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Phase composition, sintering behavior and mirowave dielectric properties of novel high *Q* $Ca_3Al_2(GeO_4)_3$ ceramic

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Keywords: Ceramics; Dielectrics; X-ray techniques

Abstract

Novel $Ca_3Al_2(GeO_4)_3$ microwave dielectric ceramic with high *Q* was prepared by a conventional solid-phase reaction method. X-ray diffraction patterns (XRD) and energy dispersive spectrometer (EDS) analysis shown that the ceramic was a single garnet phase with parameters of $a= b=c$=12.11845(16)Å, V=1779.625(69) Å^3 and Z = 8. As the sintering temperature increased from 1250 °C to 1350 °C, the bulk density (ρ), relative permittivity (ε_r) and quality factor ($Q\times f$) values increased first, reached a maximum value and then decreased. The temperature coefficient of resonator frequency (τ_f) varied slightly in a small negative range from -15 to -22 ppm/°C. The $Ca_3Al_2(GeO_4)_3$ ceramic sintered at 1325°C exhibited the best microwave dielectric properties of ε_r = 7.6, $Q\times f$ = 104,100 GHz and τ_f = -15 ppm/°C, showing that it is a good candidate for microwave devices with low dielectric loss.

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1. Introduction

Microwave dielectric ceramics are used in circuits as dielectric materials, performing one or more functions in the microwave frequency band (mainly UHF, SHF bands, 300 MHz to 300 GHz). With the rapid development of mobile communications and modern electronic devices, and the advent of the 5G communication era, the research for microwave dielectric ceramics has received more and more attention, bearing the infinite hope of future microwave devices such as electronic countermeasures, navigation, communication, radar, home satellite live TV receivers and mobile phones. [1-4].

For the microwave dielectric ceramics, low relative permittivity would reduce the reflection at the interface between air and dielectric, minimize cross-coupling with conductors, and slump the time required for electronic signal conversion to achieve low latency [5-8]. As a hotspot in microwave dielectric ceramics study in recent years, researchers have developed many ceramics with excellent microwave dielectric properties, such as $Sr_2Al_2Si_2O_7$[9], $CaAl_2Si_2O_8$(Anorthite)[10], α-$Zn_2P_2O_7$[11] and $ZnAl_2O_4$[12]. These ceramics exhibit low relative permittivity, but low $Q\times f$ values and large τ_f values also limit their further commercial applications. Therefore, many works are focused on researching new materials with high Q and near-zero τ_f.

In the present work, $Ca_3Al_2(GeO_4)_3$ ceramic was designed and prepared by the solid-state reaction method. Furthermore, the phase structure, microstructure, sintering behavior and microwave dielectric properties of ceramic were also systematically studied.

2. Experimental procedures

$Ca_3Al_2(GeO_4)_3$ ceramics samples were prepared by the solid-state reaction method. High-purity raw powders (≥99%, Guo-Yao Co. Ltd., Shanghai, China) of $CaCO_3$ GeO_2, and Al_2O were used as the starting materials. The stoichiometric ratio of raw materials was weighed separately and ball-milled in an alcohol (ethanol) medium for 4 hours with zirconia balls. After drying, the mixture was calcined in air at 1100°C for 4 h. The powders were granulated with 5 wt% polyvinyl alcohol (PVA) and pressed into a disk with a diameter of 12 mm and thickness of 5 mm under a uniaxial pressure of 150 MPa. The disks were heated to 550°C in air at a heating rate of 1°C/min to burn out PVA, and then sintered in air at 1250°C~1350°C for 4 h.

The phase structure of samples was tested by an XRD ((Model X'Pert PRO, PANalytical, Almelo, Holland). The element content of samples was tested by an XPS (Model ESCALAB 250Xi, Thermo Electron Corporation, Americe). The morphologies of the sintered ceramics were analyzed by a scanning electron microscope (JSM6380-LV, JEOL, Tokyo, Japan). The density of samples was measured at room temperature by the Archimedes method using distilled water as the buoyancy liquid. The dielectric behavior at microwave frequencies was measured using the $TE_{01\delta}$ shielded cavity method with a network analyzer (Model E5071C, Agilent Design, USA, 300K Hz to 20G Hz). The temperature coefficient of resonant frequency (τ_f) values were calculated according to the following formula:

$$\tau_f = \frac{1}{f_0} \cdot \frac{df_0}{dT} \approx \frac{f(T_1) - f(T_0)}{f(T_0)(T_1 - T_0)},$$

where f_{T1}, f_{T_0} are the resonant frequencies at the temperature of T_1 (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

Powder X-ray diffraction patterns of the $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures are shown in Figure 1(a). The XRD patterns of all samples were in agreement with the standard ICDD file no.04-008-4618, indicates that the main phase is $Ca_3Al_2(GeO_4)_3$. The ceramics are centrosymmetric crystal system with space group of Ia-3d. In order to further calculate the lattice parameters and atomic occupancy of compound, the structural refinement using the FullProf Suite program was done and the results are illustrated in Figure 1(b). Agreement factors obtained from the final refinement were as follows: R_b = 2.94%, R_p = 6.02%, R_{wp} = 7.67%, and S = 2.61, indicating that the determined structure is trustworthy. The lattice parameters and atomic occupancy of the compound after finishing are listed in Table 1. The lattice parameters of the $Ca_3Al_2(GeO_4)_3$ are a=12.11833(16)Å, b=12.11845(16)Å, c=12.11845(16)Å, V= 1779.625(69)Å^3, and Z = 8.

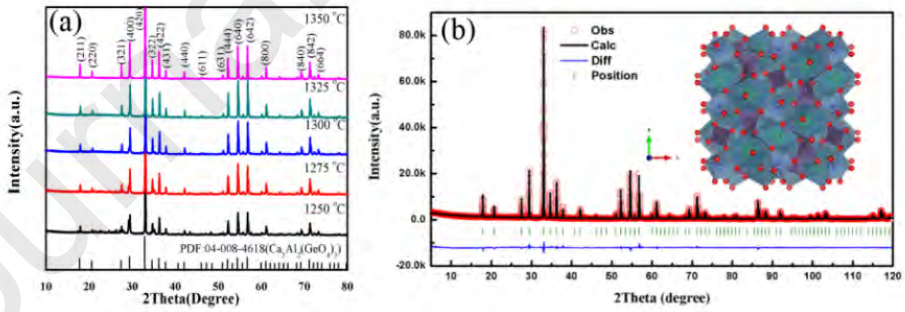

Fig. 1. (a) XRD patterns of $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures, (b)Rietveld refinement of XRD data for $Ca_3Al_2(GeO_4)_3$.

Figure 2 demonstrates the SEM pictures of $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures for 4 h. It can be seen that the grains in all samples are closely packed and few pores are observed. As the sintering temperature increased, the pores decreased, and the grain size gradually increased, showing that the microstructure

became denser. The $Ca_3Al_2(GeO_4)_3$ ceramic sintered at 1325 °C could obtain the relatively dense structure. As the sintering temperature rose to 1350 °C, almost no pores were detected, and the grains of ceramic were relatively uniform. Over-sintering occurred with further increasing the sintering temperature, resulting in the abnormal growth of some grains in ceramics.

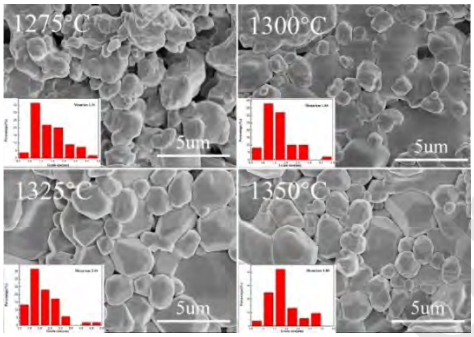

Fig. 2. SEM images of $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures.

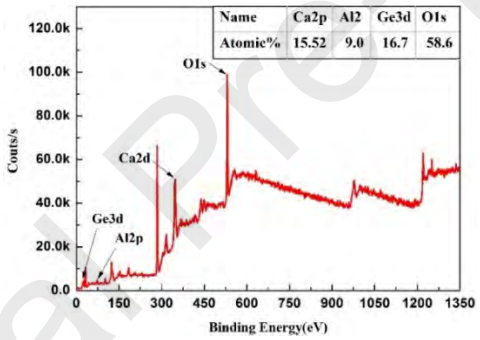

Fig. 3 X-Ray Photoelectron Spectroscopy (XPS) of different grains for $Ca_3Al_2(GeO_4)_3$ ceramics sintered at 1325 °C for 4h.

X-ray Photoelectron Spectroscopy (XPS) of $Ca_3Al_2(GeO_4)_3$ ceramics at 1325 °C for 4h was measured and the result is shown in Figure 3. The ratio of Ca:Al:Ge elements is close to 3:2:3, determining that the composition was $Ca_3Al_2(GeO_4)_3$, which agree well with the analysis of XRD.

Figure 4(a) demonstrates the bulk density and relative density of $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures. As the sintering temperature rised from 1250 °C to 1350 °C, the bulk density of $Ca_3Al_2(GeO_4)_3$ ceramics increased from 3.60 to the maximum of 4.06 g/cm^3, which is close to the theoretical density of ceramics (as

listed in Table 1), and then decreased to 3.98 g/cm^3. Figure 4(b) shows the relative permittivity, quality factor and temperature coefficient of resonant frequency of the $Ca_3Al_2(GeO_4)_3$ ceramics as a function of the sintering temperature. The relationship between the relative permittivity and sintering temperature of $Ca_3Al_2(GeO_4)_3$ ceramics is similar to that of the bulk density. When the sintering temperature was 1325°C, the relative permittivity reached the maximum value of 7.3. The grain size and density would affect the relative permittivity of ceramics. This change in relative permittivity was related to the density and structural characteristics of ceramics [13]. The $Q\times f$ value of the $Ca_3Al_2(GeO_4)_3$ sample has a close relationship with the density and grain size of the ceramic [14]. As the sintering temperature increased, the microstructure of samples became dense and the grains grew, so the quality factor increased. When the temperature increased from 1250°C to 1350°C, the $Q\times f$ values increased from 42,100 GHz to 104,100 GHz. Due to the abnormal growth and cracking of grains, the quality factor was reduced with further increasing the sintering temperatures [15].

Table 1. Details of retvield refinement result of $Ca_3Al_2(GeO_4)_3$ compound

Parameter	**Value**	**Parameter**	**Value**
formula	$Ca_3Al_2(GeO_4)_3$	symmetry	Centrosymmetric
radiation type	Cu Kα	space group	Ia-3d (NO.230)
step	0.02°	a	12.11833(16) Å
symmetry	Centrosymmetric	b	12.11845(16) Å
refinement	Rietveld method	c	12.11845(16) Å
S	2.61	β	90°
R_B	2.94%	volume	1779.625(69) Å^3
R_P	6.02%	Z	8
R_{WP}	7.67%	ρ_{calc}	4.3587 g cm^{-3}

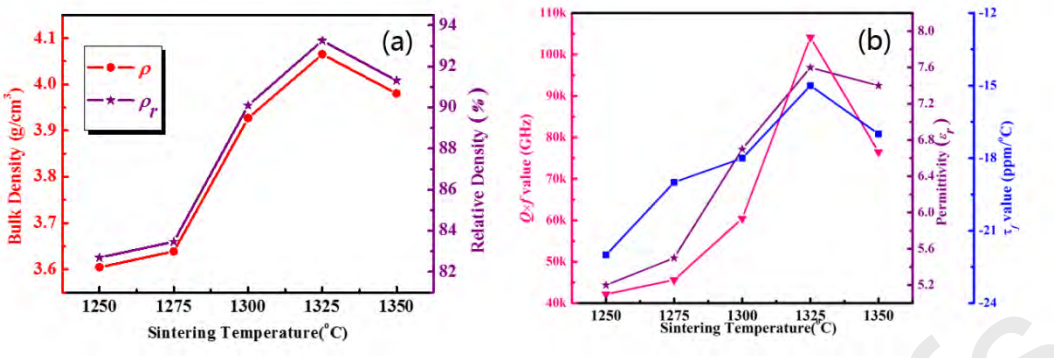

Fig. 4 (a) the bulk density(ρ) and relative density(ρ_r) of $Ca_3Al_2(GeO_4)_3$ ceramics sintered at different temperatures. (b) relative permittivity(ε_r), quality factor($Q\times f$) and temperature coefficient of resonant frequency(τ_f) of $Ca_3Al_2(GeO_4)_3$ ceramic as a function of sintering temperature.

The phase composition and structure of ceramics have a great effects on the temperature coefficient of resonant frequency(τ_f) of the materials. Because no second phase was detected, the τ_f value of $Ca_3A_{l2}(GeO_4)_3$ ceramics maintained a stable range (-22~-15ppm/°C). Table 2 lists the microwave dielectric properties of some compounds with with similar relative permittivity. Comparing with $Sr_2Al_2Si_2O_7$, $CaAl_2Si_2O_8$ (Anorthite), α-$Zn_2P_2O_7$ and $ZnAl_2O_4$ systems, $Ca_3Al_2Ge_3O_{12}$ material exhibited higher $Q\times f$ and small τ_f values, indicating that it is a good candidate for microwave devices with low dielectric loss.

Table 2 Comparison of the microwave dielectric properties for some compounds with similar relative permittivity.

Composition	ε_r	*Ts*(°C)	$Q\times f$(GHz)	τ_f (ppm/°C)	*Ref.*
$Sr_2Al_2Si_2O_7$	7.2	1525	33,000	-37	9
$Ca_3Al_2Ge_3O_{12}$	7.3	1325	104,100	-22	This work
$CaAl_2Si_2O_8$ (Anorthite)	7.4	1525	12,000	-130	10
α-$Zn_2P_2O_7$	7.5	1150	50,000	-204	11
$ZnAl_2O_4$	7.9	1700	82,000	-63	12

4. Conclusions

$Ca_3Al_2(GeO_4)_3$ ceramics have been synthesized by the traditional solid-phase routes. The ceramic exhibited a single phase of $Ca_3Al_2(GeO_4)_3$ with parameters of

$a=b=c$=12.11845(16)Å, V=1779.625(69) Å^3, and Z = 8. $Ca_3Al_2(GeO_4)_3$ ceramics sintered at 1325°C showed low bulk density of 4.06 g/cm^3 and good microwave dielectric properties of ε_r = 7.6, $Q\times f$ = 104,100 GHz, and τ_f = -15 ppm/°C. Low bulk density, small ε_r, high $Q\times f$ values, and tiny τ_f showed that $Ca_3Al_2(GeO_4)_3$ was a good candidate for 5G devices with high demands.

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Highlights

- $Ca_3Al_2(GeO_4)_3$ ceramics exhibited a single phase with cubic garnet structure.
- $Ca_3Al_2(GeO_4)_3$ ceramics exhibited excellent microwave dielectric performances.
- $Ca_3Al_2(GeO_4)_3$ ceramics sintered at 1325 °C with low dielectric loss can be used in microwave devices.

There is no interests to declare.

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Authors' contributions

Huanfu Zhou conceived and designed the study. Chengming Lu synthesized and prepared the samples. Huanfu Zhou and Chengming Lu wrote the paper. Shixuan Li tested the samples for XRD, Jiji Deng tested the samples for microwave dielectric properties and Kanguo Wang tested the samples for XPS, Huanfu Zhou and Chengming Lu reviewed and edited the manuscript. All authors read and approved the manuscript.