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Ultralow temperature cofired $BiZn_2VO_6$ dielectric ceramics doped with B_2O_3 and Li_2CO_3 for ULTCC applications

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Abstract

In this paper, $BiZn_2VO_6$ doped with sintering aids of B_2O_3 and Li_2CO_3 is investigated in order to broaden the options for ultralow temperature cofired ceramics (ULTCC). The sintering behavior, microstructure and microwave dielectric properties are studied. In combination with 1 wt% B_2O_3 and 5 wt% Li_2CO_3 dopants, the sintering temperature of the $BiZn_2VO_6$ ceramics was reduced from 780 °C to 600 °C. The co-doped $BiZn_2VO_6$ ceramics exhibited a low relative permittivity (ε_r) of 8.9 and a quality factor ($Q \times f$) of 13,000 GHz at a microwave-range frequency of 9 GHz. The temperature coefficient of resonant frequency (τ_f) was measured to be -97 ppm/°C. The average linear coefficient of thermal expansion (CTE) was 7.2 ppm/°C. With the low sintering temperature, the co-doped $BiZn_2VO_6$ ceramics are compatible to be cofired with cost-effective aluminum electrodes. This was proven in a reaction test between the $BiZn_2VO_6$-B_2O_3-Li_2CO_3 and aluminum powders, in which no chemical interaction could be detected. These promising properties make the B_2O_3-Li_2CO_3 co-doped $BiZn_2VO_6$ an ideal candidate for ULTCC applications.

Keywords: ULTCC, low-temperature sintering, sintering aid, microwave dielectric property, aluminum electrode

1. Introduction

Microwave dielectrics play a crucial role in modern society. They can be used, for example, in applications for terrestrial and satellite communications, environmental monitoring, global positioning systems (GPS) and the Internet of Things (IoT). In particular,

low-loss dielectric ceramics have triggered a revolution in the microwave wireless communication industry by reducing the size and cost of the filters, oscillators and antenna elements. Microwave dielectrics ideally need to be sintered at low temperature for the purpose of energy saving as well as for the improvement of their cofiring compatibility with cost-effective metallic electrodes.[1-3] In order to address this issue, low temperature cofired ceramics (LTCC) technology has been developed for the manufacture of miniaturized, lightweight and integrated electronic components, modules, substrates and devices.[4-6] The microwave dielectrics fabricated through the LTCC route have suitable relative permittivity (ε_r) (high for miniaturization and low for fast signal transmission), high quality factor ($Q \times f$, >5000 GHz), a quasi-zero temperature coefficient of resonant frequency (-10 ppm/°C $\leq \tau_f \leq$ +10 ppm/°C to guarantee temperature stability) and a sintering temperature below 1000 °C (compatible with Ag, Au, Cu and their alloys as electrodes).[7,8] However, compared to the preferred Al (melting point of only 660 °C), the electrode options mentioned above are still costly.

In order to incorporate Al, the dielectrics need to be able to densify at below 700 °C, making development of ultralow temperature cofired ceramics (ULTCC) very important.[9,10] The sintering temperature of ceramics can be decreased by the addition of low melting point glasses such as BBSZ (B_2O_3-Bi_2O_3-SiO_2-ZnO), LZB (Li_2O-ZnO-B_2O_3), ZBS (ZnO-B_2O_3-SiO_2) and La_2O_3-B_2O_3,[11-15] or by the addition of sintering aids. A composition containing 17 mol% B_2O_3 and 83 mol% Li_2CO_3 (equivalent to 1:5 in weight ratio) shows a low melting point of < 600 °C according to the phase diagram.[16-18] Hu *et al.*[19] added 1 wt% B_2O_3 and 5 wt% Li_2CO_3 into $BaSrTiO_3$-MgO (BSTM) ceramics and successfully reduced the

sintering temperature from 1400 °C to 920 °C whilst maintaining good dielectric and paraelectric properties.

In our previous work,[20] the LTCC $BiZn_2VO_6$ sintered at 780 °C exhibited promising microwave dielectric properties, e.g. ε_r = 15, $Q \times f$ = 20,640 GHz and τ_f = -88 ppm/°C. And the $BiVO_4$ has also been reported as a microwave dielectric material with low temperature (at 820 °C) and good dielectric properties.[21,22] The phase diagram of the ZnO-$BiVO_4$ system has been reported by Bosacka *et al.*[23] as shown in Figure 1(a). The melting point of the $BiZn_2VO_6$ compound is 805 °C. The crystal structure of the $BiZn_2VO_6$ unit cell is shown in Figure 1(b), where Bi atoms are connected with seven oxygen atoms forming [BiO_7] polyhedra. There are two types of Zn atoms. Each Type I Zn atom (grey atoms in Figure 1(b)) is bound by six oxygen atoms and Type II (green atoms in Figure 1(b)) by four oxygen atoms, forming [ZnO_6] and [ZnO_4] sharing corners, respectively. Each V atom is bound by four oxygen atoms, forming [VO_4] tetrahedra. The [VO_4] and [ZnO_4] tetrahedra share corners, while the [VO_4] tetrahedra and [BiO_7] polyhedra share edges.

In this work, based on the $BiZn_2VO_6$ matrix, 1 wt% B_2O_3 and/or 5 wt% Li_2CO_3 are added individually or collaboratively as the sintering aids. The effect of different sintering aids, i.e. 1 wt% individual B_2O_3, 5 wt% individual Li_2CO_3 and 1 wt% B_2O_3 + 5 wt% Li_2CO_3, on the sintering behavior and microwave dielectric properties of the $BiZn_2VO_6$ ceramics is discussed in detail. In addition, the chemical compatibility with Al is investigated.

2. Experimental

Reactants of Bi_2O_3 (> 99%, Alfa Aesar GmbH & Co KG, Germany), ZnO (> 99%, Alfa Aesar GmbH & Co KG, Germany) and V_2O_5 (> 99.6%, Sigma-Aldrich, Co., USA) were mixed in a ball milling machine for 4 h with zirconia balls, a polyethylene jar as the container and ethanol as the intermediary. The mixture was dried at 120 °C before being calcined at 780 °C for 4 h with a heating rate of 3 °C/min. The calcined powder was subsequently mixed with 1 wt% B_2O_3 (> 99%, Alfa Aesar GmbH & Co KG, Germany), 5 wt% Li_2CO_3 (> 98.0%, Sigma-Aldrich, Co., USA) or 1 wt% B_2O_3 + 5 wt% Li_2CO_3 through the same ball milling procedure. After drying (at 120 °C), the calcined and doped powders were pressed into green discs (10 mm diameter and 5 mm thickness) under a pressure of 100 MPa. Finally, the $BiZn_2VO_6$-B ($BiZn_2VO_6$ + 1 wt% B_2O_3), $BiZn_2VO_6$-L ($BiZn_2VO_6$ + 5 wt% Li_2CO_3) and $BiZn_2VO_6$-BL ($BiZn_2VO_6$ + 1 wt% B_2O_3 + 5 wt% Li_2CO_3) discs were sintered at 640-720 °C, 600-680 °C and 540-620 °C, respectively, for 4 h with a heating rate of 3 °C/min.

The phase composition and crystal structure of the sintered samples were analyzed by X-ray diffractometer (XRD, Bruker D8, Germany). Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were studied using an STA 499 F3 Jupiter (NETZSCH, Germany). The thermal etched surfaces of the samples were obtained at 500 °C/10 min and microstructures were observed using field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus, Germany) equipped with Energy-dispersive X-ray Spectroscopy (EDS). The bulk densities were determined by the Archimedes method. The linear shrinkage and coefficient of thermal expansion (CTE) were measured using a dilatometer (DIL 402 PC/4, NETZSCH, Germany). The ε_r and $Q \times f$ values were measured

using a vector network analyzer (10 MHz-20 GHz, ZVB20, Rohde & Schwarz, Germany). With the help of a temperature chamber (SU261, ESPEC, Japan), the τ_f and temperature coefficient of relative permittivity (τ_ε) were measured and calculated from Equations (1) and (2)[24,25] in the temperature range of 25-90 °C.

$$\tau_f = \frac{f_{90} - f_{25}}{f_{25}(T_{90} - T_{25})} \quad (1)$$

$$\tau_\varepsilon = -2(\tau_f + \mathrm{CTE}) \quad (2)$$

In Equation (1), f_{25} and f_{90} represent the resonant frequencies at temperatures T_{25} (25 °C) and T_{90} (90 °C), respectively.

Additionally, 20 wt% Al power was mixed with $BiZn_2VO_6$-BL powder in an agate mortar. The mixture was pressed into green discs and cofired at 600 °C for 4h in order to test the chemical compatibility of the powders. The temperature compensated material could be fabricated by adding an appropriate concentration of TiO_2 (rutile, >99%, Alfa Aesar GmbH & Co KG, Germany) to $BiZn_2VO_6$-BL ceramics. According to the stoichiometry (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.1, 0.15, 0.2, 0.25), TiO_2 powder was mixed with base $BiZn_2VO_6$-BL material and sintered at 600 °C for 4h.

3. Results and discussion

Figure 2 compares the linear shrinkage of the $BiZn_2VO_6$ ceramics doped with different sintering aids. Both the pure $BiZn_2VO_6$ and $BiZn_2VO_6$-B started to shrink at 600 °C, but with different saturated shrinkages of 21 % and 17 % achieved at 730 °C and 680 °C, respectively. The $BiZn_2VO_6$-L began its densification at a lower temperature (around 570 °C) than the pure $BiZn_2VO_6$ and $BiZn_2VO_6$-B. However, the shrinkage saturated at a similar level of 20 %

at a lower temperature (650 °C) compared to the samples of pure $BiZn_2VO_6$. Despite of the smallest shrinkage of 12 %, the $BiZn_2VO_6$-BL showed both the lowest shrinkage starting (525 °C) and saturation (600 °C) temperatures among all the compositions. This was due to the co-doping of B_2O_3 and Li_2CO_3 which individually proved their abilities to reduce the shrinkage temperatures to different extents, as shown in Figure 2. It also indicated that the co-doping could most effectively reduce the sintering temperature of pure $BiZn_2VO_6$.

Figure 3 shows the TGA/DSC curves of the $BiZn_2VO_6$-BL powder. In the DSC curve, two endothermic peaks were found, with the weaker at 500 °C corresponding to the melting of the B_2O_3-Li_2CO_3[16,26] while the stronger at 655 °C revealed the melting point of the powder. Because of the presence of the B_2O_3 and Li_2CO_3, the melting point was reduced from 805 °C to 655 °C. Together with those shown in Figure 2, this also indicated that co-doping of B_2O_3 and Li_2CO_3 can act as an effective sintering aid.

Figure 4 shows the XRD patterns of the $BiZn_2VO_6$ doped with different additives and sintered at different temperatures. The main phase of $BiZn_2VO_6$ with the *P-1* space group could be clearly seen in all samples. For the $BiZn_2VO_6$-L, a weak peak belonging to Li_2CO_3 (PDF# 09-0359) was detected at 21° (Figure 4(c)). The reason might be that the 5 wt% Li_2CO_3 cannot completely diffuse into the grain boundaries. The same secondary phase was not recognized in $BiZn_2VO_6$-BL, since the 1 wt % B_2O_3-5 wt% Li_2CO_3 composition started to melt at around 500 °C and may have diffused into the main phase when sintered at 600 °C.

Figure 5 consists of the thermal etched FESEM images of the $BiZn_2VO_6$–B, $BiZn_2VO_6$–L and $BiZn_2VO_6$–BL (Figure 5(a)-(c)) and the EDS spectra of the $BiZn_2VO_6$–BL. All the samples showed a relatively dense microstructure with few closed pores observed. All

grains showed identical compositions with the Bi, Zn and V elements in the ratio close to 1:2:1 due to the EDS studies.

The bulk densities and ε_r (at 9 GHz) of the $BiZn_2VO_6$–B, $BiZn_2VO_6$–L and $BiZn_2VO_6$–BL ceramic samples as a function of sintering temperature are plotted in Figure 6. The optimum densities with these three compositions were achieved after sintering at 700 °C, 660 °C and 600 °C, respectively (Figure 6(a)). The 600 °C for the $BiZn_2VO_6$-BL ceramic makes it feasible for cofiring with Al electrodes, thus enabling the ULTCC configuration. Similar trends can be found on the ε_r (Figure 6(b)), where the optimum values were obtained correspondingly with the optimum densities. It is known that the ε_r depends mainly on the density, ionic polarizability and secondary phase.[27-30] The optimum ε_r values shown in Figure 6(b) are 9.7, 9.2 and 8.9 for the $BiZn_2VO_6$-B, $BiZn_2VO_6$-L and $BiZn_2VO_6$-BL, respectively. The decreased ε_r values compared to that of the pure $BiZn_2VO_6$ (~15) may be due to the lower densities and increased doping concentration degrading the ionic polarizability.

The $Q\times f$ and τ_f values as a function of sintering temperature measured at 9 GHz for all samples are shown in Figure 7. The trends in Figure 7(a) also follow those shown in Figure 6. The decrease of $Q\times f$ beyond the optimum sintering temperature may be because of diffusion and/or evaporation of the dopants leading to the formation of extra pores, thus decreasing the density and the dielectric properties.[31,32] The $BiZn_2VO_6$-B showed the highest $Q\times f$ value of 20,160 GHz (sintered at 700 °C) among the three compositions. It then decreased with the amount of dopant (14,500 GHz for $BiZn_2VO_6$-L sintered at 660 °C and 13,000 GHz for $BiZn_2VO_6$-BL sintered at 600 °C). This may be attributed to the additional Li_2CO_3 phase with highly mobile Li^+ ions present in the composites, leading to increased leakage and dielectric

loss.[33-35] The τ_f values were also different due to the sintering temperatures (Figure 7(b)). In the range of 25-90 °C, the τ_f values of the $BiZn_2VO_6$-B, $BiZn_2VO_6$-L and $BiZn_2VO_6$-BL were -78 ppm/°C, -90 ppm/°C, and -97 ppm/°C, respectively, but showing a very linear dependence on temperature. Considering the balance between the sintering temperature and dielectric properties, the $BiZn_2VO_6$-BL is the most suitable candidate for ULTCC applications.

Apart from the above-mentioned, the coefficient of thermal expansion (CTE) is also an important factor for microwave device integration, especially when two materials are co-fired. Figure 8 shows the CTE curve of the $BiZn_2VO_6$-BL ceramic in the temperature range of 25-400 °C. The average value was calculated to be 7.2 ppm/°C. At microwave frequency the temperature dependence of relative permittivity (τ_ε) value was 179.6 ppm/°C (calculated from Equation (2)).

Figure 9 shows the XRD pattern and backscattered electron image of the cofired $BiZn_2VO_6$-BL + 20 wt% Al mixture. No emerging peak, apart from those belonging to the $BiZn_2VO_6$–BL and Al, was found in the XRD pattern, implying that there was no reaction occurring between the two compositions. This is also supported by the backscattered electron image in which two distinctive types of grains were observed. The obviously larger grains represent pure aluminum particles. This proves that the $BiZn_2VO_6$-BL ceramic is fully compatible with Al electrodes.

The microwave dielectric properties of low temperature cofired ceramics with permittivity between 8.5 and 10 are given in Table 1. It can be seen that most low temperature cofired ceramics have a high $Q \times f$ and can cofire with Ag or Al electrode.

However, a large negative τ_f is a common issue for all these low temperature cofired ceramics. Despite these facts, $BiZn_2VO_6$-BL ceramic possesses an ultralow sintering temperature of 600 °C, which is an environment-friendly and low-cost material for ULTCC applications.

To tune τ_f through zero, one of the approaches is to combine two materials having opposite τ_f values. TiO_2 has been reported to possess high positive $\tau_f \sim 460$ ppm/°C.[51] In this work, TiO_2 was add to $BiZn_2VO_6$-BL to form a (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.1, 0.15, 0.2, 0.25) composite ceramic for tuning its τ_f through zero. Figure 10 shows the XRD pattern of (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.2) ceramic sintered at 600 °C for 4h. All of the diffraction peaks match well with the $BiZn_2VO_6$ and rutile TiO_2 (JCPDS #76-0317), indicating that there was no chemical reaction between them.

Figure 11 shows the temperature dependences of the resonant frequency in the temperature range of 25−90 °C. It can be seen that the resonant frequencies of x = 0.1 and 0.15 decrease almost linearly with temperature, and their τ_f is about -51.6 and -20.7 ppm/°C. However, when x is increased to 0.2 and 0.25, their resonance frequencies increase linearly with temperature, and their τ_f is positive 5.1 and 39.8 ppm/°C. Table 2 lists the microwave dielectric properties of (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.1, 0.15, 0.2, 0.25) ceramics sintered at 600 °C for 4h. The τ_f values of (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ increased from -97 to +39.8 ppm/°C with the increase in TiO_2 content from 0 to 0.25 mol and a near zero τ_f = +5.1 ppm/°C was achieved for the composition with 20% addition of TiO_2 content.

4. Conclusions

Different sintering aids (1 wt% B_2O_3, 5wt% Li_2CO_3 and 1 wt% B_2O_3 + 5wt% Li_2CO_3) have been doped into $BiZn_2VO_6$ ceramics in order to reduce the sintering temperature. The co-doping of 1 wt% B_2O_3 and 5 wt% Li_2CO_3 has been proved to be an effective sintering aid which has reduced the densification temperature from 780 °C to 600 °C. With the co-doped $BiZn_2VO_6$, a low relative permittivity (ε_r) of 8.9, a quality factor ($Q\times f$) of 13,000 GHz (at 9 GHz), a temperature coefficient of resonant frequency (τ_f) of -97 ppm/°C and an average linear coefficient of thermal expansion (CTE) of 7.2 ppm/°C in the temperature range of 25-400 °C have been obtained. A near zero τ_f of $0.8BiZn_2VO_6$-BL-$0.2TiO_2$ ceramic was obtained at 600 °C, which has the microwave dielectric properties: $\varepsilon_r \sim 13.0$, $Q\times f \sim 10{,}050$ GHz and $\tau_f \sim +5.1$ ppm/°C. With the proven chemical inertia between the co-doped composition and 20 wt% Al, the $BiZn_2VO_6$-BL ceramic is claimed to be a suitable candidate for microwave dielectric ULTCC.

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Table 1 The metal electrodes compatibility and microwave dielectric properties of low temperature cofired ceramics with permittivity between 8.5 and 10

Compositions	Phase	S.T.[a] (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	Compatibility with metal electrodes	Reference
$Li_2Ca_2Mo_3O_{12}$	Li_2MoO_4+$CaMoO_4$	630	8.5	108,000	-89	Ag and Al	[36]
$MnMoO_4$	Pure	900	8.55	54,100	-73.91	/[b]	[37]
$LiSrBO_3$	Pure	800	8.6	60,000	-39	Ag	[38]
$ZnMoO_4$	Pure	800	8.67	49,900	-87.49	/	[37]
$LiCaBO_3$	Pure	800	8.7	75,000	-150	Ag	[38]
$Mg_3(VO_4)_2$	Pure	950	8.8	61,948	-93.2	Ag	[39]
$LiMgVO_4$	Pure	700	8.86	23,300	-140	Ag	[40]
$BiZn_2VO_6$-BL	Pure	600	8.9	13,000	-97	Al	This work
$BaCaV_2O_7$	Pure	830	8.9	31,362	-68.2	Ag	[41], [42]
$ZnCu_2Nb_2O_8$	Pure	985	8.9	23,350	-17.7	/	[43]
$BiZn_2VO_6$-L	$BiZn_2VO_6$+Li_2CO_3	660	9.2	14,500	-90	/	This work
$Ca_5Mg_4(VO_4)_6$	Pure	800	9.2	53,300	-50	/	[44]
$BaMoO_4$	Pure	900	9.3	37,200	-79.24	/	[37]
$Bi_2Ge_3O_9$	$Bi_2Ge_3O_9$+$Bi_4Ge_3O_{12}$	850	9.4	29,911	-29.5	/	[45]
$Li_3AlMo_3O_{12}$	Pure	570	9.5	50,000	-73	Ag and Al	[36]
$Ba_2V_2O_7$	Pure	840	9.6	30,315	-32	/	[46], [47]
$BiZn_2VO_6$-B	Pure	700	9.7	20,160	-78	/	This work
$Li_3InMo_3O_{12}$	Pure	630	9.8	36,000	-73	Ag and Al	[36]
$BiCa_2VO_6$	Pure	950	9.9	23,580	-71.4	Ag	[48]
$BaTeO_3$	$BaTeO_3$+$BaTeO_4$	800	10	34,000	-54	/	[49]
$NaCa_2Mg_2V_3O_{12}$	Pure	915	10	50,600	-47	Ag	[50]

[a] Sintering temperature; [b] Not studied

Table 2 Microwave dielectric properties of (1-*x*)$BiZn_2VO_6$-BL-*x*TiO_2 (*x* = 0.1, 0.15, 0.2, 0.25) ceramics sintered at 600 °C for 4h

x	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0	8.9	13,000	-97
0.1	9.9	12,300	-51.6
0.15	11.2	11,700	-20.7
0.2	13.0	10,050	+5.1
0.25	15.1	9,250	+39.8
1[51]	105	46,000	+460

Figure captions:

Figure 1 (a) Phase diagram of the ZnO-$BiVO_4$ system,[23] (b) Crystal structure of the $BiZn_2VO_6$ unit cell.

Figure 2 Dependence of linear shrinkage on sintering temperature for the $BiZn_2VO_6$ doped with different sintering aids. The inset shows the variation of shrinkage in the higher temperature area (from 400 to 800 °C).

Figure 3 TGA/DSC curves of the composition $BiZn_2VO_6$ + 1 wt% B_2O_3 + 5 wt% Li_2CO_3.

Figure 4 XRD patterns of (a) pure $BiZn_2VO_6$ sintered at 780 °C, (b) $BiZn_2VO_6$ doped with 1 wt% B_2O_3 ($BiZn_2VO_6$-B) sintered at 700 °C, (c) $BiZn_2VO_6$ doped with 5 wt% Li_2CO_3 ($BiZn_2VO_6$-L) sintered at 660 °C and (d) $BiZn_2VO_6$ doped with 1 wt% B_2O_3 and 5 wt% Li_2CO_3 ($BiZn_2VO_6$-BL) sintered at 600 °C.

Figure 5 The thermal etched FESEM images of (a) $BiZn_2VO_6$-B sintered at 700 °C, (b) $BiZn_2VO_6$-L sintered at 660 °C and (c) $BiZn_2VO_6$-BL sintered at 600 °C, (d) EDS analysis of the grains marked in (c).

Figure 6 Dependence of (a) bulk density and (b) ε_r on sintering temperature for the $BiZn_2VO_6$ ceramics doped with different additives.

Figure 7 Dependence of $Q \times f$ and τ_f on sintering temperature for the $BiZn_2VO_6$ ceramics with different dopants measured at 9 GHz.

Figure 8 Dependence of linear shrinkage on measurement temperature for the $BiZn_2VO_6$-BL ceramics with CTE value calculated and labeled.

Figure 9 XRD pattern and backscattered electron image (inset) of the $BiZn_2VO_6$-BL and 20 wt% Al powder mixture cofired at 600 °C for 4h.

Figure 10 XRD pattern of (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.2) ceramic sintered at 600 °C for 4h.

Figure 11 Resonant frequencies of (1-x)$BiZn_2VO_6$-BL-$x$$TiO_2$ (x = 0.1, 0.15, 0.2, 0.25) ceramics sintered at 600 °C over 25−90 °C.