

A novel low-firing BiZn₂VO₆ microwave dielectric ceramic with low loss

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Abstract novel low-firing microwave dielectric ceramic BiZn₂VO₆ was prepared using the solid state reaction method. The phase composition, sintering behavior, and microwave dielectric properties were investigated. BiZn₂VO₆ ceramic could be well densified at relatively low temperature 780 °C and exhibited promising microwave dielectric properties with a $\epsilon_r = 15.0$, $Q \times f = 20,640$ GHz, and $\tau_f = -88$ ppm/°C. BiZn₂VO₆ ceramic has chemically compatibility with Ag electrodes when sintered at 780 °C for 4 h.

1 Introduction

In recent years, low-temperature co-fired ceramic (LTCC) technology has been extensively investigated because it can satisfy the requirement for minimization to meet the rapid growth of wireless communication industry [1]. The development of LTCC technology has opened up a new stage for the fabrication of miniature multilayer devices [2, 3]. LTCC materials for microwave integrated circuits should possess a low sintering temperature lower than the

melting temperature of the inner electrode, such as Ag (~960 °C), a appropriate dielectric constant, a high quality factor and a near-zero temperature coefficient of resonance frequency. The addition of low-melting glass or oxide has been proved to be an effective method to reduce the sintering temperatures but at the cost of deterioration in the microwave properties [4–6]. Thus to obtain glass-free microwave dielectric ceramics with excellent microwave properties is still a challenging research.

More recently, some vanadate ceramics with good microwave dielectric properties have gained considerable attention mainly due to their relatively low sintering temperatures, such as Mg₂V₂O₇ (sintered at 900 °C, $\epsilon_r = 10.4$, $Q \times f = 31,500$ GHz, $\tau_f = -20$ ppm/°C [7], LiMVO₄ (M = Mg, Zn) (sintered at 675–750 °C, $Q \times f = 22,000$ –33,730 GHz, $\tau_f = -160$ to -110 ppm/°C [8], LiCa₃MgV₃O₁₂ (sintered at 900 °C, $\epsilon_r = 10.5$, $Q \times f = 74,700$ GHz, $\tau_f = -61$ ppm/°C [9]. BiA₂VO₆ (A = Ca, Mg, Zn, Cu or Pb) compounds constitute a family of functional materials. These compounds have been widely investigated due to their photocatalytic properties, luminescent properties, magnetic properties and nonlinear optical properties [10–13]. Up to date, however, there are few reports on the microwave dielectric properties of BiA₂VO₆ compounds. Xie et al. [14] firstly reported the microwave dielectric properties of the BiMg₂VO₆ ceramic ($\epsilon_r \sim 13.4$, $Q \times f \sim 15,610$ GHz, and $\tau_f \sim -87.2$ ppm/°C) sintered at 780 °C and its chemical compatibility with silver electrodes. Therefore, it is worthwhile to search for novel microwave dielectric ceramics with intrinsically low sintering temperature in BiA₂VO₆ system.

In this work, BiZn₂VO₆ ceramic was prepared by the conventional solid state reaction method, and its crystal structure, sintering behavior and microwave dielectric properties were studied. The chemical compatibility of BiZn₂VO₆ with silver electrodes was also investigated.

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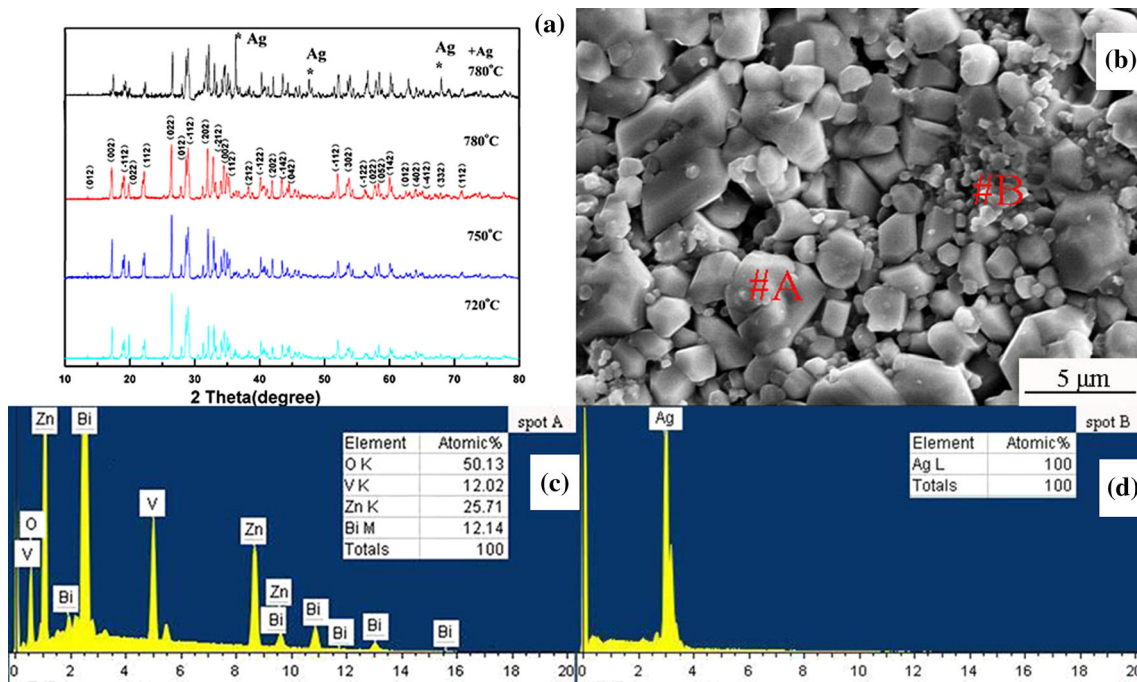


Fig. 1 **a** XRD patterns of BiZn₂VO₆ ceramics sintered at different temperatures, **b** SEM of the co-fired BiZn₂VO₆ with 10 wt% Ag sintered at 780 °C for 4 h, **c** EDS analysis of spot A, **d** EDS analysis of spot B

2 Experimental procedure

Using solid-state route, BiZn₂VO₆ was prepared from high-purity (99 %) powders of Bi₂O₃, ZnO and NH₃VO₃. Powders were milled with zirconia balls for 6 h. After dried, the mixtures were calcined at 720 °C for 4 h, followed by re-milling for 4 h. The obtained powder was mixed with 5 wt% polyvinyl alcohol as a binder and then crushed into a fine powder through a sieve with 200 mesh. The fine powder was pressed into pellets with 12 mm in diameter and 7 mm in height under a pressure of 200 MPa. The samples were heated at 550 °C for 4 h to remove the PVA and then sintered at 760–810 °C for 4 h. To research the chemical compatibility of BiZn₂VO₆ with Ag powders, 20 wt% Ag was mixed with the compound and co-fired at 780 °C for 4 h.

The crystal structure and phase composition of the specimens were analyzed with X-ray diffraction (XRD; Model X’Pert PRO, PANalytical, Almelo, the Netherlands). The bulk densities of the sintered samples were measured using Archimede’s method. The surface microstructures of the samples were performed by scanning electron microscopy (SEM; JSM6380-LV, JEOL, Tokyo, Japan). The microwave dielectric properties were measured using a network analyzer (N5230A, Agilent Co., Palo Alto, California) and a temperature chamber (Delta 9039; Delta Design, San Diego, California). The temperature

coefficient of resonant frequency τ_f values were calculated with the formula as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \quad (1)$$

where, f_{85} and f_{25} are the resonant frequencies at the measuring temperature 85 and 25 °C, respectively.

3 Results and discussion

XRD patterns of BiZn₂VO₆ ceramics sintered at different temperatures (760–810 °C) are presented in Fig. 1. Over the sintering temperature range 760–810 °C, pure BiZn₂VO₆ phase was obtained. It crystallized into a triclinic structure with space group *P-1*, which is in well agreement with the previous report by Nunes et al. [15] The XRD of the co-fired BiZn₂VO₆ ceramic with 20 wt% Ag is also shown in Fig. 1. As shown, only the peaks of BiZn₂VO₆ and Ag (JCPDS No. 004-0783) were observed, implying that BiZn₂VO₆ did not react with Ag electrodes after sintered at 780 °C for 4 h. From the EDS analysis, two distinct grains with different sizes were detected. The larger grains were rich in Bi, Zn, and V belonging to BiZn₂VO₆ phase, whereas the smaller grains were detected to be silver. This result further confirmed the chemical compatibility of BiZn₂VO₆ with Ag electrodes.

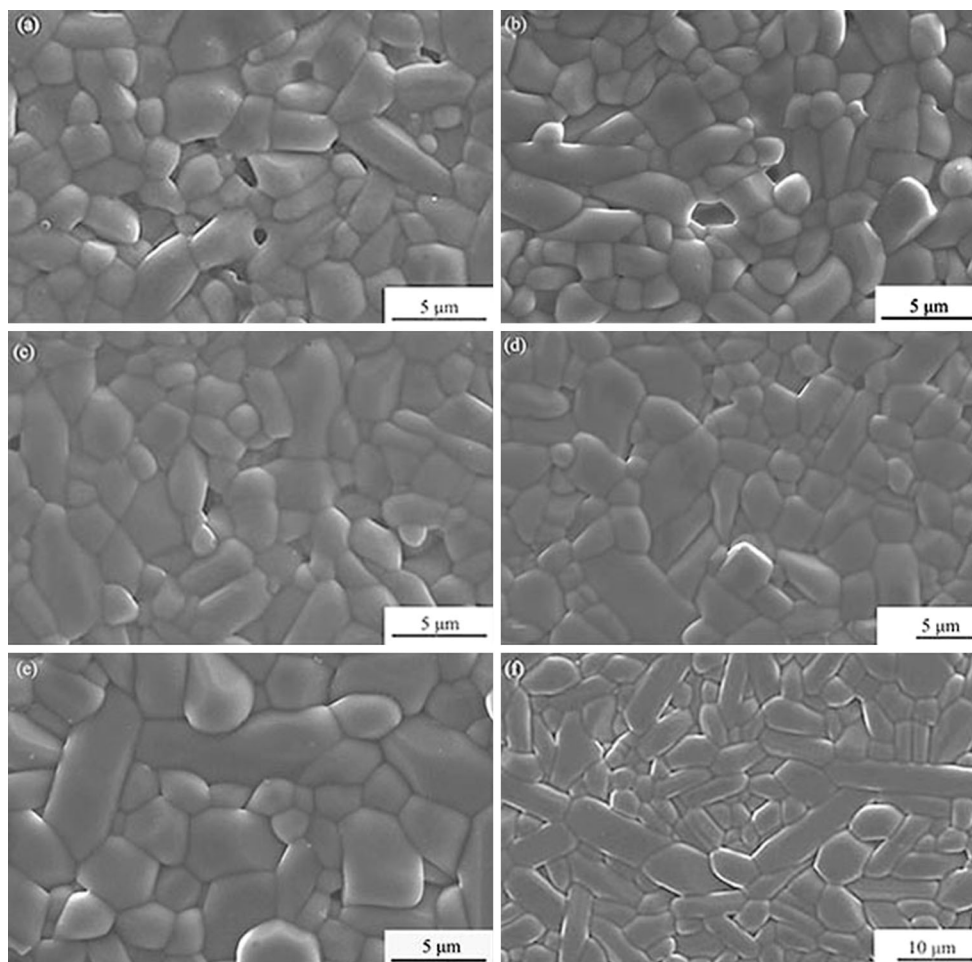
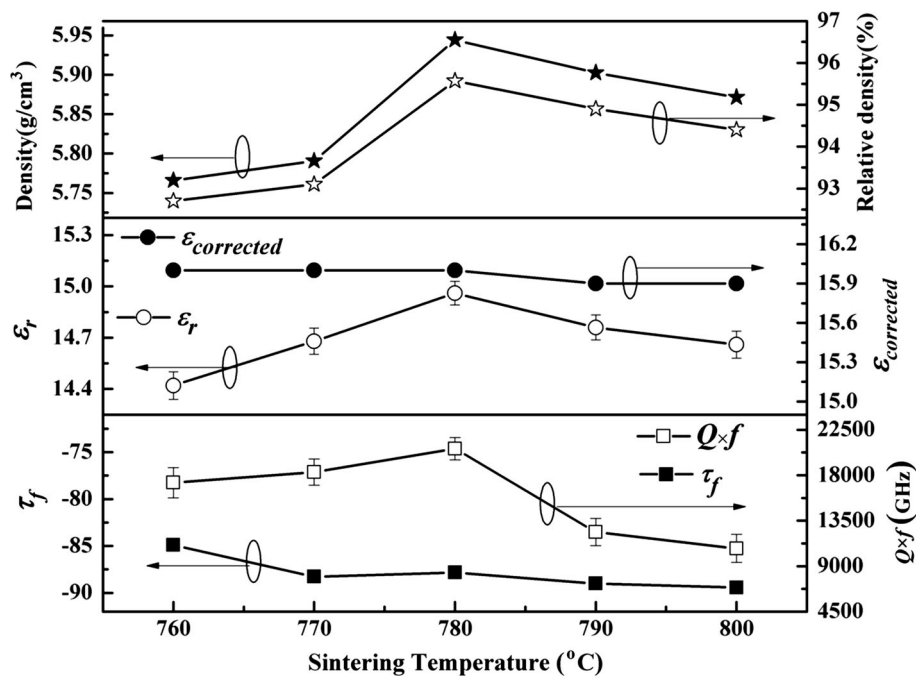


Fig. 2 SEM micrographs of BiZn_2VO_6 ceramics sintered at different temperatures: **a** 760 °C, **b** 770 °C, **c** 780 °C, **d** 790 °C, **e** 800 °C, **f** 810 °C

Fig. 3 The densities, relative densities, ϵ_r , $\epsilon_{corrected}$, $Q \times f$ values, and τ_f of BiZn_2VO_6 ceramics sintered at different temperatures



SEM micrographs of the surfaces of BiZn₂VO₆ ceramics sintered at different temperatures are shown in Fig. 2. As shown in Fig. 2a, a dense microstructure with some pores was observed in the sample sintered at 760 °C with average grain size about 2–3 μm. As the sintering temperature increased, the amount of pore decreased along with an obvious increase in the grain size. For the sample sintered at 780 and 790 °C, much denser microstructures with closely packed grains were achieved and the average grain size was in the range of 3–6 μm. Exaggerated large grains (10–15 μm) appeared in the ceramic sintered at 810 °C. The bulk densities and relative densities of BiZn₂VO₆ ceramics are shown in Fig. 3 as a function of sintering temperature. The theoretical density of BiZn₂VO₆ is 6.22 g/cm³. As seen, all the sintered ceramics had high relative densities (>92 %). The bulk density firstly increased with the sintering temperature, and then decreased thereafter, giving rise to a maximum density of 5.94 g/cm³ (95.5 % of the theoretical density) at 780 °C.

The microwave dielectric properties (ϵ_r , $Q \times f$ and τ_f) of the sintered BiZn₂VO₆ ceramics are shown in Fig. 3. As seen, both ϵ_r and $Q \times f$ values exhibited clear dependence on the sintering temperature. With increasing sintering temperature, both ϵ_r and $Q \times f$ increased firstly, reached a saturated value, and thereafter decreased. τ_f values of both ceramics did not change significantly with increasing sintering temperature and remained stable with a value about –87 ppm/°C. The best microwave dielectric properties with a $\epsilon_r = 15.0$, $Q \times f = 20,640$ GHz, and $\tau_f = -88$ ppm/°C was obtained for the sample sintered at 780 °C.

It is well known that the factors affecting the microwave dielectric properties are classified into two categories: the intrinsic factors related to the lattice vibration, and the extrinsic ones related to the secondary phases, porosity, densification, and grain boundaries, etc. [16–18]. Based on the similar variation trend in ϵ_r and $Q \times f$ values with that of the density, it is proposed that the primary factor affecting the microwave dielectric properties is densification in the present work. Similar phenomena were reported in BaMV₂O₇ (M = Mg, Zn) [19] and Ca₅A₄(VO₄)₆ (A²⁺ = Mg, Zn) [20] systems. In order to eliminate the influence of the porosity on the relative permittivity, the Bosman and Having's correction [21] equation was applied:

$$\epsilon_{corrected} = \epsilon_m(1 + 1.5P) \quad (2)$$

where, $\epsilon_{corrected}$ and ϵ_m are the corrected and measured values of permittivity, respectively. P is the fractional porosity. The porosity-corrected ϵ_r value of BiZn₂VO₆ (in the range 15.9–16.0) showed a slight variation with the sintering temperature, which further confirms that the density primarily affects the permittivity of the BiZn₂VO₆ ceramics. Moreover, the theoretical relative permittivity

was calculated according to the Clausius–Mossotti equation [22, 23]:

$$\epsilon_r = \frac{1 + 2b\alpha_D^T/V_m}{1 - b\alpha_D^T/V_m} \quad (3)$$

where $b = 4\pi/3, \alpha_D^T$ is the sum of ionic polarizabilities of individual ions and the V_m is the molar volume. The theoretical relative permittivity of BiZn₂VO₆ ceramic is 13.87. The relative error of BiZn₂VO₆ is about 7.5 % for the measured value and 13.3 % for the porosity corrected value, which implies that there is no other polarization mechanism in the BiZn₂VO₆ ceramic at microwave region beside ionic and electronic displacement polarization [24].

By comparison with BiMg₂VO₆ ceramic, the sintering temperature of BiZn₂VO₆ is comparable with that of BiMg₂VO₆ ceramic, while the relative permittivity and quality factor of BiZn₂VO₆ are a little higher. However, it should be noted that the high negative τ_f values of these materials limit their commercial applications. Further efforts are needed to tune the large negative τ_f values of BiZn₂VO₆ and BiMg₂VO₆ ceramics to be near-zero by forming a composite materials such as TiO₂ or CaTiO₃ with positive sign of τ_f values.

4 Conclusions

In summary, BiZn₂VO₆ ceramic was prepared through traditional solid-state reaction method. XRD analysis shows that at room temperature BiZn₂VO₆ crystallizes into a triclinic structure with space group $P-1$. The bulk density, the relative permittivity, and the quality factor exhibited obvious dependence on the sintering temperature, while the τ_f value was insensitive to the sintering temperature. The ceramic sintered at 780 °C exhibited good microwave dielectric properties: $\epsilon_r = 15.0$, $Q \times f = 20,640$ GHz and $\tau_f = -88$ ppm/°C. The BiZn₂VO₆ ceramic is found to be chemically compatible with Ag electrodes when sintered at 780 °C for 4 h. These results open up the possibility of BiZn₂VO₆ ceramic for LTCC application.

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