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Microwave dielectric properties of low ε_r $BaZnP_2O_7$ ceramic

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ABSTRACT

A novel microwave dielectric ceramic of $BaZnP_2O_7$ with low dielectric constant and high quality factor was synthesized by a solid-state reaction method. A dense ceramic with 96.9% relative density was obtained when the ceramic was sintered at 875 °C for 2 h. The $BaZnP_2O_7$ ceramic sintered at 875 °C for 2 h possessed good microwave dielectric properties, characterized as ε_r=8.4, $Q\times f$=27,925 GHz (at 11.1 GHz), and τ_f= −56.7 ppm/°C.

1. Introduction

The rapid development of the wireless communication industry has created a high demand for the development of new and improved components operating in the microwave spectrum. Advanced substrate materials for microwave-spectrum integrated circuits require a low dielectric constant ($\varepsilon_r < 10$) to maximize the signal propagation speed, a high quality factor ($Q\times f$) to increase the frequency selectivity, and a near-zero temperature coefficient of resonance frequency (τ_f) to ensure the stability of the frequency response across temperature changes [1,2]. At present, many low ε_r ceramics such as Al_2O_3, AO-SiO_2 (A=Ca, Mg, Zn), and $MTiO_3$ (M=Mg, Ca) have good microwave dielectric properties, but these also have a high sintering temperature, which consumes a lot of energy. Therefore, the study of microwave dielectric ceramics with low sintering temperature is useful [3–5].

Pyrophosphates are stable crystalline compounds, and have been reported to possess useful microwave dielectric properties as well as relatively low sintering temperatures [6–8]. For example, in one experiment, $SrZnP_2O_7$ ceramics sintered at 940 °C were reported to have values of ε_r=7.02, $Q\times f$=23,000 GHz, and τ_f= −84.7 ppm/°C [9]. In another, $CaZnP_2O_7$ ceramics sintered at 900 °C were found to exhibit good dielectric properties of ε_r=7.56, $Q\times f$=63,130, τ_f= −82 ppm/°C [10]. In work done by Sebastian et al. [11,12], $LiMgPO_4$ ceramic sintered at 950 °C showed an ε_r of 6.6, $Q\times f$ of 79,100 GHz and τ_f of −55 ppm/°C. $BaZnP_2O_7$ was mainly studied as a luminescence material in the literature [13,14]. To date there are no reports on the microwave dielectric properties of $BaZnP_2O_7$. In the present work, $BaZnP_2O_7$ ceramic was prepared via a solid state reaction method. The sintering behavior, microstructure, and microwave dielectric properties of the material were studied in detail.

2. Experimental

$BaZnP_2O_7$ powder was synthesized by a solid-state reaction route from analytical grade powders of $BaCO_3$, $NH_4H_2PO_4$, and ZnO (>99%, Sinopham Co. Ltd., Shanghai, China). Precursor start materials were weighed in stoichiometric ratios, then mixed and ground for 2 h, using anhydrous ethanol as grinding aid in an agate mortar and pestle. Then the powders were dried at 80 °C for 12 h, and calcined at 800 °C for 4 h in an alumina crucible. The as-calcined powders were mixed with 5 wt% PVA binder, granulated and pressed into cylinders (12 mm in diameter and 3 mm in height) under a uniaxial pressure of 10 MPa. Ceramics of $BaZnP_2O_7$ were sintered in an air atmosphere at 850–950 °C for 2 h. Powder X-ray diffraction (XRD) patterns were taken at room temperature using a Bruker D8 Advance diffractometer with Cu Kα radiation. The microstructure of the ceramic surface was evaluated by field emission scanning electron microscopy (SEM) (Quanta 600 FEG, FEI, USA) at an accelerating voltage of 20 keV. The bulk densities of sintered pellets were measured by Archimedes' method. Microwave dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method, using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25–85 °C. The temperature coefficient of the resonant frequency τ_f

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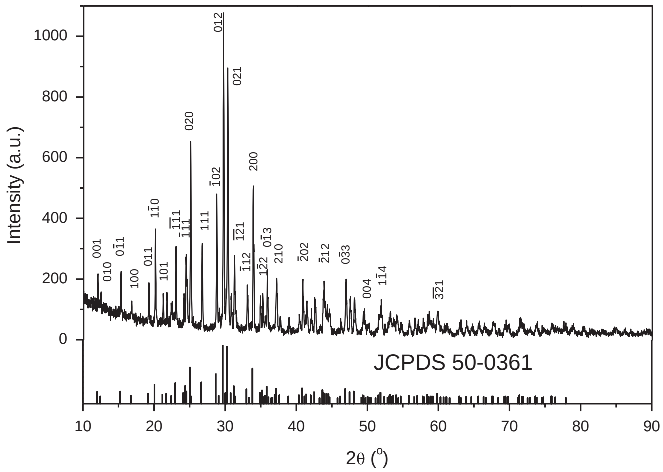

Fig. 1. XRD patterns of $BaZnP_2O_7$ powders calcined at 800 °C for 4 h in air.

value (ppm/°C) was calculated using the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \text{ppm}/°\text{C} \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of $BaZnP_2O_7$ powders calcined at 800 °C for 4 h. All the peaks in the figure's X-ray diffraction patterns can be indexed based on the JCPDS no. 50-0361 of $BaZnP_2O_7$.

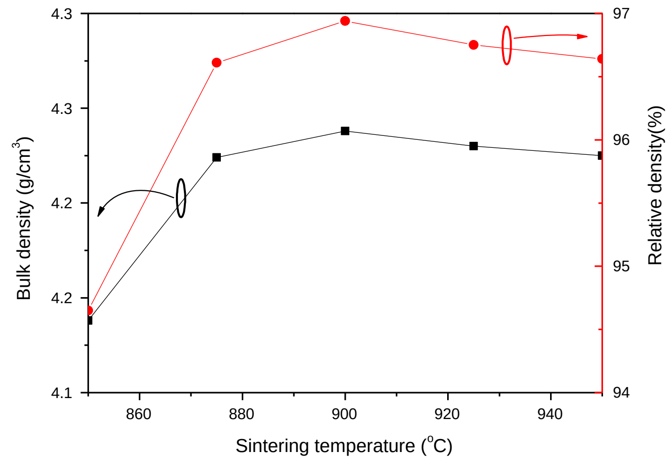

Fig. 3. Variation of bulk density and relative density with sintering temperature of $BaZnP_2O_7$ ceramic.

No additional peaks were found in the patterns, indicating that there were no other impurity phases in the powders. The XRD results showed that $BaZnP_2O_7$ powders calcined at 800 °C crystallized into the triclinic structure with space group $P\bar{1}$ (No. 2).

Fig. 2(a)–(e) presents the surface SEM images of $BaZnP_2O_7$ ceramics sintered at different temperatures. It can be observed that the samples showed a dense microstructure with almost no pores, at all the sintering temperatures tested. The grain size of the sample sintered at 850 °C showed random variation from 1.5 μm to 10 μm with distinct grain boundaries. As the sintering temperature increased, the grain size also clearly increased. At a sintering temperature of 925 °C, abnormal grain growth of the ceramics was observed, which indicates that a sintering temperature

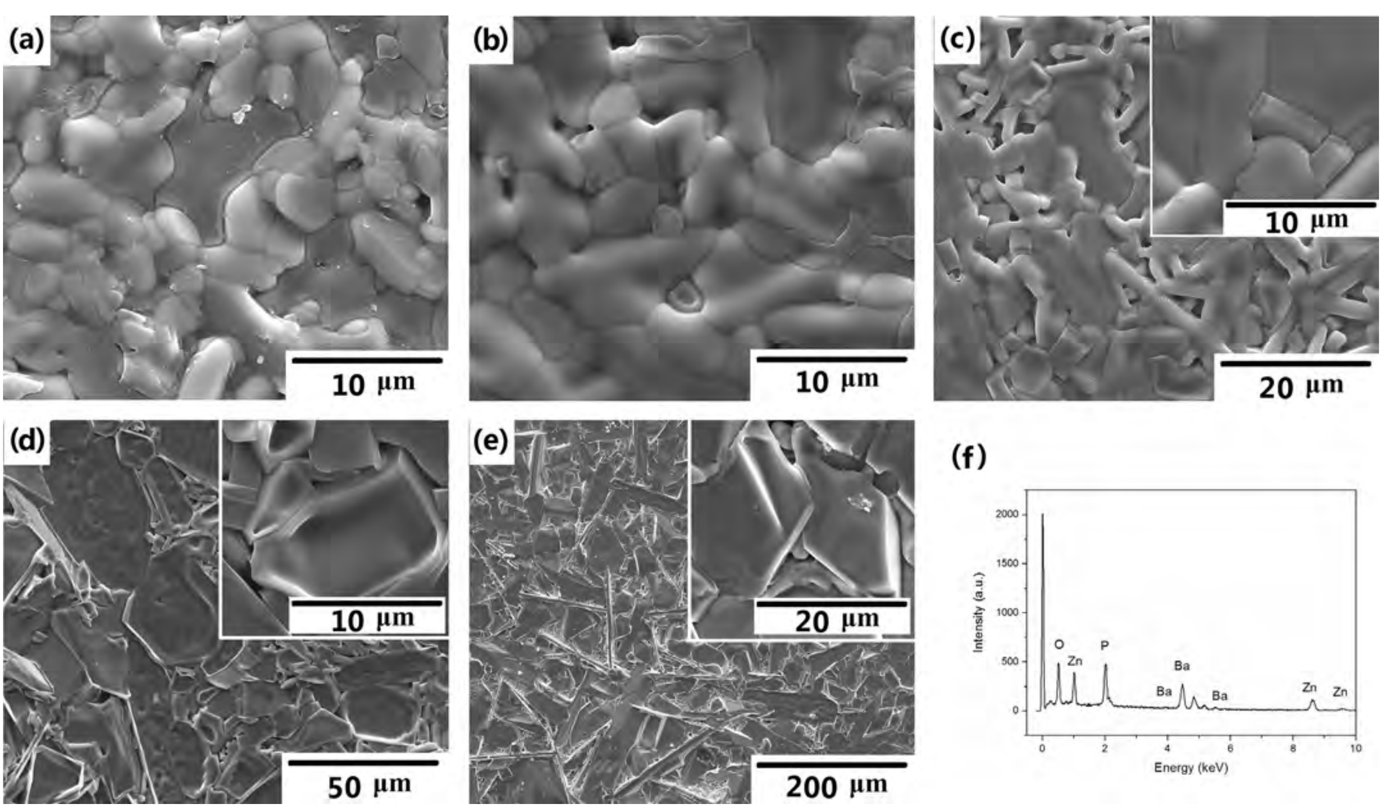

Fig. 2. (a–e) SEM images of the $BaZnP_2O_7$ ceramics sintered at (a) 850 °C/2 h, (b) 875 °C/2 h, (c) 900 °C/2 h, (d) 925 °C/2 h, (e) 950 °C/2 h, (f) EDS spectra of the sample sintered at 875 °C.

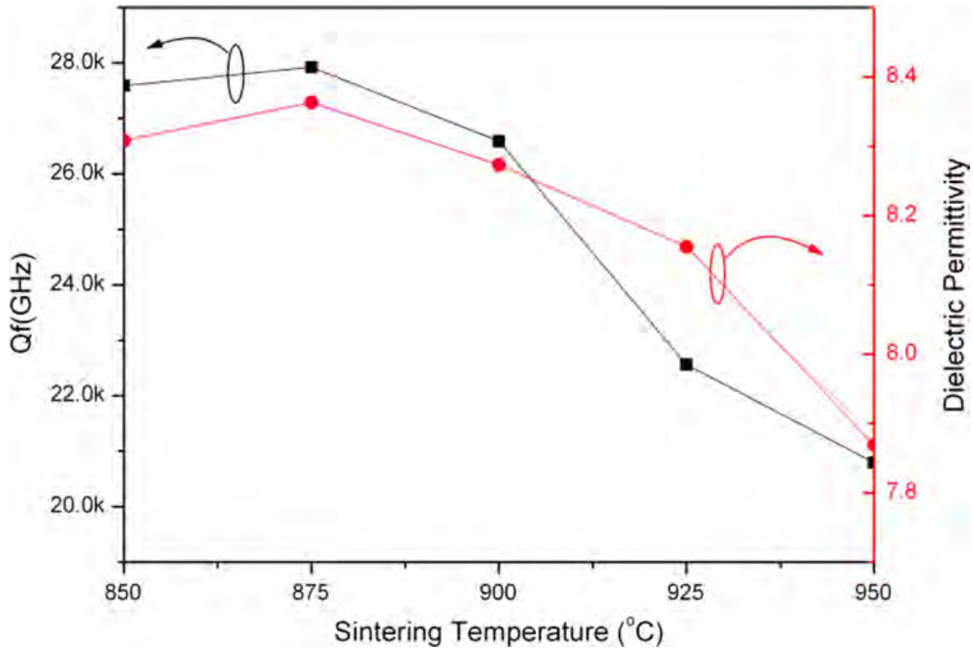

Fig. 4. Microwave dielectric characteristics of $BaZnP_2O_7$ ceramic as functions of sintering temperature.

of 925 °C is too high for $BaZnP_2O_7$ ceramics. Fig. 2(f) presents the energy dispersive spectroscopy (EDS) analysis of the $BaZnP_2O_7$ ceramics at 875 °C. EDS analysis shows the atomic ratio of Ba:Zn:P:O was 9.01:13.89:16.65:60.46 (1.0:1.54:1.85:6.71), which is close to the ideal value of 1:1:2:7.

Fig. 3 presents the apparent and relative densities of $BaZnP_2O_7$ ceramics as a function of sintering temperature. As can be seen, as sintering temperature increased, the relative density initially increased as pores were eliminated, reaching a maximum of 96.9% at 900 °C. The relative density decreased slightly with the further increase of sintering temperature, which may be due to over-burning and abnormal grain growth. The high relative density indicated that $BaZnP_2O_7$ was easily densified.

Fig. 4 illustrates the microwave relative dielectric permittivities and $Q \times f$ values of the ceramics as a function of sintering temperature. As the sintering temperature increased, the permittivity initially increased and then reached a maximum value of 8.4, at the optimum sintering temperature of 875 °C. In general the dielectric constant in the microwave frequency spectrum was dependent on the density, second phases, and the crystal structure. Higher density led to a greater dielectric constant. In addition the quality factor showed a similar trend to that seen in the dielectric constant, and the highest quality factor was observed for the highest densification. The ceramic of $BaZnP_2O_7$ sintered at 875 °C presented an optimum $Q \times f$ value of 27,925 GHz (at 11.1 GHz) with a TCF value of −56.7 ppm/°C calculated from Eq. (1). Generally speaking, the $Q \times f$ value of microwave dielectric ceramics is determined by the intrinsic loss and extrinsic loss. The intrinsic loss depends on lattice vibrational modes, and the extrinsic loss is influenced by many defects, such as pore size, density, second phases, grain sizes, and impurities [15,16]. High densification, homogeneous phase and uniform grain microstructure led to a high $Q \times f$ value due to reduced extrinsic loss; however, the second phase and abnormal grain growth produced a low $Q \times f$ value. The degradation of $Q \times f$ at higher temperatures might be attributed to the rapid grain growth of $BaZnP_2O_7$ as observed in Fig. 2 (d) and (e).

4. Conclusions

Ceramics of $BaZnP_2O_7$ were synthesized by a solid-state reaction method. The ceramics could be satisfactorily sintered at a low temperature of 850 °C. $BaZnP_2O_7$ ceramic sintered at 875 °C for 2 h exhibited good microwave dielectric properties, characterized as ε_r=8.4, $Q \times f$=27,925 GHz (@11.1 GHz), and τ_f=−56.7 ppm/°C. This material has a low permittivity, high quality factor, and medium negative τ_f values, which suggest that it is an attractive candidate for use as a microwave substrate.

Acknowledgments

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