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Preparation and microwave dielectric properties of cristobalite ceramics

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Abstract

Dense SiO_2 ceramics with cristobalite phase were prepared by the solid state sintering route, and the microwave dielectric properties were evaluated. The dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f) of the pure cristobalite ceramics showed little dependence on the sintering temperature. While, the Qf value increased significantly with increasing the sintering temperature, and it was due to the increasing grain size. The optimized microwave dielectric properties with very low ε_r of 3.81, high Qf value of 80,400 GHz and low τ_f of −16.1 ppm/°C were obtained for the cristobalite ceramics sintered at 1650 °C for 3 h. It was indicated that cristobalite ceramic was a promising candidate as a low-dielectric-constant microwave material for applications in microwave substrates.

Keywords: D. SiO_2; Cristobalite; Microwave dielectric properties

1. Introduction

Microwave dielectric ceramics have been widely used in various wireless communication systems as resonators, filters, antennas, and substrates [1]. Recently, low-dielectric-constant microwave materials have attracted much attention for their applications as substrates in microwave integrated circuits [1–3]. The microwave substrate material should have a low dielectric constant (ε_r) to minimize the cross coupling with conductors and shorten the time for the signal transmission. High Qf value is also a key parameter for maintaining the overall high Q value of the microwave circuits by lowering the power dissipation. Furthermore, the substrate material should have low temperature coefficient of resonant frequency (τ_f) considering the temperature stability of the microwave circuits.

Among the microwave substrate materials, microwave dielectric ceramics with low dielectric constant and high Qf value including alumina [4,5], aluminates [6,7] and silicates [5,8–10] are of the most importance. Such materials are usually of dielectric constants of 6.6–9.8 and Qf values higher than 50,000 GHz, while their temperature coefficients of resonant frequency are at a high level of −50 to −80 ppm/°C. Material with large τ_f such as TiO_2 is usually used to tune the temperature coefficient to near zero. However, significant increase in dielectric constant is always accompanied due to the high dielectric constant of TiO_2 [6–8,10]. Low temperature cofired ceramics [3] and polymer–ceramic composites [11] with low dielectric constants are also potential candidates as substrate materials, while their Qf values are usually relatively low.

SiO_2 is an important insulator with low dielectric constant and low dielectric loss, and its polymorphs and phase transitions are quite complex. Quartz is the stable phase of SiO_2 at temperatures lower than 573 °C, while cristobalite and amorphous phase also exist at room temperature as metastable phases for high-purity SiO_2 [12]. Quartz single crystal is of excellent microwave dielectric properties with $\varepsilon_{r\perp} = 4.443$, $Qf_{\perp} = 1{,}400{,}000$ GHz, $\tau_{\varepsilon\perp} = 9$ ppm/°C, $\varepsilon_{r||} = 4.644$, $Qf_{||} = 2{,}100{,}000$ GHz and $\tau_{\varepsilon||} = 28.7$ ppm/°C, where τ_ε is the temperature coefficient of dielectric constant, and the subscripts "⊥" and "||" represent the directions perpendicular and parallel to the c axis, respectively [13]. Furthermore, good microwave dielectric properties with $\varepsilon_r = 3.72$–3.90, $Qf = 44{,}300$–$122{,}100$ GHz and $\tau_f = -15.3$–-5.7 ppm/°C have been achieved for the SiO_2 amorphous bulks prepared by different approaches [14]. It is also an interesting and important issue to investigate the microwave dielectric properties of SiO_2 ceramics. To our knowledge, however, no such work has been reported till now, and it may be due to the difficulty for preparing the dense SiO_2 ceramics caused by the complex polymorphs and phase transformations of SiO_2.

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It is well known that the high-purity SiO_2 amorphous phase and crystalline quartz may transfer to high cristobalite at high temperatures below the melting point, and it transfers to low cristobalite as a metastable phase instead of the stable quartz phase when cooled to room temperature at normal cooling rates [15–17]. So it is difficult to prepare the SiO_2 ceramics with quartz phase. In the present work, SiO_2 ceramics with cristobalite phase were prepared by the solid state sintering route, and the microwave dielectric properties were investigated, together with the phase constitution and microstructure.

2. Experimental procedure

The cristobalite ceramics were prepared by the standard solid state sintering route. SiO_2 amorphous powder with high purity (>99.99%) was used as the raw material. To prepare the cristobalite powder, the amorphous raw powder was placed in an alumina crucible and calcined at 1150 and 1200 °C in air for 3 h with a heating rate of 5 °C per minute, ball milled with agate media in ethanol for 24 h, and then dried. The raw and calcined SiO_2 powders with polyvinyl alcohol water solution were pressed into cylindrical compacts with the diameter of 12.5 mm under a uniaxial pressure of 100 MPa. The compacts were placed in an alumina crucible and heated to the sintering temperatures varying from 1100 to 1675 °C with a rate of 5 °C per minute. After sintered for 3 h in air atmosphere, the compacts were cooled to 1000 °C with a rate of 2 °C per minute, and then freely cooled down to room temperature inside the furnace.

The sample density was determined by the volume method. The phase constitution was identified by the powder X-ray diffraction (Rigaku 2550/PC, Rigaku Co., Tokyo, Japan). The microstructures were observed on the as-sintered surfaces with a field emission scanning electron microscopy (Hitachi S-4800, Hitachi, Tokyo, Japan). Cylindrical samples with the diameter of about 9.5 mm and thickness of about 5 mm were used for evaluating the microwave dielectric properties. The dielectric constant was measured by the paralleling plate method [18,19] at about 22 GHz using a vector network analyzer (Agilent E8363B, Agilent Technologies Inc., Santa Clara, CA, USA),

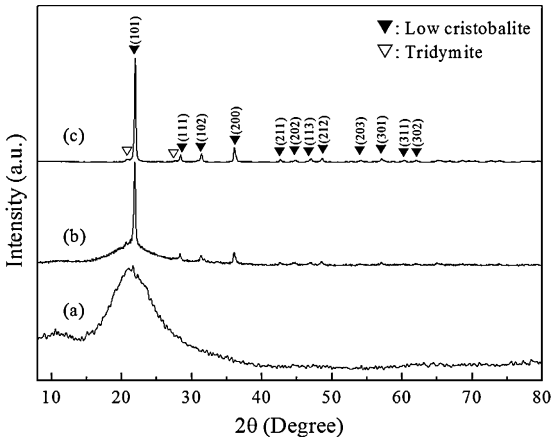

Fig. 1. XRD patterns of (a) SiO_2 amorphous raw powder and powders calcined at (b) 1150, and (c) 1200 °C for 3 h.

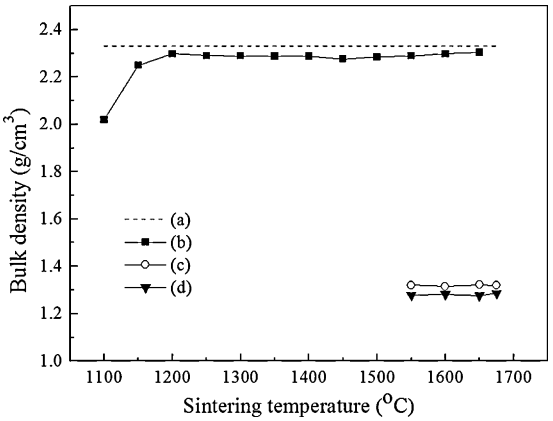

Fig. 2. (a) Theoretical density of low cristobalite, and measured bulk densities of the sintered samples from (b) uncalcined SiO_2 amorphous raw powder, and those calcined at (c) 1150, and (d) 1200 °C for 3 h.

and the temperature coefficient of resonant frequency was determined between 20 and 80 °C by the same method. The Qf value was measured by the resonant cavity method [18,20] at about 13 GHz.

3. Results and discussion

The XRD patterns of SiO_2 raw powder and the powders calcined at 1150 and 1200 °C for 3 h are shown in Fig. 1. Only a diffusion peak is observed for the SiO_2 raw powder, which indicates the pure amorphous phase. While, the amorphous

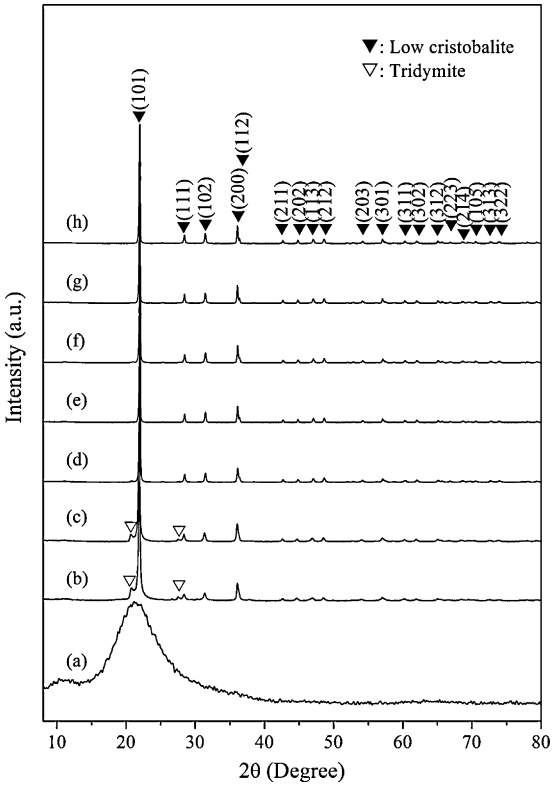

Fig. 3. XRD patterns of samples from SiO_2 raw powder sintered at (a) 1100, (b) 1150, (c) 1200, (d) 1250, (e) 1350, (f) 1450, (g) 1550, and (h) 1650 °C for 3 h.

phase transfers into low cristobalite phase partially for the powder calcined at 1150 °C, and only crystalline phases (low cristobalite major phase with a small amount of tridymite secondary phase) are observed when the calcining temperature increases to 1200 °C. As shown in Fig. 2, the sintered samples prepared from the uncalcined SiO_2 amorphous raw powder exhibit much higher densities than those from the calcined powders, and the densities for the latter are not higher than 1.32 g/cm^3 even the sintering temperature is as high as 1675 °C. This is due to the increasing particle size of the powder and the emergence of the crystalline phases with low free energy [21], which lower the activity of the powder and hinder the sintering process. So in the following work, the samples are prepared from the uncalcined SiO_2 amorphous raw powder.

Fig. 3 shows the XRD patterns of the sintered samples from the uncalcined amorphous raw powder. Phase transition is not

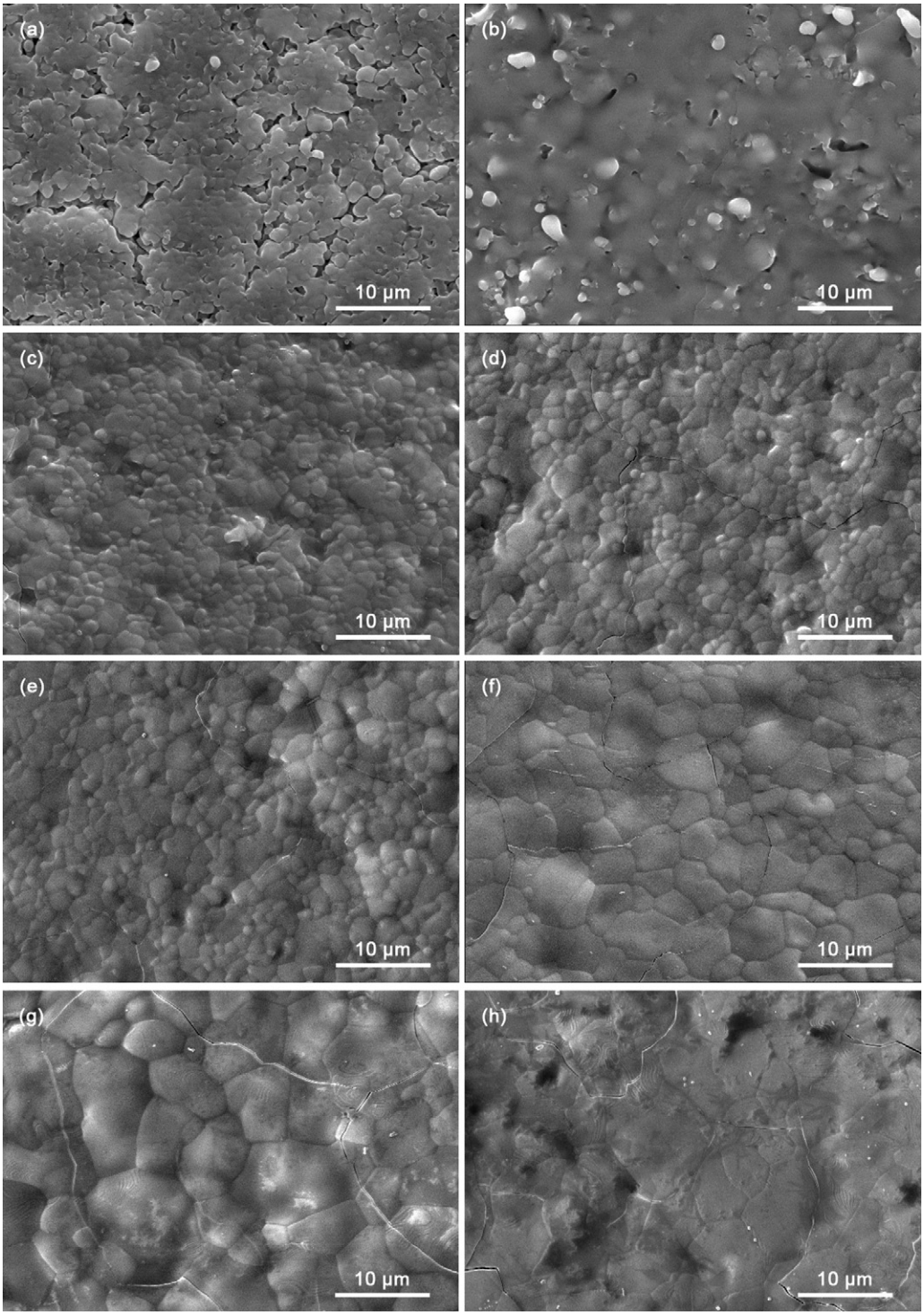

Fig. 4. SEM images on as-sintered surfaces of samples from SiO_2 raw powder sintered at (a) 1100, (b) 1150, (c) 1200, (d) 1250, (e) 1350, (f) 1450, (g) 1550, and (h) 1650 °C for 3 h.

observed for the sintering temperature of 1100 °C. When the sintering temperature increases to 1150 °C, the low cristobalite major phase is observed, together with a small amount of the tridymite secondary phase. The diffraction peaks of tridymite are weakened with increasing sintering temperature to 1200 °C, and only the low cristobalite single phase is indicated for the sintering temperatures higher than 1250 °C. As shown in Fig. 2(b), the sample density increases rapidly from 2.02 to 2.30 g/cm^3 with increasing the sintering temperature from 1100 to 1200 °C, and it changes little with further increasing the sintering temperature. Considering that the theoretical density of low cristobalite is 2.33 g/cm^3 [22], the relative densities of the pure cristobalite ceramics sintered at temperatures higher than 1250 °C are at a high level of 97.6–98.8%.

Fig. 4 shows the SEM images on the as-sintered surfaces. The sample sintered at 1100 °C is composed of agglomerated particulates which should be the amorphous SiO_2. Inhomogeneous microstructures with bright areas in Fig. 4(b) are observed for the sintering temperature of 1150 °C, which indicates the occurrence of the crystalline secondary phases, and this is consistent with the result from the XRD pattern. With further increasing the sintering temperature, the typical grains are observed, and the grain size increases significantly, as shown in Fig. 4(c)–(h). When the sintering temperature is as high as 1650 °C, unclear grain boundaries are observed. The high sintering temperature of 1650 °C is near to the melting point of cristobalite (1723 °C). Meanwhile, the minor impurities may lower the melting point of SiO_2. Thus, a small amount of liquid phase may occur during the sintering process, and lead to the final unclear grain boundaries on the as-sintered surface, as shown in Fig. 4(h). Furthermore, microscopic cracks are observed for the sintering temperatures higher than 1150 °C, and they are due to the stresses originated from the high cristobalite-low cristobalite phase transition during the cooling process after sintering, which occurs at about 265 °C and is accompanied by a large volume change of about −3.2% [16,23,24]. The microscopic cracks are deteriorated with increasing the sintering temperature, and this can be explained by the increasing grain size with temperature and the toughening effect of fine grains [25].

The microwave dielectric properties of the sintered samples as function of the sintering temperature are shown in Fig. 5. With increasing the sintering temperature from 1100 to 1200 °C, the dielectric constant increases from 3.56 to 3.81, and it changes little for higher sintering temperature, which is consistent with the bulk density (see Fig. 2). On the whole, the Qf value increases significantly with increasing the sintering temperature, except that it is only 13,300 GHz for the sintering temperature of 1150 °C. The sudden decrease in Qf value should be attributed to the inhomogeneous microstructures (see Fig. 4(b)), which are originated from the coexistence of the amorphous and crystalline phases. For the pure cristobalite ceramics, the Qf value increases from 43,200 to 80,400 GHz with increasing the sintering temperature from 1250 to 1650 °C. The increasing grain size with sintering temperature (see Fig. 4(d)–(h)) is responsible for the increasing Qf value of the cristobalite ceramics, which weakens the microwave scattering of the grain boundaries and decreases their effect

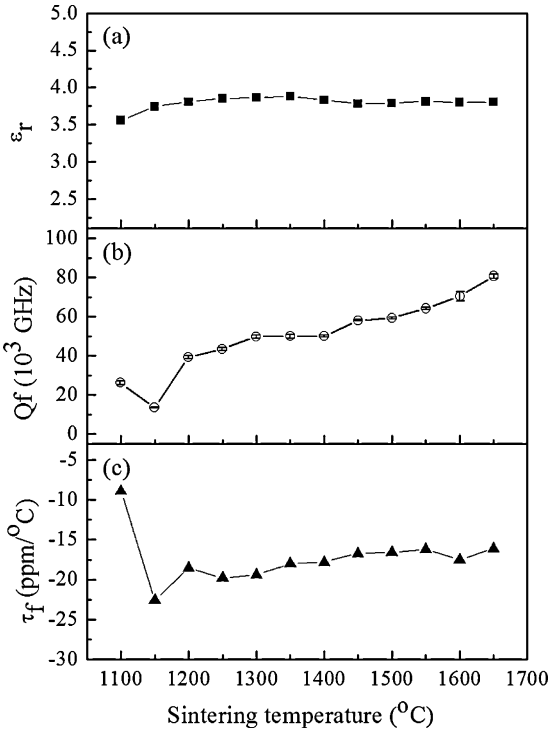

Fig. 5. Microwave dielectric properties of samples prepared from SiO_2 raw powder as function of sintering temperature: (a) dielectric constant, (b) Qf value, and (c) temperature coefficient of resonant frequency.

on the dielectric loss [26]. Meanwhile, the microscopic cracks are deteriorated with increasing the sintering temperature, which decreases the Qf value through strengthen the microwave scattering of the interfaces. It is indicated that the deteriorated microscopic cracks have a reverse and minor effect on the Qf value comparing with the increasing grain size. The temperature coefficient of resonant frequency of the pure cristobalite ceramics sintered at temperatures higher than 1250 °C shows a low negative value and varies slightly between −19.8 and −16.1 ppm/°C. The optimized microwave dielectric properties with very low dielectric constant of 3.81, high Qf value of 80,400 GHz and low temperature coefficient of resonant frequency of −16.1 ppm/°C are obtained for the cristobalite ceramics sintered at 1650 °C. It is indicated that the cristobalite ceramic is a promising candidate as a low-dielectric-constant microwave material for applications in microwave substrates. It should be noted that the existence of the microscopic cracks in the cristobalite ceramics is a serious problem that should be solved in the further work. Meanwhile, further improved Qf value is expected for the crack-free cristobalite ceramics.

4. Conclusions

Dense SiO_2 ceramics with pure low cristobalite phase have been prepared from the SiO_2 amorphous powder by the solid state sintering route, and the microwave dielectric properties have been investigated. The dielectric constant and temperature coefficient of resonant frequency of the pure cristobalite ceramics are not sensitive to the sintering temperature, while the Qf value increases significantly with increasing the

sintering temperature, and it is due to the increasing grain size and decreasing effect of the grain boundaries on dielectric loss. The optimized microwave dielectric properties with very low ε_r of 3.81, high Qf value of 80,400 GHz and low τ_f of −16.1 ppm/°C are obtained for the cristobalite ceramics sintered at 1650 °C, which indicates that the cristobalite ceramic is a promising candidate as a low-dielectric-constant microwave material. The existence of the microscopic cracks in the cristobalite ceramics is a serious problem that should be solved in the further work, and the improved Qf value is expected for the crack-free cristobalite ceramics.

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