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Microwave Dielectric Properties of Ultra-Low Temperature Fired Li_3BO_3 Ceramics

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Abstract

A ultra-low firing Li_3BO_3 microwave dielectric ceramics with monoclinic structure were prepared by the conventional solid-state reaction method, and the phase assemblages, microstuctures and microwave dielectric properties were investigate. Samples were sintered at 580–640^oC for 2–8 h which is extremely lower than 960^oC. The XRD patterns of sintered specimens showed the main phase Li_3BO_3 coexisted with HBO_2 and $Li_6B_4O_9$ secondary phases were observed. Large number of HBO_2 secondary phase increased when the sintering temperature and time over 600^oC and 6 h, respectively. The variations in the microwave dielectric properties of Li_3BO_3 ceramics were depended on the secondary phases. Li_3BO_3 ceramics sintered at 600^oC for 6 h possessed an optimal microwave dielectric properties of ε_r = 5, $Q\times f$ = 37,200 GHz, and τ_f = 3.1 ppm/^oC. The good microwave dielectric properties and relatively low sintering temperature would make Li_3BO_3 ceramics promising candidate for LTCC integration applications.

Keywords: Li_3BO_3 ceramics, microwave dielectric properties

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1. Introduction

With the rapid development of wireless communication devices using microwave frequencies, the requirement of miniaturization and integration of microwave components have widely increased. Low-temperature cofired ceramics (LTCC) technology offers significant benefits to meet the demand. The microwave dielectric materials used in LTCC field need to have a low dielectric constant (ε_r, typically < 10) to maximize signal propagation speed, a high quality factor ($Q \times f \geq 5000$ GHz) for frequency selectivity, and a near zero temperature coefficient of the resonant frequency ($|\tau_f| \leq 10$ ppm/^{o}C) for stability of the frequency response across temperature changes. The alternating dielectric ceramics and internal metallic electrode layers formed LTCC multilayer devices [1]. Silver (melting point ~ 961^{o}C) is usually used as the internal metallic electrode because of its high conductivity and low cost. For this purpose, low-temperature sinterable materials (below 960^{o}C) with suitable dielectric properties have been widely investigated.

Most of the traditional ceramics with good microwave dielectric properties have too high sintering temperature to satisfy in LTCC applications [2]. Three commonly used method to lower the sintering temperature are low melting temperature glasses addition, chemical processing, and small particle size of starting materials. The addition of low softening temperature glasses is the most effective and cheap method to realize the low temperature sintering. However, the presence of some amorphous phase in glass-ceramic route deteriorated the quality factor of ceramics. In addition, the different thermal expansion coefficients between ceramics and glasses would cause cracks during the sintering process as the glass addition content is more than 5 wt% [3-4], which also might degrade the microwave dielectric properties. The use of fine powders prepared by wet chemical processing is the seldom method owing to the complicacy of the fabrication process and an increase of the cost.

Therefore, a glass-free ceramic with low dielectric constant and appropriate microwave dielectric properties is a hot challenge in LTCC material research. Currently, to reduce processing

time, fabrication cost, and save energy, developing interest has been focused on researching the materials with ultra-low sintering temperatures (< 650^{o}C). Some low-fire crystalline oxides such as Li_2O-, TeO_2-, Bi_2O_3-, WO_3-, and MoO_3-based compounds with intrinsically low sintering temperature and promising microwave dielectric properties have been extensively studied in this context [5-9]. This present paper is adopt B_2O_3 and Li_2CO_3 , which possess low melting point below 750^{o}C, to prepare Li_3BO_3 ceramics. The effect of different sintering conditions on crystallization and microwave dielectric properties of Li_3BO_3 ceramics were investigated.

2. Experimental Procedure

Li_3BO_3 ceramics were synthesized by a conventional solid-state reaction method using above 99.9% high-purity powders of Li_2CO_3 and B_2O_3. The powder were mixed according to the desired stoichiometry and ball-milled using agate balls in distilled water for 24 h in a polyethylene jar. The resulting slurry were dried at 80^{o}C for overnight. After drying, the powders for Li_3BO_3 were forced thought a 200-mesh sieve, and then calcined at 600^{o}C for 4 h. Phase identification on the calcined powders was performed using X-ray diffraction (XRD, Siemens D5000). The calcined powders were added with a 3 wt.% of a 10% solution of PVA as a binder and screened by a 200-mesh again. The granulated powders were subsequently pressed into cylinders with dimensions of 11 mm in diameter and 5 mm in thickness at a pressure of about 150 MPa. These pellets were preheated at 550^{o}C for 1 h to remove the organic binder and sintered at temperatures of 580−640^{o}C for 2−8 h in air. The heating and the cooling rates were both set at 10^{o}C/min.

The crystal structure of fired ceramics was investigated via an X-ray diffractometer (XRD, Siemens D5000) with Cu-Kα radiation and a graphite monochromator in the 2θ range of 20−60^{o}. Prior to examination sintered pellets were crushed in a mortar and pestle to powder. The microstructure of the sintered sample was observed by a scanning electron microscopy (SEM, Philips XL□40FEG, Eindhoven. the Netherlands) and an energy dispersive X-ray spectrometer (EDS).

The dielectric properties were measured at microwave frequencies by the Hakki-Coleman dielectric resonator method, as modified and improved by Courtney [10-11] with an HP 8757D network analyzer. The temperature coefficients of the resonant frequencies (τ_f) were obtained in the temperature range from 20 to 80^{o}C, with a heating rate of 1^{o}C/min for heating and the residence time was 10 min at each time. The τ_f (ppm/°C) was calculated from the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \qquad (1)$$

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

3. Results and Discussions

Fig. 1(a) and (b) show the X-ray diffraction patterns of the Li_3BO_3 ceramics sintered at 580–640^{o}C for 6h and 600^{o}C for 2–8 h, respectively. Three types of phases can be observed in the obtained Li_3BO_3 ceramics. A monoclinic phase of Li_3BO_3 type (JCPDS #70–2459), belonging to the space group $P2_1/c$ (14), can be classified as the main phase. HBO_2 (JCPDS #76–0746) and $Li_6B_4O_9$ (JCPDS #18–0721) as secondary phases were detected in all specimens. When B_2O_3 dissolved in water, the solution would release a lot of heat and generate metaboric acid (HBO_2) and boric acid (H_3BO_3). Further heating above 170^{o}C, boric acid would decompose into water and metaboric acid (HBO_2). As shown in Fig. 1(a), it could be found that the HBO_2 increased with increasing sintering temperature, which coincided well with above mention results, meanwhile $Li_6B_4O_9$ decreased. The HBO_2 also increased with increasing sintering time. Moreover, the secondary phase contents of specimens sintered for 6h are much less than that of other sintering time.

$$B_2O_3 + H_2O \rightarrow 2HBO_2 \qquad \Delta H^o = -199.2\ \text{kJ/mol} \qquad (2)$$

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3 \qquad (3)$$

$$H_3BO_3 \rightarrow HBO_2 + H_2O \qquad (4)$$

The SEM micrographs of Li_3BO_3 ceramics sintered at 580–640^{o}C for 2–8 h are illustrated in

Fig. 2. The surface of the Li_3BO_3 ceramics was porous sintered at low sintering temperature and short sintering time as shown in Fig. 2 (a)–(c), resulting an insufficient densification. The increase of sintering time and temperature promoted the grain growth, and uniform grain morphology was produced at 600^{o}C with sintering for 6 h (Fig. 2(d)). There is the same uniform grain phenomenon when specimens sintered at 600^{o}C for other time. However, more rod-like grains and granular grains with some abnormal grain growth in the sintered body could be observed due to high sintering temperature and long sintering time. To clarify m the diamond-shaped and rod-like grains, an energy dispersive spectroscopy (EDS) analysis for marked spots was performed for the Li_3BO_3 specimens, as illustrated in Fig. 2(f). All the EDS results such as a ratio B : O = 30.32 : 69.68, 29.86 : 71.04, and 30.82 : 69.18 at.% respectively for spot A-C, approximately 1 : 2, which indicated that the rod-like grains were HBO_2. It was in agreement with the XRD analysis. The $Li_6B_4O_9$ is difficult to detect by EDS because the grain did not grow well at low sintering temperature and short sintering time.

Fig. 3 shows the bulk density of Li_3BO_3 ceramics with various sintering conditions. The densities increased remarkable with an increase sintering temperature. These results are due to the decrease of porosity. On the other hand, it could be seen that the densities of the Li_3BO_3 specimens gradually increased with extending sintering time up to 6 h, and then decreased because of the least amount of second phase. To compare Fig. 1, the variations of densities with sintering time were found to be well correlated.

Fig. 4 presents the dielectric constants of Li_3BO_3 ceramics sintered for 2–8 h as a function of sintering temperature. The ε_r values of specimens increased with increasing sintering temperature. Among them, the dielectric constant of specimens sintered for 6 h increased from 4.7 to its maximum 7.3 as sintering temperature increased from 580 to 640^{o}C. However, there is an increase in ε_r with an increase in sintering time up to 6 h, and then decreased as further prolonging sintering time. The variation in ε_r values exhibited similar trend as that of densities with sintering time and temperature. The higher density would lead to higher dielectric constant owing to lower porosity.

Hence, the densities played a dominant role in the ε_r values of Li_3BO_3 ceramics in this research.

Fig. 5 shows the $Q\times f$ values of Li_3BO_3 ceramics sintered for 2–8 h as a function of sintering temperature. The quality factor ($Q\times f$ value) depends on extrinsic factors and intrinsic parameters. The intrinsic losses are mainly caused by lattice vibration modes while the extrinsic losses are dominated by second phases, grain sizes, and porosities or densification [12]. The relationship between the $Q\times f$ value of Li_3BO_3 ceramics and sintering time reveals a trend similar to that of density and sintering time. The $Q\times f$ value of Li_3BO_3 specimens sintered for 6 h had the best value because of the relatively less amount of second phases in specimens. Higher density indicated lower porosity and higher $Q\times f$ value. However, it was observed that the $Q\times f$ values of Li_3BO_3 ceramics first increased, reached a maximum value, and then decreased with further increasing sintering temperature. The enhanced $Q\times f$ value could be attributed to the enlarged grain size to obtain uniform grain morphology, and its deterioration could be involved in abnormal grain growth and large amount of HBO_2 second phases. In addition, to evaluate the variation in the $Q\times f$ value of Li_3BO_3 ceramics, the packing fractions (PFs) were calculated using the following formula:

$$\text{Packing fraction (\%)} = \frac{\text{Volume of packed ions}}{\text{Volume of primitive unit cell}} \quad (5)$$

A higher packing fraction resulted in a higher $Q\times f$ value. The volumes of primitive unit cell for specimens sintered at 6h are smaller than others because of fewer secondary phase contents compared with other sintering time. Furthermore, the $Q\times f$ values of Li_3BO_3 ceramics sintered for 6 h are higher than that of specimens sintered for other time. As shown in Fig. 5, the $Q\times f$ value of Li_3BO_3 ceramics sintered at 600°C for 6 h has a maximum value of 37,200 GHz.

Fig. 6 shows the temperature coefficient of the resonant frequency (τ_f) of Li_3BO_3 ceramics sintered for 2–8 h as a function of sintering temperature. It can be seen that the τ_f value was insensitive to the sintering time. The τ_f value would remain in the range from 0 to 5 ppm/°C for specimens sintered at 580–600°C. It trended clearly to be increased to about 25 ppm/°C with sintering temperature increased to 640°C. It is known that τ_f value is influenced by the additives and

the second phase of the materials [13]. Therefore, the reason for the above result might be attributed to the large amount of HBO_2 second phases. For LTCC applications, one of the most important dielectric property of microwave dielectric materials is the low temperature coefficient of the resonant frequency (τ_f near zero) [14]. A near-zero τ_f of 3.1 ppm/^oC can be obtained for Li_3BO_3 ceramics sintered at 600^oC for 6 h.

4. Conclusion

The microwave dielectric properties of ultra-low firing Li_3BO_3 ceramics have been studied in this paper. The main monoclinic phase Li_3BO_3 ceramics were obtained, accompanied by HBO_2 and $Li_6B_4O_9$ secondary phases for all compositions. The HBO_2 increased with increasing sintering temperature, meanwhile $Li_6B_4O_9$ decreased. Moreover, the secondary phase contents of specimens sintered for 6h are much less than that of other sintering time. The sintering density and microwave dielectric properties were found to strongly correlate with the amount of HBO_2 and $Li_6B_4O_9$ secondary phases. At ultra-low firing 600^oC/6 h, Li_3BO_3 ceramics possesses good microwave dielectric properties with an ε_r of 5, a $Q\times f$ value of 37,200 GHz and near-zero τ_f of 3.1 ppm/^oC.

Acknowledgments

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Figure Caption

Fig. 1 The XRD patterns of Li_3BO_3 ceramics sintered at (a) 580-640^oC for 6h and (b) 600^oC for 2-8 h.

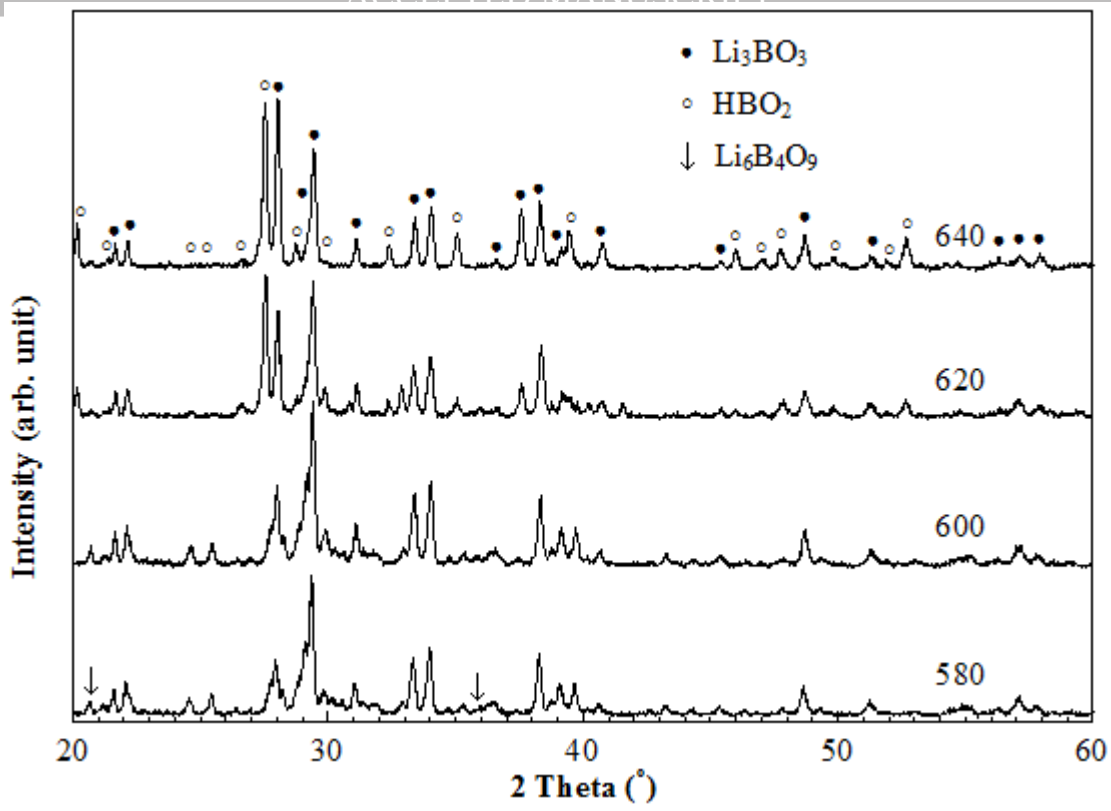
Fig. 2 The SEM micrographs of Li_3BO_3 ceramics sintered at 580-640^oC for 2-8 h.

Fig. 3 Densities of Li_3BO_3 ceramics sintered at different sintering conditions.

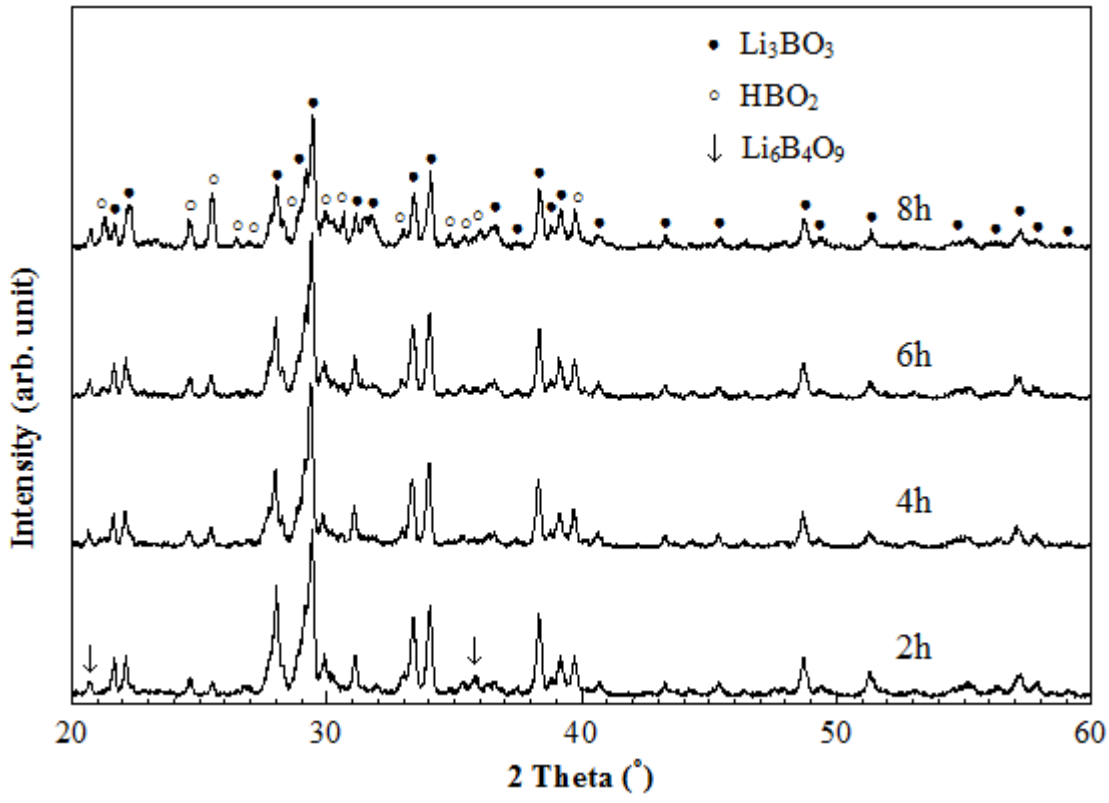
Fig. 4 Dielectric constant of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.

Fig. 5 Quality factor of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.

Fig. 6 τ_f value of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.



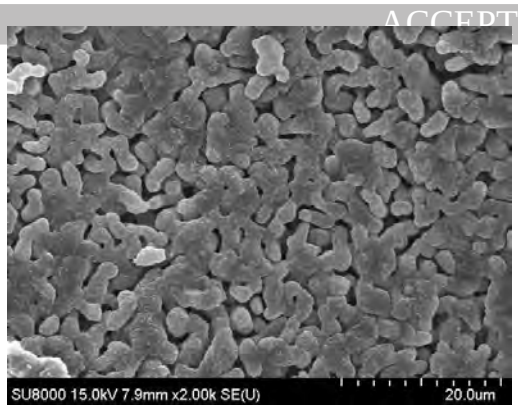
(a)



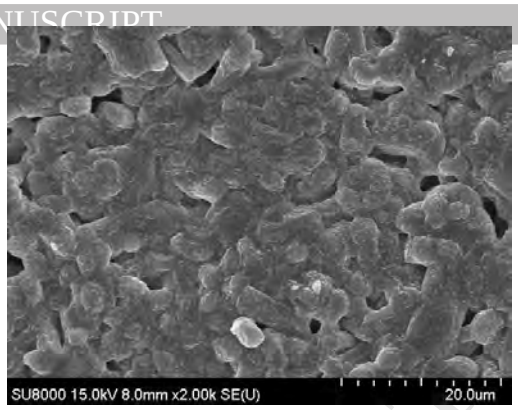
(b)

Fig. 1 The XRD patterns of Li_3BO_3 ceramics sintered at (a) 580-640^oC for 6h and (b) 600^oC for 2-8

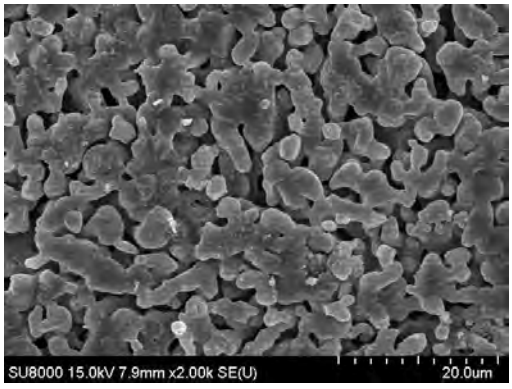
h.



(a) 600°C /2h

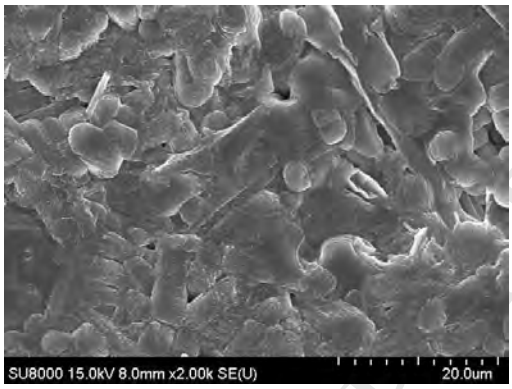


(b) 600°C /4h



(c) 580°C /6h

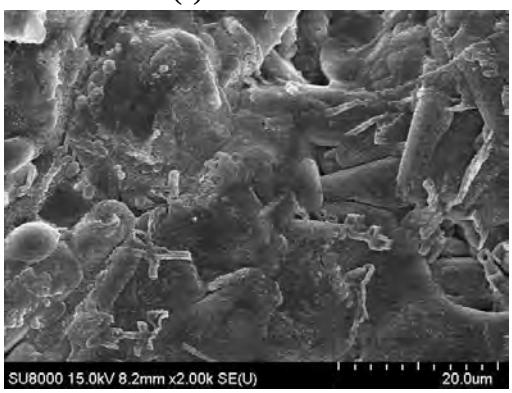
(d) 600°C /6h



(e) 620°C /6h

(f) 640°C /6h

(g) 600°C /8h



(h) 620°C/8h

Fig. 2 The SEM micrographs of Li_3BO_3 ceramics sintered at 580-640°C for 2-8 h.

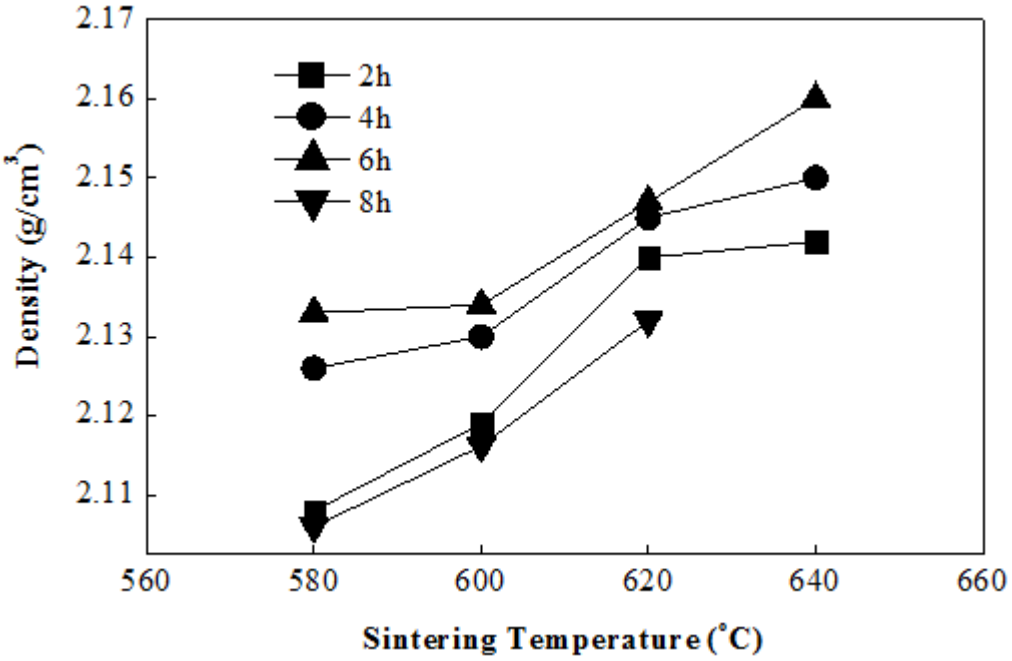


Fig. 3 Densities of Li_3BO_3 ceramics sintered at different sintering conditions.

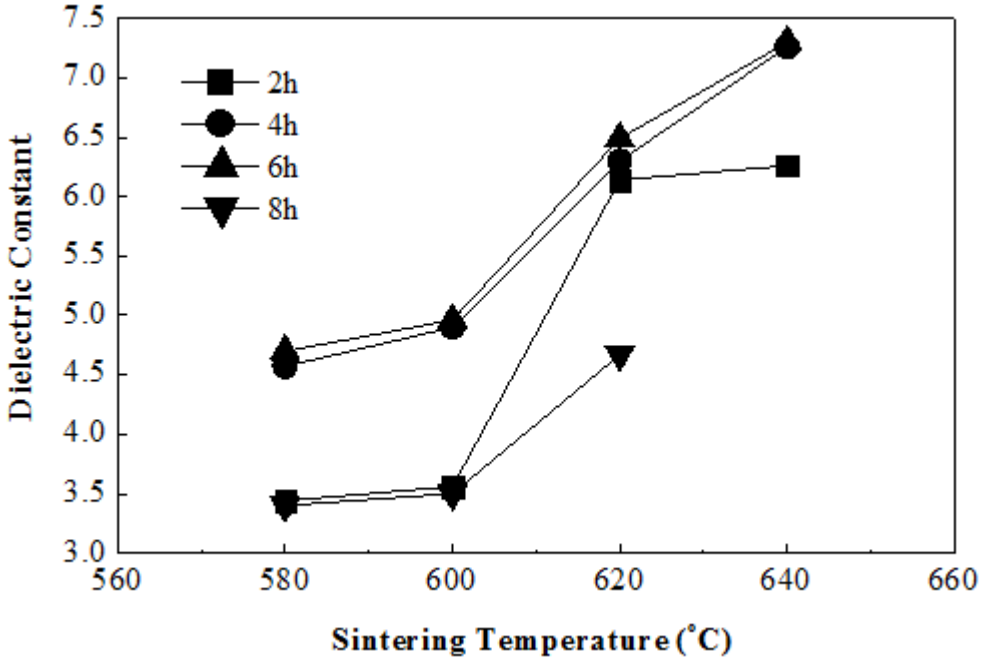


Fig. 4 Dielectric constant of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.

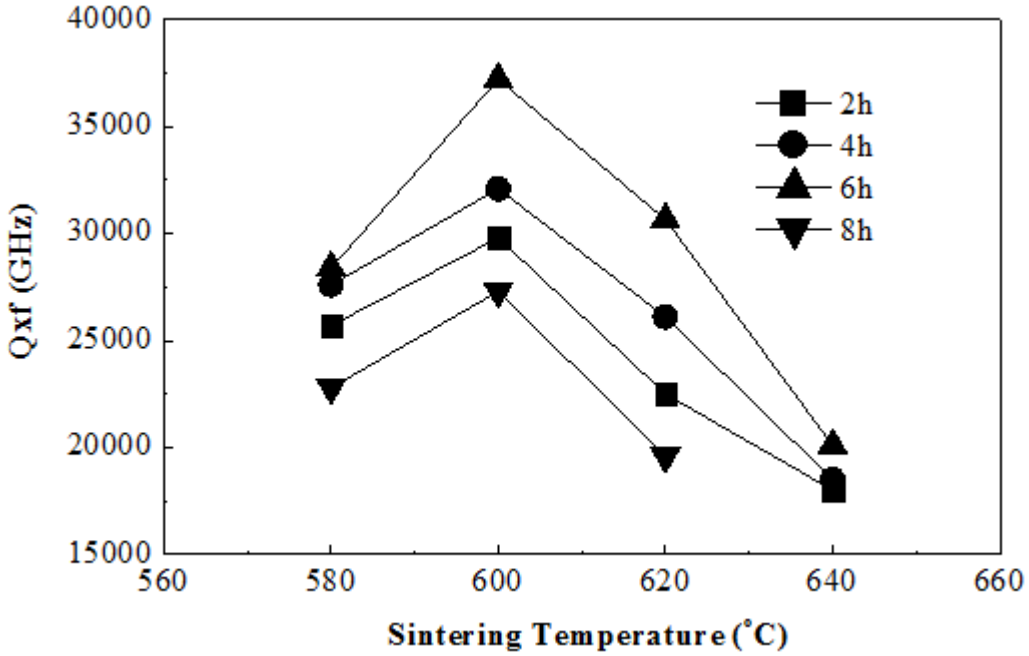


Fig. 5 Quality factor of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.

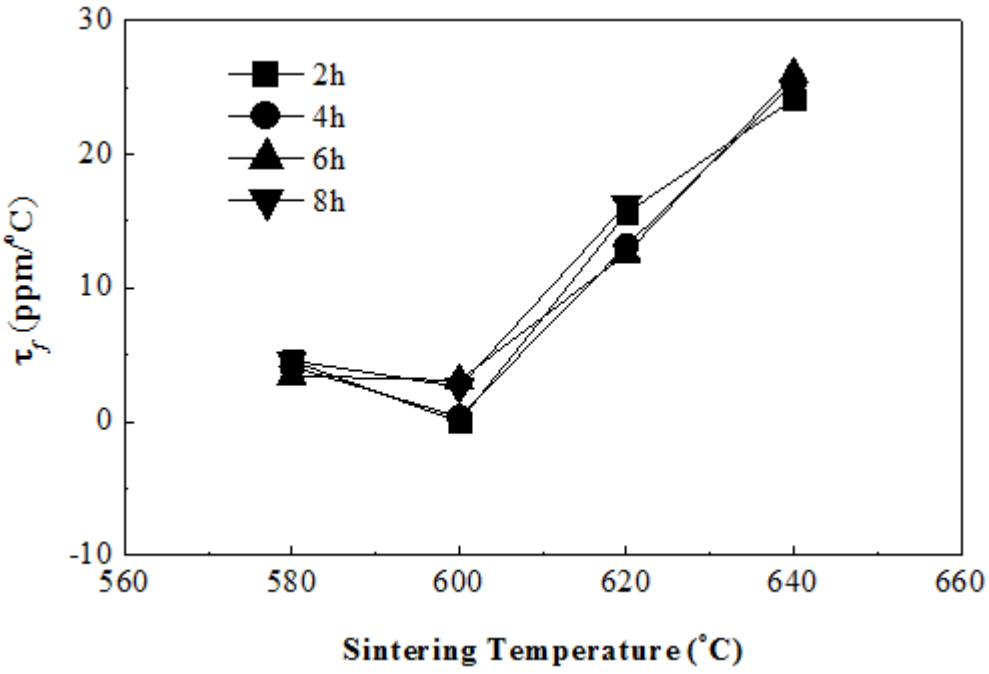


Fig. 6 τ_f value of Li_3BO_3 ceramics sintered at different temperatures for 2−8 h.

1. New microwave dielectric properties of Li_3BO_3 ceramics were investigated.

2. Second phases were formed and affected the dielectric properties of Li_3BO_3 system.

3. Li_3BO_3 ceramics sintered at 600^oC for 6 h possessed an optimal microwave dielectric properties.

4. The ε_r of 5, $Q \times f$ value ~ 37200 GHz, and zero τ_f = 3.1 ppm/^oC were obtained for Li_3BO_3 ceramics.