升综合性能提供了一种简单有效且可满足实际生产应用的解决方案。

关　键　词: 氧化镁陶瓷; 介电强度; 烧结温度; 生长激活能

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