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Adjustable dielectric properties of $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$ to 1) ceramics with low sintering temperature

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Abstract

Single-phase dielectric ceramics $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$–1) were synthesized by the conventional solid-state ceramic route. All the solid solutions adopted $Li_2MTi_3O_8$ cubic spinel structure in which Li/M and Ti show 1:3 order in octahedral sites whereas Li and M are distributed randomly in tetrahedral sites with the degree of Li/M cation mixing varying from 0.5 to 0.3. The substitution of Cu for Zn effectively lowered the sintering temperatures of the ceramics from 1050 to 850 °C and significantly affected the dielectric properties. As x increased from 0 to 0.5, τ_f gradually increased while the dielectric constant (ε_r) and quality factor value ($Q\times f$) gradually decreased, and a near-zero τ_f of 1.6 ppm/°C with ε_r of 25.2, $Q\times f$ of 32,100 GHz could be achieved for $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ ceramic sintered at 950 °C, which make it become an attractive promising candidate for LTCC application. As x increases from 0.5 to 1, the dielectric loss significantly increases with AC conductivity increasing up to 2.3×10^{-4} S/cm (at 1 MHz).
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1. Introduction

In the last few decades, the microwave-based wireless communications industry has been revolutionized with the continuing requirement of miniaturization. Dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of high frequency devices. For application to resonators, microwave dielectric materials require a high dielectric constant (ε_r) to facilitate circuit miniaturization, a high quality factor values ($Q\times f$) to increase their selectivity, and a near-zero temperature coefficient of the resonant frequency (τ_f) to ensure the stability of the frequency against temperature changes[1]. Recently, there is a considerable interest in lowering the sintering temperatures of dielectric ceramics for co-firing with cheaper and highly conductive internal electrode metals such as Ag (the melting point 961 °C) and Cu (the melting point 1050 °C) [2,3], however, the sintering temperatures of most of commercial microwave dielectric ceramics such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $CaTiO_3$–$NdAlO_3$[4,5]are usually above 1300 °C. Therefore, it is necessary to search new systems with lower melting points, and many studies have been focused on Li-containing compounds which have low sintering temperature and excellent microwave dielectric properties, such as $LiZnNbO_4$ [6], $Ba_4LiNb_3O_{12}$ [7] and Li_2MgSiO_4 [8].

More recently, the microwave dielectric properties of cubic spinels $Li_2ATi_3O_8$ (A = Zn, Mg, Co) and their solid solution ceramics have been reported [9–12]. These ceramics are well sintered below 1100 °C, and exhibit good microwave dielectric properties with ε_r in the range 25.6–28.9, $Q\times f$ up to 72,000 GHz and low τ_f in the range −15–3.2 ppm/°C. Furthermore, these materials are advantageous in terms of low cost of raw materials, low sintering temperature and low bulk density compared to commercially available ceramics.

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However, the sintering temperature of these materials is still too high to preclude their application for LTCC technology.

Considering the Shannon's effective ionic radii of Cu^{2+} (0.745 Å) are very similar to that of Zn^{2+} (0.74 Å) [13], and Cu substitutions for Zn in the $Yb_2Ba(Cu_{1-x}M_x)O_5$ (M = Zn, Ni) ceramics has been reported to effectively reduce the sintering temperature and adjust the microwave dielectric properties [14], then Cu^{2+} substituted for Zn^{2+} in $Li_2ZnTi_3O_8$ system might explore new materials to meet the requirement of LTCC. However, there has been no report on sintering behaviors and microwave dielectric properties of Cu substituted Li-spinels. In the present work, the ceramics of $Li_2Cu_xZn_{1-x}Ti_3O_8$ (x = 0–1) solid solutions were prepared, and the effect of Cu substitution on sintering behavior, structure and dielectric properties were investigated.

2. Experimental procedures

$Li_2Cu_xZn_{1-x}Ti_3O_8$ ceramics were prepared by conventional mixed oxide route from the high-purity oxide powders of Li_2CO_3 ($\geq$ 99.9%), CuO ($\geq$ 99.9%), ZnO ($\geq$ 99.9%) and TiO_2 ($\geq$ 99.9%). Stoichiometric amounts of the powders were weighed and milled in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 750 °C for 4 h. The calcined powders were ground well and mixed with 5 wt% of polyvinyl alcohol solution as the binder. The powders were then uniaxially pressed into cylindrical disks of 12 mm diameter and 6–7 mm height under a pressure of 150 MPa. The samples were heated at 600 °C for 4 h to remove the organic binder and then sintered at 800–1075 °C for 2 h.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The phase compositions of sintered samples were determined using an X-ray diffractometer (XRD) ($CuK\alpha_1$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland). The surface micrographs of the samples were examined using a scanning electron microscope (SEM, Model JSM6380-LV, JEOL, Tokyo, Japan). The microwave dielectric properties were measured using a network analyzer (Model N5230A, Agilent Co., Palo Alto, CA) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). Thin disks of about 2 mm thickness were used as a capacitor to determine the dielectric constant at low frequency (1 kHz to 10 MHz) using a Precision Impedance Analyzer (Agilent 4249 A) at room temperature. Silver paste was applied to the surfaces of these disks, then dried at 600 °C for 30 min and cooled naturally to room temperature. The ac conductivity of these samples were calculated using the equation $\sigma = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta$, where f is the measured frequency, ε_0 is the permittivity of free space, ε_r is the dielectric constant and $\tan\delta$ is the dielectric loss of the sample. The microwave dielectric properties were obtained using a network analyzer (Model N5230A, Agilent Co., Palo Alto, CA). The τ_f were measured by noting the variation of resonant frequency of the TE_{011} resonant mode over the temperature range of 25–85 °C

3. Results and discussion

The room temperature XRD patterns recorded for the $Li_2Cu_xZn_{1-x}Ti_3O_8$ (x = 0–1) ceramics sintered at different temperatures using $CuK\alpha$ radiation are shown in Fig. 1. The patterns are similar and match well with PDF files No. 01–086–1512 of $Li_2ZnTi_3O_8$. All of the peaks were indexed and there was no evidence of any secondary phases present, which indicated that the single phase solid solutions of $Li_2Cu_xZn_{1-x}Ti_3O_8$ are easily formed for all x values since Zn^{2+} and Cu^{2+} are isovalent and their Shannon's effective ionic radii are similar [13]. The relative diffraction intensity of (110) and (220) peaks decrease with x while that of (111) increases toward that of $Li_2CuTi_3O_8$, which might be related to different occupancy of cation sites. The crystal structures of lithium spinels $Li_2MTi_3O_8$ (M = Zn, Mg, Co, Cu) have been reported West et al. [15], and $Li_2MTi_3O_8$ have a cubic spinel structure with space group $P4_332$. The cation distributions may be expressed by the formula, $Li_{1-Y}M_Y[(Li_YM_{0.5-Y})Ti_{1.5}]O_4$ ($0 \leq Y \leq 0.5$) [16], Y therefore denotes the degree of cation mixing in tetrahedral sites, Li and M are distributed randomly in tetrahedral 8c sites and octahedral 4b sites, and Ti is situated only in octahedral 12d sites. For $Li_2ZnTi_3O_8$, Y = 0.5; there is complete 1:3 order of Li and Ti in octahedral sites. As for $Li_2CuTi_3O_8$, Y = 0.3; Li and Cu are distributed in tetrahedral sites whereas Li/Cu and Ti show 1:3 order in octahedral sites [16].

Fig.2 presents the relative densities of the $Li_2Cu_xZn_{1-x}Ti_3O_8$ (x = 0–1) ceramics as a function of sintering temperature from 825 °C to 1075 °C. As the sintering temperature increases, the relative density of the specimen gradually increases to an optimized value above 96% and thereafter slightly decreases. The optimized sintering temperature decreases gradually from 1050 °C to 850 °C as the amount of Cu increases. The microstructure of the $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$

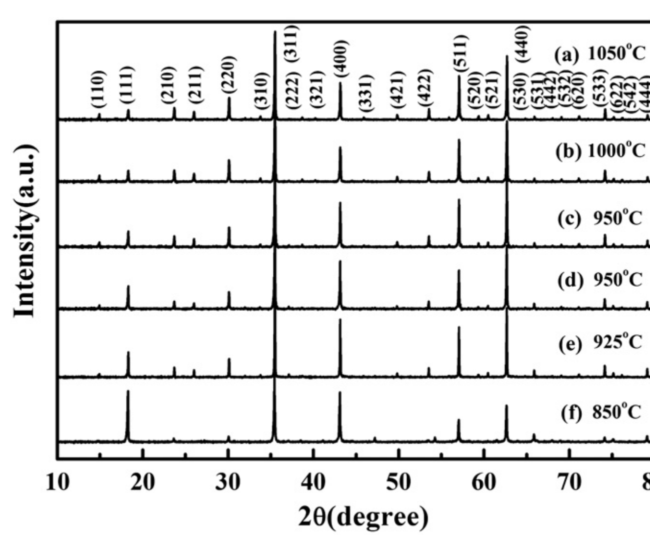

Fig. 1. X-ray diffraction patterns of the $Li_2Cu_xZn_{1-x}Ti_3O_8$ (x = 0–1) ceramics sintered at different temperatures for 2 h: (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.2, (e) x = 0.5 and (f) x = 1.

ceramics sintered at different temperatures for 2 h investigated using SEM is shown in Fig.3. It is notable that the grain size of $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ ceramics increases with increasing sintering temperatures. The microstructure is observed with several pores, and most of the grain sizes are small at 900 °C, approximately 3 μm, as shown in Fig. 3(a). The dense microstructures were formed as the sintering temperature increases from 900 °C to 975 °C. A well-sintered and uniform microstructure with grain sizes in the range 8–20 μm can be achieved at 950 °C. However, abnormal grain growth occurs as the sintering temperature exceeds 950 °C. A few large grains with an average size of 40 μm are observed, as shown in Fig. 3(d).

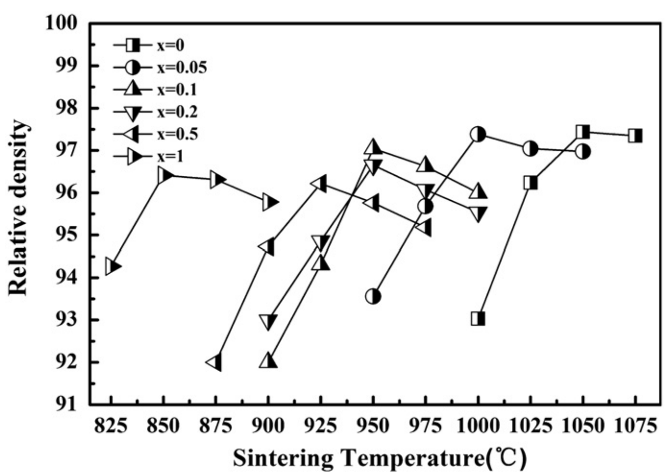

Fig. 2. The relative density of $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$–1) ceramics as a function of sintering temperature.

The dielectric properties of the $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$–1) ceramics have been measured in the low frequency region (up to 10 MHz) at the room-temperature was shown in Table 1. It was notable that dielectric loss ($\tan\delta$) gradually increases from 0.0003 to 3.9 and AC conductivity (σ_{ac}) increases from 5.7×10^{-9} S/cm to 2.3×10^{-4} S/cm as x increases. It is well known that practically all the physical and chemical properties of the metal oxide materials are directly related to their elemental composition, crystal structure and cationic distribution, lithium spinels $LiNiGe_3O_8$ (with $Y=0$) has been reported to exhibit high σ_{ac} of 3.4×10^{-3} S/cm at room temperature due to interconnected octahedral and tetrahedral that would provide pathways for lithium ion mobility[15]. The increase of $\tan\delta$ and σ_{ac} might be attributed to the decreasing Y values from 0.5 for $x=0$ to 0.3 for $x=1$ [15]. Further, the electrochemical properties of the $Li_2CuTi_3O_8$ will be investigated in the future.

The microwave dielectric properties are only measured for the $Li_2Cu_xZn_{1-x}Ti_3O_8$ ceramics with $x\leq0.5$ since other ceramics did not show any resonance. The microwave dielectric properties of the ceramics sintered at optimized temperature are summarized in Table 1. As x increases from 0 to 0.5, the ε_r slightly decreases the ceramics vary from 26.9 to 24.6 and τ_f increases form -13.2 ppm/°C to 30.4 ppm/°C, which are similar to the trends reported in $Yb_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions[14]. The $Q\times f$ significantly decreases from 74,000 to 9400 GHz which may be ascribed to the increasing ionic conductivity. It is worth noting that a near-zero τ_f of 1.6 ppm/°C with ε_r of 25.2, $Q\times f$ of 32,100 GHz could be achieved for $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ ceramic sintered at

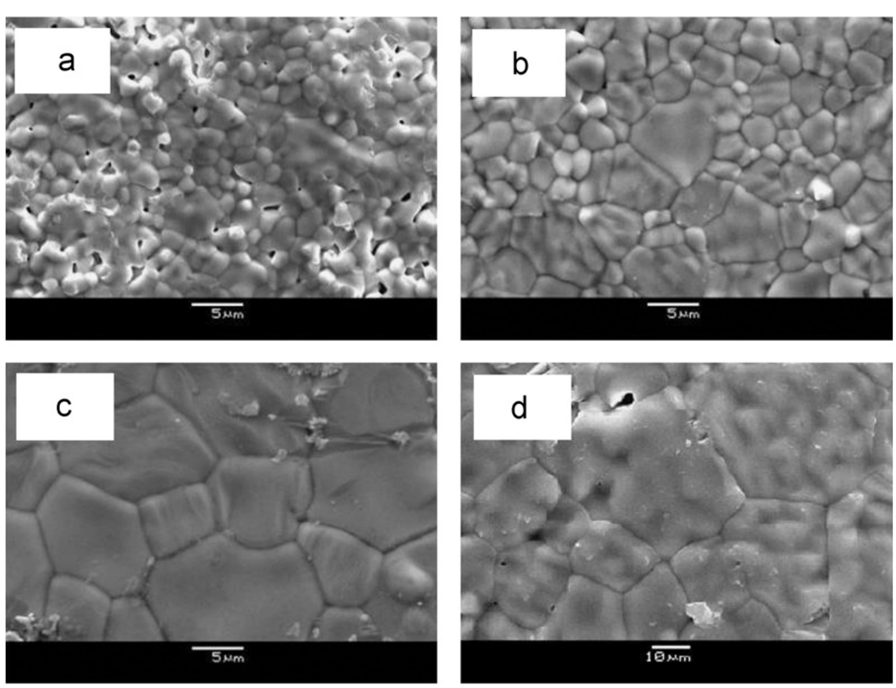

Fig. 3. Scanning electron micrographs of the $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ ceramics sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C and (d) 975 °C.

Table 1
Sintering temperatures and dielectric properties of the $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$–1) ceramics.

Composition x	Sintering temp. (°C)	Relative density (%)	Microwave dielectric properties			ε_r 1 MHz	tan δ 1 MHz	σ (S/cm)
			ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)			
$x=0$	1050	97.4	26.9	74,000	−13.2	30.8	0.0003	5.7×10^{-9}
$x=0.05$	1000	97.3	26.5	48,180	−4.7	29.7	0.0011	1.8×10^{-7}
$x=0.1$	950	97	25.2	32,100	1.6	27.6	0.0019	3.2×10^{-7}
$x=0.2$	950	96.6	24.9	18,784	12	26.4	0.0026	6.6×10^{-7}
$x=0.5$	925	96.4	24.6	9432	30.4	32.9	0.0122	7.9×10^{-6}
$x=1$	850	96.2	*	*	*	1842.3	3.939	2.3×10^{-4}

*cannot be measured.

950 °C, which might be an attractive promising candidate for LTCC application.

4. Conclusions

The $Li_2Cu_xZn_{1-x}Ti_3O_8$ ($x=0$–1) solid solution system with cubic spinel structure has been prepared by the conventional solid-state ceramic route. Cu substituted for Zn effectively lowered the sintering temperatures of the ceramics from 1050 to 850 °C and significantly affected the dielectric properties. As x increased the τ_f increased from −13.2 ppm/°C for $x=0$ to 30.4 ppm/°C for $x=0.5$ while ε_r decreased from 26.9 to 24.6 and $Q\times f$ decreases from 74,000 to 9400 GHz. As x increases from 0.5 to 1, the dielectric loss significantly increases with AC conductivity increasing from 7.9×10^{-6} to 2.3×10^{-4} S/cm. The ceramic $Li_2Cu_{0.1}Zn_{0.9}Ti_3O_8$ with $x=0.1$ sintered at 950 °C/2 h exhibits an excellent combination of microwave dielectric properties with ε_r of 25.2, $Q\times f$ of 32,100 GHz and τ_f of 1.6 ppm/°C, which might be an attractive promising candidate for LTCC application, and further studies are in progress to investigate its compatibility with silver electrode.

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