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Ceramics International 38 (2012) 5493–5496

CERAMICS INTERNATIONAL

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Effects of microwave sintering on the properties of $0.87(Mg_{0.7}Zn_{0.3})TiO_3$–$0.13(Ca_{0.61}La_{0.26})TiO_3$ ceramics

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Received 8 March 2012; received in revised form 25 March 2012; accepted 26 March 2012
Available online 1 April 2012

Abstract

$0.87(Mg_{0.7}Zn_{0.3})TiO_3$–$0.13(Ca_{0.61}La_{0.26})TiO_3$ (referred to as 87MZCLT) ceramics were prepared by microwave sintering and conventional sintering. The experimental results demonstrated that the sintering cycle of 87MZCLT ceramics was greatly shortened and the impurity phase $(Mg_{0.7}Zn_{0.3})Ti_2O_5$ was eliminated by microwave sintering. Moreover, the 87MZCLT ceramics prepared by microwave sintering show more uniform, fine-grained microstructure as well as much less Zn evaporation. As a result, the quality factor was increased by 40% compared with conventional sintering. All samples were sintered at 1275 °C for 20 min with heating and cooling rate of 15 °C/min and gave excellent microwave dielectric properties: $\varepsilon_r = 26.21$, $Q \times f = 120{,}000$ GHz, $\tau_f = -3$ ppm/°C.

Keywords: Microwave sintering; Dielectric constant; Quality factor; Ceramics

1. Introduction

Microwave dielectric ceramics have become a new trend in dielectric materials research with the widespread use of them in resonators, filters and other devices in mobile communication systems. Moreover, Microwave dielectric ceramics are important basic materials for developing multilayer microwave components. The microwave ceramics of the dielectric constant of 20–27 and resonance frequency at 7–9 GHz are demanded largely in recent years, as they are widely used in communication systems such as cellular phone, direct broadcasting satellite and global positioning systems [1–3].

The benefits of using complex perovskite and ilmenite ceramics are reportedly associated with their excellent dielectric properties at microwave frequencies [6–11]. $(Mg_{0.7}Zn_{0.3})TiO_3$ ($\varepsilon_r = 18.6$, $Q \times f = 90{,}000$ GHz and $\tau_f = -51 \times 10$–6/°C) ceramic has been studied extensively which has a negative τ_f value [4], $Ca_{0.61}La_{0.26}TiO_3$ ($\varepsilon_r = 109$, $Q \times f = 17{,}600$ GHz and $\tau_f = 212 \times 10$–6/°C) [5], having a large positive τ_f value, was added to $(Mg_{0.7}Zn_{0.3})TiO_3$ to compensate its τ_f. $0.85(Mg_{0.95}Zn_{0.05})TiO_3$–$0.15Ca_{0.61}Nd_{0.26}TiO_3$ ceramics were studied associated with their excellent dielectric properties at microwave frequencies [6]. $(1 - x)(Mg_{0.7}Zn_{0.3})TiO_3$–$x(Ca_{0.61}La_{0.26})TiO_3$ ceramics were synthesized using the conventional mixed-oxide method and sintering process. The results indicated that $0.87(Mg_{0.7}Zn_{0.3})TiO_3$–$0.13(Ca_{0.61}La_{0.26})$-$TiO_3$ ceramics possessed excellent performance in our previous work [12].

Nowadays, the study of microwave sintering of ceramic materials, both at home and abroad, has just begun. In this paper, $0.87(Mg_{0.7}Zn_{0.3})TiO_3$–$0.13(Ca_{0.61}La_{0.26})TiO_3$ (referred to as 87MZCLT) ceramics was prepared by conventional mixed-oxide method and microwave sintering. The sintered properties, dielectric properties, microstructure and the element changes of the samples were studied. A comparison between microwave sintering and conventional sintering with terms of 87MZCLT ceramics was conducted.

2. Experimental procedure

AR grade powders La_2O_3, $CaCO_3$, TiO_2, ZnO and MgO of purity better than 99% were used as starting materials. They were weighed according to the stoichiometric ratio of $(Mg_{0.7}Zn_{0.3})TiO_3$, $(Ca_{0.61}La_{0.26})TiO_3$ and ball milled for 6 h in distilled water. Then the mixture was dried and ground before

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.03.062

it was calcined at 1100 °C for 3 h. According to the molar ratio of $0.87(Mg_{0.7}Zn_{0.3})TiO_3$–$0.13(Ca_{0.61}La_{0.26})TiO_3$, the calcined powder was re-milled for 6 h using PVA solution as a binder. The obtained powder was then crushed into a fine powder through a sieve with a 60 mesh. The obtained fine powder was pressed to pellets with a diameter of 12 mm and a thickness of 5 mm under a press of 300 MPa. These pellets were sintered at temperatures 1275 °C for 20 min using microwave sintering with heating and cooling rate of 15 °C/min. For a comparison, 87MZCLT ceramics were also prepared by conventional sintering at temperatures 1275 °C for 3 h. The microwave furnace used in this study consisted of 2.45 GHz magnetrons with maximum power of 3 kW (MW-L0316V, Changsha Longtech Co. Ltd., China). The 87MZCLT ceramics samples were placed on a silicon carbide plate. They were surrounded by a hollow silicon carbide cylinder, which was used as the susceptor to enhance microwave heating through efficient coupling. The entire assembly was covered with ceramics fiber insulation.

The crystalline phases of the sintered ceramics were identified by XRD using Cu $K\alpha$ radiation (at 40 kV and 38 mA). The microstructures of the sintered samples were performed by a scanning electron microscopy (SEM; JEOL, JSM-5900). The composition analysis of the sintered samples was performed by XRF. The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant and the quality factor values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [13].

3. Results and discussion

3.1. Sintering behavior

Fig. 1 shows the comparison of the time–temperature profiles for 87MZCLT ceramics in microwave sintering (MWS) and conventional sintering (CS) at the best craft conditions. The total sintering cycle of MWS was just about 4 h. It had just taken 50 min to heat the samples to 1275 °C. Furthermore, the soaking time was just 20 min and the process of cooling was shorter. For CS it had taken at least 10 h to heat the samples to 1275 °C and its cooling rate was much slower, which lead to the sintering cycle was more than 20 h.

Table 1
Comparison between CS and MWS for 87MZCLT ceramics.

Parameters	MWS	CS
Sintering temperature (°C)	1275	1275
Soaking time (h)	0.33	4
Total cycle time (min)	240	>1200
Bulk densities (g/cm^3)	4.27	4.25
Dielectric constant	26.21	26.22
Quality factor (GHz)	120,000	86,011
Resonant frequency temperature coefficient (ppm/°C)	−3	−6

The bulk densities of 87MZCLT ceramics prepared at the best craft conditions with different sintering processes are shown in Table 1. As can be seen from this table, the bulk density of MWS sample is much higher than that of CS sample at the same sintering temperature. Compared with CS, Heat was produced by the sample itself during MWS process. Under the radiation of microwave, electric field and energy density in the area of pores between grains will enhance instantaneously, which greatly reduces the diffusion barrier of ions, allowing ions to migrate faster and accelerating diffusion of grain boundary and densification rate [14,15]. Thus 87MZCLT ceramics with higher bulk density were obtained by MWS for a much shorter soaking time.

3.2. Dielectric properties

Microwave dielectric properties of 87MZCLT ceramics prepared by different sintering processes are also shown in Table 1. As we can see, there is no obvious difference in dielectric constant for the MWS samples and the CS samples. The quality factor was increased by 40 percent by microwave sintering. Moreover, resonant frequency temperature coefficient (τ_f) of MWS samples was also closer to zero than that of CS samples. Therefore, the microwave-sintered 87MZCLT ceramics showed better bulk density, lower dielectric loss and almost zero frequency temperature coefficient.

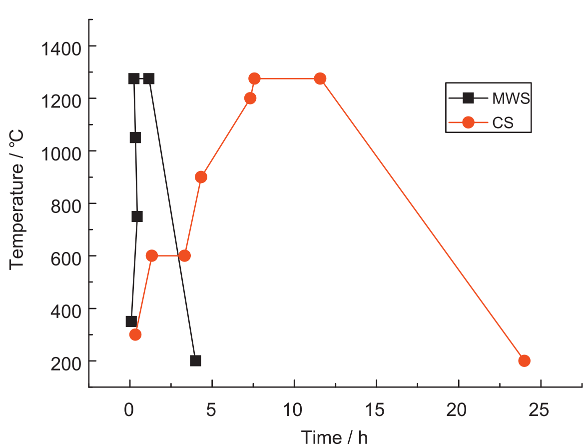


Fig. 1. Time–temperature sintering profiles for MWS and CS of 87MZCLT ceramics.

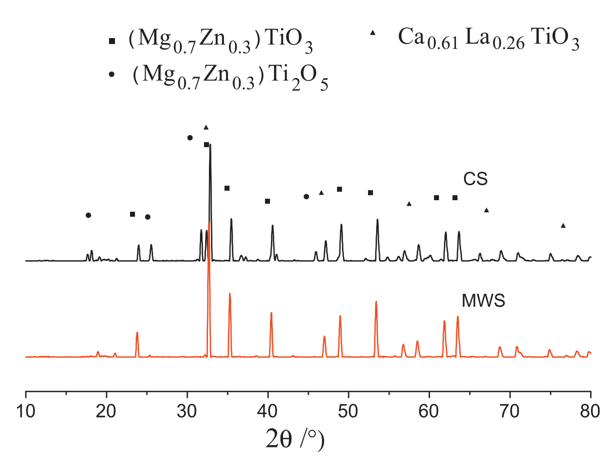
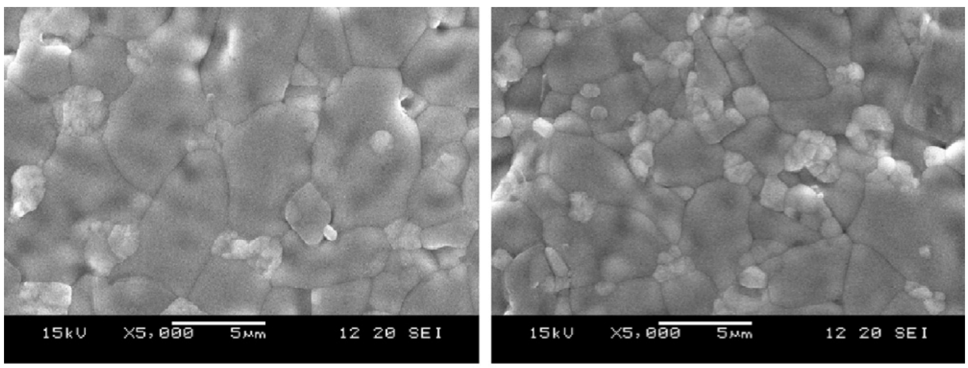


Fig. 2. XRD patterns of 87MZCLT ceramics with different sintering processes.

Table 2
Variation in composition before and after different sintering processes.

Element	Mass ratio before CS (%)	Mass ratio after CS (%)	Changes during CS (%)	Mass ratio before MWS (%)	Mass ratio after MWS (%)	Changes during MWS (%)
Zn	14.00	13.35	4.64	14.01	13.85	1.14
Mg	13.74	13.83	0.66	13.74	13.68	0.44
Ti	31.46	31.89	1.36	31.45	31.72	0.86
La	3.10	3.01	2.90	3.09	3.02	2.27
Ca	2.36	2.31	2.12	2.37	2.32	2.11
Impurities	35.34	35.61	0.76	35.34	35.41	0.20



(a) the CS (b) the MWS

Fig. 3. SEM of 87MZCLT ceramics with different sintering processes.

3.3. Phase composition, microstructure and composition analysis

Fig. 2 illustrates the room-temperature X-ray diffraction (XRD) patterns recorded from 87MZCLT ceramics with different sintering processes at the best craft conditions. What we can learn from the patterns is that the major crystalline phases of all the sintered samples were ilmenite $(Mg_{0.7}Zn_{0.3})TiO_3$ and perovskite $(Ca_{0.61}La_{0.26})TiO_3$. In CS samples, a small quantity of $(Mg_{0.7}Zn_{0.3})Ti_2O_5$, the impurity phase of the products was proved by the lower values of diffraction peak at the 18°, 27°, 32° and 46°. However, in MWS samples, $(Mg_{0.7}Zn_{0.3})Ti_2O_5$ was not identified, which was one of the prime reasons for the dramatic increase in the quality factor.

SEM micrographs of the 87MZCLT ceramics prepared by different sintering processes at the best craft conditions are shown in Fig. 3. Compared with CS, the grain shape of the MWS samples changed little, but the grain size of the latter (about 5 μm) was smaller than that of the former (about 8 μm). This is due to the fact that in microwave heating the sintering time and heating rates are much shorter than in the conventional heating, and hence there is not enough time for the grains to grow and one finds much finer microstructure in microwave sintered products.

Zn is easy to volatile at high temperatures [16] which will influence the composition and properties of the materials. The change of composition tested by the fluorescence analyzer is shown in Table 2. The variation of the Zn content is our main concern. From the table, we can see that the composition of the samples do change in different extents in CS and MWS process. A relatively large decrease of 4.64% in Zn content was observed for CS, whereas it was only 1.14% for MWS, which is attributed to the shorter soaking time and faster heating and cooling rate. Therefore, much less evaporation of Zn, and consequently composition deviation occurs for MWS compared with CS, which also contributes to the dramatic improvement in quality factor.

4. Conclusion

Compared with the conventional sintering, the sintering cycle of microwave sintering was greatly shortened and the impurity phase $(Mg_{0.7}Zn_{0.3})Ti_2O_5$ was eliminated. Moreover, the 87MZCLT ceramics prepared by microwave sintering show more uniform, and fine-grained microstructure as well as much less Zn evaporation. As a result, excellent dielectric properties of 26.21 for ε_r, 120,000 GHz for $Q \times f$, and -3 ppm/°C for τ_f were obtained by microwave sintering at 1275 °C for 20 min. Especially, the quality factor ($Q \times f$) was increased by 40% compared with conventional sintering. Microwave sintering shows great potential in preparing 87MZCLT ceramics with high performance and lower cost.

Acknowledgement

This work was supported by a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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