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Microwave dielectric properties and low temperature sintering of the $ZnO–V_2O_5$ doped $Ba_3Ti_2(Mg_{1/3}Nb_{2/3})_2Nb_4O_{21}$ ceramics

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Abstract

The ZnO and V_2O_5 co-doped $Ba_3Ti_2(Mg_{1/3}Nb_{2/3})_2Nb_4O_{21}$ (BTMNN-2) microwave dielectric ceramics were successfully prepared via a conventional solid-state reaction method. The effect of the 2 $ZnO–V_2O_5$ complex additive on the sintering temperature and microwave dielectric properties was specially investigated. The X-ray diffraction analysis reveals that the BTMNN-2 ceramics doped with 2 $ZnO–V_2O_5$ form a single hexagonal structure phase without visible secondary phases. A small amount of 2 $ZnO–V_2O_5$ additive can significantly lower the sintering temperature of BTMNN-2 ceramics owing to the formation of a liquid phase in the BTMNN-2 matrix, as clearly evidenced by the SEM micrographs. Meanwhile, the experimental results show that the microwave dielectric properties of the samples were strongly dependent on the densification, crystalline phases, and grain size. The 5 wt% 2 $ZnO–V_2O_5$ doped BTMNN-2 ceramics can be sintered at 900 °C and own good microwave dielectric properties of $\varepsilon_r=47$, $Q\times f=10{,}500$ GHz and $\tau_f=16$ ppm/°C, showing a potential for applications in mid-permittivity low temperature co-fired ceramics.

Keywords: A. Sintering; D. Ceramics; Microwave dielectric properties; LTCC

1. Introduction

With the rapid development of global microwave communication in recent years, low temperature co-fired ceramic (LTCC) technology has become an excellent solution to the miniaturization of microwave dielectric components. LTCC multilayer devices consisting of alternating microwave dielectric ceramics and internal metallic electrode layers have been extensively investigated for applications related to satellite communications, wireless local area networks, and car collision avoidance systems. The critical requirements for LTCC materials include a low sintering temperature (below 960 °C), good microwave dielectric properties, as well as an excellent chemical compatibility with electrode materials [1]. Several microwave dielectric ceramic systems, including $ZnNb_2O_6$, $MgO–TiO_2$, $BaO–TiO_2$, $Ca[(Li_{1/3}Nb_{2/3}),Ti]O_{3-\delta}$, $Li_2O–Nb_2O_5–TiO_2$ and $BaO–Ln_2O_3–TiO_2$ (Ln = La, Nd, Sm) have been studied by using low-melting glass frits or oxides to lower their sintering temperatures [2–7]. However, among the reported LTCC systems, the mid-permittivity LTCC materials with a relatively high dielectric constant ($\varepsilon_r \geq 45$) and a high quality factor ($Q\times f \geq 10{,}000$ GHz) are still few.

Groult reported that $Ba_3Ti_4Nb_4O_{21}$ (BTN) exhibited a hexagonal crystal structure and pointed out that it belonged to the family of $A_3M_8O_{21}$ ($A=K$, Ba; M = Nb, Ti, Cr, Fe, Ni, Mg, Zn) [8]. Sebastian [9] first reported its microwave dielectric properties of $\varepsilon_r=55$, $Q\times f=9000$ GHz and the temperature coefficient of resonant frequency $\tau_f=100$ ppm/°C. However, this material cannot be widely used as the LTCC material because of its large τ_f value and high sintering temperature. Several studies were carried out to tune its microwave dielectric properties. However, either the τ_f value was still quite positive (~50 ppm/°C) or the $Q\times f$ value was decreased seriously [10–12]. In our previous work, we found that the microwave dielectric properties of BTN ceramics could be effectively modified by substitutingfor Ti^{4+} ($\varepsilon_r=66–41$, $Q\times f=10{,}500–22{,}500$ GHz and $\tau_f=56–15$ ppm/°C), and investigated the influence of $BaCu(B_2O_5)$ (BCB) additives on the sintering temperature and the phase composition of

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BTMNN-2 ceramics (50% Ti^{4+} was replaced by) [13]. The BTMNN-2 ceramics doped with 1.5 wt% BCB can be well sintered at 950 °C and own desirable dielectric properties of $\varepsilon_r = 50$, $Q \times f = 10{,}500$ GHz and $\tau_f = 18$ ppm/°C. However, more BCB additive would have an adverse effect on the electrical properties due to the presence of the impurity phases. For the purpose to lower the sintering temperature close to 900 °C and simultaneously to maintain good dielectric properties, the current work was focused on the effect of $ZnO–V_2O_5$ additives on the BTMNN-2 ceramics because some compounds in $ZnO–V_2O_5$ binary system have a high quality factor and a low sintering temperature [14]. We first carried out a comparative study on the influence of 2 $ZnO–V_2O_5$, $ZnO–V_2O_5$ and $ZnO–2V_2O_5$ additions on the sintering behavior of BTMNN-2 ceramics. It was then found that the addition of 2 $ZnO–V_2O_5$ should be most effective in reducing the sintering temperature, which is consistent with the result of other reports [14,15]. Finally, we successfully developed a mid-permittivity LTCC microwave dielectric based on 2 $ZnO–V_2O_5$ doped BTMNN-2 ceramics.

2. Experimental

The BTMNN-2 ceramic specimens were prepared by means of a conventional solid-state reaction route using the high-purity powders of $BaCO_3$, TiO_2, $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, and Nb_2O_5. The stoichiometric mixture of the above raw materials was first weighed and milled in ethanol medium for 24 h using zirconia balls. After drying, the slurry was then calcined at 1100 °C for 4 h. Finally, different percentages (1–6 wt%) of 2 $ZnO–V_2O_5$ additive and 5 wt% PVA were added to BTMNN-2 powders. After ball-milling for 24 h, the powders were dried, granulated and subsequently uniaxially pressed into cylinders of 10 mm in diameter and 6 mm in thickness. The as-pressed samples were sintered in the temperature range of 875 °C–975 °C for 4 h in air at a heating and a cooling rate of 5 °C/min.

The bulk densities of the sintered specimens were measured by the Archimedes method. The crystal structures of the sintered samples were determined by an X-ray powder diffractometer (XRD, Rigaku D/Max-II, Japan) using CuK_α radiation. The microstructure of the samples was observed by a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). An Agilent N5230C network analyzer (Agilent, Santa Clara, CA, USA) was used for the measurement of microwave dielectric properties by means of a Hakki–Coleman method [16,17]. The τ_f value of the samples was measured in the temperature range from 30 to 80 °C. It can be calculated by the following relationship: where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the relative density of the BTMNN-2 ceramics as a function of the content of 2 $ZnO–V_2O_5$ additive and the sintering temperature. It can be seen that the relative density of all samples increased with increasing the sintering temperature

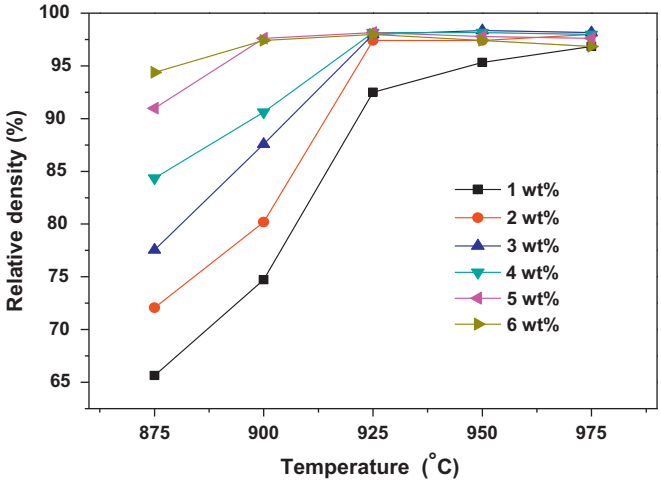

Fig. 1. The relative density of BTMNN-2 ceramics doped with various contents of 2 $ZnO–V_2O_5$ as a function of sintering temperature.

and then slightly decreased after a maximum value. The increase in density should be mainly attributed to the reduction in porosity and the uniform grain growth. Moreover, the optimum sintering temperature was reduced with increasing the amount of the additive. The decrease in density at a relatively high sintering temperature can be attributed to the rapid grain growth. This can be clearly seen in the microstructure observation infra. The rapid grain growth tends to reduce the driving force for further densification since the intrinsic sintering potential is inversely proportional to the grain size. The results in Fig. 1 definitely exhibits that the 2 $ZnO–V_2O_5$ additive is an effective aid in lowering the sintering temperature of BTMNN-2 ceramics. As only 5 wt% 2 $ZnO–V_2O_5$ was added, the sample density of up to 97% could be obtained at 900 °C for 4 h.

Fig. 2 indicates the SEM micrographs of 2 $ZnO–V_2O_5$ doped BTMNN-2 ceramics. On the one hand, it can be seen that the microstructure became more and more dense but grains grew only slightly. With increasing the amount of 2 $ZnO–V_2O_5$ additive, the content of the residual liquid phase can be seen more clearly in the microstructure (Fig. 2(d)). Because there is a low eutectic point in $ZnO–V_2O_5$ binary system, the liquid phase can be formed at a relatively low temperature and tends to promote the rearrangement of the particles and the mass transportation during sintering. However, excessive amount of 2 $ZnO–V_2O_5$ additive not only tends to degrade the densification owing to the rapid grain growth, but also leaves much more glass phase in the final microstructure. On the other hand, as the content of 2 $ZnO–V_2O_5$ was fixed at 5 wt%, the increase of sintering temperature obviously induced inhomogeneous grain growth, which would degrade the sintering behavior of the samples. It is indicated that the SEM observation exhibited a good consistency with the measurement of the relative density in Fig. 1.

Fig. 3 illustrates the XRD patterns of the x wt% 2 $ZnO–V_2O_5$ doped BTMNN-2 ceramics sintered at 900 °C for 4 h. Compared to the standard card, it can be seen that all

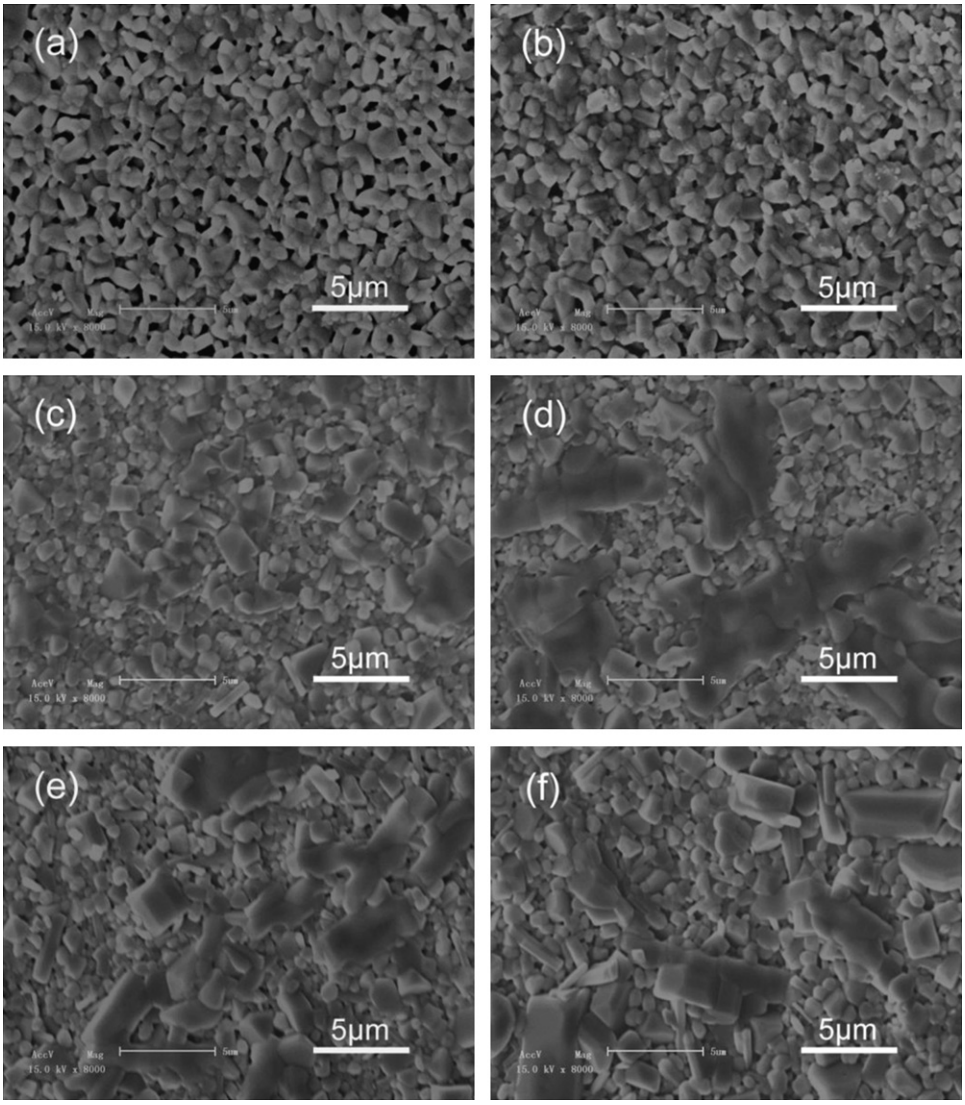

Fig. 2. SEM micrographs of BTMNN-2 samples doped with x wt% 2 ZnO–V_2O_5 sintered at 900 °C for 4 h: (a) $x=1$ wt%, (b) $x=3$ wt%, (c) $x=5$ wt%, (d) $x=6$ wt%, and doped with 5 wt% 2 ZnO–V_2O_5 sintered at different sintering temperatures: (e) 950 °C for 4 h and (f) 975 °C for 4 h.

samples showed a single hexagonal structure without detectable secondary phases. Moreover, it is interesting to note that the lattice parameters did not obviously change because a detectable shift of diffraction peaks was not observed. The results probably indicate that there was not an obvious reaction between BTMNN-2 and 2 ZnO–V_2O_5 additive. Most of the 2 ZnO–V_2O_5 liquid phase formed at high temperatures probably transforms into the glass phase at room temperature, as can be seen from Fig. 2. It is still possible that a slight amount of 2 ZnO–V_2O_5 liquid phase changed into the crystalline phase although it was not detected by XRD, which might have an effect on the electrical properties of the ceramics.

The dielectric constant ε_r of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics as a function of sintering temperature is illustrated in Fig. 4. The dielectric constant of all samples increased with the increase of sintering temperature and then reached a platform particularly as the doping content of 2 ZnO–V_2O_5 was in the range from 1 to 4 wt%, showing a similar tendency to the bulk density. This is because the ε_r values are highly dependent on the relative density of the sintered bodies. Glass phases or porosities with low ε_r values tend to degrade the dielectric property based on the mixing rule of dielectrics [18,19] as expressed by the Maxwell–Wagner's equation. As the 2 ZnO–V_2O_5 liquid phase existed in the form of glass phase, the dielectric constant of the samples would be degraded even if the sintering behavior was obviously improved. The maximum values of ε_r in the studied sintering temperature range slightly decreased from 51.6 to 45.8 with the increase of 2 ZnO–V_2O_5 content. The 5 wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics have an ε_r value of 47 as sintered at 900 °C.

Fig. 5 indicates the quality factors of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics as a function of sintering temperature. With the increase of sintering temperature, the $Q \times f$ value of the specimens increased to a maximum value,

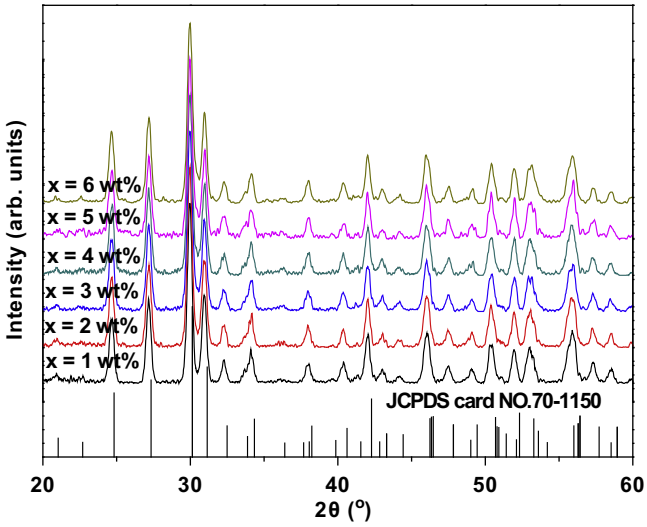

Fig. 3. XRD patterns of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics sintered at 900 °C for 4 h.

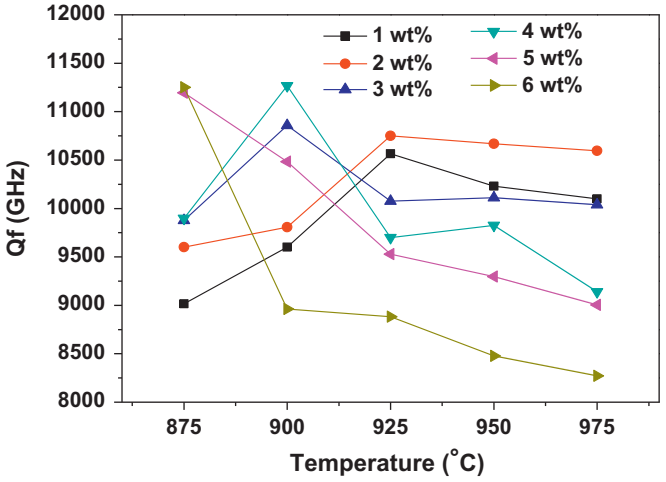

Fig. 5. The quality factors of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics as a function of sintering temperature.

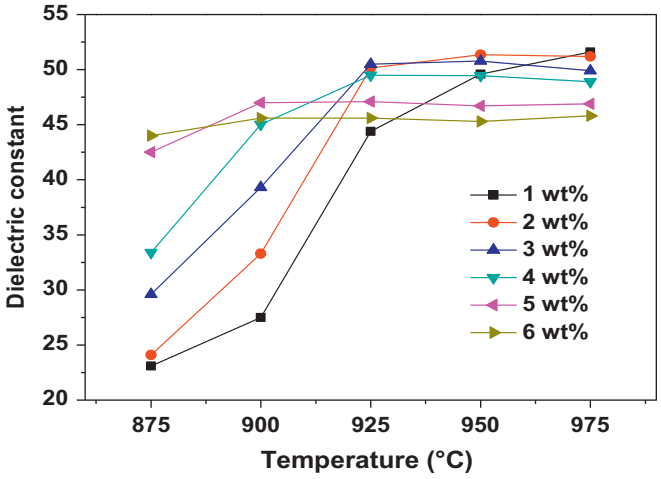

Fig. 4. Dielectric constants of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics as a function of sintering temperature.

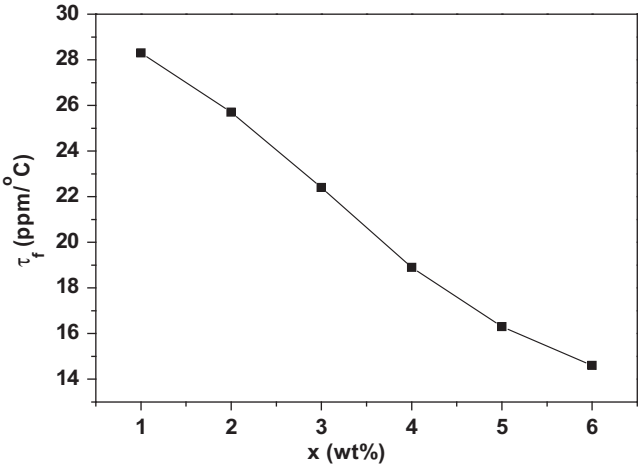

Fig. 6. The τ_f value of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics sintered at their optimum sintering temperatures.

and decreased thereafter. The increase of the $Q \times f$ value can be attributed to the reduction of the extrinsic loss, such as the crystal defects and grain boundaries [20,21], as the densification increased during sintering. The temperature, at which the $Q \times f$ value reaches the maximum, obviously decreased with increasing the content of 2 ZnO–V_2O_5 additive because of the optimum densification behavior. Glass phases from the 2 ZnO–V_2O_5 liquid phase may decrease the quality factor, yet some ZnO–V_2O_5 compounds were reported to have a high quality factor [14] although these compounds were not clearly detected from the XRD patterns. The deterioration of the $Q \times f$ values was mainly caused by the inhomogeneous grain growth, as shown in Fig. 2(f). In addition, it can be seen that all samples had $Q \times f$ values of more than 8000 GHz. The 5 wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics had a $Q \times f$ value of 10,500 GHz. In addition, the τ_f value of the x wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics sintered at their optimum sintering temperatures is shown in Fig. 6. It can be seen that the τ_f value of BTMNN-2 ceramics slightly declined with increasing the 2 ZnO–V_2O_5 content. The τ_f value is known to be governed by the composition, additive and secondary phase of the materials [22]. The higher 2 ZnO–V_2O_5 content seems to reduce the τ_f value of BTMNN-2 ceramic. The τ_f value could reach ~16 ppm/°C as the additive content increased to 5 wt%. From the above results, one can see that ZnO–V_2O_5 complex additive proves to be an effective sintering aid, and simultaneously maintains its good microwave dielectric properties.

4. Conclusions

The BTMNN-2 ceramics sintered at 1270 °C exhibited good microwave dielectric properties of $\varepsilon_r = 57$, $Q \times f = 18{,}500$ GHz and $\tau_f = 25$ ppm/°C, but their sintering temperature was too high to be used in LTCC devices. When 2 ZnO–V_2O_5 was added, the BTMNN-2 ceramics could be well sintered at

temperatures between 900 and 950 °C. The XRD analysis reveals that the 2 ZnO–V_2O_5 doped BTMNN-2 ceramics formed a single hexagonal structure without any detectable secondary phase. The SEM micrographs indicate that the improvement of sintering behavior could be attributed to the formation of ZnO–V_2O_5 liquid phases. The 5 wt% 2 ZnO–V_2O_5 doped BTMNN-2 ceramics can be sintered at 900 °C and exhibit good microwave dielectric properties of $\varepsilon_r = 47$, $Q \times f = 10{,}500$ GHz, and $\tau_f = 16$ ppm/ °C. These results demonstrate that the 2 ZnO–V_2O_5 doped BTMNN-2 ceramics could be a good mid-permittivity material for LTCC applications.

Acknowledgements

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