Ba₉Y₂Si₆O₂₄: A new silicate dielectric ceramic for microwave communication application

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Abstract

A novel Ba₉Y₂Si₆O₂₄(BYS) ceramic was fabricated by solid-state reaction process for the first time. Rietveld refinement of powder diffraction data suggest that BYS

crystallize into a layered structure with space group of R-3(148). The microwave dielectric properties of BYS ceramics were found strongly related to the sintering temperature. The BYS samples sintered at 1400°C exhibit good microwave dielectric properties with relative permittivity (ϵ_r) of 14.9, $Q \times f$ value of 22440 GHz(at 8.4 GHz), and medium positive τ_f value of 35.8 ppm/°C, which indicates BYS may have potential in the application of microwave technology.

Keywords: Ceramics, Silicates, Crystal structure, Microwave dielectric properties

1. Introduction

Microwave dielectric ceramics are widely used in radar, base station, satellite and mobile communication technology because of their excellent performances and very important role in the communication industry [1-2]. As rapid development of modern communication technology, many new dielectric ceramics with low dielectric constant (ϵ_r), high quality factor ($Q \times f$), and near zero temperature coefficient of resonant frequency(τ_f) compliment the requirements of dielectric resonators, filters and substrates used in microwave-millimeterwave wireless communications [3-6].

Recently various dielectric ceramics, such as Mg_2SiO_4 [7], BaMgP_2O_7 [8], Zn_2SiO_4 [9], $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ [10], $\text{Sr}_2\text{Al}_2\text{SiO}_7$ [11], etc., have been reported for applications of microwave and millimeter wave devices. In previous work, BYS has been reported as a novel orthosilicate phosphor[12]. However, its microwave dielectric properties and crystal structure have not been reported. In this work, BYS ceramics were fabricated by solid-state reaction, and their microwave dielectric properties, microstructure, and the

crystal structure were investigated in detail. Comparing to other silicates like Mg_2SiO_4 ($\tau_f = -67 \text{ ppm}/^\circ\text{C}$), Zn_2SiO_4 ($\tau_f = -61 \text{ ppm}/^\circ\text{C}$) and $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ($\tau_f = -34 \text{ ppm}/^\circ\text{C}$), **BYS** has a positive temperature coefficient of resonant frequency (τ_f) of $35.8 \text{ ppm}/^\circ\text{C}$, which acts as a dielectric to tune other dielectrics with negative temperature coefficients, and can be used in potential application as resonators, filters and substrates.

2. Experimental

The **BYS samples** were prepared by solid-state reaction with raw materials of BaCO_3 (99.8%), SiO_2 (99.99%), Y_2O_3 (99.9%). The raw materials were weighed stoichiometrically, mixed in alcohol and milled with zirconia balls for 24 h. Then the mixtures were dried at 100°C for 8 h to evaporate alcohol. After drying and screening, the powder was loaded in the corundum crucibles, and calcined at 1200°C for 4 h in the furnace for initial reaction. The calcined powder was milled again in alcohol for 24 h. After that, 5 wt% polyvinyl alcohol was added as a binder. Then the calcined powder was pressed into cylindrical tablets with a diameter of 12 mm and a height of 6-8 mm under a uniaxially pressure of 100 MPa. The tablets were calcined at 650°C for 2 h to remove the organic binder and then sintered to 1250°C – 1475°C for 4 h at heating rate of $4^\circ\text{C}/\text{min}$ in the air.

The bulk densities of the sintered samples were measured by the Archimedes method. The microstructure of samples was measured by using scanning electron microscope (SEM; JEOL JSM6380-LV, Tokyo, Japan). The crystalline phases of the sintered samples were determined by powder X-ray diffraction technique (XRD; 40kV,

30mA, $\lambda=1.54056$ Å. Geiger Counter, RIGAKU D/max 2550/PC; Rigaku Co., Tokyo, Japan). Refined crystal structure was obtained by the Rietveld refinement method. The relative permittivity (ϵ_r) and temperature coefficient of resonant frequency (τ_f) values were measured by the Hakki-Coleman method. The quality factor Q (often using $Q \times f$ values index) was evaluated by the resonant-cavity in the TE_{01δ} mode, with a silver-coated cavity and a network analyzer (E8362B; Agilent Technologies, Palo Alto, CA). The τ_f values were measured at temperatures from 25°C to 85°C. The τ_f values were calculated by formula: $\tau_f = (f_{85} - f_{25}) / (f_{25} \times 60)$. Where f_{85} and f_{25} are the resonant frequencies at the measuring temperatures of 85°C and 25°C, respectively.

3. Results and Discussions

Figure 1 shows the XRD pattern of BYS samples sintered at different temperatures for 4h. All XRD spectra show an identical profile of Ba₉Sc₂Si₆O₂₄ (BSS, PDF No.82-1119), which belongs to the trigonal structure with space group of R-3(148). The crystal structure of BYS was further refined by the Rietveld method based on GSAS software. The refined profile of the sample sintered at 1400°C for 4h was given in Figure 2. The final weighted R-factor R_{wp} , the profile R-factor R_p and the goodness-of-fit indicator χ^2 were 5.04%, 3.32%, and 2.16 respectively, confirming that this compound is a single phase and isostructural to the known crystal structure of BSS. The inset Figure 2 shows the crystal structure of BYS. It shows a single layer of rhombohedral structure made of YO₆ octahedra linked by SiO₄ tetrahedra. The YO₆ octahedra are arranged in a nearly hexagonal array. The vertices of YO₆ octahedron are

corner-shared with the SiO_4 tetrahedra. The barium ions occupy three different coordination sites in the structure: Ba(1) ions are coordinated with 12 oxygen atoms, Ba(2) ions coordinated with 9 oxygen atoms, and Ba(3) ions coordinated with 10 oxygen atoms. The Ba(1) and Ba(2) ions are arrayed in chains in the interlayer gap, and the Ba(3) ions occupy a general position in the Y-Si-O layer.

Fig. 1. XRD pattern of BYS powder sintered at different temperature in air for 4h.

Fig. 2. Rietveld refinement of BYS sample sintered at 1400°C. The inset depicts the crystal structure of BYS and the coordination environments of Ba^{2+} ions.

Figure 3 shows the SEM images of the surfaces of BYS samples sintered at different temperatures. As shown in Fig.3 (a), the grain boundary is not clear. In Fig.3 (b)-(d), with the increase of sintering temperature from 1300°C -1400°C, the grain boundaries become clear and distinct. The grains grow up and the sizes become more uniform. After that, as shown in Fig.3 (e), glass phase appears and precipitates at boundaries of grains due to liquid phase sintering effect at 1450 °C. Especially, as Fig.3

(f) shows, when the sintering temperature increases up to 1475°C, the oversintering phenomenon appears, which exaggerates the abnormal grain growth.

Fig. 3. The SEM images of BYS samples sintered at different temperatures.

The quality factors ($Q \times f$ values), dielectric constants (ϵ_r), bulk relative densities, τ_f values of the samples as function of the sintering temperature are shown in Fig.4. The relative densities ($\rho_{rel} = \rho_{mea} NV / ZM$, where, ρ_{rel} is the relative densities, ρ_{mea} is the densities measurements, N is the Avogadro number, V is the volume of the unit cell, Z is the number of atoms per unit cell and M is the molar weight) of BYS samples increase with increasing sintering temperature from 1250°C to 1400°C, and reach a maximum value (94.6%) at 1400°C, then decrease as the sintering temperature exceeds 1400°C. It can be obviously seen that the optimum point for sintering temperature is 1400°C. These results are in agreement with the varying trend of SEM. The low densities of samples which were sintered at 1250°C, 1300°C and 1350°C mainly due to high porosity, whereas for the high temperatures of 1450°C and 1475°C, the densities of samples were significantly affected by glass phase and abnormal grain growth. The variation of quality factors ($Q \times f$ values) and the dielectric constants (ϵ_r) with the sintering temperature exhibit similar trends with the relative densities. It signifies the density has an remarkable contribution to the microwave dielectric properties in BYS

ceramics. ϵ_r increases from 12.5 to 14.9 with the sintering temperature increase from 1250°C to 1400°C and then decrease to 12.7 at 1475°C.

Fig.4. The relative densities, $Q \times f$ values, ϵ_r and τ_f values of BYS ceramics as function of sintering temperature.

As Fig. 4 shows, the $Q \times f$ value of BYS samples sintered at 1400 °C has a maximum value of 22,440 GHz. However, the $Q \times f$ values decrease with further increasing the sintering temperature. The enhanced quality factor could be attributed to the increasing density, and its deterioration could be attributed to the appearance of glass phase due to the oversintering. The value of τ_f varies from +35.8 ppm/°C to +40.7 ppm/°C when the samples sintered in the temperature range of 1250 °C – 1475 °C. In the further work, we are planning to improve the temperature coefficient of resonant frequency and increase the $Q \times f$ values via introducing different additives.

4. Conclusions

The BYS ceramic had been fabricated by solid-state reaction. Rietveld refinement of XRD data confirms that BYS crystallize into the BSS structure that belongs to the trigonal system with space group of R-3(148). The permittivity, $Q \times f$ values and a positive τ_f value are measured to be 14.9, 22440 GHz, and 35.8 ppm/°C, respectively. These good properties indicate that BYS has potential applications in microwave communication.

5. Acknowledgements

The present work was supported by the National Science Foundation of China (51212021, 51302056, 61376005), and Project of science and technology of Zhejiang Province, China (2016C31110), and National Science Foundation of Zhejiang province, China (LY16E020009).

References

- [1] Zhang YD, Zhou D, Guo J, Xi HH, He B, Mater Lett 2014;132:200-2.
- [2] Yang H, Zhang QL et al, J Chin Ceram Soc 2003;10:965-73.
- [3] Zhou HF, Liu XB, Chen XL et al, J Eur Ceram Soc 2012;32:261-5.
- [4] Chen Q, Shen Y, Zhang SH et al, Annu Rev Mater Res 2015;45:433-58.
- [5] Xu WH, Ding YC, Jiang SH et al, Polym Compos 2016;37:794-801.
- [6] Ohsato H, Tsunooka T, Ando M, Ohishi Y, Miyauchi Y, Kakimoto K, J Kor Ceram Soc 2003;40:350-3.
- [7] Zhang C, Zuo RZ, Zhang J, Wang Y, J Am Ceram Soc 2014;98:702-10.
- [8] Xie HD, Chen C, Tian R, Xi HH, Mater Lett 2015;162:91-3.
- [9] Jin-Seong K, Ngoc-Huan N, Jong-Bong L, Dong-Soo P, Sahn N, J Am Ceram Soc 2008;91:671-4.
- [10] Wu S, Song KX, Liu P, Lin HX, Zhang FF, Zheng P et al, J Am Ceram Soc 2015;98:1842-7.
- [11] Manu KM, Ananthakumar S, Sebastian MT, Ceram Int 2013;39:4945-51.
- [12] Park S, Mater Lett 2014;135:59-62.