Microwave dielectric properties of Na^+-substituted $CaMg_{0.9}Li_{0.2}Si_2O_6$ ceramics

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Abstract. Ceramics with low dielectric constant are widely used in high frequency substrates. The low temperature sintered $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics with low dielectric constant and dielectric loss were prepared by the traditional solid-state reaction method, with 0.5wt%LBSCA additive. The XRD patterns of the samples were obtained by X-ray diffraction and it was found that there were three ceramic components, $CaMgSi_2O_6$, $CaSiO_3$ and Na_2MgSiO_4, which indicated that the experimental sample was a multiphase ceramic system. Through the trend of bulk density as functions of the content of substitution and the change of SEM morphology, it could be found that appropriate amount of Na^+ substitution can promote the grain growing and the densification of ceramics. Results demonstrated that both the $Q \times f$ and ε_r were relevant to bulk density and the second phase. The τ_f was also affected by the second phase to some extent. In particular, the ceramics sintered at 925℃ for 3h possessed the desirable microwave dielectric properties for LTCC application: ε_r = 7.03, $Q \times f$ = 17,956 GHz, and τ_f = −79 ppm/℃.

1 Introduction

Dielectric ceramics have been widely used in microwave devices because of their low dielectric loss, serialized dielectric constant and temperature coefficient of resonant frequency which can be adjusted to near zero. In the field of 5G communication and the Internet of Things, microwave dielectric ceramics with low dielectric constant are often used in microwave substrates, because according to $T_d = L\sqrt{\varepsilon_r}/c$(where L is the distance travelled by the signal, and c is the speed of light), low dielectric constant can effectively reduce the time delay of high-frequency signals during transmission[1, 2]. At the same time, LTCC technology, which requires sintering temperature below 950℃, has been paid more attention in the research of microwave dielectric ceramics to follow the development trend of device miniaturization and integration[3-5].

$CaMgSi_2O_6$ ceramic (ε_r = 7.46, $Q \times f$ = 59,638 GHz, and τ_f = −46 ppm/℃) prepared by Sun et.al, is a promising candidate for LTCC substrate[6]. Thereafter, a variety kinds of researches have been performed on the diopside with monoclinic structure, reducing

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sintering temperature and improving $Q \times f$ values[7-9]. Lai et.al reported that Cu^{2+} substituting for Mg^{2+} could effectively reduce the sintering temperature as well as the dielectric loss[10]. Mn^{2+} has also been proved to enhance the performance of $CaMgSi_2O_6$ ceramics when substituted in Mg site[11]. However, the influence of Na^+ on the properties and composition of $CaMgSi_2O_6$ ceramics has not been investigated yet. Recent reports have found that the substitution of Na^+ for Mg^{2+} improved the properties and reduced the sintering temperature of $MgWO_4$ ceramics[1].

In this work, Na^+-substituted $CaMg_{0.9}Li_{0.2}Si_2O_6$($x$ = 0-0.05, 0.1) ceramics were synthesized with 0.5wt% LBSCA glass addition. Then the phase composition, microstructure and microwave dielectric properties of the prepared ceramic samples were further investigated.

2 Experimental and methods

$CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics were synthesized via conventional solid-state reaction method. The raw material, $CaCO_3$(99.5%), MgO(99%), SiO(99.9%), Na_2CO_3(99.8%) and Li_2CO_3(99%) was ball-milled with deionized water for 12h after weighing according to the stoichiometric ratio. The slurry was dried in air for 24h and then grinded, and calcined at 925℃ for 3h. The presintered powder was added with 0.5wt% LBSCA glass and ball-milled for a second time for 6h. The mixture was dried again before it was mixed with polyvinyl alcohol (PVA) at a concentration of 12% and pressed into cylindrical sheets of 12 mm in diameter and 6 mm in thickness under pressure of 10MPa. The cylinder were sintered from 900 °C to 950 °C for 3h.

The phase composition was detected by X-ray diffractometer (Bruker D8 advance). Based on Archimedean principle, the bulk densities were measured with distilled water as a buoyancy liquid. The morphology pictures of sintered ceramic samples were taken by a scanning electron microscope at an acceleration voltage of 15 kV. Microwave dielectric properties, resonance frequency f, ε_r and dielectric loss $tg\delta$ were measured using the Hakki-Coleman dielectric resonator method combining a network analyzer (Agilent N5230A, USA). The temperature coefficient of resonant frequency was calculated using the equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 \ (ppm/°C),$$

where f_1 and f_2 represent the resonant frequencies at temperatures T_1 and T_2 respectively.

3 Results and discussions

Fig. 1. shows the XRD patterns of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics sintered at 925℃. It is obvious that all the specimens are polycrystalline system: diopside $CaMgSi_2O_6$(PDF#11-0654, space group: C2/c(15)) with monoclinic structure occupied the main phase, accompanied by a small amount of second phase $CaSiO_3$(PDF#19-0249, space group:P1(1)) when x value changes from 0 to 0.1; When x≥0.04, the phase Na_2MgSiO_4(PDF#19-0249) was produced, indicating the limited solid solubility of Na^+ in the $CaMgSi_2O_6$ ceramics that is resulted from the relative big radius difference between Na^+(1.13Å) and Mg^{2+}(0.72 Å).

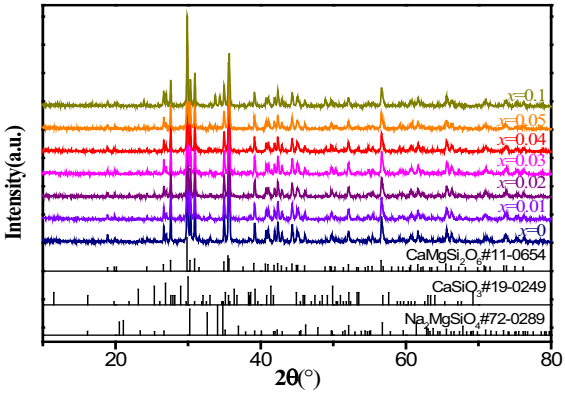

Fig. 1. The XRD diffraction patterns of the $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics sintered at 925℃.

Fig. 2. shows the bulk density of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics sintered at different temperatures. It could be easily seen from the curves that the bulk density changes with the sintering temperature which is in the range of 900-950 ℃ due to the densification process. At 900 ℃ and 925 ℃, the bulk density values of the ceramics reach their maximum at x=0.05; However, for samples sintered at 925 ℃ and 950 ℃, there are two bulk density peaks at x=0.01 and 0.05. The peak valley at x=0.03 could be ascribed to different mechanisms of action of Na^+ in the $CaMg_{0.9}Li_{0.2}Si_2O_6$ ceramics: when x≤0.03, Na^+ is solidly dissolved in the lattice, while when x≥0.04, the phase Na_2MgSiO_4 is formed. The results prove that appropriate amount of Na^+ substitution for Mg^{2+} could promote the densification of ceramics.

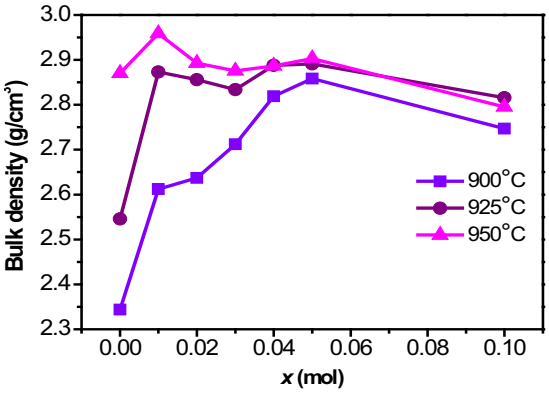

Fig. 2. The bulk density of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics sintered at 925℃.

The SEM micrographs of the $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics sintered at 925℃ are showed in Fig. 3. Fig. 3(a) shows that although there are few pores, most of the grains are round and have not grown fully. From Fig. 3(b)-(g), the grains gradually present a clear shape, but the grain size distribution is becoming more and more uneven. In addition, it could be seen that the changing trend of the microscopic morphology of ceramics is consistent with the one of the bulk density in Fig. 2. Results show that Na^+ could promote the growth of grain.

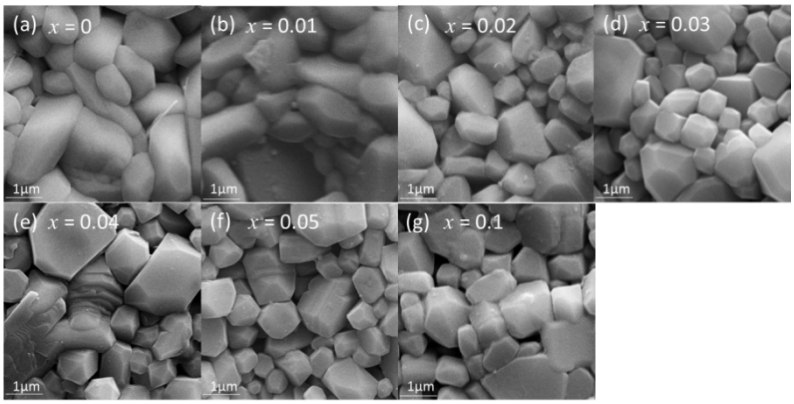

Fig. 3. SEM images of the $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics sintered at different temperature.

Fig. 4(a) illustrates the ε_r of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$($x$ = 0-0.05 and 0.1) ceramics sintered at different temperature. The dielectric constant is usually determined by both the external causes including porosity, the density and the second phase of the sample, and internal factors such as ion polarizability. In this study, the external factors play a critical role on the dielectric constant which is distinctly influenced by the bulk density and the second phase. Combined with Fig. 2, it is clear that the trend of ε_r is in accordance with that of density at sintering temperature 900 ℃ and 925 ℃, demonstrating the great effect of density on the dielectric constant. However, at 925 ℃, the ε_r value of ceramics is determined not only by the density but the second phase. The decreasing trend of ε_r when x changes from 0.04 to 0.1 is reasonable related to the increasing Na_2MgSiO_4 phase according to the mixture rule: $\ln \varepsilon_r = V_1 \ln \varepsilon_{r_1} + V_2 \ln \varepsilon_{r_2}$ [12].

Fig. 4(b) shows the $Q \times f$ values of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics as functions of Na^+ doped content and sintering temperatures. In general, the $Q \times f$ value is influenced by both intrinsic and extrinsic factors[13]. Extrinsic factors include second phase, density and grain size distribution, while the intrinsic factors consist of crystal structure and the lattice vibration. The $Q \times f$ values of sintered $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ composites in this work are nearly dependent on the density and the second phase, which could be seen from the Fig. 4(b) when considering the XRD patterns and Fig. 2. With regard to the second phase, the XRD patterns demonstrate that when x=0.01 there is no Na_2MgSiO_4 phase appearing and the density of the certain samples is high when taking the density into account, leading to the maximum $Q \times f$ value at 900 and 925 ℃. So given the results of the trends, the $Q \times f$ value is determined by more second phase than the density when Na^+ substitution content exceeds 0.06mol.

Fig. 4(c) shows the τ_f values of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics sintered at 925 ℃. Notably, the τ_f value changes non-linearly with the Na^+ substitution. However, it shows a slight upward trend in the entire sample range. So it could be speculated that the τ_f value is related to the second phase on the grounds of Lichtenecker empirical logarithmic rule: $\tau_f = V_1\tau_{f_1} + V_2\tau_{f_2}$. The optimal $Q \times f$ value samples sintered at 925℃ was obtained at x=0.01, corresponding to the τ_f value of -79. Therefore, the τ_f value need to be adjusted to meet the requirements of LTCC application in subsequent work.

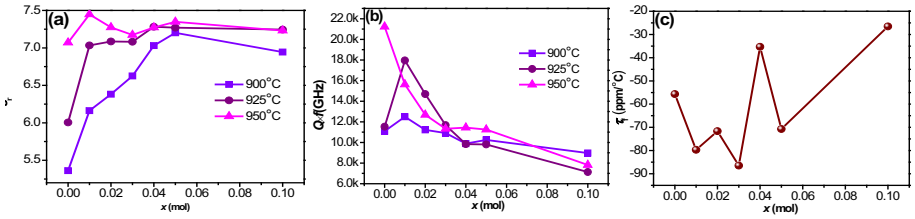

Fig. 4. (a) ε_r and (b) $Q \times f$ trend of $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics as functions of Na^+ doped content and sintering temperatures; (c) The τ_f values of the $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics sintered at 925℃.

4 Conclusion

In this work, low temperature sintering $CaMg_{0.9-x}Na_{2x}Li_{0.2}Si_2O_6$ ceramics were synthesized via solid state reaction method. And the phase structure, bulk density, microstructure and the microwave dielectric properties were investigated in detail. There were totally three phases detected by the X-ray diffraction in the entire samples sintered at 925℃ and $CaMgSi_2O_6$ was the major phase as expected. From the bulk density and SEM pictures, it could be concluded that suitable Na^+ substitution promoted growth of the grains and eliminated the pores. The second phase and density play an important role on the properties of the ceramics and the excellent microwave dielectric properties was obtained at x=0.01: ε_r = 7.03, $Q \times f$ = 17,956 GHz, and τ_f = −79 ppm/℃ when considering the actual technological requirements.

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