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Microwave dielectric properties of B_2O_3 doped $LaAlO_3$ ceramics at low sintering temperature

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The microwave dielectric properties and the microstructures of $LaAlO_3$ ceramics with B_2O_3 additions (0.25–1 wt%) prepared with conventional solid-state route have been investigated. Doping with B_2O_3 (up to 0.5 wt%) can effectively promote the densification of $LaAlO_3$ ceramics. It is found that $LaAlO_3$ ceramics can be sintered at 1400°C due to the liquid phase effect of B_2O_3 addition. The $Q \times f$ value as well as the dielectric constant decreases at higher B_2O_3 doping level (1 wt%) due to the increase of boundary phases. At 1460°C, $LaAlO_3$ ceramics with 0.5 wt% B_2O_3 addition possesses a dielectric constant (ε_r) of 22.9, a $Q \times f$ value of 44700 (at 9 GHz) and a temperature coefficients of resonant frequency (τ_f) of -36 ppm/°C. The B_2O_3-doped $LaAlO_3$ ceramics can find applications in microwave devices requiring low sintering temperature. *© 2003 Kluwer Academic Publishers*

1. Introduction

Recently, many researchers have been focusing on developing dielectric materials with high quality factor ($Q \times f$), high dielectric constant (ε_r) and zero temperature coefficient of resonant frequency (τ_f) for the use of dielectric resonator and microwave device substrate. High dielectric constant material can effectively reduce the size of resonators since that the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_o) in vacuum ($\lambda = \lambda_o/\sqrt{\varepsilon_r}$). The inverse of the dielectric loss ($Q = 1/\tan\delta$) is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter components and small temperature coefficient of the resonant frequency is to ensure the stability of the microwave components at different working temperature. Several compounds such as (Zr, Sn)TiO_4, $Ba(Mg_{1/3}Ta_{1/3})O_3$ and (Mg, Ca)TiO_3 have therefore been developed [1–3]. Rare-earth aluminates $LaAlO_3$, has been widely used as substrate for superconducting microwave devices since it provides a high quality factor, excellent lattice matching and a good matching for thermal expansion. A phase transition of $LaAlO_3$ occurs at ~800 K from the high temperature cubic phase (space group Pm3m) to the rhombohedral phase (space group $R\bar{3}c$) [4]. It possesses suitable microwave dielectric properties ($\varepsilon_r \sim 23$, $Q \times f$ ~65000 GHz, $\tau_f \sim -44$ ppm/°C) [5] for applications in dielectric resonators. However, it also requires high sintering temperatures (1550–1650°C). The crystal structure of $LaAlO_3$ exhibits rhombohedral symmetry.

Chemical processing and small particle sizes of the starting materials are generally advantageous to reduce the sintering temperature of dielectric materials [6–8]. However, they required a flexible procedure not only expansive but time consuming in the fabrication of dielectric resonator. In this paper, B_2O_3 was selected as a sintering aid in $LaAlO_3$ material since the liquid phase sintering by adding glass or other low melting point material can effectively lower the sintering temperature of ceramics [7]. Moreover, the microwave dielectric properties of dielectric resonators could be affected due to the development of a particular microstructure linked to the reaction between host material and addition or the sintering with a liquid phase. The crystalline phases, the microstructures and the microwave dielectric properties of B_2O_3-doped $LaAlO_3$ ceramics were investigated.

2. Experimental

Samples of $LaAlO_3$ were synthesized by conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of B_2O_3 (0.25–1 wt%) was added as a sintering aid. High purity oxide powders (>99.9%) La_2O_3, Al_2O_3 and B_2O_3 were weighted and mixed for 24 h with distilled water. The mixture was dried at 100°C and thoroughly milled before it was calcined at 1100°C for 2 h. The calcined powder was ground and sieved through 100-mesh screen. Phase formation of $LaAlO_3$ was confirmed using X-ray diffraction. The fine powder together with the organic binder was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness. These pellets were sintered at temperatures of 1340–1460°C for 2 h in air. The heating rate and the cooling rate were both set at 10°C/min.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III. V) spectra were collected using Cu Kα radiation (at 30 Kv and 20 mA) and a graphite monochromator in the 2θ range of 20° to 60°. The microstructural observations and the analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk relative densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki-Coleman [9] dielectric resonator method as modified and improved by Courtney [10]. The dielectric resonator was positioned between two brass plates. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25°C to +80°C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf),

$$\tau f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 0.25 wt% B_2O_3-doped $LaAlO_3$ ceramics at different sintering temperatures (1340–1460°C). All of the XRD profiles of the ceramics samples can be indexed by pseudo-cubic unit cell of the perovskite structure. The X-ray diffraction patterns of the $LaAlO_3$ ceramics have not significant change with 0.25 wt% B_2O_3 addition at sintering temperatures 1340–1460°C. Second phase was not observed by XRD at the level of 0.25 wt% B_2O_3 addition.

The X-ray diffraction patterns of $LaAlO_3$ ceramics with different amounts of B_2O_3 additions sintered at 1460°C are illustrated in Fig. 2. Identical XRD patterns were observed for the ceramics regardless the amount of B_2O_3 additions.

The SEM photographs of B_2O_3-doped $LaAlO_3$ at sintering temperatures of 1340–1460°C are shown in Fig. 3. The grain size increased with the increase of sintering temperature as well as amount of B_2O_3 addition due to the liquid phase effect. With 0.25–0.5 wt% B_2O_3 additions, porous specimens were observed for $LaAlO_3$ ceramics sintered at temperatures 1340–1400°C. Dense samples can be obtained at sintering temperatures above 1430°C. However, the grain boundary phases were pronounced product with 1 wt% B_2O_3 addition. It may directly affect the microwave dielectric properties of the ceramic samples.

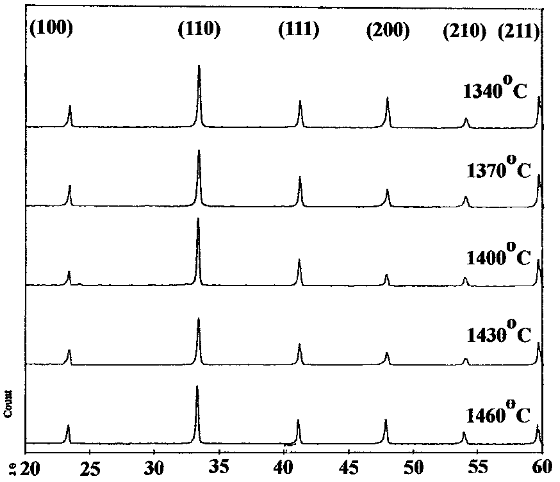


Figure 1 X-ray diffraction patterns of 0.25 wt% B_2O_3-doped $LaAlO_3$ ceramics at different sintering temperatures.

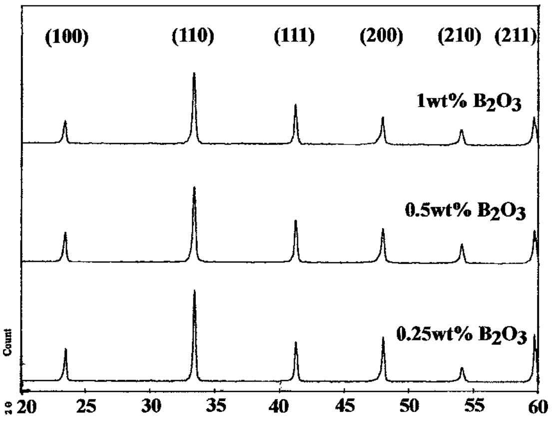


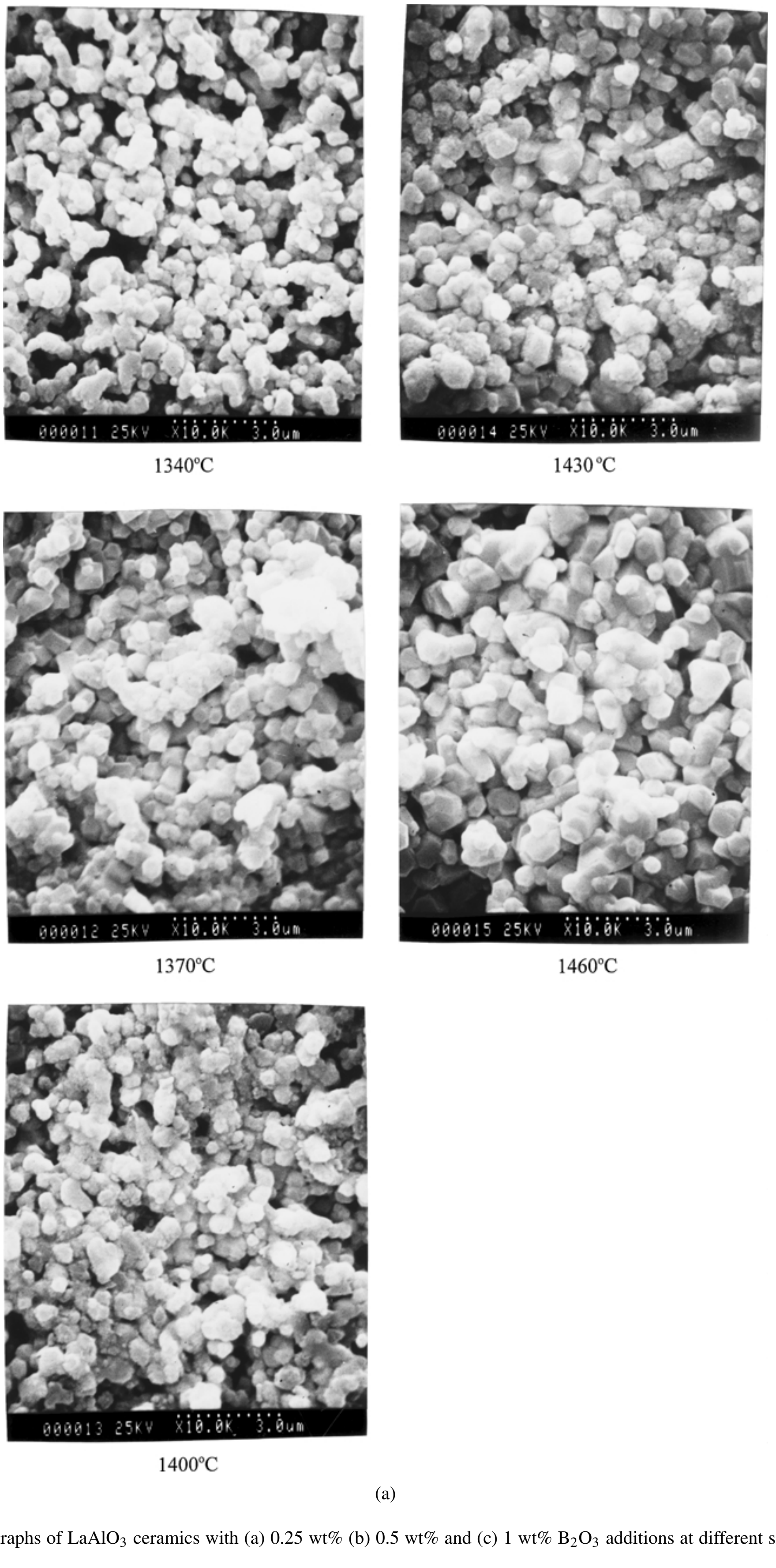
Figure 2 X-ray diffraction patterns of $LaAlO_3$ ceramics with different amount of B_2O_3 addition sintered at 1460°C.

The relative density of the B_2O_3-doped $LaAlO_3$ ceramics at different sintering temperatures is shown in Fig. 4. It indicated that relative densities of 91.4%–99% were obtained for B_2O_3-doped $LaAlO_3$ ceramics at sintering temperatures from 1340°C to 1460°C. The relative density increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 3, and was also affected by the B_2O_3 addition. Higher B_2O_3 doping level formed more liquid phase, which would enhance the densification resulted in a higher ceramic relative density. Moreover, the relative density also related to the porosity and increased with the decrease of porosity. As the sintering temperature increased, the relative density slightly increased and reached 98% at 1460°C with 0.5 wt% B_2O_3 addition.

Fig. 5 demonstrates the dielectric constants of $LaAlO_3$ ceramics with different amount of B_2O_3 additions as functions of their sintering temperatures. The relationships between ε_r values and sintering temperatures revealed the same trend with those between relative densities and sintering temperatures since higher relative density means lower porosity. The dielectric constants slightly increased with increasing sintering temperature. The increase in the ε_r value could be explained owing to higher relative densities. However, a dramatic degradation in the ε_r value appeared at 1 wt% B_2O_3 doping level. It was attributed to the low dielectric constant of the liquid phase. With 0.5 wt% B_2O_3 addition, an ε_r value of 22.9 was obtained for $LaAlO_3$ ceramics sintered at 1460°C.

Fig. 6 shows the $Q \times f$ values of $LaAlO_3$ ceramics with various B_2O_3 additions at different sintering temperatures. At low level of B_2O_3 additions (0.25–1 wt%), the $Q \times f$ values of $LaAlO_3$ ceramics increased with increasing sintering temperature.

However, higher $Q \times f$ values were observed at 0.5 wt% B_2O_3 doping level. With increasing B_2O_3 content, the $Q \times f$ value increased to a maximum value of 44700 (GHz) at 0.5 wt% and thereafter decreased. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and the secondary phases. Smaller grain size as well as higher porosity degraded the $Q \times f$ values of the as-sintered samples with 0.25 wt% B_2O_3 addition. Relative density also plays an important role



1340°C

1430°C

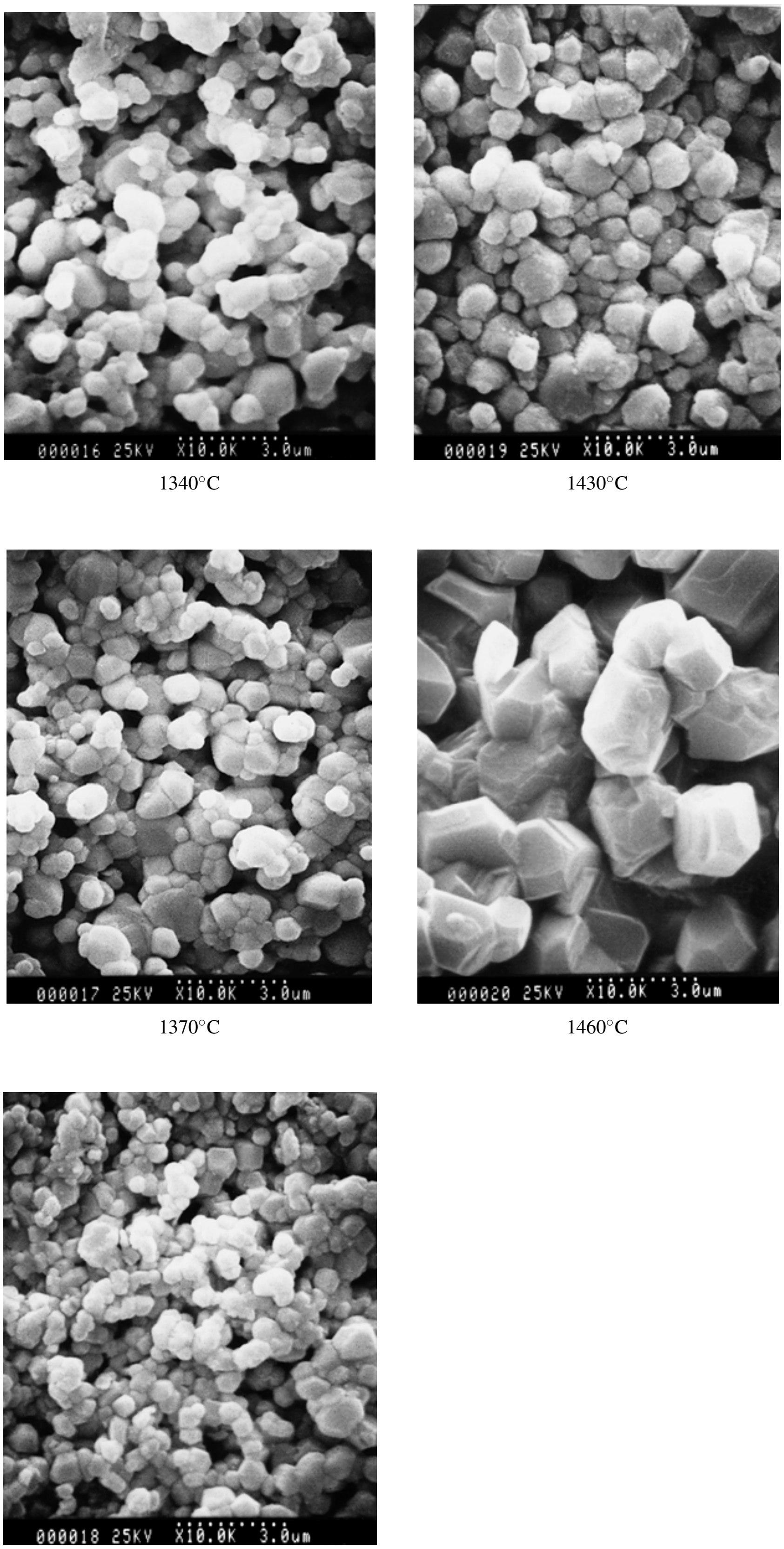
1370°C

1460°C

1400°C

(a)

Figure 3 SEM photographs of $LaAlO_3$ ceramics with (a) 0.25 wt% (b) 0.5 wt% and (c) 1 wt% B_2O_3 additions at different sintering temperatures. (*Continued*)



1340°C 1430°C

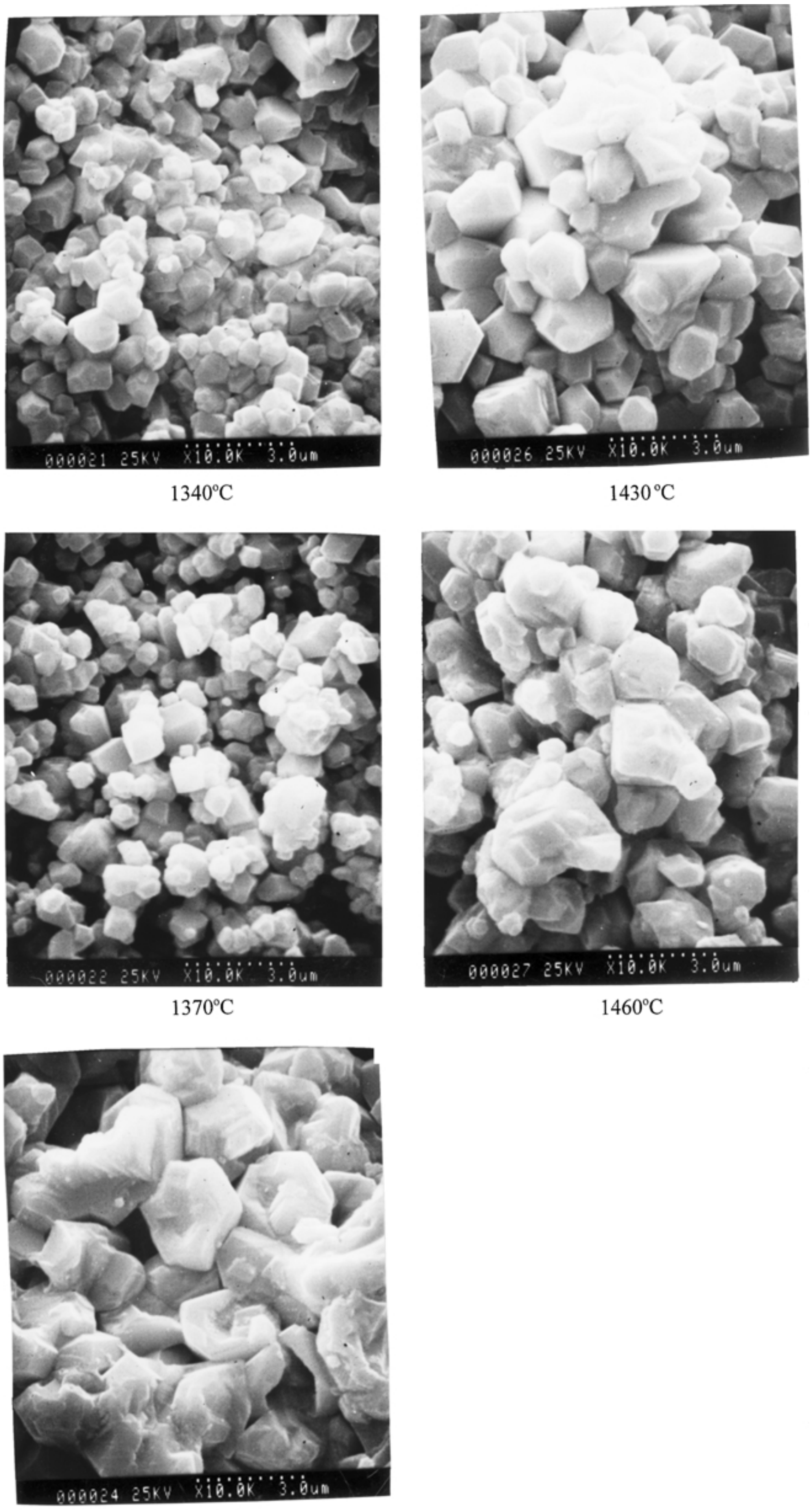
1370°C 1460°C

1400°C

(b)

Figure 3 (*Continued*).

in controlling the dielectric loss and has been shown for other microwave dielectric materials. With 0.5 wt% B_2O_3 addition, the $Q \times f$ value increased from 21000 to 44700 (GHz) as the sintering temperature increased from 1340 to 1460°C for 2 h. It was consistent with the variation of relative density. Furthermore, higher B_2O_3 content would degrade the $Q \times f$ value of $LaAlO_3$ ceramics since the grain boundary phases were pronounced product at higher sintering temperatures as observed in Fig. 3. That would explain the decrease in



1340°C

1430°C

1370°C

1460°C

1400°C

(c)

Figure 3 (*Continued*).

$Q \times f$ values for $LaAlO_3$ ceramics with 1 wt% B_2O_3 addition. The quality factors of B_2O_3-doped $LaAlO_3$ ceramics were relatively lower than that of pure $LaAlO_3$ ceramics due to the grain boundary phase.

The temperature coefficients of resonant frequency (τ_f) of B_2O_3-doped $LaAlO_3$ ceramics at different sintering temperatures are illustrated in Fig. 7. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. The τ_f value, as presented, was a function of the B_2O_3 content. It varied from average −26 to −35 ppm/°C as the amount of B_2O_3

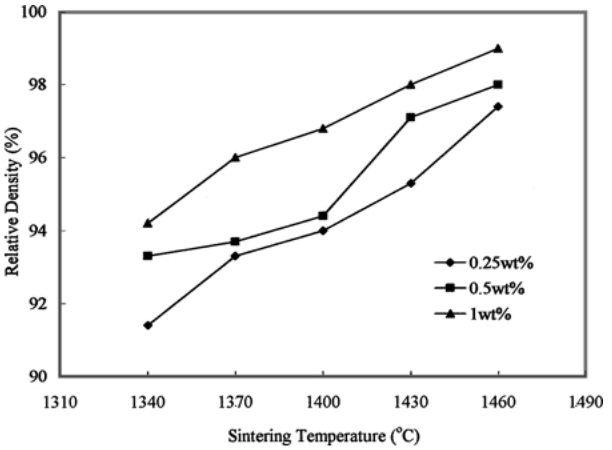


Figure 4 Dependence of sintering temperature of $LaAlO_3$ ceramics on relative density with various B_2O_3 additions.

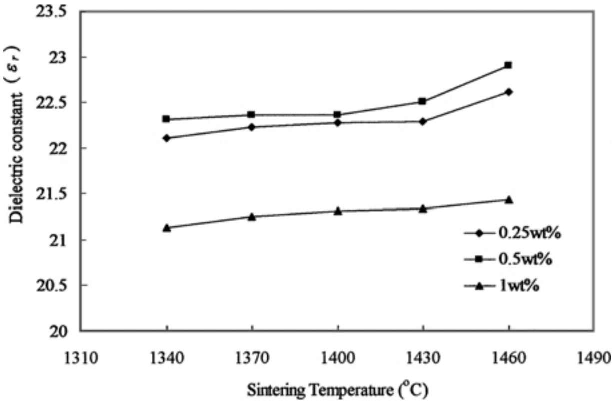


Figure 5 Dependence of sintering temperature of $LaAlO_3$ ceramics on dielectric constant with various B_2O_3 additions.

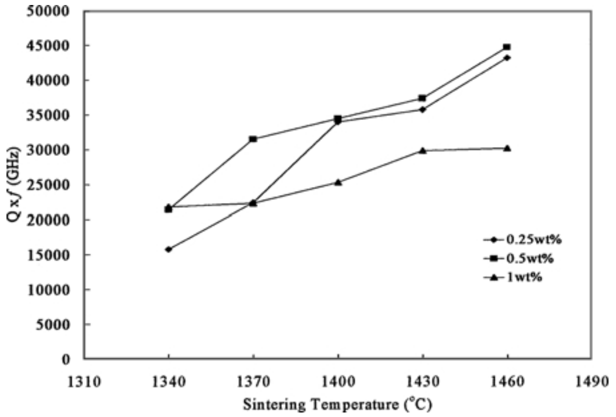


Figure 6 Dependence of sintering temperature of $LaAlO_3$ ceramics on quality factor ($Q \times f$) with various B_2O_3 additions.

addition increased from 0.25 to 0.5–1 wt%. Significant change was not observed in the τ_f value with fixed B_2O_3 addition at different sintering temperatures. It implies that the τ_f value was not sensitive to the sintering temperature.

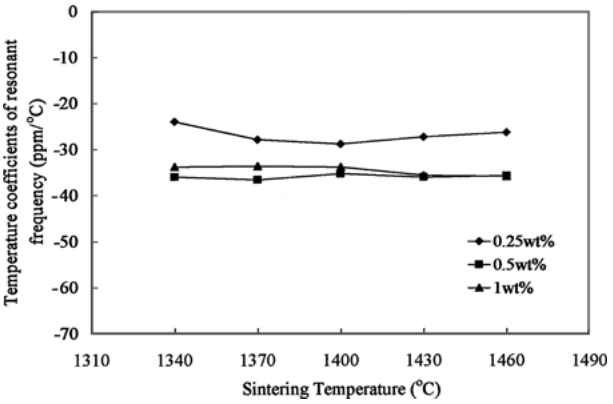


Figure 7 Dependence of sintering temperature of $LaAlO_3$ ceramics on τ_f value with various B_2O_3 Additions.

4. Conclusion

The dielectric properties of B_2O_3-doped $LaAlO_3$ ceramics were investigated. $LaAlO_3$ ceramics exhibited perovskite structure with pseudo-cubic unit cell. A tremendous sintering temperature reduction (100–200°C) can be achieved by adding B_2O_3 to the $LaAlO_3$ ceramics. With 0.5 wt% B_2O_3 addition, a dielectric constant of 22.9, a $Q \times f$ value of 44700 (GHz) and a τ_f value of -36 ppm/°C were obtained for $LaAlO_3$ ceramics at 1460°C for 2 h. The decrease in $Q \times f$ value at higher B_2O_3 addition (1 wt%) was owing to that the grain boundary phases were pronounced product.

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