

## Synthesis and microwave dielectric properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ceramics by the reaction-sintering process

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$\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics were prepared by reaction-sintering process (calcination free). The crystal phase and microstructure were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). A pure phase of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics sintered at 1075 °C-1150 °C with cubic spinel structure was confirmed by XRD. The microwave dielectric properties ( $\epsilon_r$ ,  $Q \times f$ ) of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics were strongly dependent on the densification and grain size. The  $\tau_f$  of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics was almost independent with the sintering temperatures. In particular,  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics by reaction-sintering method sintered at 1125 °C for 5 hrs exhibited good combination microwave dielectric properties of  $\epsilon_r = 21.7$ ,  $Q \times f = 70\,500$  GHz (at 7.5 GHz) and  $\tau_f = -13$  ppm/°C.

**Key words:** reaction-sintering,  $\text{Li}_2\text{ZnTi}_3\text{O}_8$ , dielectric properties.

### Introduction

Microwave dielectric materials are advantageous in terms of compactness, light weight, temperature stability and low cost in the production of microwave devices. With the development of wireless communication, low cost microwave dielectric materials with high quality factor ( $Q \times f$ ), high relative dielectric constant ( $\epsilon_r$ ) and near-zero temperature coefficient of resonant frequency ( $\tau_f$ ) are strongly desired. In spite of any of these requirements alone can be satisfied in a broad range of materials, whereas their combination severely limits the number of available options [1, 2].

In recent years, the dielectric materials in  $\text{Li}_2\text{O-ZnO-TiO}_2$  system have attracted much attention, since they crystallize in many different structure types and exhibit interesting physical and chemical properties [3-5]. For example, the crystal structure of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  was first reported by Virginia [6]. Recently, George et al. first reported its microwave dielectric properties of  $\epsilon_r = 25.6$ ,  $Q \times f = 72,000$  GHz and  $\tau_f = -11.2$  ppm/°C [7]. The comparatively intrinsic low sintering temperature (~1100 °C) and excellent combination dielectric properties make it promising for application in microwave dielectric resonators, filters and a new low-temperature co-fired ceramics material [8]. Presently active works have been done to decrease its sintering temperature, improve the microwave dielectric properties of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics by adding various additives or suitable ions substitution [9-12].

Reaction-sintering (hereafter referred to as RS) has increased in popularity for its high efficiency by avoiding calcination and re-milling process. The reactions between constituent phases take place during sintering process at high temperatures [13]. Several materials, such as  $(\text{MgCo})\text{TiO}_3$ ,  $\text{BaTi}_5\text{O}_{11}$  and  $\text{MgAl}_2\text{O}_4\text{-CoAl}_2\text{O}_4$ , have been successfully prepared using this method [14-16]. Although the spinel structure  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics has been studied by some researchers, however, works of this ceramics by the RS process are not readily available. In the present work,  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics was prepared using RS method. The resultant microwave dielectric properties were analyzed based on the densification, phase constituents and microstructures of the ceramics.

### Experimental

The starting materials are high-purity oxide powders (> 99.9%):  $\text{Li}_2\text{CO}_3$ ,  $\text{ZnO}$  and  $\text{TiO}_2$ . Predried raw materials were weighed in stoichiometric  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  and ball milled for 7 h in a nylon jar with agate balls and ethanol as media. The milled powders were dried. After drying, the powders with 5 wt% PVA as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness under a pressure of 200 MPa. The green compacts were sintered between 1075 °C and 1150 °C in air with a heating rate of 5 °C/min.

The bulk densities of the sintered ceramics were measured by Archimedes' method. The crystal structures were analyzed using XRD with Cu K $\alpha$  radiation (Rigaku D/MAX2550, Japan). The microstructure of pellets was investigated using SEM (Fei Quanta 200, Holland). The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20,

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Rohde & Schwarz, Germany) with the TE<sub>01ā</sub> shielded cavity method. The temperature coefficient of resonant frequency ( $\tau_f$ ) was calculated with the following equation:

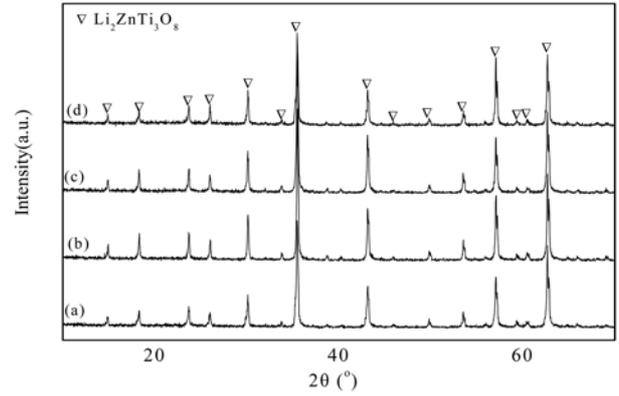
$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

## Results and Discussion

Figure 1 shows the XRD patterns of Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics sintered at different temperatures. As it can be seen, a pure phase cubic spinel structure with space group P<sub>4</sub>32 was detected within the detectable level of XRD, and the crystal structure of ceramic samples kept stable in the sintering temperature range of 1075 °C–1150 °C. The lattice parameters were calculated to be  $a = 8.3808 \text{ \AA}$ , which are a little larger than that reported earlier [4].

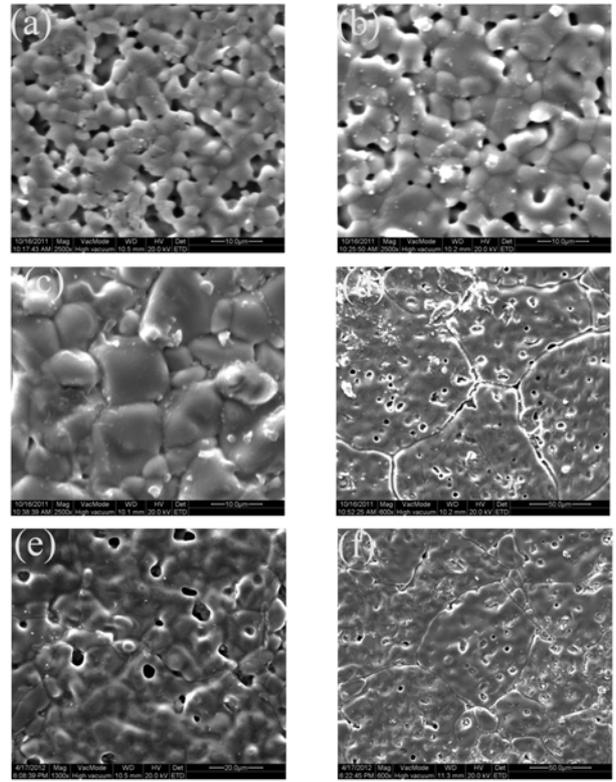
Figure 2 demonstrates the surface SEM micrographs of Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics sintered at various temperatures and at 1125 °C with different soaking times. A porous structure with small grain size (about 1 ~ 4 μm) was observed at temperature lower than 1100 °C, as shown in Figs. 2(a-b). As the sintering temperature was up to 1125 °C, a noticeable grain growth and a relatively uniform surface morphology were developed, as seen in Fig. 2(c). However, when the samples were sintered at temperature higher than 1125 °C or at 1125 °C with dwell time longer than 5 hrs, abnormal grain growth and entrapped pores were apparently observed as illustrated in Figs. 2(d-f). Similar abnormal grain growth was also observed in A<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> (A = Mg, Ni) by RS process [17]. The entrapped pores in grain were attributed to the evaporation of Li at elevated temperature [9, 12, 18]. These changes in microstructure were found to affect the microwave dielectric properties of the Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics as discussed later.

The bulk density and microwave dielectric properties of Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics as a function of sintering temperature are exhibited in Fig. 3. The density increased with increasing sintering temperature, reached a maximum value at 1125 °C (around 86.5% of theoretical density), and then decreased with a further increase in the temperature. The improvement in density could be due to the decrease of pores in the ceramics and the increase of grain size, as shown in Figs. 2(a-c). The decrease of density at higher sintering temperature might be attributed to the trapped pores by the evaporation of lithium as well as the abnormal grain growth, as seen in Figs. 2(d-f). In addition, in our experiment the maximum bulk density of the Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> samples was smaller than that one reported by the traditional solid-state reaction [7]. The essence of the calcination in the traditional solid-state reaction is to form a pre-phase of a given composition and to avoid the formation of closed pores and cracks caused



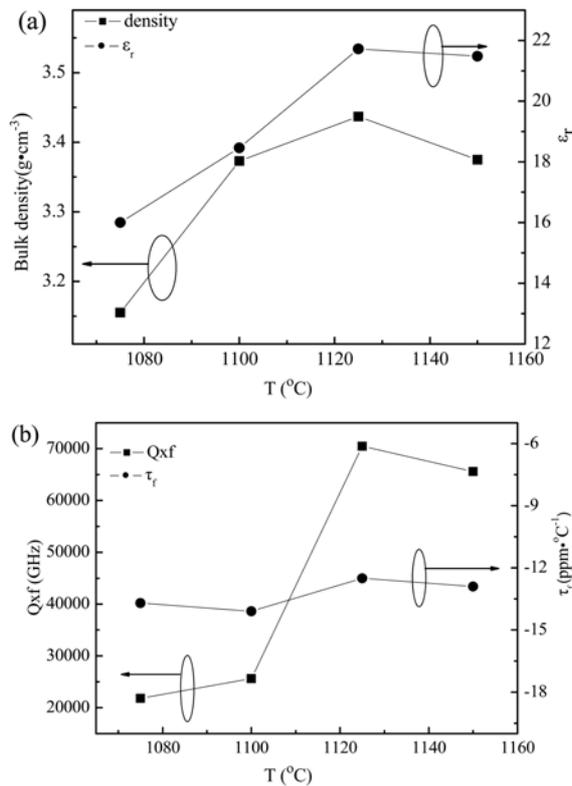
**Fig. 1.** XRD patterns of Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics sintered at different temperatures:

(a) 1075 °C, (b) 1100 °C, (c) 1125 °C, (d) 1150 °C.



**Fig. 2.** Typical surface SEM micrographs of Li<sub>2</sub>ZnTi<sub>3</sub>O<sub>8</sub> ceramics sintered at various temperatures for 5 hrs: (a) 1075 °C, (b) 1100 °C, (c) 1125 °C, (d) 1150 °C, and at 1125 °C with different soaking times: (e) 3 hrs, (f) 8 hrs.

by rapid shrinking during sintering [19, 20]. Practically, the closed pores and cracks directly result in the decrease of density. Therefore, the lower densification in present work maybe connected with the RS process. From Fig. 3, the variation in  $\epsilon_r$  and Qxf with sintering temperature was consistent with the trend in bulk density with sintering temperature. It is because both the  $\epsilon_r$  and Qxf of the samples are influenced much by many of the same extrinsic factors such as densification/porosity, secondary phases, and grain size etc [21, 22]. The effect of secondary phase might be neglected because



**Fig. 3.** Variations of bulk density and microwave dielectric properties of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics as a function of sintering temperature.

**Table 1.** Density and microwave dielectric properties of  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics sintered at 1125 °C with different soaking times.

Soaking time (h)	density ( $\text{g}/\text{cm}^3$ )	$\epsilon_r$	Qxf (GHz)	$\tau_f$ (ppm/°C)
3	3.432	21.74	55800	-13.3
5	3.437	21.72	70500	-12.5
8	3.435	21.75	65600	-10.4

there was no one in the ceramic bodies confirmed by the XRD patterns (see Fig. 1). Therefore, the improvements in  $\epsilon_r$  and Qxf values can be attributed to the increase in the density as well as grain growth, whereas the deterioration might be caused by the abnormal grain growth coupled with a decrease in density [23, 24]. The  $\tau_f$  did not change remarkably with increasing sintering temperature and remained stable at about -13 ppm/°C, which is due to that the  $\tau_f$  is well known related to the composition and the secondary phase of the material [25].

The influences of soaking times on the density and microwave dielectric properties of the  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics sintered at 1125 °C are also investigated and summarized in Table I. As can be seen, with increased dwell times, the density and Qxf values increased firstly and then decreased. At the same time both the  $\epsilon_r$  and  $\tau_f$  values were found to be independent of soaking

time (Table 1). In summary,  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics prepared by RS and sintered at 1125 °C for 5 hrs exhibits good microwave dielectric properties of  $\epsilon_r=21.7$ , Qxf=70 500 GHz (at 7.5 GHz), and  $\tau_f=-13$  ppm/°C. In addition, the obtained  $\epsilon_r$  values by RS method are somewhat lower than previously reported by the classic solid-state reaction, which may be due to the poor densification, as stated previously, because a higher density results in a lower porosity and thus a higher dielectric constant [26].

## Conclusions

Reaction-sintering process was proved to be a simple and effective method to prepare phase-pure  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics. The density and grain size play a significant role to control  $\epsilon_r$  and Qxf in  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramics system. With increasing sintering temperature, the bulk density, the  $\epsilon_r$  and  $Q \times f$  increased firstly and then decreased, while  $\tau_f$  changed slightly. A fine combination microwave dielectric properties of  $\epsilon_r=21.7$ ,  $Q \times f=70$  500 GHz (at 7.5 GHz) and  $\tau_f=-13$  ppm/°C can be obtained in  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  ceramic sintered at 1125 °C for 5 hrs.

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