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Letter

Synthesis and microwave dielectric properties of $Ca_3SnSi_2O_9$ ceramics

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ABSTRACT

$Ca_3SnSi_2O_9$ ceramics were synthesized and their microwave dielectric properties were investigated. Non-stoichiometric compositions (molar ratio of Ca:Sn:Si = 1:1.2:1) were employed to synthesize pure monoclinic $Ca_3SnSi_2O_9$ phase when sintering temperature varied between 1400 and 1525 °C. The $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at 1500 °C exhibited microwave dielectric properties: a dielectric constant (ε_r) of 8.44, a quality factor ($Q \times f$) of 92,000 GHz and a temperature coefficient of resonant frequency (τ_f) of −60 ppm/°C. Monoclinic $Ca_3SnSi_2O_9$ phase ceramics have a wide sintering temperature region, excellent sintering behavior and high quality factor. They are promising candidate materials for millimeter-wave devices.

1. Introduction

Microwave dielectric ceramics have been widely used in passive component [1,2], local area network and intelligent transport systems. Microwave ceramic materials include Al_2O_3 [3], silicate [4,5], MAl_2O_4 (M = Mg, Zn), $Mg_4Nb_2O_9$ system. Al_2O_3 has a strong raw material and processing sensitivity. MAl_2O_4 needs a high sintering temperature of 1550–1650 °C [6]. Addition of TiO_2 into the spinel $ZnAl_2O_4$ improved its properties and the τ_f approached zero for 0.83 $ZnAl_2O_4$–0.17 TiO_2. This temperature compensated composition has excellent microwave dielectric properties ($\varepsilon_r = 12.67$, $Q_u = 9950$ at 10.075 GHz) [7]. For $x = 0.25$ in $(1-x)MgAl_2O_4$–$xTiO_2$, the microwave quality factor reaches a maximum value of $Q \times f = 105{,}400$ GHz at 7.5 GHz, where $\varepsilon_r = 11.035$ and $\tau_f = -12$ ppm/°C [8]. Magnesium niobate has a low Q value ($Q \times f = 26{,}069$ GHz) [9]. The microwave dielectric properties of $Mg_4Nb_2O_9$ + 3 wt.% LiF sintered at 850 °C for 10 h were: $\varepsilon_r = 12.6$, $Q \times f = 103{,}607$ GHz, $\tau_f = -70.5$ ppm/°C [10].

Silicates, such as magnesium silicate ($MgSiO_3$), forsterite (Mg_2SiO_4), zinc silicate (Zn_2SiO_4) and wollastonite ($CaSiO_3$) have low dielectric constant and high quality factor. $MgSiO_3$ ceramics have excellent dielectric properties: $\varepsilon_r = 6.7$, $Q \times f = 121{,}200$ GHz, $\tau_f = -17$ ppm/°C [11], however, they are easy to be powdered due to the inevitable phase transformation. The microwave properties of Mg_2SiO_4 ceramics containing 0.5 wt.% LMZBS glass were: $\varepsilon_r = 7.3$, $Q \times f = 121{,}200$ GHz [12]. $(Mg_{0.4}Zn_{0.6})_2SiO_4$ ceramics indicate a good combination of microwave dielectric characteristics: $\varepsilon_r = 6.6$, $Q \times f = 95{,}650$ GHz, and $\tau_f = -60$ ppm/°C [13]. Mg_2SiO_4 ceramics have a strong processing sensitivity [4,14]. Zn_2SiO_4 ceramics with excellent properties were synthesized by a cold isostatic pressing (CIP) at a pressure of 200–300 MPa [15–18]; however, its quality factor was low ($Q \times f = 15{,}000$ GHz) when the conventional solid-state method was employed [18]. $CaSiO_3$ ceramics have a low sintering temperature (1320 °C) and low dielectric constant (6.69); however, the low densification and porous microstructure of $CaSiO_3$ led to a low quality factor ($Q \times f = 25{,}398$ GHz) [19]. Ternary silicates contain Li_2MgSiO_4 and $Sr_2ZnSi_2O_7$. Li_2MgSiO_4 mixed with 1 wt.% LBS sintered at 925 °C/2 h had $\varepsilon_r = 5.5$ and $\tan\delta = 7 \times 10^{-5}$ at 8 GHz [20]. Excellent dielectric properties ($\varepsilon_r = 8.4$, $Q \times f = 105{,}000$ GHz (at 12.628 GHz) and $\tau_f = -51.5$ ppm/°C were obtained for the composition $Sr_2ZnSi_2O_7$ when sintered at 1475 °C/2 h [21,22].

For microwave ceramic capacitors, the low dielectric constant and high quality factor were helpful for the high self-resonant frequency (SRF) and low dielectric loss of component because of the low parasitic inductance and low insertion loss. Low dielectric constant would reduce the relaxation time and enhance the signal propagation speed when microwave ceramics were supplied in multilayer packaging system. The simple synthesis process and stable dielectric properties of ceramics were also important problems. Therefore, it is an urgent task to find a new silicate material system for microwave/millimeter-wave application.

Even though various studies were conducted on silicates, dielectric properties of monoclinic $Ca_3SnSi_2O_9$ materials were seldom investigated. In the present work, we reported the synthesis, characterization, and microwave dielectric properties of $Ca_3SnSi_2O_9$ ceramics.

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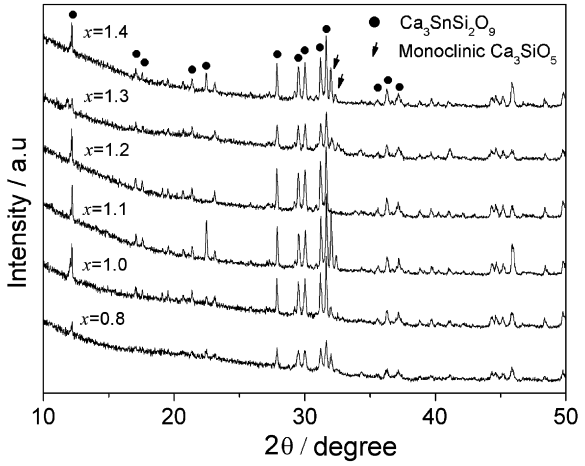

Fig. 1. XRD patterns of $Ca_3Sn_xSi_2O_{9+\delta}$ ceramic materials with various compositions at 1400 °C.

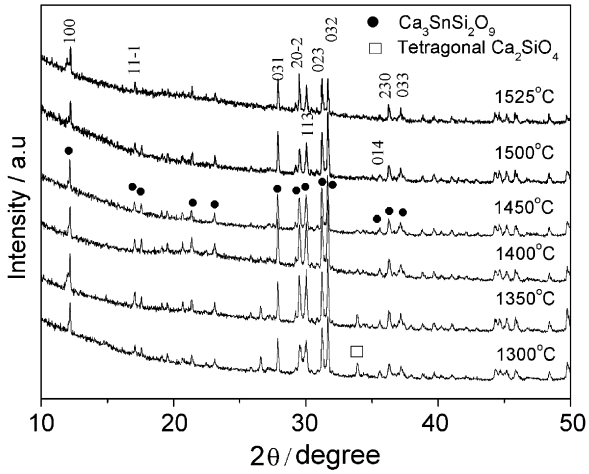

Fig. 2. XRD patterns of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramic materials sintered at various temperatures.

2. Experimental

$Ca_3SnSi_2O_9$ microwave ceramics were synthesized by the conventional solid-state method. $CaCO_3$, nano-SnO_2 particles ($d_{50} = 0.2$ μm by laser size distribution analyzer, Aladdin, Shanghai, China) and nano-SiO_2 (7 nm, Degussa, Auckland, New Zealand) were mixed with a proper molar ratio, and then milled with zirconia balls for 4 h on a planetary milling machine (QM-3SP2, Zhenguang, Nanjing, China). The mixtures were dried, and then calcined at 1100 °C for 2 h. The calcined ceramic powders were re-milled for 4 h, dried, then granulated with paraffin binder, and final pressed into cylindrical disks of 8 mm diameter and 3 mm thickness under 10 MPa pressure isostatically with a hydrostatic press (KSTY70, Haixiang, Changzhou, China). The samples were sintered at 1300–1525 °C for 4 h in air with a high temperature electric furnace (SSJ-1600, Shenjia kiln, Luoyang, China).

The crystalline phases of specimen were analyzed by X-ray diffraction (XRD) (D8 ADVANCE, Bruker, Germany) with Cu Kα radiation of 2θ from 10 to 80°. The microstructure observations of the ceramic surfaces were performed under a scanning electron microscope (SEM) (LEO 1530 VP, Zeiss, Vertrieb Deutschland, Germany). The bulk density of ceramics was measured by the Archimedes method. Microwave dielectric constants (ε_r) and the quality factor values ($Q \times f$) at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using a Network Analyzer (N5230 PNA-L, Agilent, Santa Clara, CA, USA). Temperature coefficient of resonant frequency (τ_f) was also measured by the same method with a changing temperature from 25 to 75 °C, and calculated by the following Eq. (1):

$$\tau_f = \frac{f_{75} - f_{25}}{f_{25} \times 50} \times 10^6 \ (\text{ppm/°C}) \quad (1)$$

where f_{75} and f_{25} represent the resonant frequency at 75 °C and 25 °C, respectively.

3. Results and discussion

3.1. Phase identification of $Ca_3Sn_xSi_2O_{9+\delta}$ ceramics

Fig. 1 shows the XRD patterns of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 0.8$–1.4) ceramics sintered at 1400 °C with different amounts of SnO_2. According to the XRD patterns, monoclinic $Ca_3SnSi_2O_9$ phase (JCPDS no. 46-0812) was the main crystal phase at $x = 0.8$–1.1, accompanied with small amount of monoclinic Ca_3SiO_5 (JCPDS no. 49-0442). The Ca_3SiO_5 diffraction peaks disappeared and a pure monoclinic $Ca_3SnSi_2O_9$ phase occurred at $x = 1.2$; however, trace monoclinic Ca_3SiO_5 phase appeared at $x = 1.3$–1.4. Monoclinic $Ca_3SnSi_2O_9$ has a monoclinic structure with space group P21/c (14), and lattice parameters of $a = 0.7327$ nm, $b = 1.0067$ nm, and $c = 1.0432$ nm.

Fig. 2 shows the XRD patterns of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at different sintering temperatures (T_s). According to the XRD patterns, monoclinic $Ca_3SnSi_2O_9$ phase was the main crystal phase at $T_s = 1300$–1350 °C, accompanied with a small amount of tetragonal Ca_2SiO_4 (JCPDS no. 39-0298). The pure monoclinic $Ca_3SnSi_2O_9$ phase could be obtained when the sintering temperature was above 1400 °C. In this work, non-stoichiometric compositions (molar ratio of Ca:Sn:Si = 1:1.2:2) were employed to synthesize pure monoclinic $Ca_3SnSi_2O_9$ phase ceramics, which has a very wide sintering region (about 125 °C). The possible reason for the excessive SnO_2 was the strong evaporation of SnO_2 at high temperature [23,24].

3.2. SEM studies

The microstructures of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at various temperatures were investigated using SEM, as shown in Fig. 3. For the specimen sintered at 1400–1450 °C, a porous microstructure was developed with a large number of pores and the no clear crystal grains could be observed. The densification and grain size increased as the sintering temperature increased. When the temperature was 1500 °C, the grain size of the specimen increased to 5 μm, and the dense microstructure was developed (see Fig. 3(3)). The uniform large grain microstructures and clear grain boundaries could be observed. When the sintering temperature was 1525 °C, $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics began to melt. Abnormal grain growth occurred and porous microstructure appeared, as exhibited in Fig. 3(4).

3.3. Microwave dielectric properties

Fig. 4 shows the relative density, dielectric constant (ε_r), quality factor ($Q \times f$) and τ_f values of the $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at various temperatures for 4 h, respectively. The relative density for the specimen sintered at 1300 °C was low (63%), then increased markedly with increasing sintering temperature to a maximum value of 96.2% of the theoretical density for the specimen sintered at 1500 °C (see Fig. 4(1)). The ε_r value was low (4.93) for the specimen sintered at 1300 °C, probably due to the porous microstructure. Dielectric constant of ceramics increased with increasing sintering temperature to a maximum value of 8.44 for the specimen sintered at 1500 °C, then decreased to 7.74 at 1525 °C (see Fig. 4(2)) because of the decreased relative density (89% of the theoretical density). The dielectric constant could be evaluated by the well-known mixing rule [15].

The $Q \times f$ value of the $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at 1300 °C lower to 12,000 GHz (at 16.6 GHz) due to the low density and porous microstructure. However, it increased considerably with increasing sintering temperature, to a value of 92,000 GHz (at 15.1 GHz) for the specimens sintered at 1500 °C, then decreased as the sintering temperature was 1525 °C, as exhibited in Fig. 4(3).

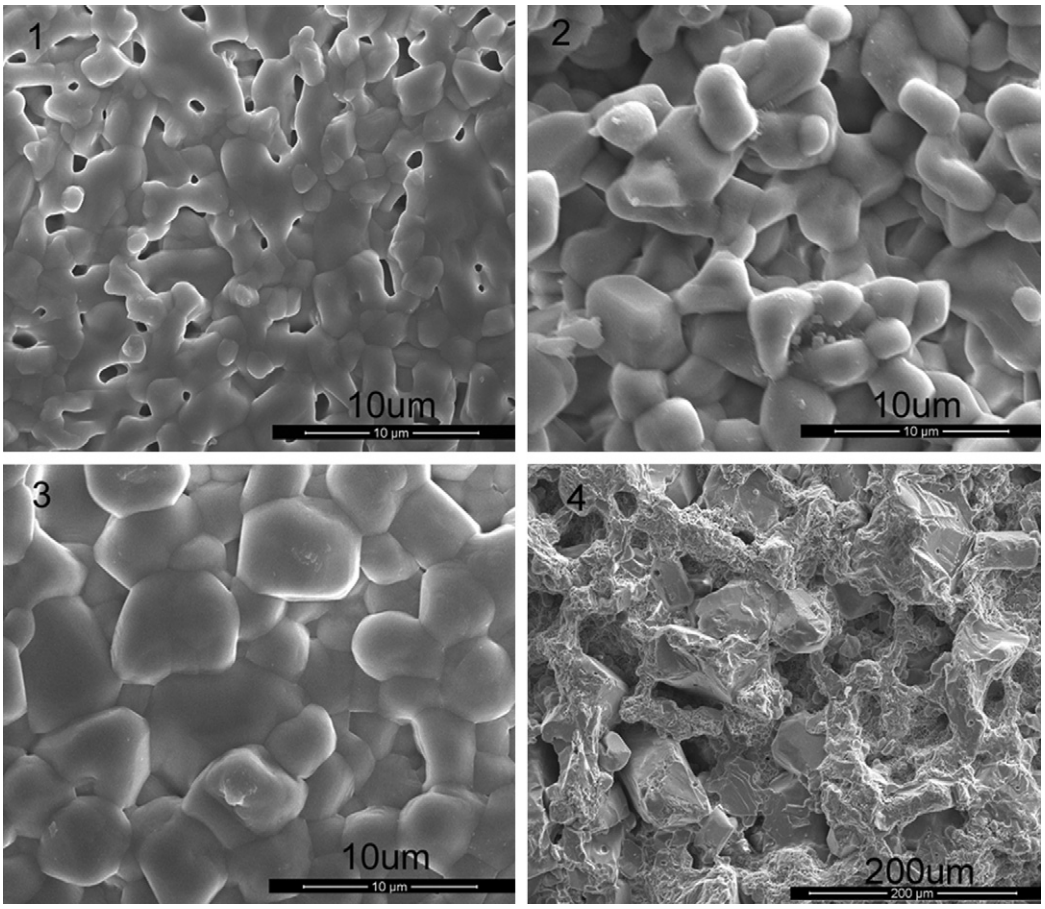

Fig. 3. SEM photographs of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramic materials sintered at: (1) 1400 °C, (2) 1450 °C, (3) 1500 °C, (4) 1525 °C.

The XRD results revealed the development of inhomogeneous phases consisting of monoclinic $Ca_3SnSi_2O_9$ ceramics (major phase) and Ca_2SiO_4 (minor phase) when the sintering temperature was less than 1400 °C. As the temperature increased, the pure monoclinic $Ca_3SnSi_2O_9$ phase appeared, and the densification of specimens increased. Generally speaking, high densification, homogeneous phases and uniform grain microstructure led to a high $Q \times f$ value due to less extrinsic loss; however, the second phase and abnormal grain growth produced a low $Q \times f$ value. Therefore, the decreased $Q \times f$ value of specimen sintered at

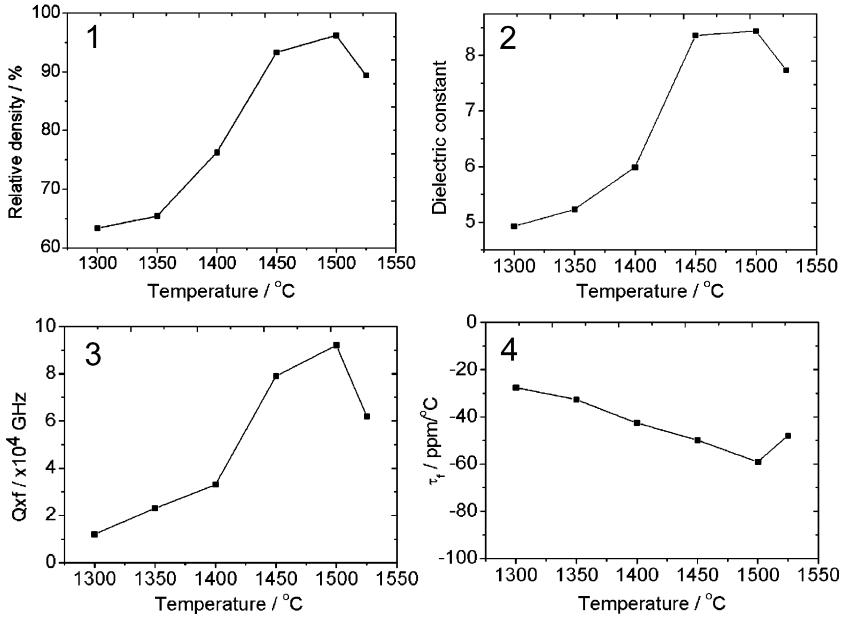

Fig. 4. (1) Relative density and (2) ε_r, (3) $Q \times f$, and (4) τ_f values of the $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at various temperatures.

1525 °C may have related to the low densification, abnormal grain growth and porous microstructure derivate from the melting of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics. The τ_f values of the $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at various temperatures are also shown in Fig. 4(4). The τ_f values of pure monoclinic $Ca_3SnSi_2O_9$ phase varied between −50 and −60 ppm/°C.

Even though the $Q \times f$ value of the $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics was slightly lower than that for $MgSiO_3$ [10], Mg_2SiO_4 [13] or Zn_2SiO_4 [14] ceramics, it was higher than that of $CaSiO_3$ ceramics [18]. The τ_f value of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) is high and immediate application in millimeter wave communication is limited; however, it may be possible to lower the τ_f value by adding suitable additives such as TiO_2 or $CaTiO_3$. In this work, we synthesized pure monoclinic $Ca_3SnSi_2O_9$ phase ceramics using the conventional solid-state method. $Ca_3SnSi_2O_9$ ceramics have a wide sintering temperature region (1400–1525 °C), excellent sintering behavior and high quality factor ($Q \times f = 92{,}000$ GHz at 15.1 GHz).

4. Conclusions

Monoclinic $Ca_3SnSi_2O_9$ phase ceramics were synthesized with the conventional solid-state method. The crystal phase evolution, sintering behavior and microwave dielectric properties of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 0.8$–1.4) ceramics were investigated. Pure monoclinic $Ca_3SnSi_2O_9$ phase ceramics could be synthesized at 1400–1525 °C when non-stoichiometric compositions (molar ratio of Ca:Sn:Si = 1:1.2:1) were employed. As temperature increased to 1525 °C, $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics began to melt and porous microstructure appeared. The relative density, second phase and microstructures have large influences on microwave dielectric properties of $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics. The $Ca_3Sn_xSi_2O_{9+\delta}$ ($x = 1.2$) ceramics sintered at 1500 °C exhibited the following microwave dielectric properties: $\varepsilon_r = 8.44$, $Q \times f = 92{,}000$ GHz (at 15.1 GHz) and $\tau_f = -60$ ppm/°C. Monoclinic $Ca_3SnSi_2O_9$ phase ceramics have a wide sintering temperature region and high quality factor. They could be considered as promising candidate materials for millimeter-wave devices.

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