

Effect of Ga³⁺ Doping on Crystal Structure Evolution and Microwave Dielectric Properties of SrAl₂Si₂O₈ Ceramic

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Abstract: The feldspar-based microwave dielectric ceramic with low relative permittivity (ϵ_r) and excellent mechanical properties has attracted much attention in the fifth-generation wireless communication technology. In this work, a series of microwave dielectric ceramic SrAl_{2-x}Ga_xSi₂O₈ ($0.1 \leq x \leq 2.0$) was synthesized using the traditional solid-state method. X-ray diffraction pattern indicates that Ga³⁺ can be dissolved into Al³⁺, forming a solid solution. Meanwhile, substitution of Ga³⁺ for Al³⁺ can promote the space group transition from I2/c ($0.1 \leq x \leq 1.4$) to P21/a ($1.6 \leq x \leq 2.0$) with coefficient of thermal expansion (CTE) increasing from $2.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $5.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. During this substitution, the phase transition can significantly improve the structural symmetry to enhance the dielectric properties and mechanical properties. Rietveld refinement results indicate that Ga³⁺ averagely occupied four Al³⁺ compositions to form solid solution. All ceramics have a dense microstructure and high relative density above 95%. An ultralow ϵ_r of 5.8 was obtained at $x=1.6$ composition with high quality factor ($Q \times f$) of 50700 GHz and negative temperature coefficients of resonant frequency (τ_f) of approximately $-35 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The densification temperature can be reduced to 940 $^\circ\text{C}$ by adding 4% (in mass) LiF, resulting in good chemical compatibility with Ag electrode. Meanwhile, negative τ_f can be tuned to near-zero ($+3.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) by adding CaTiO₃ ceramic.

Key words: ion substitution; microwave dielectric ceramic; dielectric property; low-temperature co-fired ceramic

The frequency range of 8–12 GHz was determined as the X band in accordance with the IEEE 521-2002 criterion^[1-3]. The primary advantage of the X band is its capability for ultralong transmission distance, which positions it as a key frequency range for applications in areas such as space exploration, satellite broadcast, wireless communication, and satellite communication. Among these applications, wireless communication has rapidly developed because of the increasing requirements of autonomous automobiles and artificial intelligence. The emergence of 5G technology, characterized by high data transfer speed and minimal signal latency, is a typical representative^[4-6]. Considering that the signal delay is relevant to ϵ_r as $t_d = \sqrt{\epsilon_r} l_0 / c$ where t_d , l_0 , and c represent

signal delay time, transmission distance, and velocity of light, the rapid development of wireless communication networks has provided a substantial drive for the exploration of low permittivity dielectric ceramics^[7-10]. Given their importance, there is a strong demand for microwave dielectric ceramics with comprehensive dielectric properties.

Among silicates, a novel microwave dielectric ceramic, namely SrGa₂Si₂O₈ with low permittivity of 6.3, was reported in our previous work^[10]. An intriguing observation is that SrAl₂Si₂O₈ has a relatively high permittivity of 7.3 compared with SrGa₂Si₂O₈, although the ion polarizability of Al³⁺ ($0.79 \text{ } \text{\AA}^3$) is lower than that of Ga³⁺ ($1.5 \text{ } \text{\AA}^3$)^[11-15]. Based on previous works, SrAl₂Si₂O₈ underwent a non-reversible phase transition from hexacelsian (hexagonal)

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to celsian (monoclinic) at 1200 °C^[16]. By contrast, the SrGa₂Si₂O₈ ceramic has a low phase transition temperature around 900 °C. To lower the transition temperature and densification temperature of SrAl₂Si₂O₈ ceramic, Ga³⁺ was substituted for Al³⁺. The phase composition, structure evolution, microstructure, and microwave dielectric properties were investigated.

1 Experimental

The raw powders of SrCO₃, Al₂O₃, Ga₂O₃, and SiO₂ (99.99%, Aladdin Industrial Corporation) were weighed and subsequently ball-milled for 6 h. The slurries were dried at 80 °C for 8 h and then calcined at 1100 °C for 6 h. The calcined powders were re-milled, dried and then mixed with 5% (in mass) polyvinyl alcohol (PVA). The powders were pressed into a cylinder. The green specimens were firstly sintered at 550 °C for 2 h, followed by sintering at temperatures ranging from 1150 to 1450 °C for 6 h to achieve adequate densification.

The phase composition was determined using X-ray diffraction (XRD) with CuK α radiation (χ 'Pert PRO). The Rietveld refinement was employed using FullProf software. The thermal etching microstructure was observed using a scanning electron microscope (SEM, Quanta 200). The density was measured *via* Archimedes method. The relative permittivity and quality factor were measured using a network analyzer (Model N5230 A)^[17]. τ_f were measured within the temperature range from room temperature T_1 (25 °C) to T_2 (85 °C) and calculated based on the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent resonant frequency at 25 and 85 °C, respectively. CTE was measured by NETZSCH DIL402C thermal expansion instrument.

2 Results and discussion

Fig. 1 shows the room temperature XRD patterns of SrAl_{2-x}Ga_xSi₂O₈ ($0.1 \leq x \leq 2.0$) powders sintered at 1150 °C for 6 h. The diffraction peaks were well-indexed to the SrAl₂Si₂O₈ phase, which indicates a monoclinic structure (space group of I2/c) for the composition range of $x=0.1$ –1.4. Upon further doping with Ga³⁺, the space group transforms from I2/c to P21/a at $x=1.6$, which is attributed to SrGa₂Si₂O₈ (PDF #76-0672). The enlarged patterns in the 2θ range from 26.6° to 28.0°, as shown in Fig. 1(b), feature a slight shift towards lower angles, which is ascribed to the larger ion radius of Ga³⁺ ($R=0.47$ Å,

C.N.=4) compared to Al³⁺ ($R=0.39$ Å, C.N.=4). All results indicated that Ga³⁺ can be fully incorporated into Al³⁺ sites, forming a solid solution and triggering a phase transition.

Fig. 2 shows the CTE for the compositions of $x=1.0$ and $x=1.6$ which represent the space groups of I2/c and P21/a, respectively. For $x=1.0$ composition, the CTE is measured at 2.9×10^{-6} °C⁻¹ within the temperature range of 100–315 °C, increasing to around 7×10^{-6} °C⁻¹ at elevated temperatures. In contrast, $x=1.6$ composition exhibits a significantly higher CTE of 5.2×10^{-6} °C⁻¹ from 100 to 280 °C, rising to around 11×10^{-6} °C⁻¹ at higher temperature. These results indicate that the P21/a structure has a large CTE compared to I2/c structure.

To investigate the phase composition and structure of

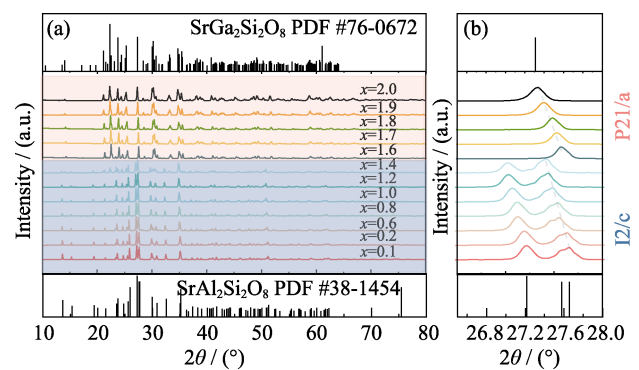


Fig. 1 (a) XRD patterns of SrAl_{2-x}Ga_xSi₂O₈ ($0.1 \leq x \leq 2.0$) ceramics sintered at 1150 °C for 6 h and (b) enlarged patterns in $2\theta=26.5^\circ$ –28.0°

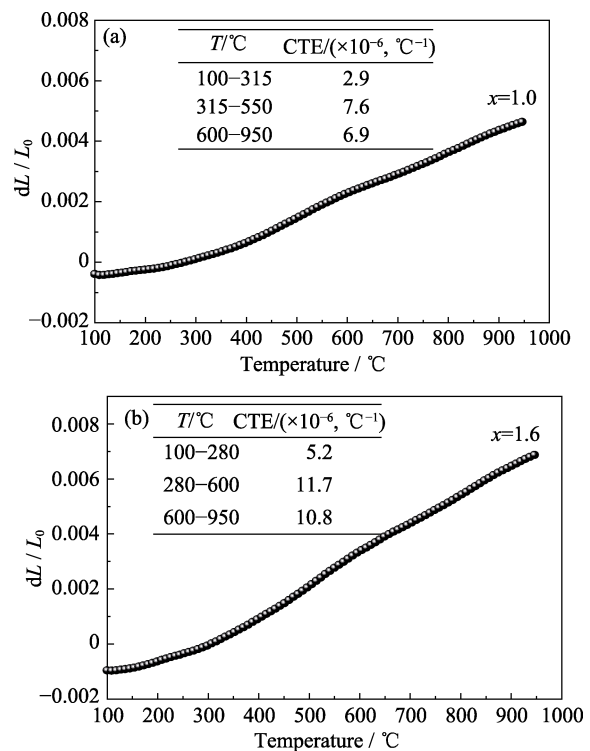


Fig. 2 CTE of SrAl_{2-x}Ga_xSi₂O₈ ceramics with (a) $x=1.0$ and (b) $x=1.6$

$\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ ceramic, Rietveld refinement was carried out on the XRD data using FullProf software. As reported in previous works, Al^{3+} in $\text{SrAl}_2\text{Si}_2\text{O}_8$ has four different positions. Based on the crystallography, it is assumed that Ga^{3+} equally occupies these four positions. Fig. 3(a-d) show the representative refinement results of compositions $x=0.1, 1.0, 1.6$, and 1.9 . The good agreement between measured and calculated data, accompanied by a low difference (yellow line), indicates the high reliability of the refinement results. The inset shows the enlarged pattern around $2\theta=22^\circ$, where a splitting peak appears with Ga^{3+} doping and subsequently disappears at $x=1.6$ composition. This observation confirms our hypothesis that Ga^{3+} is distributed equally among the four Al^{3+} positions. Fig. 3(e) shows the variations of cell parameters, β , and cell volume as a function of x . In the range of $0.1 \leq x \leq 1.4$, the cell parameters gradually increase with Ga^{3+} doping, leading to the increase of cell volume. The β angle also gradually increases from 115.358° (at $x=0.1$) to 115.375° (at $x=1.4$). A sharp change in parameters occurs at $x=1.6$ composition, which is attributed to the space group transition from $\text{I}2/\text{c}$ to $\text{P}21/\text{a}$.

Fig. 4 shows the polished and thermally etched surface morphologies of $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ ceramics sintered at their optimum temperature. For $x=0.1$, the $\text{SrAl}_{1.9}\text{Ga}_{0.1}\text{Si}_2\text{O}_8$ ceramic presents a non-uniform grain distribution, characterized by small grains interspersed with large grains. All grains display a square morphology, tightly packed together. With Ga^{3+} doping increasing to

$x=1.6$, the microstructure remarkably changes, and square grains are linked together to form a uniform and dense morphology, which indicates that a high concentration of Ga^{3+} can promote grain growth.

Fig. 5 shows the density and microwave dielectric properties of $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ ceramics as a function of x . As shown in Fig. 5(a), bulk density gradually increases from 2.74 g/cm^3 (at $x=0.1$) to 3.60 g/cm^3 (at $x=2.0$). Notably, the relative density of all ceramics exceeds 95%, which is an important factor influencing the physical and dielectric properties. Fig. 5(b) shows the variation of measured relative permittivity, which gradually decreases from 7.3 to 6.6 in the range of $0.1 \leq x \leq 1.4$, followed by a sharp decline to 5.8 at $x=1.6$. Beyond this composition, the relative permittivity slightly increases to over 6.0. The ultralow relative permittivity at $x=1.6$ can be attributed to the space group transition, while the subsequent increase can be due to the higher polarizability of Ga^{3+} ($\alpha=1.5 \text{ \AA}^3$) compared with Al^{3+} ($\alpha=0.79 \text{ \AA}^3$)^[9, 18-19]. As reported by previous research, the theoretical relative permittivity can be estimated based on the Clausius-Mossotti equation^[8-9, 20].

$$\varepsilon_r = (1 + 2b\alpha_D^T / V_m) / (1 - b\alpha_D^T / V_m) \quad (2)$$

$$\alpha_D^T = \alpha(\text{Sr}^{2+}) + (2-x)\alpha(\text{Al}^{3+}) + x\alpha(\text{Ga}^{3+}) + 2\alpha(\text{Si}^{4+}) + 8\alpha(\text{O}^{2-}) \quad (3)$$

where V_m represents the cell volume, $b=4\pi/3$ while α_D^T is the total polarizability which can be obtained from equation (3). As shown in Fig. 5(b), the theoretical

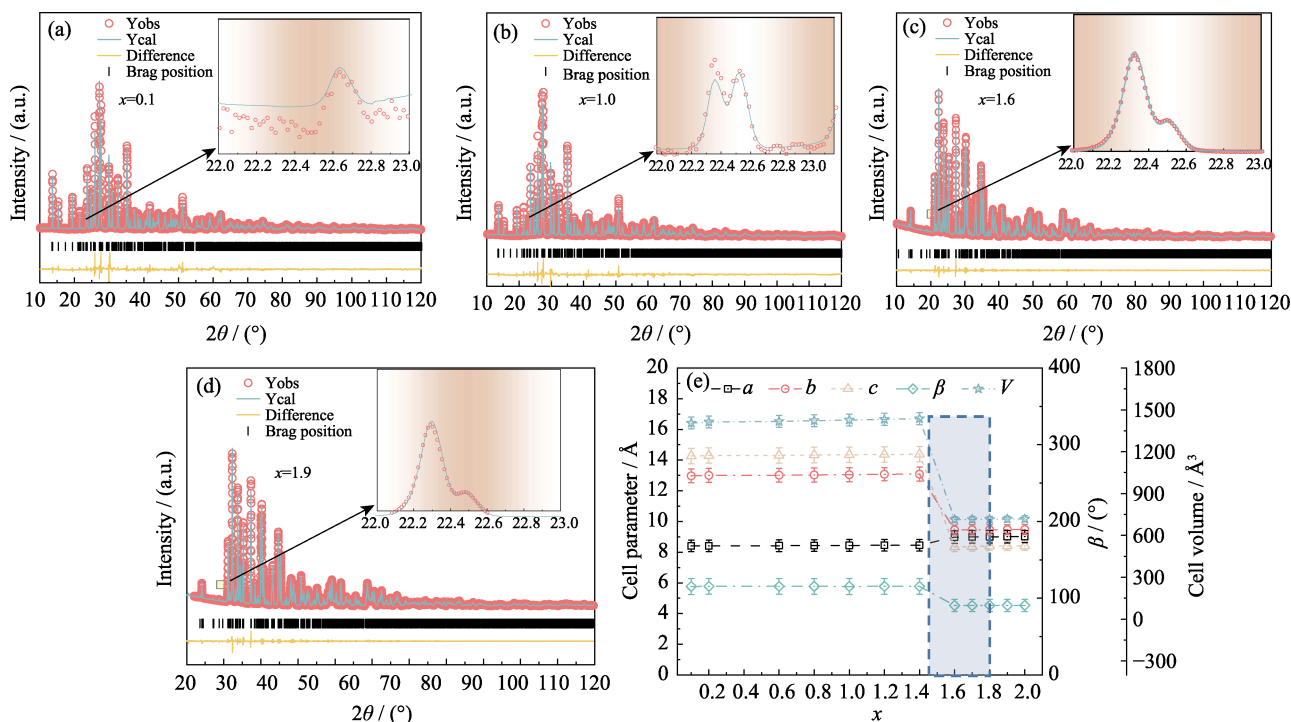


Fig. 3 (a-d) Rietveld refinement patterns of $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ ceramics; (e) Variation trends of cell parameters, β , and cell volume as a function of x

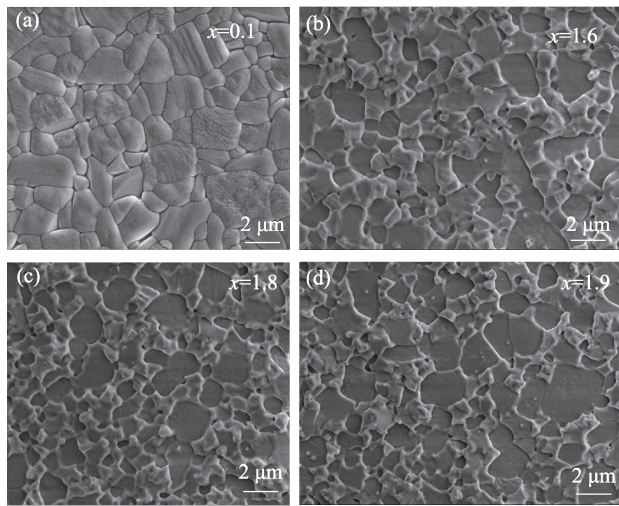


Fig. 4 SEM morphologies of SrAl_{2-x}Ga_xSi₂O₈ ceramics after being polished and etched
(a) $x=0.1$; (b) $x=1.6$; (c) $x=1.8$; (d) $x=1.9$

values demonstrate an increasing trend with Ga³⁺ doping. However, the theoretical values are slightly lower than the measured ones, which exhibit a decreasing trend. According to Shannon *et al.*, the large difference can be attributed to the “Rattling” or “Compressed” cations in the lattice. The decreasing trend of measured permittivity is due to the low polarizability of Al³⁺ ($\alpha=0.79 \text{ \AA}^3$) compared with Ga³⁺ ($\alpha=1.5 \text{ \AA}^3$). The influence of porosity on relative permittivity can be estimated using Bosman Having’s method^[21-24]:

$$\varepsilon_{\text{corr}} = \varepsilon_r (1 + 1.5P) \quad (4)$$

where P represents the fractional porosity. The corrected relative permittivity, as shown in Fig. 5(b), is slightly higher than the measured values, suggesting that relative density plays a crucial role in determining relative permittivity.

Fig. 5(c) exhibits the variation of $Q \times f$ as a function of x . With Ga³⁺ doping, the $Q \times f$ value initially increases gradually and then exhibits a sharp increase from 37500 GHz (at $x=1.4$) to 96600 GHz (at $x=2.0$). The $Q \times f$ value is determined by both extrinsic factors, such as density, porosity, grain size, and second phase, and intrinsic factors, including lattice vibration and packing fraction (P.F.)^[25-27]. Based on the XRD and SEM results, the influence of the second phase and density can be ruled out. To estimate the effect of intrinsic factors, the P.F. can be employed, which is defined as the summation of the volume of packed ions over the volume of a primitive unit cell. Higher P.F. results in reduced interspace for lattice vibration, thus reducing the dielectric loss and increasing the quality factor. As shown in Fig. 5(c), all compositions have high P.F., exceeding 55%, despite a slightly decreased trend, indicating other factors are also determining the quality factor. Notably, the P.F. also sharply increases at $x=1.6$, with a $Q \times f$ value of 50700 GHz.

τ_f is approximately $-35 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, which shows limited dependence on the sintering temperature and composition (Fig. 5(d)). The substantial absolute value $|\tau_f|$ immensely constrains the application of microwave dielectric ceramics. Two strategies have been constantly exploited to tune τ_f . Firstly, a composite ceramic with

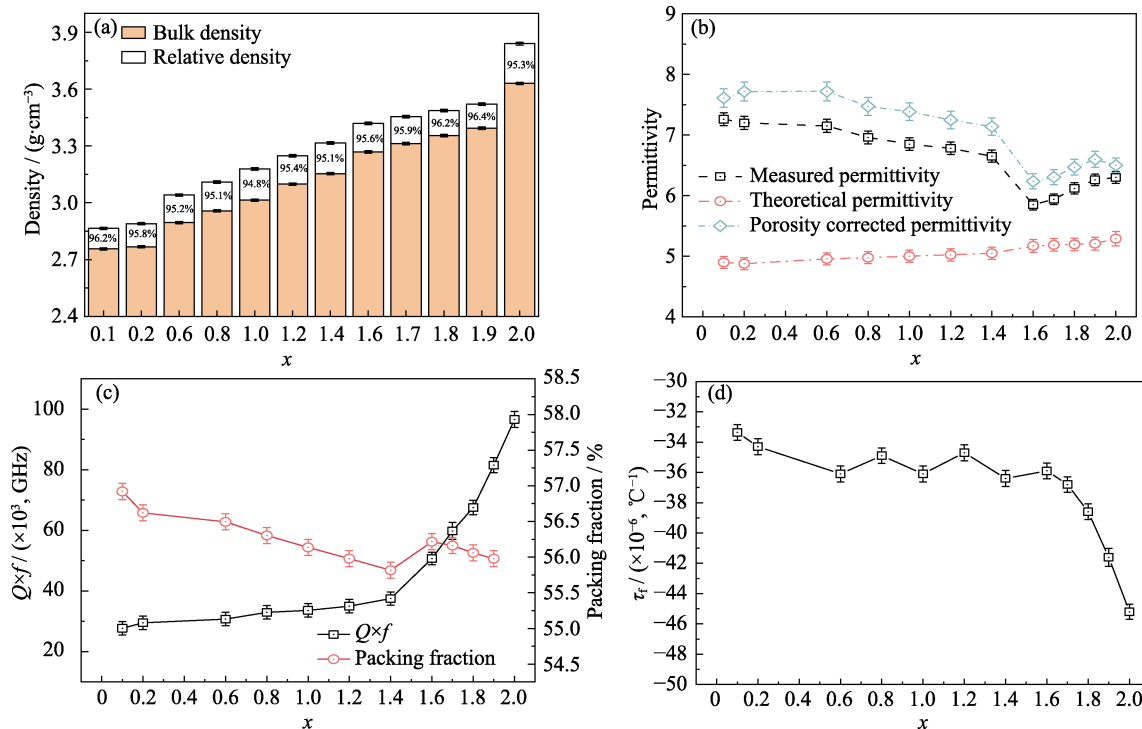


Fig. 5 Densities and microwave dielectric properties of SrAl_{2-x}Ga_xSi₂O₈ ceramics as a function of x
(a) Density; (b) Permittivity; (c) $Q \times f$ and packing fraction; (d) τ_f

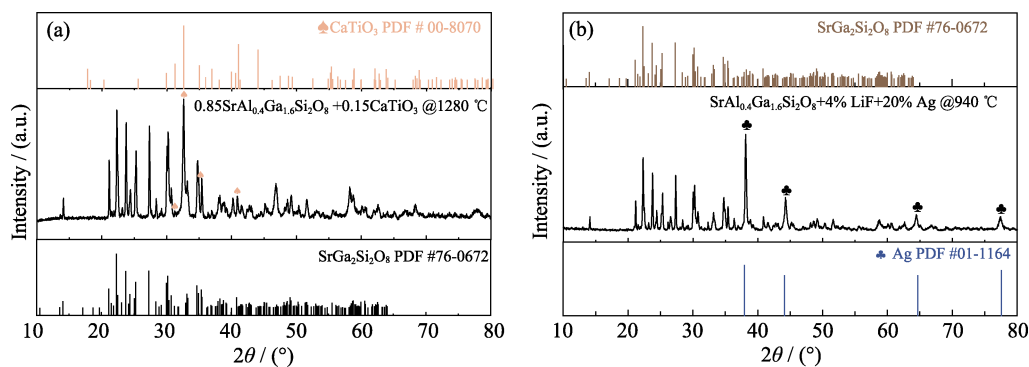


Fig. 6 (a) XRD patterns of $0.85\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8+0.15\text{CaTiO}_3$ ceramic sintered at $1280\text{ }^\circ\text{C}$;
(b) $\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8+4\%$ (in mass) LiF co-fired with 20% (in mass) Ag at $940\text{ }^\circ\text{C}$

Table 1 Microwave dielectric properties of $(1-y)\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8+y\text{CaTiO}_3$ ceramics sintered at their optimum temperature

y	ε_r	$Q \times f/\text{GHz}$	$\tau_f/(\times 10^{-6},\text{ }^\circ\text{C}^{-1})$
0.03	6.1	50300	-31.6
0.06	6.3	49800	-24.4
0.09	6.5	49400	-12.8
0.12	6.7	48900	-5.7
0.15	7.0	48400	+3.7

inverse τ_f is formed. Notably, TiO_2 ($\tau_f \sim 460 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$) and CaTiO_3 (CTO, $\tau_f \sim 800 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$) are commonly used^[28-29]. Secondly, a solid solution is formed by ionic substitution to alter the crystal structure by modifying the bond valence and polyhedron distortion. Although the substitution of Ga^{3+} for Al^{3+} has caused transition of space group, the negative τ_f cannot be tuned.

In this study, the CTO ceramic was selected as the compensator to buffer the negative τ_f of $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$. The $x=1.6$ composition was selected as a representation. Fig. 6(a) exhibits the XRD patterns of the composite ceramic with 15% (in mass) CTO sintered at $1280\text{ }^\circ\text{C}$ for 6 h. Only the peaks of $\text{SrGa}_2\text{Si}_2\text{O}_8$ and CTO are present, indicating their coexistence without any additional phase peaks. Table 1 shows the microwave dielectric properties of the composite ceramics sintered at their optimum temperature. The increase of relative permittivity and decrease of quality factor can be attributed to the microwave dielectric properties of CTO ($\varepsilon_r \sim 162$, $Q \times f \sim 8700\text{ GHz}$, $\tau_f \sim +800 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$). Notably, a near-zero τ_f of $+3.7 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$ is achieved at $y=0.15$.

The low-temperature co-fired ceramic (LTCC) technology has become the standard for passive integration and miniaturization because of its high-frequency characteristics, thermal stability, multi-function, high assembly density, *etc.* The LTCC technology primarily requires low densification temperature, which must be lower than the

melting points of commonly used electrodes, such as Ag ($\sim 960\text{ }^\circ\text{C}$) and Cu ($\sim 1060\text{ }^\circ\text{C}$)^[30-31]. In this work, LiF as the sintering aid was added to reduce the densification temperature of the $\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8$ ceramic. Fig. 6(b) shows the XRD pattern of the $\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8$ ceramic sintered at $940\text{ }^\circ\text{C}$ with 4% (in mass) LiF. Only the peaks belonging to $\text{SrGa}_2\text{Si}_2\text{O}_8$ (PDF #76-0672) and Ag (PDF #01-1164) can be detected, which indicates the absence of any chemical reaction between them. All results suggest that $\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8$ microwave dielectric ceramics with a low relative permittivity and high quality factor possess a large application potential in the LTCC technology.

3 Conclusions

In this work, a series of microwave dielectric ceramics of $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ were fabricated using conventional solid-state method. Based on the XRD patterns and Rietveld refinement results, the Ga^{3+} is averagely entered into four Al^{3+} positions to form solid solution in a wide range ($0.1 \leq x < 1.6$). Meanwhile, the space group has transformed from I2/c to P21/a at $x=1.6$, coinciding with an increase in the CTE from 2.9×10^{-6} to $5.2 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$. The microwave dielectric properties are significantly influenced by the lattice structure, resulting in a gradual decrease in relative permittivity to a minimum value of 5.8 at $x=1.6$, despite the greater polarizability of Ga^{3+} ($\alpha=1.5\text{ \AA}^3$) compared to Al^{3+} ($\alpha=0.79\text{ \AA}^3$). The quality factor reaches a maximum value of 96600 GHz at $x=2.0$. The negative τ_f can be tuned to $+3.7 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$ by adding 15% CaTiO_3 ceramic. The densification temperature also can be reduced to $940\text{ }^\circ\text{C}$ by adding 4% LiF as the sintering aid, which exhibits good chemical compatibility with Ag electrode. All results indicate that the $\text{SrAl}_{0.4}\text{Ga}_{1.6}\text{Si}_2\text{O}_8$ has a large application potential in LTCC technology.

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Ga^{3+} 掺杂对 $\text{SrAl}_2\text{Si}_2\text{O}_8$ 陶瓷晶体结构 及微波介电性能的影响

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摘要: 长石基微波介质陶瓷以其较低的相对介电常数(ϵ_r)和优异的力学性能在 5G 通信技术中备受关注。本工作采用传统固相法合成了系列微波介质陶瓷 $\text{SrAl}_{2-x}\text{Ga}_x\text{Si}_2\text{O}_8$ ($0.1 \leq x \leq 2.0$)。XRD 分析表明, Ga^{3+} 能够进入 Al^{3+} 晶格并形成固溶体。此外, Ga^{3+} 取代 Al^{3+} 可以促使空间群由 I2/c ($0.1 \leq x \leq 1.4$) 转变为 P21/a ($1.6 \leq x \leq 2.0$), 热膨胀系数(CTE)由 $2.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ 升高到 $5.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ 。空间群演变有效提高了晶体结构的对称性, 从而改善了材料的介电性能和力学性能。Rietveld 精修结果表明, Ga^{3+} 平均占据 4 个 Al^{3+} 晶格位置。所有陶瓷样品均具有致密的显微结构和较高的相对密度(超过 95%)。 $x=1.6$ 所获得的材料具有超低 ϵ_r (5.8), 品质因数($Q \times f$)为 50700 GHz, 以及负的谐振频率温度系数(τ_f 约为 $-35 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$)。通过添加质量分数 4% 的 LiF, 陶瓷致密化温度可降低至 940 $^\circ\text{C}$, 并且该复合陶瓷与 Ag 电极之间展现出良好的化学兼容性。同时, 通过添加 CaTiO_3 陶瓷, 可以将负 τ_f 调整到接近零($+3.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$)。

关键词: 离子取代; 微波介电陶瓷; 介电性能; 低温共烧陶瓷

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