Crystal structure and microwave dielectric properties of CaTiO_3 modified $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ cordierite ceramics

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ABSTRACT

In this work, CaTiO_3 modified $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (MAS) of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0 \leq x \leq 0.35$) cordierite ceramics were fabricated by traditional solid phase sintering method. The densification sintering temperatures of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ceramics are effectively lowered from 1460°C to 1250°C with increasing addition of CaTiO_3 . X-ray diffraction spectra show that $(1-x)\text{MAS}-x\text{CaTiO}_3$ ceramics present cordierite phase as $0 < x \leq 0.05$, and the composite phases of cordierite, perovskite-structured CaTiO_3 and monoclinic feldspar phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ as $0.10 \leq x \leq 0.35$. Rietveld refinement of XRD data show the six-membered rings of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ transit from non-symmetry rings to centro-symmetry equilateral rings in $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0 < x \leq 0.10$). The optimal dielectric properties of $Q \times f = 55490 \text{ GHz}$ (at 15.3 GHz), $\epsilon_r = 7.2$ and $\tau_f = -28.3 \text{ ppm}/^\circ\text{C}$ are obtained at $x=0.5$, which are better than those of pure MAS cordierite ceramics.

Keywords: Microwave dielectric ceramic; Silicate; $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$; Low dielectric constant.

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1. Introduction

Microwave dielectric materials for communication applications such as cellular phones, direct broadcasting satellites, wireless local area networks, global positioning systems and intelligent transport systems, etc., have been rapidly developed in the past decades. Operating frequency has also gradually increased from microwave to millimeter-wave range because more information is capable to be transported with higher speed [1]. Novel dielectric resonator materials for millimeter-wave application are required to satisfy the requirements of high quality value ($Q \times f$), low dielectric constant (ϵ_r) and near-zero temperature coefficient of resonant frequency (τ_f) for frequency stability [2,3].

Due to strong covalent bond effects in basic structure units of $[\text{SiO}_4]$ tetrahedrons [4], silicates usually have low dielectric constants less than 10. In recent years, many kinds of new materials with $[\text{SiO}_4]$ tetrahedrons such as cristobalite (SiO_2) [5], $\text{Sr}_2\text{Al}_2\text{SiO}_7$ [6], Sr-feldspar ($\text{SrAl}_2\text{Si}_2\text{O}_8$) [7], forsterite (Mg_2SiO_4) [8,9], willemite (Zn_2SiO_4) [10], cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) [11,12], anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) [13], mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) [14] and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_6$) [15] have been fabricated for the application of microwave and millimeter-wave dielectric materials. Among these silicates, cordierite is a promising alternative material which is usually synthesized at 1350-1475 °C. The polymorph of cordierite (Cccm) is a low symmetry orthorhombic phase with $[(\text{Si},\text{Al})\text{O}_4]$ tetrahedrons arranging orderly on six-membered rings of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$. Alternate layers of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings are connected via one $[\text{MgO}_6]$ octahedrons, one $[\text{SiO}_4]$ tetrahedron and two $[\text{AlO}_4]$ tetrahedrons, as shown in Fig.1 [16,17]. Most of natural cordierites are not pure and contain other cations or molecules which either substitute Mg^{2+} , Al^{3+} and Si^{4+} ions or

stay in the interstitial channel sites of cordierite framework [18,19]. Mio Terada et al. had reported that Ni-doping cordierite ceramic fabricated by isostatic cool pressing presents obvious improvement of $Q \times f$ values from 39,000 GHz to 99,000 GHz, while temperature coefficient of resonance frequency deteriorated from -32 ppm/°C to -43 ppm/°C [20]. In our previous work, the influences of SrTiO₃ addition on phase composition and microwave dielectric properties of cordierite ceramics have been investigated. We had reported the (1-x)MAS-xSrTiO₃ (x=0.10) ceramic has good microwave dielectric properties: $\epsilon_r = 6.53$, $Q \times f = 80600$ GHz, $\tau_f = -18$ ppm/°C [21].

Because of the positive τ_f value of +800 ppm/°C of CaTiO₃ [22], according to the dielectric complex rules, it is reasonable to add CaTiO₃ into MAS to adjust its negative temperature coefficient. In addition, Ca²⁺ ions can easily substitute Mg²⁺ sites to form [CaO₆] octahedrons, and Ti⁴⁺ ions substitute Si⁴⁺ ions to form [TiO₄] tetrahedrons, which may be useful to enhance its dielectric constant. Herein, CaTiO₃ was added to tune temperature coefficient and quality factor of cordierite ceramics. The dependence of CaTiO₃ addition on sintering behaviors, microstructures and microwave dielectric properties of cordierite ceramic are investigated in detail.

2. Experimental Procedure

(1-x)MAS-xCaTiO₃ (x=0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.35) samples were synthesized by conventional solid-state method using high-purity MgO (99.99%), SiO₂ (99.99%), Al₂O₃ (99.99%) and CaTiO₃ (99.5%). MgO was additionally calcinated at 1000 °C for 2 hours to remove water and CO₂ due to its hygroscopic property. The raw materials were weighed stoichiometrically, mixed in alcohol ethanol and milled for 24 h. Then the mixtures were dried at 100°C to evaporate

ethanol. Then the powder was calcinated at 1400 °C for 3h to obtain MAS samples, then grounded and added the CaTiO₃ powder to make the (1-x)MAS-xCaTiO₃ composite powder. The weighed raw materials of (1-x)MAS-xCaTiO₃ composite powder were mixed by ball milling with zirconia media in ethanol for 24h. After drying, the mixtures were calcinated at 1300°C in air for 3h. After it being remilled and dried, the powder was added with 7wt% polyvinyl alcohol, pressed into disks of 12mm in diameter and 2-6mm in height. Finally, these disks were sintered at 1200-1500°C in air for 3h. After cooling from the sintering temperature to 1100°C at a rate of 2°C/min, and then the sintered ceramics were cooled in the air inside the furnace.

The bulk densities of sintered samples were measured by Archimedes method. All the samples were selected at each densification sintering temperatures to characterize their physical parameters. The crystal structures of (1-x)MAS-xCaTiO₃ samples were identified by X-ray diffraction (XRD) using CuKα₁ radiation (40 kV, 30 mA, Geiger Counter, RIGAKU D/max 2550/PC, Rigaku Co., Tokyo, Japan). The XRD data for Rietveld refinement were collected in the 2θ range of 5°-120° at a step size of 0.02° with a dwelling time of 4 s for each step. Rietveld refinements were carried out by GSAS Program [23]. The morphology of samples was analyzed by using scanning electron microscope (SEM, Model JSM6380-LV; JEOL, Tokyo, Japan). The dielectric constant (ϵ_r) and temperature coefficient of resonant frequency (τ_f) value were measured by the Hakki–Coleman method. The quality factor Q was evaluated by the resonant-cavity method in the TE₀₁₁ resonant mode [24,25], using a silver-coated cavity connected to the network analyzer (E8362B, Agilent Technologies, Palo Alto, CA). The τ_f values were measured at temperatures from 25 °C to 85 °C. The τ_f values were calculated by Eq (1):

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \quad (1)$$

Where, f_{85} , f_{25} were the temperature coefficients of resonant frequency at 85 °C and 25 °C, respectively.

3. Results and Discussion

Fig.2 shows the bulk densities of (1-x)MAS-xCaTiO₃ samples sintered at different temperatures. It can be seen that the densities of all samples increase to a maximum value and then decrease with increasing sintering temperature. The optimal sintering temperature of samples with x=0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 are 1460°C, 1400°C, 1350°C, 1325°C, 1300°C, 1275°C, 1275°C, and 1250°C, respectively. The average bulk densities at these temperature points are 2.5041 g/cm³, 2.5293 g/cm³, 2.5484 g/cm³, 2.5641 g/cm³, 2.5746 g/cm³, 2.5929 g/cm³, 2.6137 g/cm³, and 2.6425 g/cm³, respectively. The addition of CaTiO₃ obviously reduces the densification sintering temperature and enhances the densities of (1-x)MAS-xCaTiO₃ ceramics.

The XRD patterns of (1-x)MAS-xCaTiO₃ (x=0~0.35) samples sintered at each densification temperatures are shown in Fig.3. The prominent peaks are clearly indexed as the cordierite phase for MAS (JCPDS #13-0294) with x=0 to 0.35. Minor secondary phases of CaTiO₃ and CaAl₂Si₂O₈ are also found when x ≥ 0.10. With increasing x, the peak intensities of CaAl₂Si₂O₈ phase gradually increase, which indicates that CaAl₂Si₂O₈ becomes a considerable phase in the samples.

To further investigate the structure information of cordierite solid solution with x=0 to 0.10, the profile fits were conducted using Rietveld refinements for three samples with x= 0, 0.05 and 0.10. The refined crystal structures are illustrated in Fig.4. The lattice parameters and bond angles

are listed in Table 1. In cordierite crystal structure, the $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings are composed by six corner sharing $[(\text{Si}/\text{Al})\text{O}_4]$ tetrahedrons viewing along c axis. The ordered $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings of cordierite samples with $x=0$ are shown in Fig.4(a), which depicts the arranging series of $[-\text{Si}(3)\text{O}_4-\text{Si}(2)\text{O}_4-\text{Al}(2)\text{O}_4-\text{Si}(3)\text{O}_4-\text{Si}(2)\text{O}_4-\text{Al}(2)\text{O}_4-]$. However, the shape of the rings of samples with $x=0.05$ is closer to equilateral hexagons than those of $x=0$ and $x=0.10$ (shown in Fig.4), which is measured by the method of standard deviation σ values using the data of bond angles in Table 1. The lower standard deviation σ value implies that $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ ring has the higher equilateral hexagon. The standard deviation σ value is calculated by Eq (2):

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - x_0)^2} \quad (2)$$

Where x_0 is the average value of six angles in the hexagon, and x_i is one of the six angles in hexagons. The average value of x_0 in hexagons is 120° and N is six. The calculated σ values are plotted in Fig.4(d) as a function of x . It indicates that the $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0.05$) ceramic is much isotropic than those of $x=0$ and 0.10 . The slight deformation of the $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings would change the values of ε_r , $Q \times f$ and τ_f in $(1-x)\text{MAS}-x\text{CaTiO}_3$ ceramics. Correspondingly, the relative permittivity of ε_r , quality factor of $Q \times f$ and temperature coefficient of resonant frequency of τ_f should also be sensitive to the secondary phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and additional phase of CaTiO_3 with the scope of $0.10 < x \leq 0.35$.

Fig.5 further verifies this kind of microstructure transformation via calculating the volumes of three kinds of $[\text{SiO}_4]/[\text{Al}(2)\text{O}_4]$ tetrahedrons and $[\text{MgO}_6]$ octahedrons. Fig.5(a) demonstrates that the volumes of $[\text{Si}(3)\text{O}_4]$ tetrahedrons gradually decrease, while the $[\text{Si}(2)\text{O}_4]$ tetrahedrons increases as x values increase from $x=0$ to 0.10 . Meanwhile, the volumes of $[\text{Al}(2)\text{O}_4]$ tetrahedrons decrease to the minimum and that of $[\text{MgO}_6]$ octahedrons increase to the maximum at

$x = 0.10$ (as shown in Fig.5(a) and Fig.5(b)). Considering that Ti^{4+} and Si^{4+} have the same chemical valences amongst the increase of $[\text{Si}(2)\text{O}_4]$ tetrahedrons volume, it can be concluded that some Ti^{4+} cations may substitute $\text{Si}(2)^{4+}$ cations to form $[\text{Si}(2)/\text{TiO}_4]$ in the channels of hexagonal rings. Because the ionic radius of Ti^{4+} is bigger than that of $\text{Si}(2)^{4+}$, the volumes of neighboring $[\text{Si}(3)\text{O}_4]$ and $[\text{Al}(2)\text{O}_4]$ tetrahedrons are squeezed to be smaller ones. As $x = 0.10$, the connected $[\text{O}_6]$ rings obtain the maximum centro-symmetry of close to equilateral hexagonal structure. Besides, Mg^{2+} and Ca^{2+} ions are both alkaline earth elements, and Ca^{2+} ions with a relative large radius ($R_{\text{Ca}^{2+}} = 0.099 \text{ nm}$) are often used to substitute the Mg^{2+} ions ($R_{\text{Mg}^{2+}} = 0.072 \text{ nm}$) to form solid solution. However, the radius differences between both kinds of ions are more than 15%, which could only form a limited solid solution [26]. Some Ca^{2+} ions may occupy the Mg^{2+} sites to form $[\text{CaO}_6]$ octahedrons. Hence, the substitution of a little amount of larger radius of Ca^{2+} ions would induces the increasing volume of the $[\text{MgO}_6]$ octahedrons. It can be concluded that as $x = 0.05$, the $[(\text{Si}_4\text{Al}_2)]$ rings obtained the maximum centro-symmetry close to equilateral hexagonal structure.

The SEM images of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0\sim0.35$) samples sintered at each densification temperatures are shown in Fig.6. As shown in Fig.6(a), the MAS sample has homogeneous grains. Smaller and more homogeneous grains are distributed in Fig.6(b) and Fig6(c). And all grains are in the range of 1-2 μm . With a further increase of CaTiO_3 addition, big size of grains can be seen in Fig.6(d) -Fig.6(h), which bring about the non-uniform grain morphology.

The ε_r values of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ceramics are presented in Fig.7(a). The relative dielectric constants increase from 6.14 to 7.68 within $0 \leq x \leq 0.10$, then gradually decrease from 7.34

to 6.25 with the increasing CaTiO_3 addition in the range of $0.15 \leq x \leq 0.35$. When x is < 0.10 , Ti^{4+} ions enter the channels of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings, forming the titanium-containing tetrahedrons similar to $[(\text{Si}(2)/\text{Ti})\text{O}_4]$ types. Ti^{4+} ions have stronger dielectric polarizabilities of ions than that of Si^{4+} ions and stronger dipole moment in the equilibrium position [27]. Furthermore, Ca^{2+} ions also possess higher ionic polarizability than Mg^{2+} ions. Hence, the ϵ_r values increase from 6.14 to 7.68 within $0 \leq x \leq 0.10$. Although the precipitated CaTiO_3 has high dielectric constant ($\epsilon_r \sim 170$) as $0.10 \leq x \leq 0.35$, secondary phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ with a very low dielectric constant ($\epsilon_r \sim 5$) [27] appears. The relative dielectric constants of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0.15 \leq x \leq 0.35$) ceramics gradually decrease under the effects of Ca-feldspar $\text{CaAl}_2\text{Si}_2\text{O}_8$ phase and CaTiO_3 phase together, but it is still higher than that of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0$).

The $Q \times f$ values of the $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0 \leq x \leq 0.35$) samples are shown in Fig.7(a). The $Q \times f$ values are evidently improved from 39000 GHz to 55490 GHz from $x=0$ to 0.05, then decreased from 53100 GHz to 28250 GHz from $x=0.10$ to 0.35. These changes indicate that optimal CaTiO_3 addition ($0 < x \leq 0.05$) can improve the microwave dielectric properties of cordierite ceramics by adjusting microstructures of cordierite solid solution ceramics. However, excessive CaTiO_3 addition ($0.10 < x \leq 0.35$) would degrade the quality factor of $Q \times f$ values due to the appearance of the secondary phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and CaTiO_3 . It is well known that the dielectric losses are always accompanied with strong spontaneous polarization, which is caused by large displacements and distortions of atoms or other polyhedrons. Herein, as the centro-symmetry of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings increases shown as in Fig 4, the crystal symmetry of cordierite solid solution will be further improved. It can be concluded that the strength of the spontaneous polarization of the $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings will decrease to the minimum, where the $Q \times f$

values arrive at maximum value of 55490 GHz at $x=0.05$. However, when x continues to increase, due to the poor quality factor of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ ($Q \times f$: $\sim 6500\text{GHz}$) and CaTiO_3 ($Q \times f$: $\sim 3600\text{GHz}$) [28,29], the $Q \times f$ values of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0.10 \leq x \leq 0.35$) ceramics exhibit the decreasing trend.

The τ_f values of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0 \leq x \leq 0.35$) samples are shown in Fig.7(b). The τ_f values of the cordierite solid solution increase from $-32.8 \text{ ppm}/^\circ\text{C}$ to $-21.6 \text{ ppm}/^\circ\text{C}$ as x is from 0 to 0.25, then deteriorate with increasing addition. These behaviors can be explained by the mixture rules of $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - CaTiO_3 phases, which includes the positive τ_f value of CaTiO_3 ($\tau_f = +800 \text{ ppm}/^\circ\text{C}$) and negative τ_f value of cordierite ($\tau_f = -32 \text{ ppm}/^\circ\text{C}$) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ ($\tau_f = -140 \text{ ppm}/^\circ\text{C}$). The τ_f values of the $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0.30 \leq x \leq 0.35$) composite ceramics are deteriorated when $x \geq 0.30$, which could be attributed to the contribution of $\text{CaAl}_2\text{Si}_2\text{O}_8$.

4. Conclusions

The effects of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ rings on the microwave dielectric properties of CaTiO_3 modified cordierite ceramics are investigated. XRD results show that the system of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($0 \leq x \leq 0.05$) is cordierite solid solution, secondary phases of CaTiO_3 and $\text{CaAl}_2\text{Si}_2\text{O}_8$ feldspar are detected when $x \geq 0.10$. The centro-symmetry of $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ six-membered rings in cordierite is adjusted to optimum value at $x = 0.05$. The improvement of centro-symmetry in $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ six-membered rings reduces the strength of spontaneous polarization and enhances $Q \times f$ values of cordierite ceramics. These results indicate that the appropriate amount of CaTiO_3 addition is beneficial to the improvement of microwave dielectric properties of cordierite ceramics. The optimal microwave dielectric properties of $Q \times f = 55490 \text{ GHz}$, $\varepsilon_r = 7.2$ and $\tau_f = -28.3 \text{ ppm}/^\circ\text{C}$ are

obtained at $x=0.05$, which is better than those of pure cordierite ceramic of $Q \times f = 39000\text{GHz}$, $\varepsilon_r=6.2$ and $\tau_f=-33\text{ ppm}/^\circ\text{C}$.

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References

- [1] J. Tony, M.T. Sebastian, J. Am. Ceram. Soc. 93 (2010) 147-154.
- [2] S. Wu, K.X. Song, P. Liu, H.X Lin, F.F Zhang, P. Zheng, H.B. Qin, J. Am. Ceram. Soc. 98 (2015) 1842-1847.
- [3] N.X. Xu, J.H. Zhou, H. Yang, Q.L. Zhang, M.J. Wang, L. Hu, Ceram. Int. 40 (2014) 15191-15198.
- [4] H. Ohsato, T. Tsunooka, T. Sugiyama, K.I. Kakimoto, H. Ogawa, J. Electroceram. 17 (2006) 445-450.
- [5] Y. Fang, L. Li, Q. Xiao, X.M. Chen, Ceram. Int. 38 (2012) 4511-4515.
- [6] K.M. Manu, C. Karthik, R. Uric, M.T. Sebastian, J. Am. Ceram. Soc. 96 (2013) 3842-3848.
- [7] X.C. Wang, W. Lei, R. Ang, W.Z. Lu, Ceram. Int. 39 (2013) 1707-1710.
- [8] K.X. Song, X.M. Chen, Mater. Lett. 62 (2008) 520-522.
- [9] K. Kakimoto, T. Tsunooka, H. Osato, H. Sugiyama, H. Ogawa, K. Kakimoto, H. Tsunooka, J.

Ceram. Soc. Jpn. 112 (2004) S1637-S1640.

[10] Y. Guo, H. Ohsato, K.I. Kakimoto, J. Eur. Ceram. Soc. 26 (2006) 1827-1830.

[11] H. Ikawa, T. Otagiri, O. Imai, M. Suzuki, K. Urabe, S. Udagawa, J. Am. Ceram. Soc. 69 (1986) 492-498.

[12] A. Srivastava, V.K. Singh, V. Kumar, P.H. Kumar, H. Tripathi, A. Chaudhary, K. Asiwal, R. Pandey, S.K. Suman, J. Alloy. Compd. 586 (2013) 581-587.

[13] H. Wang, J. Chen, W. Yang, S. Feng, H. Ma, G. Jia, S. Xu, J. Eur. Ceram. Soc. 32 (2012) 541-545.

[14] M.A. Bei-Yue, L.I. Ying, S.G. Cui, Y.C. Zhai, Trans. Nonferrous. Met. Soc. China. 20 (2010) 2331-2335.

[15] T. Joseph, M.T. Sebastian, H. Sreemoolanadhan, V.K.S. Nageswari, Int. J. Appl. Ceram. Tec. 7 (2010) E98-E106.

[16] S. Li, Y. Zhang, J. Han, Y. Zhou, Int. J. Refract. Met. H. 35 (2012) 257-261.

[17] M.D. Karkhanavala, F.A. Hummel, J. Am. Ceram. Soc. 36 (1953) 389-392.

[18] G. Gibbs, Am. Mineral. 51 (1966) 1068-1087.

[19] A. Putnis, Contrib. Mineral. Petr. 74 (1980) 135-141.

[20] M. Terada, K. Kawamura, I. Kagomiya, K.I. Kakimoto, H. Ohsato, J. Eur. Ceram. Soc. 27 (2007) 3045-3048.

[21] K.X. Song, S. Wu, P. Liu, H.X. Lin, Z.H. Ying, P. Zheng, J.X. Deng, L. Zheng, H.B. Qin, J. Alloy. Compd. 628 (2015) 57-62.

[22] C.L. Huang, C.L. Pan, S.J. Shium, Mater. Chem. Phys. 78 (2003) 111-115.

[23] B.H. Toby, J. Appl. Crystallogr. 34 (2001) 210-213.

[24] B.W. Hakki, P.D. Coleman, IEEE. T. Microw. Theory. 8 (1960) 402-410.

- [25] W.E. Courtney, IEEE. T. Microw. Theory. 18 (1970) 476-485.
- [26] Y.C. Chen, C.Y. Wu, Int. Ceram. 39 (2013) 1877-1883.
- [27] R.D. Shannon, J. Appl. Phys. 73 (1993) 348-366.
- [28] M.M. Krzmanc, M. Valant, B. Jancar, D. Suvorov, J. Am. Ceram. Soc. 88 (2005) 2472-2479.
- [29] M.M. Krzmanc, M. Valant, D. Suvorov, J. Eur. Ceram. Soc. 25 (2005) 2835–2838.

Table 1. Refined structural lattice parameters of (1-x)MAS-xCaTiO₃ (x=0, 0.05, and 0.10) samples and selected bond lengths and bond angles for [(Si₄Al₂)O₁₈] six-membered ring.

	x= 0	x= 0.05	x= 0.10
Lattice Parameters			
a (Å)	17.0491(5)	17.0517(5)	17.0232(8)
b (Å)	9.7438(8)	9.7443(3)	9.7321(5)
c (Å)	9.3281(8)	9.3257(2)	9.3147(3)
Volume (Å ³)	1549.61	1549.53	1543.18(12)
Bond Angles			
Si(2)–Al(2)–Si(3) (°)	125.497(1)	123.853(1)	123.674(1)
Si(3)–Si(2)–Al(2) (°)	114.349(3)	115.697(1)	116.780(2)
Si(2)–Si(3)–Al(2) (°)	120.155(7)	120.450(1)	119.546(2)
Bond Angles			
O(5)–O(4)–O(6) (°)	128.943(5)	126.555(2)	129.078(3)
O(4)–O(6)–O(5) (°)	117.941(7)	117.880(1)	112.919(2)
O(6)–O(5)–O(4) (°)	113.116(6)	115.565(1)	118.003(2)

Notes: (a) R_{wp} =6.37%, R_p =4.73%, χ^2 =1.14 for (1-x)MAS-xCaTiO₃ (x= 0). (b) R_{wp} =7.07%, R_p =5.42%, χ^2 =2.38 for (1-x)MAS-xCaTiO₃ (x=0.05). (c) R_{wp} =8.24%, R_p =6.43%, χ^2 =2.40 for (1-x)MAS-xCaTiO₃ (x= 0.10); (R_{wp} : Weight profile, R_p : Profile, χ^2 : Goodness of fit).

Figure

Fig.1. The crystal structure of cordierite six-membered ring

Fig.2. The bulk densities of (1-x)MAS -xCaTiO₃ samples sintered at different temperatures

Fig.3. The XRD patterns of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0\sim0.35$) samples sintered at each densification temperatures

Fig.4. (1-x)MAS-xCaTiO₃ (x=0 (a), 0.05 (b) and 0.10 (c)) solid solution crystal structures performed by the profile fits of Rietveld refinements, (d) standard deviation for [O₆] and [(Si₄Al₂)O₁₈] six-membered ring

Fig.5. (a) The volumes of $[\text{Al}(2)\text{O}_4]$ tetrahedrons, $[\text{Si}(2)\text{O}_4]$ tetrahedrons and $[\text{Si}(3)\text{O}_4]$ tetrahedrons of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0, 0.05, 0.10$), (b) The volumes of $[\text{MgO}_6]$ octahedrons of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0, 0.05, 0.10$)

Fig.6. The SEM images of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0\sim0.35$) samples sintered at each densification temperatures

Fig.7. (a) The $Q \times f$ values, ϵ_r of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0\sim0.35$) samples, (b) the τ_f values of $(1-x)\text{MAS}-x\text{CaTiO}_3$ ($x=0\sim0.35$) samples.