Microwave dielectric properties of doped Zn$_3$Nb$_2$O$_8$ ceramics sintered below 950 °C and their compatibility with silver electrode

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Abstract

Zn$_3$Nb$_2$O$_8$ has been considered as candidate microwave materials due to its high quality factor. However, Zn$_3$Nb$_2$O$_8$ has to be sintered above 1200 °C. We have lowered Zn$_3$Nb$_2$O$_8$ sintering temperature to 950 °C by using 3 wt.% of BC additives (0.29BaCO$_3$–0.71CuO). The doped Zn$_3$Nb$_2$O$_8$ exhibits good microwave properties at 8.3 GHz ($\varepsilon_r = 14.7$, $Q \times f = 8200$ GHz). The interfacial behavior between Zn$_3$Nb$_2$O$_8$ dielectric and silver was investigated by using X-ray diffractometer, scanning electronic microscope, and electronic probe microanalyzer. No new crystalline phase and no silver migration behavior were found after cofiring doped Zn$_3$Nb$_2$O$_8$ and silver electrode at 950 °C for 4 h. The low sintering temperature BC doped Zn$_3$Nb$_2$O$_8$ with high $Q \times f$ value has a potential for microwave applications.

Keywords: Zn$_3$Nb$_2$O$_8$; Microwave materials; Dielectric properties; Diffusion; Silver; Powders solid state reaction

1. Introduction

Most conventional ceramics that have excellent microwave dielectric properties such as BMT (BaMg$_{1/3}$Ta$_{2/3}$O$_3$), BNT (BaO–Nd$_2$O$_3$–TiO$_2$), etc. have sinterability above 1300 °C. Because of the high sintering temperature, Ag–Pd electrode is the only choice for multilayer ceramic components (MLCCs). In the microwave frequency range, the dielectric loss of components is mostly attributed to the electrode. The good conductivity of the electrode is important for MLCCs. Thus, it is desirable to replace the poor conductivity and high cost Ag–Pd electrode with the better properties and lower cost of silver electrodes. However, the melting temperature of silver is low (961 °C). A low sintering temperature material is required to cofire with the silver.

Recently, Zn$_3$Nb$_2$O$_8$ has emerged as a good microwave material because it exhibits high quality factor [1–5]. The sintering temperature can be further decreased to 850 °C by adding 2 mol% V$_2$O$_5$ to Zn$_3$Nb$_2$O$_8$, but silver migration behavior was found after firing the mixture of V$_2$O$_5$ doped Zn$_3$Nb$_2$O$_8$ and silver to determine whether the CuO-based additives for Zn$_3$Nb$_2$O$_8$ can be cofired with silver. X-ray diffractometer, scanning electron microscope, and electronic probe micro-analyzer were used to evaluate the extent of silver migration. The results are reported here.

2. Experimental

Copper oxide has been known as a good sintering aid and less reactive toward silver [5–9]. Therefore, we studied two eutectic compounds of CuO, 0.81MoO$_3$–0.19CuO [10] and 0.29BaCO$_3$–0.71CuO [11] as sintering aid to lower the sintering temperature of Zn$_3$Nb$_2$O$_8$. We also investigated the interfacial behavior between the doped Zn$_3$Nb$_2$O$_8$ and silver to determine whether the CuO-based additives for Zn$_3$Nb$_2$O$_8$ can be cofired with silver. X-ray diffractometer, scanning electron microscope, and electronic probe micro-analyzer were used to evaluate the extent of silver migration. The results are reported here.
Fig. 1. XRD patterns of Zn$_3$Nb$_2$O$_8$ powders calcined at different temperatures for 4 h.

The dielectric properties of sintered Zn$_3$Nb$_2$O$_8$ series tablets were evaluated by network analyzer (Hewlett Packard, 8722ES Network Analyzer, USA).

For the silver migration study, samples were prepared by printing silver electrode over dense Zn$_3$Nb$_2$O$_8$ series tablets and cofiring the products at various temperatures for 4 h. The diffusion distance and concentration of silver were determined by electronic probe micro-analyzer (EPMA) equipped with wavelength dispersive spectrometer. The microstructures of sintered samples were evaluated by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (Philips, XL-30, The Netherlands).

3. Results and discussion

The Zn$_3$Nb$_2$O$_8$ has been prepared by the solid mixing method. The Zn$_3$Nb$_2$O$_8$ powder was calcined at 900, 1000 and 1100 $^\circ$C, respectively. The calcined Zn$_3$Nb$_2$O$_8$ powders were investigated with XRD. As shown in Fig. 1, a pure single phase of Zn$_3$Nb$_2$O$_8$ was formed when the powder was sintered at 1100 $^\circ$C. At 900 $^\circ$C, a phase of ZnNb$_2$O$_6$ containing ZnO was formed. At 1000 $^\circ$C, a major phase of ZnNb$_2$O$_6$ combined with a secondary phase of Zn$_3$Nb$_2$O$_8$ was found. The existence of secondary phase or other component degraded the dielectric

Table 1 Specific surface area and particle size of Zn$_3$Nb$_2$O$_8$ series powders

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m$^2$ g$^{-1}$)</th>
<th>Particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_3$Nb$_2$O$_8$</td>
<td>3.33</td>
<td>0.89</td>
</tr>
<tr>
<td>3.0 wt.% BC doped Zn$_3$Nb$_2$O$_8$</td>
<td>3.37</td>
<td>0.87</td>
</tr>
<tr>
<td>3.0 wt.% MC doped Zn$_3$Nb$_2$O$_8$</td>
<td>3.87</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Fig. 2. SEM surface structures of BC doped Zn$_3$Nb$_2$O$_8$ at (a) 1.0 wt.% (b) 3.0 wt.% and MC doped Zn$_3$Nb$_2$O$_8$ at (c) 1.0 wt.% (d) 3.0 wt.% at 950 $^\circ$C for 4 h.
Table 2
Molar ratio of Zn$_3$Nb$_2$O$_8$ series ceramics measured by EPMA

<table>
<thead>
<tr>
<th>Material</th>
<th>Sintering condition</th>
<th>Molar ratio of Zn$_3$Nb$_2$O$_8$ series ceramics sintered at 950 °C</th>
<th>Zn</th>
<th>Nb</th>
<th>Cu</th>
<th>Ba</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_3$Nb$_2$O$_8$</td>
<td>1150 °C, 4 h</td>
<td>3.0</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.0 wt.% BC doped Zn$_3$Nb$_2$O$_8$</td>
<td>950 °C, 4 h</td>
<td>3.0</td>
<td>2.0</td>
<td>0.01</td>
<td>0.03</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.0 wt.% MC doped Zn$_3$Nb$_2$O$_8$</td>
<td>950 °C, 4 h</td>
<td>3.0</td>
<td>2.0</td>
<td>0.01</td>
<td>–</td>
<td>0.02</td>
<td>–</td>
</tr>
</tbody>
</table>

properties of Zn$_3$Nb$_2$O$_8$; therefore, all Zn$_3$Nb$_2$O$_8$ powders were calcined at 1100 °C.

The chemical composition of calcined Zn$_3$Nb$_2$O$_8$ powder was analyzed by ICP-Mass and EPMA equipped with wavelength dispersive spectrometer. The amount of Zn and Nb remained the same before and after calcination. The specific surface area and particle size of the Zn$_3$Nb$_2$O$_8$ series powders are shown in Table 1.

The BC doped Zn$_3$Nb$_2$O$_8$ and MC doped Zn$_3$Nb$_2$O$_8$ ceramics were sintered at 950 °C for 4 h. Table 2 shows the chemical compositions of doped Zn$_3$Nb$_2$O$_8$ ceramics after sintering at 950 °C, which are the same as before sintering. Thus, the doped Zn$_3$Nb$_2$O$_8$ ceramics exhibit good composition stability. The choice of 950 °C sintering temperature is for the purpose of cofiring ceramics with silver.

The BC doped Zn$_3$Nb$_2$O$_8$ ceramics were sintered from 925 to 1050 °C for 4 h. Their dielectric properties are shown in Fig. 3. The microwave dielectric properties of BC doped Zn$_3$Nb$_2$O$_8$ ceramics are improved with increasing sintering temperature. However, their quality factor degraded when the amount of BC additives was more than 3.0 wt.%. Their XRD patterns indicate that the degradation was due to the existence of secondary phase (MoO$_3$).

For the silver migration study, samples of Zn$_3$Nb$_2$O$_8$ ceramics cofired with silver electrodes were analyzed by EPMA and...
Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Sintering condition</th>
<th>Relative density (%)</th>
<th>/GHz</th>
<th>/GHz</th>
<th>×</th>
<th>f (GHz)</th>
<th>Ag diffusion distance (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn3Nb2O8</td>
<td>1150 °C, 4 h</td>
<td>92.7</td>
<td>7.8</td>
<td>17.1</td>
<td></td>
<td>32500</td>
<td>0</td>
</tr>
<tr>
<td>3.0 wt.% BC doped Zn3Nb2O8</td>
<td>950 °C, 4 h</td>
<td>92.1</td>
<td>8.3</td>
<td>14.7</td>
<td></td>
<td>8200</td>
<td>0</td>
</tr>
<tr>
<td>3.0 wt.% MC doped Zn3Nb2O8</td>
<td>950 °C, 4 h</td>
<td>93.5</td>
<td>8.2</td>
<td>15.9</td>
<td></td>
<td>10200</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 4. Microwave dielectric properties of MC doped Zn3Nb2O8 ceramics were measured by network analyzer (a) dielectric constant, (b) Q × f value.

XRD. As shown in Table 3, there are no silver migrations in pure Zn3Nb2O8 and BC doped Zn3Nb2O8 ceramics. However, the MC doped Zn3Nb2O8 exhibited a silver migration with an average distance of 6 µm. The silver migration was possible due to the reaction between Ag and MoO3 to form Ag–Mo oxide compounds [8,9]. We tried to use XRD to confirm the formation of Ag–Mo oxide compounds. However, the concentration was too low to detect it.

4. Conclusion

Eutectic compounds 0.81MoO3–0.19CuO (MC) and 0.21BaCO3–0.79CuO (BC) are good sintering aids for Zn3Nb2O8. At 3.0 wt.% level, the sintering temperature can be reduced from 1150 to 950 °C. The MC additive is a better sintering aid than BC additive in terms of densification and dielectric properties of Zn3Nb2O8. However, an active MoO3 ingredient causes a silver migration, when the MC doped Zn3Nb2O8 was cofired with silver electrode at 950 °C. The BC doped Zn3Nb2O8 exhibited good overall properties such as low sintering temperature, inert to silver, and high quality factor (Q × f = 8200 GHz). It has a potential for microwave applications.

Acknowledgments


References