Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Temperature stability and high-Qf of low temperature firing Mg_2SiO_4–Li_2TiO_3 microwave dielectric ceramics

Yuanming Lai, Caiyun Hong, Lichuan Jin, Xiaoli Tang, Huaiwu Zhang, Xin Huang, Jie Li, Hua Su*

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

ARTICLE INFO

Keywords:
Microwave dielectric ceramic
Temperature stability
High-Qf value
Low temperature firing

ABSTRACT

In this work, a series of low-temperature-firing $(1-x)Mg_2SiO_4$–xLi_2TiO_3–8 wt% LiF (x = 35–85 wt%) microwave dielectric ceramics was prepared through conventional solid state reaction. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses showed that the Li_2TiO_3 phase was transformed into cubic phase $LiTiO_2$ phase and secondary phase Li_2TiSiO_5. Partial substitution of Mg^{2+} ions for Ti^{3+} ions or Li^+Ti^{3+} ions increased the cell volume of the $LiTiO_2$ phase. The dense microstructures were obtained in low Li_2TiO_3 content ($x \le 65$ wt%) samples sintered at 900 °C, whereas the small quantity of pores presented in high Li_2TiO_3 content ($x \ge 75$ wt%) samples sintered at 900 °C and low Li_2TiO_3 content ($x = 45$ wt%) sintered at 850 and 950 °C. Samples at $x = 45$ wt% under sintering at 900 °C for 4 h showed excellent microwave dielectric properties of $\varepsilon_r = 10.7$, high $Q \times f = 237{,}400$ GHz and near-zero $\tau_f = -3.0$ ppm/°C. The ceramic also exhibited excellent chemical compatibility with Ag. Thus, the fabricated material could be a possible candidate for low temperature co-fired ceramic (LTCC) applications.

1. Introduction

LTCC technology plays an important role in microelectronic applications. This technology requires materials with moderate dielectric constant (ε_r), high Q × f values, near-zero temperature coefficients of resonant frequency ($\tau_f \le \pm 10$ ppm/°C) and low firing temperature (~ 961 °C to co-fire with Ag) for practical application [1–5]. Forsterite (Mg_2SiO_4) is an important candidate for microwave applications because of its high Q × f value (Q × f = 240,000 GHz) [6–9]. However, Mg_2SiO_4 ceramics require high sintering temperatures (1350–1450 °C) and negative temperature coefficients of resonance frequency ($\tau_f = -67$ ppm/°C) to satisfy LTCC application requirements [10–12]. Several glass types, such as lithium borosilicate glass, calcium borosilicate and lithium magnesium zinc borosilicate glasses, are used to reduce the sintering temperature of Mg_2SiO_4 ceramics [13–15]. However, these glass additives exhibit the following two disadvantages: (i) deterioration of microwave dielectric properties [13], and (ii) high sintering temperature requirement (1325 °C for 4 h) [14]. LiF is widely used as sintering aid for microwave ceramics because of its low melting point (~ 848 °C) and retention of remarkable microwave properties [16–20]. According to dielectric complex rules, $CaTiO_3$ and TiO_2 are widely utilized to adjust the τ_f value to zero because of their large positive τ_f of approximately + 800 and + 430 ppm/°C, respectively. But additives of $CaTiO_3$ and TiO_2 can deteriorate dielectric properties [16,21].

The rock salt-type Li_2TiO_3 has attracted considerable attention in microwave dielectric ceramics because of its positive τ_f value, relatively high Q × f value and low sintering temperature [22,23]. However, pure Li_2TiO_3 ceramics with high densification is very difficult to obtain by conventional solid-state method because of porous microstructures and microcracks formed through lithium evaporation and order–disorder phase transition at high temperatures [23–26]. Several approaches have been employed to improve the densification of Li_2TiO_3 ceramics; such approaches include the use of nanosized particles and sintering aids [23,27,28]. Nevertheless, adjustment of the negative τ_f of microwave dielectric ceramics by using Li_2TiO_3 has been rarely reported.

In this work, Mg_2SiO_4 and Li_2TiO_3 composite was obtained by solid phase reaction. The Mg_2SiO_4 and Li_2TiO_3 composites were added with LiF to decrease the sintering temperature. The temperature stability, high-Qf and low-temperature firing of Mg_2SiO_4–Li_2TiO_3 microwave dielectric ceramics were assessed. XRD patterns, XPS spectra, SEM images and Vector Network Analyzer were used to analyze phase composition, microstructure, microwave dielectric properties and chemically compatible with Ag electrode material.

2. Experimental procedure

Mg_2SiO_4 and Li_2TiO_3 ceramics were prepared through solid-state ceramic route. Analytically pure MgO, TiO_2, Li_2CO_3(Shanghai Aladdin

---

* Corresponding author.
E-mail address: uestcsh77@163.com (H. Su).

http://dx.doi.org/10.1016/j.ceramint.2017.08.192
Received 6 August 2017; Received in revised form 14 August 2017; Accepted 29 August 2017
0272-8842/ © 2017 Published by Elsevier Ltd.

Please cite this article as: Lai, Y., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.08.192

Biological Technology Co., LTD) and SiO_2 (Sinopharm Chemical Reagent Co., Ltd) were used as starting materials, weighed and wet mixed in distilled water by using zirconia balls in a plastic container for 4 h. The slurry of Mg_2SiO_4 and Li_2TiO_3 was dried and calcined in alumina crucibles at 1350 °C and 850 °C, respectively, for 4 h. The calcined powders were mixed in accordance with the (1-x)Mg_2SiO_4–$x$$Li_2TiO_3$–8 wt% LiF ($x$ = 35, 45, 55, 65, 75 and 85 wt%) and ground into fine particles. The samples were then pressed under a uniaxial pressure of 10 MPa into cylindrical disks with 12 mm diameter and 4–5 mm height. Sintering was carried out at temperatures between 850 and 950 °C for 4 h.

The crystalline phase of the ceramics was confirmed using PANalytical X'Pert PRO with Cu K_α radiation ($\lambda = 1.54$ Å) at room temperature. The XRD patterns were measured in the 2θ angle range between 10° and 120° with a step of 0.02° and a time per step of 1.0 s. Structural refinements were conducted through Rietveld method using FullProf software. The titanium XPS spectra of $x = 45$ wt% sintered at 900 °C were recorded with a Kratos XSAM800 spectrometer with monochromatic Al Kα radiation. The microstructures and morphology of the sintered samples were analysed by a scanning electron microscope (SEM) (JSM-7001F; JEOL, Japan) at an accelerating voltage of 20 kV. In order to analyze distribution of element, EDS mapping of $x =$ 45 wt% sintered at 900 °C were also recorded. The density of each sample was measured at room temperature by the Archimedes method using distilled water as the buoyancy liquid. Microwave dielectric properties were assessed by a Vector Network Analyzer (N5230, Agilent Technologies, USA). The relative dielectric constants (ε_r), quality factor ($Q \times f$) and temperature coefficient of resonance frequency (τ_f) of the samples were determined through Hakki–Coleman dielectric resonator method.

3. Results and discussion

The XRD patterns of the (1-x)Mg_2SiO_4–$x$$Li_2TiO_3$–8 wt% LiF ($x$ = 35, 45, 55, 65, 75 and 85 wt%) ceramics are shown in Fig. 1. Notably, the main phases include Mg_2SiO_4 (ICDD no. #04–0768), $LiTiO_2$ (ICDD no. #16-0223) and Li_2TiSiO_5 (ICDD no. #82-1955) with increasing x. It is well known that Li_2TiO_3 phase in three modifications: the metastable cubic α-Li_2TiO_3, ordered monoclinic β-Li_2TiO_3 and disordered cubic γ-Li_2TiO_3. α-Li_2TiO_3 phase transforms to the monoclinic β-Li_2TiO_3 at 300 °C and, after which the reversible transition of the β-Li_2TiO_3 to γ-Li_2TiO_3 occurs at 1150–1215 °C. As low Li_2TiO_3 content, the Mg_2SiO_4 additive lead to transformation of Li_2TiO_3 phase into a cubic $LiTiO_2$ phase. Similar changes were obtained for the Li_2TiO_3 ceramics, along with the excess MgO, ZnO and NiO (> 30 wt%) [24–26]. Moreover, since the LiF has a face centered cubic rock salt structure which is similar with that of Li_2TiO_3 (superstructure with edge-sharing cation oxygen octahedral), solid solutions between Li_2TiO_3 and part of LiF can be formed [29]. In the case of high LiF content (8 wt%), a slight amounts of excess Li^+ ions and F^- ions were derived from LiF. These ions enter into Li_2TiO_3 lattice result in Li_2TiO_3 phase present disordered cubic structure ($LiTiO_2$). This can be a main reason the Li_2TiO_3 phase also transform into a cubic $LiTiO_2$ phase with high Li_2TiO_3 content. Similar results were obtained for the (1-x)Li_2TiO_3–xLiF ceramics (when $0.15 \le x \le 0.4$) [30]. In addition, the diffraction peaks of $LiTiO_2$ at the lattice plane were inclined toward the lower diffraction angles. This pattern indicates that the unit cell volumes can increase with increasing x because of the substitution of a larger Mg^{2+} ($R = 0.72$ Å) for a smaller Ti^{3+} ($R = 0.67$ Å) or Li^+Ti^{3+} ($R_{av} = 0.715$ Å), and the replacement mechanism could be proposed as $2Ti^{3+} \leftarrow 3Mg^{2+}$ or $Li^+Ti^{3+} \leftarrow 2Mg^{2+}$ [24]. Moreover, the $MgSiO_3$ phase was detected in calcined powder of Mg_2SiO_4 (Fig. 2(a)). But the $MgSiO_3$ phase unexpectedly disappeared when Mg_2SiO_4 calcined power was sintered with Li_2TiO_3 and LiF. Thus, it can be deduced that the Li_2TiSiO_5 phase may be produced as a result of chemical reaction between $MgSiO_3$ and Li_2TiO_3 phases:

$$Li_2TiO_3 + 2MgSiO_3 \rightarrow Li_2TiSiO_5 + Mg_2SiO_4$$

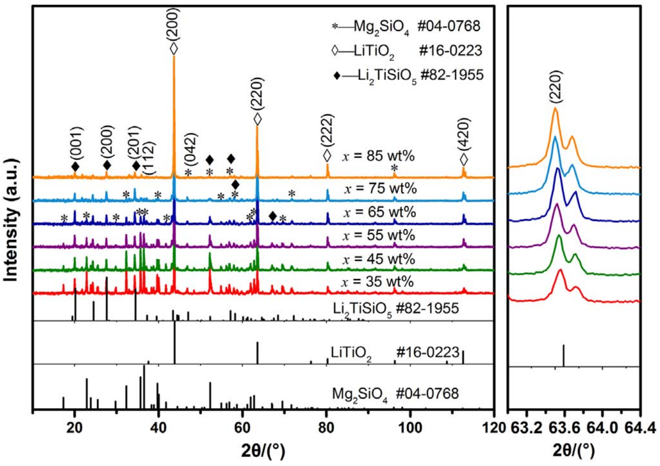

Fig. 1. The XRD patterns of the(1-x)Mg_2SiO_4–$x$$Li_2TiO_3$–8 wt% LiF ceramic sintered at 900 °C for 4 h.

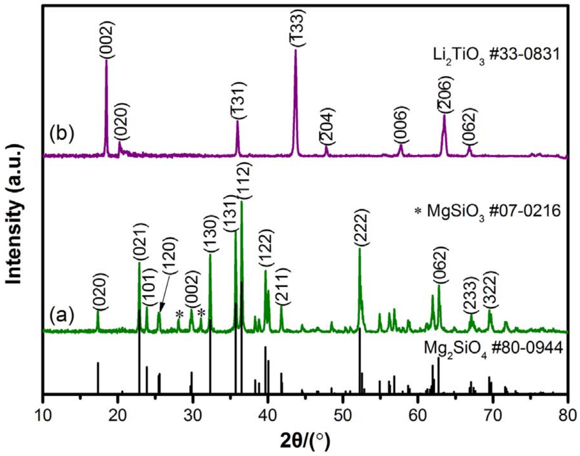

Fig. 2. The XRD patterns of Mg_2SiO_4 (a) and Li_2TiO_3 (b) calcined at 1350 °C and 850 °C, respectively.

The Li_2TiSiO_5 phase were also found between Mg_2SiO_4 and TiO_2 phases with LiF in the previous report [16]. The impure phase may deteriorate the dielectric properties. Furthermore, the phase-containing F ions were not detected by XRD when 8 wt% LiF was added. This result may be due to two main reasons. First, partial substitution of O^{2-} ions by F^- ions may have occurred. Second, the LiF may have formed an amorphous phase because the sintering temperature exceeded the compound's melting point (848 °C). Previous research has indicated that the solid solubility limit of F^- in Li_2TiO_3 is about 4 wt%, and when LiF > 6 wt%, a large extent of liquid phase during sintering process inhibit the entrance or occupation of Li^+ and F^- in the Li_2TiO_3 lattice [23,30]. In this work, both of these are likely to really happen because of the LiF content up to 8 wt%. In addition, the EDS elemental mapping analysis of $x = 45$ wt% ceramic sintered at 900 °C for 4 h are plotted in Fig. 3. It is obvious that F element is uneven distributions in the samples, and partial segregations in some specific regions can be observed.

To obtain the structure, lattice parameter and unit cell volume, the whole XRD pattern was refined using the Fullprof program [31]. Such refinement involved constraining within the orthorhombic, cubic and tetragonal structural models of Mg_2SiO_4 ($a = 4.7600$ Å, $b = 10.2000$ Å and $c = 5.9900$ Å), $LiTiO_2$ ($a = b = c = 4.1400$ Å) and Li_2TiSiO_5 ($a = b = 6.4379$ Å, $c = 4.4003$ Å) with the space groups *Pbnm*, *Fm-3m* and *P4/nmm*, respectively. As representative data, the refined XRD patterns of the $x = 45$ wt% ceramics are shown in Fig. 4. All the fitted curves

Download English Version:

https://daneshyari.com/en/article/5437243

Download Persian Version:

https://daneshyari.com/article/5437243

Daneshyari.com