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Preparation and microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramics

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Abstract Single phase of $Bi_2Ti_4O_{11}$ ceramics, which belong to meta-stable phase compounds, were synthesized by controlling the reaction time through conventional solid-state method. The effects of annealing time on phase composition of $Bi_2Ti_4O_{11}$ ceramic powders and sintered ceramics were studied by XRD analysis. Second phase $Bi_2Ti_2O_7$ appeared when the annealing time shorter than 4 h. However, pure phase of $Bi_2Ti_4O_{11}$ powders can be formed by prolonging the annealing time to 6 h at 1,000 °C. The sintering temperatures on microstructure and microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramics were investigated. The results show that ceramics sintered at 1,075–1,175 °C are single phase of $Bi_2Ti_4O_{11}$ and present two different sizes of prismatic shape grains. Smaller size crystals grow into larger ones with increasing sintering temperature. The ceramics sintered at 1,125 °C reach a maximum density and have a microwave dielectric properties of $\varepsilon_r = 51.2$, $Q \times f = 3{,}050$ GHz and $\tau_f = -297$ ppm/°C.

1 Introduction

With the fast growth of microwave communication in the past decades, there is an ever-increasing demand for low-cost and high-performance dielectric ceramics. Which are key materials for the manufacturing of microwave components such as resonators, filters, oscillators, wave guides and antennas [1]. The properties required for high performance dielectric ceramics are high dielectric constant (ε_r), high quality factor ($Q \times f$) and near zero temperature coefficient of resonant frequency (τ_f) [2]. Therefore, light weight and low cost ceramics attracting the component manufacturers' attention and a large number of dielectric has been developed [3]. In the low-cost Bi_2O_3–TiO_2 system, several compounds, such as $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_{12}TiO_{20}$ and $Bi_2Ti_4O_{11}$, have been found and most of them have special electronic properties [4–6]. Furthermore, due to the low sintering temperature and high relative dielectric constant, these compounds have potential electronic devices applications.

Several researchers have attempted to prepare $Bi_2Ti_4O_{11}$ ceramics and investigate their properties. The polymorphism and dielectric properties at 1 MHz of $Bi_2Ti_4O_{11}$ was studied by Subbarao in 1962 [7]. Single crystal of $Bi_2Ti_4O_{11}$ with platelike and prismatic shape were prepared by Barsukova et al. [8]. Using different staring materials and process, the microwave dielectric properties of Bi_2O_3–$Bi_2Ti_4O_{11}$ composite ceramics were researched by Axelsson and co-workers [9]. Akimov studied the effect of pressing pressures and heating rate on the synthesis and sintering of $Bi_2Ti_4O_{11}$. And found that the formation of $Bi_2Ti_4O_{11}$ begins at 900 °C and follows with a diffusion mechanism [10]. However, $Bi_2Ti_4O_{11}$ is one kind of meta-stable compounds, and it is difficult to synthesize the single phase by conventional oxides reaction method.

Moreover, $Bi_2Ti_4O_{11}$ possess two phases, the high-temperature β-$Bi_2Ti_4O_{11}$ and low-temperature α-$Bi_2Ti_4O_{11}$ phase. Preparation of $Bi_2Ti_4O_{11}$ without calcinations processes will lead to a weight loss greater than 1 % when the sintered temperature above 1,100 °C due to the volatilization of Bi_2O_3 [11]. And TiO_2 is not soluble in the high-temperature form of $Bi_2Ti_4O_{11}$ [12]. For these reasons, phase pure $Bi_2Ti_4O_{11}$ is very difficult to prepare for short

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calcinations time and low temperature and the preparation processes on the dielectric properties of the ceramics are remains unknown. In order to prepare phase pure $Bi_2Ti_4O_{11}$ powders, we attempted to increase the calcinations time at 1,000 °C by solid state reaction method and investigate the effects of sintering condition on microstructure and microwave dielectric properties of the ceramics.

2 Experimental

The powders of $Bi_2Ti_4O_{11}$ were prepared by conventional solid state reaction method from high purity oxides of Bi_2O_3 (>99 %) and TiO_2 (>99 %). Stoichiometric ratios of Bi_2O_3 and TiO_2 were mixed and ball-milled in ethanol with zirconia balls for 6 h. After drying, the mixed powders were calcined in covered alumina crucible at 1,000 °C for 1–6 h in air, respectively. The heating and cooling rate of calcinations process was 5 °C/min. Ceramics were prepared from phase pure $Bi_2Ti_4O_{11}$ powders which calcined at 1,000 °C for 6 h. The powders were remilled for 6 h and dried then press into pellets of 10 mm in diameter and 6 mm in thickness at 100 MPa. The pellets were sintered at 1,075–1,175 °C for 2 h in air with a heating rate of 5 °C/min.

Crystal structure of calcined powders and sintered ceramics were examined by X-ray diffraction (XRD, Rigaku, DMAX-RB, Japan) using Cu K_α radiation with a scan speed of 10 °C/min. The apparent densities of sintered samples were measured by Archimedes' method. Microstructures of $Bi_2Ti_4O_{11}$ ceramics were studied by scanning electron microscopy (SEM, JSM-6480LV). Microwave dielectric properties of ceramic samples were measured with a HP8720ES network analyzer at 3-8 GHz using Hakki-Coleman's dielectric resonator method, as modified and improved by Courney and Kobayashi et al. [13–15].

3 Results and discussion

Figure 1 shows the XRD patterns of powders calcined with different holding time and ceramics sintered at various temperatures. When the mixed powders were calcined at 1,000 °C for 1 h, the reaction products consist of main phase of $Bi_2Ti_4O_{11}$ (JCPDS, File No. 83-0672) and a small amount of second phase $Bi_2Ti_2O_7$ (JCPDS, File No. 32-0118). The amount of $Bi_2Ti_2O_7$ decreased with increasing holding time, and finally disappeared as the holding time is 6 h. Because the low melting point of Bi_2O_3 (860 °C), the calcinations process at 1,000 °C may be consider as the reaction of TiO_2 and liquid Bi_2O_3, and the growth of $Bi_2Ti_4O_{11}$ is diffusion-controlled reaction.

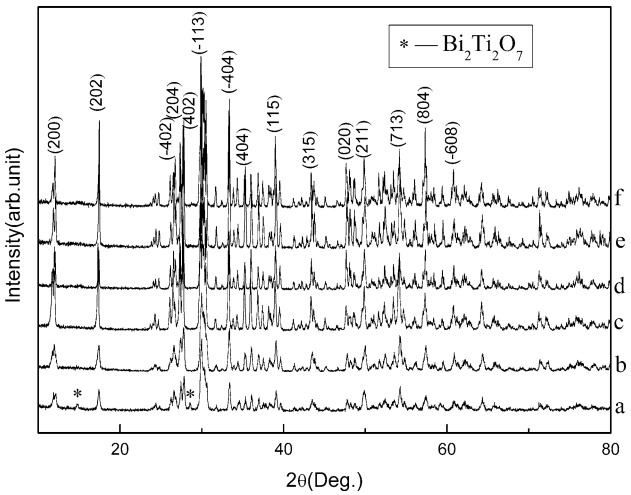

Fig. 1 XRD patterns of $Bi_2Ti_4O_{11}$ powders and ceramics: (*a*), (*b*), (*c*) powders calcined at 1,000 °C for 1, 4, and 6 h; (*d*), (e), (*f*) ceramics sintered at 1,075, 1,125 and 1,175 °C, respectively

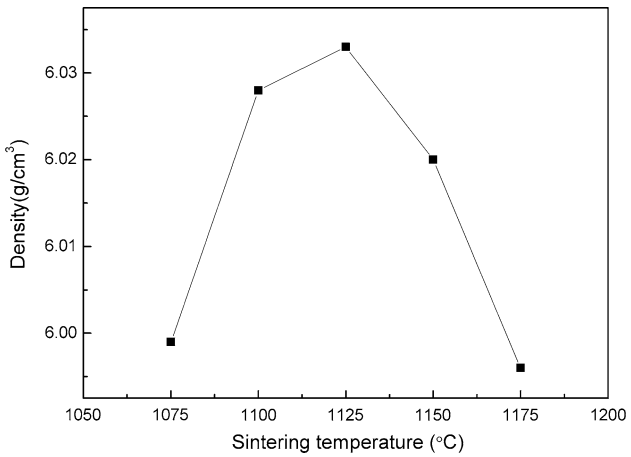

Fig. 2 Densities of $Bi_2Ti_4O_{11}$ ceramics as a function of sintering temperature

According to Lu's [16] study of interface compound of Bi_2O_3 and TiO_2, $Bi_4Ti_3O_{12}$ forms fast and then $Bi_2Ti_4O_{11}$ arise between TiO_2 and $Bi_4Ti_3O_{12}$ when the heating time is 0.5 h, after that $Bi_2Ti_2O_7$ appeared for longer holding time. However, both of $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ have not been detected in the calcined powders of Bi_2O_3 and TiO_2, and pure phase of $Bi_2Ti_4O_{11}$ can be obtained after 6 h calcination. Ceramics prepared using the above powders sintered at various temperature also show a single $Bi_2Ti_4O_{11}$ phase, and no second phases was detected in the ceramics sintered at 1,075–1175 °C. Therefore, for preparing single phase $Bi_2Ti_4O_{11}$ ceramics, the key process is obtain single phase $Bi_2Ti_4O_{11}$ powders by controlling the calcining temperature and holding time.

Densities of $Bi_2Ti_4O_{11}$ ceramics sintered at different temperature for 2 h in air are shown in Fig. 2. All the ceramics samples sintered at 1,075–1,175 °C reach above

95 % of the theoretical density. They increase with the increasing of sintering temperature and then decline after reaching a maximum at 1,125 °C. The maximum density of 6.033 g/cm^3 (96 % of the theoretical density) can be obtained for samples sintered at 1,125 °C, which suggests that the $Bi_2Ti_4O_{11}$ ceramics can be sintered at a low temperature.

Surface SEM photographs of $Bi_2Ti_4O_{11}$ ceramics sintered at different temperature are shown in Fig. 3. All samples sintered at the temperature in this study present two different sizes of prismatic shape crystals. The sizes of those grains increased with increasing sintering temperature and the smaller size crystals transform into larger ones. In early studies of single crystal of $Bi_2Ti_4O_{11}$ by hydrothermal method, Barsukova found that platelike crystal of $Bi_2Ti_4O_{11}$ appeared when Bi_2O_3 excesses in the Bi_2O_3–TiO_2 system and prismatic crystal obtained in other conditions [8]. However, in this study, single phase $Bi_2Ti_4O_{11}$ powders were used to prepare ceramics by solid reaction method, and the crystals in the ceramics exhibit only prismatic shape except that they have different sizes.

Effect of sintering temperature on microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramics is shown in Fig. 4. Both of the dielectric constant (ε_r) and quality factor ($Q \times f$) increase below 1,125 °C, and then decreased with increasing of the sintering temperature. These results are similar to the effect of sintering temperature on the density of $Bi_2Ti_4O_{11}$ ceramics. However, temperature coefficient of resonant frequency (τ_f) has negative value and decreasing with the sintering temperature near linearly. This result illuminates that increasing sintering temperature will bring on the increase of τ_f values for $Bi_2Ti_4O_{11}$ ceramics. As the sintering temperature is 1,125 °C, $Bi_2Ti_4O_{11}$ ceramics exhibits a microwave dielectric properties: $\varepsilon_r = 51.2$, $Q \times f = 3{,}050$ GHz and $\tau_f = -297$ ppm/°C. In previous study, Fukuda et al. [17] reported that $Bi_2Ti_4O_{11}$ ceramic

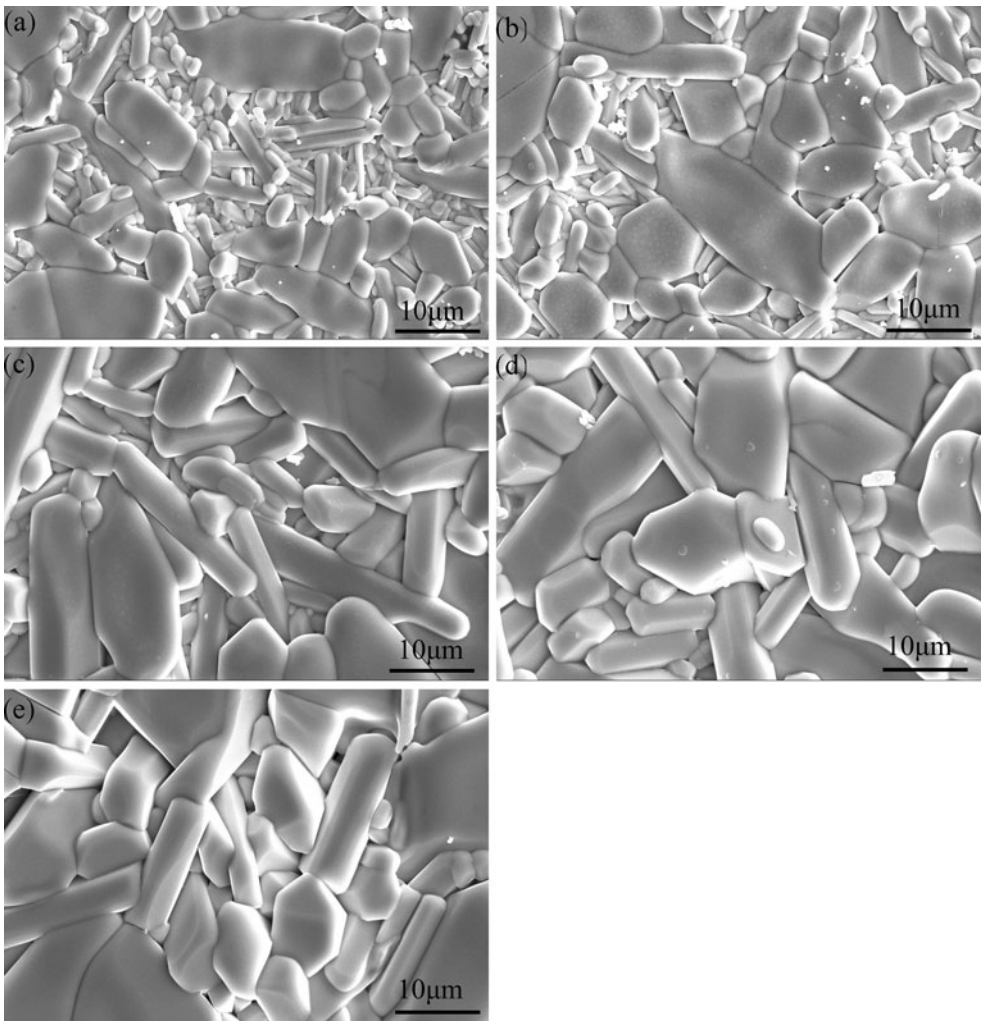

Fig. 3 Surface SEM photographs of $Bi_2Ti_4O_{11}$ ceramics sintered at different temperature: **a** 1,075 °C, **b** 1,100 °C, **c** 1,125 °C, **d** 1,150 °C, **e** 1,175 °C

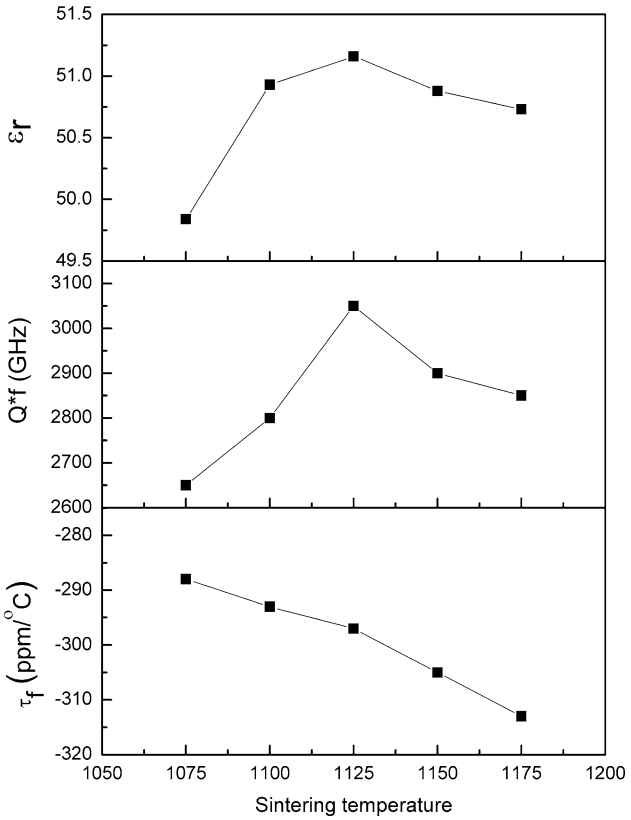

Fig. 4 Microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramics as a function of sintering temperature from 1,075 to 1,175 °C

have $\varepsilon_r = 53.2$, $Q \times f = 4{,}500$ GHz and $\tau_f = -550$ ppm/°C . However, the XRD patterns of $Bi_2Ti_4O_{11}$ they provided presents a trace of $Bi_2Ti_2O_7$ phase. The values of ε_r and $Q \times f$ obtained in this study are somewhat lower and temperature coefficient of resonant frequency is higher than their result. The reasons may be the different calcinations and sintering temperature and during times.

4 Conclusions

Single phase $Bi_2Ti_4O_{11}$ powders can be synthesized by controlling the calcining temperature and holding time through solid-state reaction method. It was found that second phase $Bi_2Ti_2O_7$ appeared when the holding time below 4 h, and the single phase of $Bi_2Ti_4O_{11}$ powders can be obtained by calcining the mixture of stoichiometric Bi_2O_3 and TiO_2 at 1,000 °C for 6 h. $Bi_2Ti_4O_{11}$ ceramics sintered at different temperature present two different sizes of prismatic shape crystals, and smaller ones grow into larger sizes ones when raising the sintering temperature. The sintering temperatures have a significant effect on microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramics. Both of ε_r values and $Q \times f$ values increase with increasing sintering temperature, and present a maximum value of 51.2 and 3,050 GHz at 1,125 °C, respectively. Increasing sintering temperature will bring on the increase of τ_f values for $Bi_2Ti_4O_{11}$ ceramics. The microwave dielectric properties of $Bi_2Ti_4O_{11}$ ceramic sintered at 1,125 °C are: $\varepsilon_r = 51.2$, $Q \times f = 3{,}050$ GHz and $\tau_f = -297$ ppm/°C.

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References

1. R.C. Pullar, J. Am. Ceram. Soc. **92**, 563 (2009)
2. S.B. Narang, S. Bahel, J. Ceram. Process Res. **11**, 316 (2010)
3. M.T. Sebastian, H. Jantunen, Int. Mater. Rev. **53**, 57 (2008)
4. S. Miyazawa, T. Tabata, J. Cryst. Growth **191**, 512 (1998)
5. T.M. Bruton, J. Solid State Chem. **9**, 173 (1974)
6. J.R. Esquivel-Elizondo, B.B. Hinojosa, J.C. Nino, Chem. Mater. **23**, 4965 (2011)
7. E.C. Subbarao, J. Am. Ceram. Soc. **45**, 564 (1962)
8. M.L. Barsukova, V.A. Kuznetsov, A.N. lobachev, Y.V. Shaldin, J. Cryst. Growth **13–14**, 530 (1972)
9. A.K. Axelsson, M. Sebastian, N.M. Alford, J. Korean Ceram. **40**, 340 (2003)
10. A.I. Akimov, G.K. Savchuk, Inorg. Mater. **40**, 716 (2004)
11. V. Kahlenberg, H. Böhm, Acta Crystallogr. Sect. B: Struct. Sci. **51**, 11 (1995)
12. C.E. Bamberger, G.M. Begun, H.W. Dunn, J. Am. Ceram. Soc. **69**, C93 (1986)
13. B.W. Hakki, P.D. Coleman, IEEE T. Microw. Theory **8**, 402 (1960)
14. W.E. Courtney, IEEE T. Microw. Theory **18**, 476 (1970)
15. Y. Kobayashi, M. Katoh, IEEE T. Microw. Theory **33**, 586 (1985)
16. C.D. Lu, L.S. Chang, Y.F. Lu, F.H. Lu, Ceram. Int. **35**, 2699 (2009)
17. K. Fukuda, R. Kitoh, I. Awai, J. Appl. Phys., Part 1 **32**, 4584 (1993)