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A low-firing microwave dielectric material in Li_2O–ZnO–Nb_2O_5 system

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ABSTRACT

$LiZnNbO_4$ ceramic was fabricated by the conventional solid state reaction method and its microwave dielectric properties were reported for the first time. The phase structure, microstructure, and sintering behavior were also investigated. The $LiZnNbO_4$ ceramic could be well densified at around 950 °C and demonstrated high performance microwave dielectric properties with a low relative permittivity ~14.6, a high quality factor (resonant frequency/dielectric loss) ~47, 200 GHz (at 8.7 GHz), and a negative temperature coefficient of resonant frequency approzmiately −64.5 ppm/°C. The $LiZnNbO_4$ ceramic is chemically compatible with Ag electrode material at its sintering temperature. It can be a promising microwave dielectric material for low-temperature co-fired ceramic technology.

1. Introduction

To achieve the miniaturization of microwave components for wireless communication, low-temperature co-fired ceramic (LTCC) technology becomes an important method because of its predominance in enabling the fabrication of three-dimensional ceramic modules with low dielectric loss and co-fired metal electrodes. In order to use the most common electrode silver, the ceramic must have a low sintering temperature below 960 °C and chemical compatibility with Ag [1,2].

Traditionally high performance microwave dielectrics have high sintering temperatures (above 1000 °C) [3–7]. The addition of sintering aids, such as glasses, is the most often used method to lower the sintering temperatures [8–10]. Besides this, considerable attention has been paid recently to developing new microwave dielectrics with low or ultra-low sintering temperature [11–20], such as Li_2O-rich compounds, TeO_2-rich compounds, and MoO_3-rich compounds.

A great number of Lithium-based binary or ternary compounds have been developed as low-firing microwave dielectric ceramics, such as $LiNb_3O_8$ [13], Li_3NbO_4 [14], Li_2MoO_4, $(Li_{0.5}Bi_{0.5})$ MoO_4, $Li_8Bi_2Mo_7O_{28}$ [20], and Li_2O–Nb_2O_5–TiO_2 system [21,22]. The phases in the ternary system Li_2O–ZnO–Nb_2O_5 were explored fragmentarily [23–27]: $LiZnNbO_4$, $Li_{2.98}Zn_{0.51}Nb_2O_7$, $Li_6ZnNb_4O_{14}$, and $LiZnNb_4O_{11.5}$. Konovalova et al. [26] reported that the $Li_6ZnNb_4O_{14}$ is a conducting phase with conductivity 1.2×10^{-2} S cm^{-1}. The relationship between crystal structure and electric property for $LiZnNbO_4$ ceramic was studied by González et al., [23] and the result showed that $LiZnNbO_4$ is not a solid electrolyte. The $LiZnNbO_4$ compound has a tetragonal spinel structure belonging to the space group $P4_122$, and it is an ordering type with the niobium and lithium ions occupying the octahedral B sites and the cations Zn^{2+} occupying the tetrahedral A positions. In this work, the microwave dielectric properties of $LiZnNbO_4$ ceramic were reported for the fist time, and its chemical compatibility with silver electrode was investigated to check whether the $LiZnNbO_4$ ceramic is suitable for LTCC technology.

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of Li_2CO_3, ZnO, and Nb_2O_5 with high-purity (>99%) were prepared by mixed-oxide approach according to the stoichiometric $LiZnNbO_4$ composition. The final powders were calcined at temperatures between 900–950 °C for 5 h and the cylinder specimens (10 mm in diameter and 5 mm in height) were sintered in air at temperatures 875–1025 °C for 3 h.

The crystalline structures were investigated using X-ray diffraction (XRD) with Cu–Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The apparent densities were measured by Archimedes' method. The dielectric properties were measured at microwave frequency by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency (TCF) was calculated by the following formula:

$$TCF = \frac{f_{85}-f_{25}}{f_{25}(85-25)}\times 10^6 (\text{ppm}/^{\circ}\text{C}), \quad (1)$$

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where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

To check the chemical compatibility of $LiZnNbO_4$ ceramic with the silver powder, 20 wt.% powdered silver was mixed and homogenized with the ceramic powder [28], and then the mixture was pressed into pellets and fired at 950 °C for 3 h to achieve equilibrium. In addition to the XRD analysis, micro-structural study was conducted via scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan) coupled with energy-dispersive X-Ray spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows the XRD pattern of the $LiZnNbO_4$ ceramic sintered at its specific optimal sintering temperature. All the diffraction peaks of the $LiZnNbO_4$ ceramic could be indexed as a tetragonal structure ($P4_122$) without a second phase, and the lattice parameters were calculated as $a = 6.0835$, $c = 8.4172$, which agreed well with the result reported by González et al. [23].. SEM micrograph (the insert part of Fig. 1) of the as-fired surface demonstrates the microstructure of the $LiZnNbO_4$ ceramic sintered at 950 °C. It shows that well densified $LiZnNbO_4$ ceramic with little pores was obtained after being sintered at 950 °C for 3 h. The grain sizes were found to lie between 2 and 6 μm.

The bulk density and the relative density of $LiZnNbO_4$ ceramic vs. sintering temperature are shown in Table 1. When the $LiZnNbO_4$ ceramic was sintered at 950 °C, the bulk density reached up to 4.75 g/cm^3 and the relative density was as high as 97%, which indicated that the densified temperature of $LiZnNbO_4$ ceramic was around 950 °C, lower than the melting temperature of silver (960 °C).

Table 1 also presents the microwave dielectric properties of $LiZnNbO_4$ ceramics. As the sintering temperature increased from 875 to 950 °C, the permittivity increased continually from 13.4 to 14.6, and it reached saturation when the sintering temperature increased further. The maximum Qf value (quality factor, $Q = 1$/dielectri loss (tan δ), and f = resonant frequency) of about 47,200 GHz (at 8.7 GHz) was obtained in the $LiZnNbO_4$ ceramic sintered at 950 °C. The TCF value was stable with the sintering temperature, and it remained around −65 ppm/°C. Comparing with the materials with permittivity of 14–15 (as shown in Table 1), $LiZnNbO_4$ ceramic is an environment-friendly and low-cost material, and it possesses much lower sintering temperature.

The chemical compatibility with the electrode material was assessed by mixing 20 wt.% Ag powders with the $LiZnNbO_4$ compound which were co-fired at 950 °C under air atmosphere. Fig. 2 presents the XRD pattern together with the backscattered electron imaging (BEI) of the fractured surface of the co-fired ceramic. It was seen that there were only diffraction peaks of the $LiZnNbO_4$ phase and the cubic silver phase in the co-fired ceramic. It indicates that the $LiZnNbO_4$ phase did not react with the Ag powders and no other phase was formed when they were co-fired at 950 °C for 3 h. In the BEI micrograph of Fig. 2(b), it is

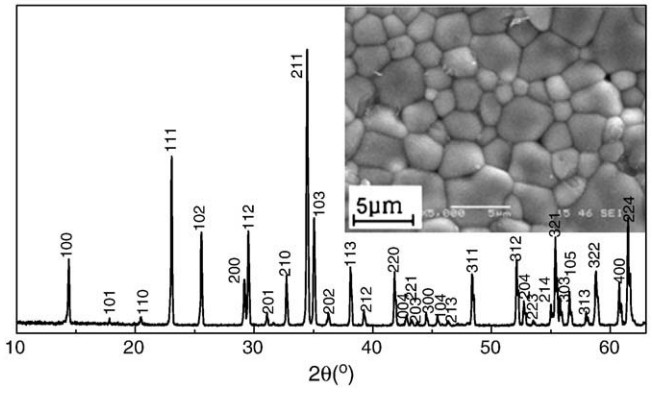

Fig. 1. XRD pattern and SEM micrograph (the insert part) of $LiZnNbO_4$ ceramic sintered at 950 °C.

Table 1
Density and microwave dielectric properties of $LiZnNbO_4$ ceramics and some alternative materials.

Composition	S. T. (°C)	Density (g/cm^3)	R. D. (%)	Permittivity	Qf (GHz)	TCF (ppm/°C)
$LiZnNbO_4$	875	4.50	92.2	13.4	27100	−66.2
	900	4.58	93.7	13.9	39800	−65.3
	925	4.69	96.0	14.4	44100	−66.0
	950	4.75	97.2	14.6	47200	−64.5
	975	4.76	97.3	14.6	45000	−63.4
	1000	4.76	97.4	14.7	32850	−66.3
	1025	4.76	97.4	14.7	27700	−64.2
$Mg_4Ta_2O_9$ [4]	1200	–	–	14	350000	−60
$LaMgAl_{11}O_{19}$ [5]	1700	–	–	14	28000	−12
$Yb_2BaCu_{0.5}Zn_{0.5}O_5$ [29]	1270	—	—	14.2	110665	−41.5
$MnWO_4$ [30]	1000	—	—	14.5	32000	−64
$LiYW_2O_8$ [31]	900	–	–	14.8	9550	−64

S. T.: Singtering Temperature; R. D. — Relative Density.

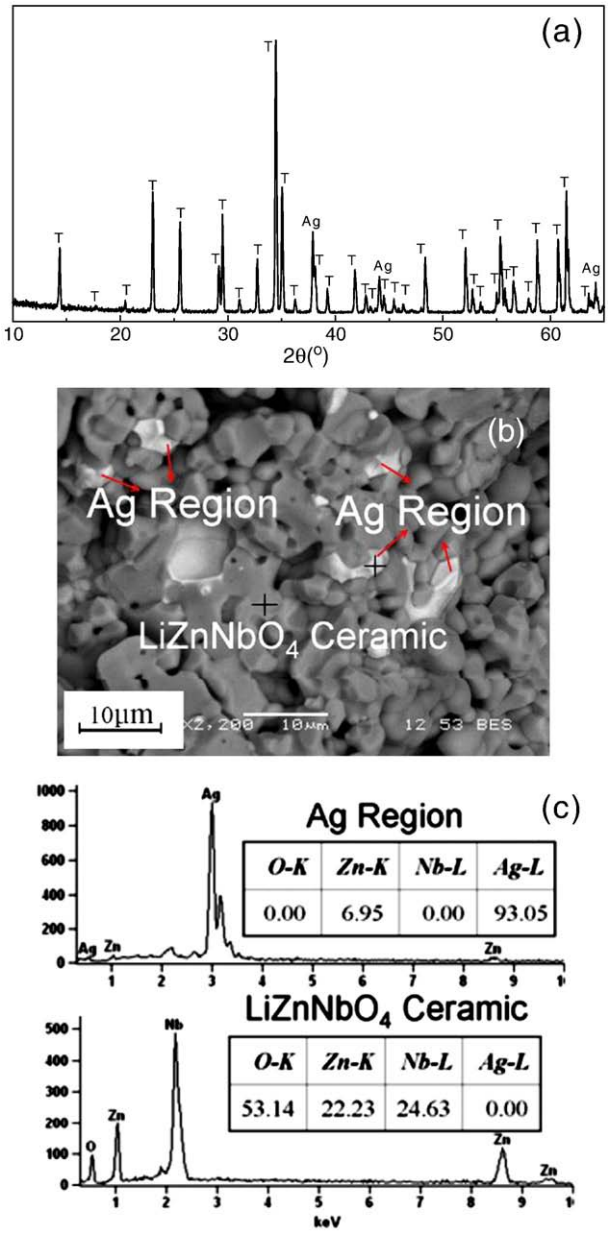

Fig. 2. XRD pattern (a), BEI micrograph (b) and EDS spectrums (c) of the fractured surface of the co-fired ceramic ($LiZnNbO_4$ with 20 wt.% Ag powders sintered at 950 °C for 3 h).

obviously seen that there were two kinds of grains. From the EDS analysis (Fig. 2(c)), it was identified that the grains with grey color belonged to the $LiZnNbO_4$ phase and the grains with bright color were found to be silver. On the other hand, a small amount of Zinc were detected in the silver region, which might result from the measurement error of EDS or the diffusion of Zn element from $LiZnNbO_4$ phase into the silver region. This result is tolerable during the LTCC procedures and $LiZnNbO_4$ ceramic can be recognized as a promising dielectric material for LTCC application.

4. Conclusions

$LiZnNbO_4$ microwave dielectric ceramic was prepared by the conventional solid state reaction method and well densified at about 950 °C. The phase structure, microstructure, sintering behavior, and microwave dielectric properties were characterized. The best microwave dielectric properties was obtained in the $LiZnNbO_4$ ceramic sintered at 950 °C for 3 h with a low permittivity of 14.6, a high *Qf* value of 47,200 GHz, and a negative TCF value of −64.5 ppm/°C. The XRD, BEI, and EDS analysis shows that the $LiZnNbO_4$ ceramic can co-fire with the silver electrode at 950 °C. The $LiZnNbO_4$ ceramic can be a promising dielectric material for LTCC application.

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