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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),

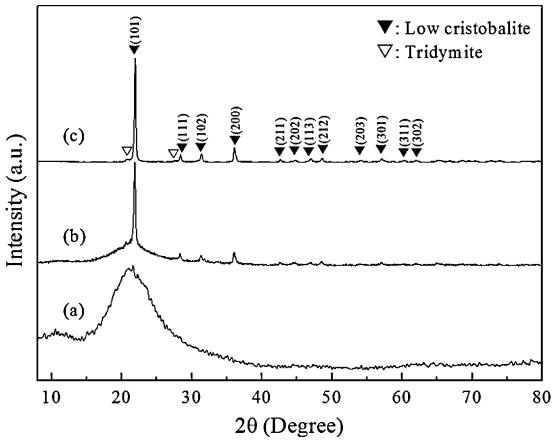

Fig. 1. XRD patterns of (a) SiO_2 amorphous raw powder and powders calcined at (b) 1150, and (c) 1200 °C for 3 h.

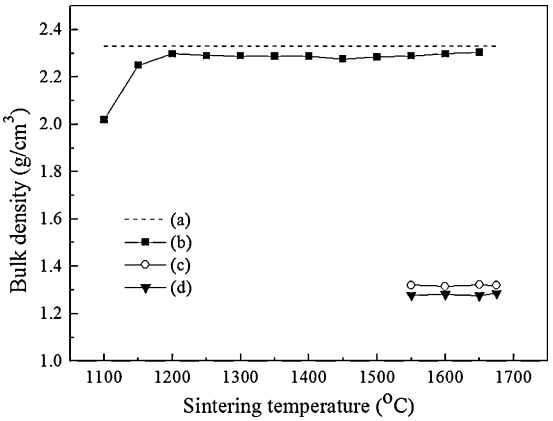

Fig. 2. (a) Theoretical density of low cristobalite, and measured bulk densities of the sintered samples from (b) uncalcined SiO_2 amorphous raw powder, and those calcined at (c) 1150, and (d) 1200 °C for 3 h.

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

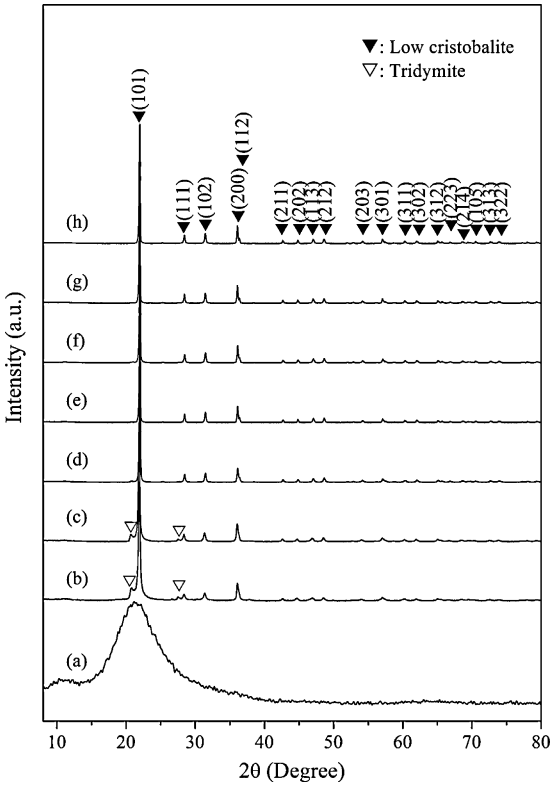

Fig. 3. XRD patterns of samples from SiO_2 raw powder sintered at (a) 1100, (b) 1150, (c) 1200, (d) 1250, (e) 1350, (f) 1450, (g) 1550, and (h) 1650 °C for 3 h.