International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 3, Mar 2012, Page 245
DOI: 10.1007/s12613-012-0546-x

Microwave sintering of $Ca_{0.6}La_{0.2667}TiO_3$ microwave dielectric ceramics

Jia-mao Li[1,2] *and Tai Qiu*[1]

1) College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, China
2) School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan 243002, China

(Received: 23 March 2011; revised: 23 May 2011; accepted: 24 May 2011)

Abstract: $Ca_{0.6}La_{0.2667}TiO_3$ ceramics were prepared by conventional and microwave sintering techniques and their sinterability, microstructure, and microwave dielectric properties were investigated in detail for comparison. Densified $Ca_{0.6}La_{0.2667}TiO_3$ ceramics were obtained by microwave sintering at 1350ºC for 30 min and by conventional sintering at 1450ºC for 4 h. An unusual phenomenon was found that some larger grains (grain size range: 8-10 μm) inclined to assemble in one area but some smaller ones (grain size range: 2-4 μm) inclined to gather in another area in the microwave sintered ceramics. The microwave dielectric properties of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared by microwave sintering at 1350ºC were as follows: dielectric constant (ε_r) = 119.6, quality factor (Qf) = 17858.5 GHz, and temperature coefficient of resonant frequency (τ_f) = 155.5 ppm/ºC. In contrast, the microwave dielectric properties of the ceramics prepared by conventional sintering at 1450ºC were ε_r = 117.4, Qf = 13375 GHz, and τ_f = 217.2 ppm/ºC.

Keywords: perovskite; microwave sintering; microstructure; dielectric properties

[*This work was financially supported by A Priority Academic Program Development of Jiangsu Higher Education Institutions.*]

1. Introduction

With the rapid growth of the wireless telecommunication industry, dielectric ceramics are playing an important role in microwave components such as filters, resonators, oscillators, and dielectric antennas. Three basic properties, namely, high quality factor (Qf), high dielectric constant (ε_r), and near-zero temperature coefficient of resonant frequency (τ_f), are required for microwave dielectric ceramics to practical application. The demand for the miniaturization of microwave components can be met by increasing the ε_r value since the size of microwave components is inversely proportional to $1/\sqrt{\varepsilon_r}$. Therefore, many efforts have been made to develop microwave ceramics with high ε_r. In the early 1990s, a number of microwave ceramics with high ε_r, such as $(A^{1+}_{1/2}A^{3+}_{1/2})TiO_3$, $BaO\text{-}Ln_2O_3\text{-}TiO_2$, $CaO\text{-}Li_2O\text{-}Ln_2O_3\text{-}TiO_2$, and Pb-based ceramics were developed [1-4]. Among these materials, $Ca_{1-x}La_{2x/3}TiO_3$, a solid solution system where Ca^{2+} ions are substituted by La^{3+} ions in $CaTiO_3$, is a promising material with high ε_r and Qf values. Huang *et al.* [5] prepared $Ca_{1-x}La_{2x/3}TiO_3$ ceramics by a conventional solid state reaction method and obtained the best microwave dielectric properties of ε_r = 109 and Qf = 17600 GHz at x = 0.4 ($Ca_{0.6}La_{0.2667}TiO_3$) in 2001. However, $Ca_{0.6}La_{0.2667}TiO_3$ ceramics require a high sintering temperature of about 1450ºC, which is time and energy consuming for industry production. Therefore, it is necessary to explore new preparation methods to reduce the sintering temperature of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics.

One alternative route is microwave sintering, which offers several advantages over conventional sintering, including faster heating rate, lower sintering temperature, enhanced densification, smaller average grain size, and an apparent reduction in activation energy in sintering. It is well known that microwave sintering is fundamentally different from conventional sintering owing to its unique heating mechanism. In the microwave process, the heat is produced by an interaction of electromagnetic waves with molecules

Corresponding author: Tai Qiu E-mail: qiutai@njut.edu.cn

and is directly transferred to the material. In contrast, the heat is transferred between objects by the mechanisms of conduction, radiation and convection in the conventional process. In the conventional heating process, the surface of materials is first heated, and then the heat moves inward, which leads to a temperature gradient from the surface to the inside. Nevertheless, microwave heating generates heat within the material first and then transfers to the entire volume [6].

In the past 20 years, the microwave sintering technique has received much attention and has been employed to prepare some important dielectric ceramics such as $Ba_2Ti_9O_{20}$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $CaCu_3Ti_4O_{12}$, and $Li_{0.5}La_{0.5}TiO_3$ [7-10]. However, the synthesis and dielectric properties of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared *via* microwave sintering have never been studied. Therefore, the present work aims to investigate the processing, sinterability, microstructure, and dielectric properties of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared *via* microwave sintering and reveal the differences from those of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared *via* conventional sintering.

2. Experimental

$Ca_{0.6}La_{0.2667}TiO_3$ ceramics were prepared by conventional sintering and microwave sintering techniques for comparison. High-purity (≥ 99%) oxide powders of $CaCO_3$, La_2O_3, and TiO_2 were used as starting materials. These powders were weighed according to the desired stoichiometry of $Ca_{0.6}La_{0.2667}TiO_3$ and then wet ball milled in ethanol for 12 h in polyethylene bottles with zirconia balls. All mixtures were dried and calcined at 1100ºC for 3 h in an alumina crucible. Then the calcined powders were remilled for 12 h, dried, and mixed with a 7wt% polyvinyl alcohol solution as a binder. After passing through a 40-mesh screen, the powders were uniaxially pressed at 100 MPa, and then cold isostatically pressed into pellets of 11 mm in diameter and 5 mm in height at 300 MPa to obtain homogeneous and better compaction of green pellets. For the conventional sintering method, one batch of these pellets was sintered finally at 1350-1500ºC for 4 h in a conventional muffle furnace with the heating rate and cooling rate controlled at 2 ºC/min. In case of the microwave sintering technique, another batch of green pellets was sintered at 1250-1450ºC for 30 min in a microwave oven (a frequency of 2.45 GHz and a maximum power of 4 kW). Meanwhile, the heating rate and the cooling rate were both kept at 20ºC/min (by controlling the input power to the microwave oven) for the microwave sintering process. During preparing the microwave sintered samples, the binder in the green pellets was carefully expelled at 600ºC for 2 h in a conventional electrical resistance furnace, and then the debound pellets were moved in a small alumina crucible and covered with an alumina lid. Subsequently, they were surrounded by SiC coarse powder and covered with another big alumina crucible. The SiC coarse powder acts as a secondary heater because it can readily absorb microwave and cause a rapid temperature rise of the pellets at a lower temperature. Temperature measurements in the microwave furnace were carried out using a digital infrared pyrometer. Sintering temperature profiles of the microwave sintering and conventional sintering process are illustrated in Fig. 1.

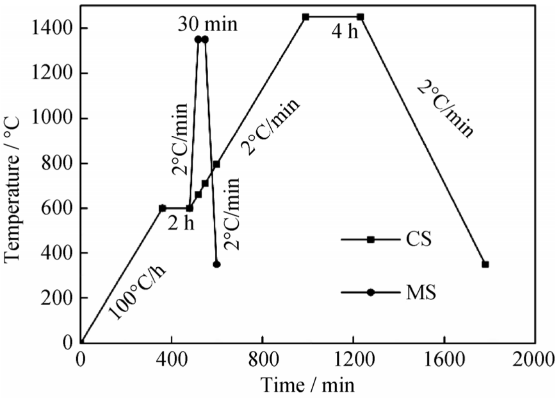

Fig. 1. Sintering temperature profiles of the conventionally and microwave sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics. MS—microwave sintering; CS—conventional sintering, hereinafter the same.

The bulk densities of the sintered pellets were measured by the Archimedes method. The theoretical density of 4.604 g/cm^3 was used for calculation of relative densities. The crystalline phases of the sintered pellets were identified by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructures of the sintered pellets were observed by scanning electron microscopy (SEM, JEOL JSM 6490, Japan). All pellets for SEM observation were polished and thermally etched at a temperature which was 100ºC lower than the sintering temperature. Grain size for these pellets was measured using the line-intercept method [11]. The ε_r and unloaded Q values at microwave frequencies were measured using Hakki-Coleman dielectric resonator method, as modified and improved by Courtney *et al.* [12-13]. The τ_f was measured in the temperature range from 25 to 80ºC.

3. Results and discussion

The relative densities of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics synthesized by conventional sintering at 1350-1500ºC for 4 h and those prepared by microwave sintering at 1250-1400ºC for 30 min are illuminated in Fig. 2, respectively. It can be seen that $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared by microwave sintering exhibit enhanced densification, compared with those prepared by conventional sintering at below 1450ºC. For example, the relative density of the sample by microwave sintering at 1350ºC can reach the maximum value of 97.23% whereas that of the sample by conventional sintering at the same temperature is only 82.96%. In contrast, the conventionally sintered sample at 1450ºC can reach the 97% theoretical density, which is comparable to that obtained by microwave sintering at 1350ºC. This may be due to the better sinterability in the microwave sintering process at a lower temperature than the conventional sintering method. In microwave sintering process, the activation energy for sintering is reduced and the densification mechanisms of volume and grain boundary diffusion appear due to a microwave effect in the presence of an external electrical field at a relative lower sintering temperature. In fact, the temperature increase of $Ca_{0.6}La_{0.2667}TiO_3$ samples at low temperatures (<800ºC) is primarily by thermal radiation from the SiC susceptance powder because $Ca_{0.6}La_{0.2667}TiO_3$ is a low dielectric loss material at low temperature. At higher temperatures, the radiation cooling of $Ca_{0.6}La_{0.2667}TiO_3$ occurs, while the continuing temperature increase is due to microwave power absorption by $Ca_{0.6}La_{0.2667}TiO_3$ with increasing dielectric loss. It is obvious that if the resultant densities from heating the samples in the microwave oven would be due only to indirect heating from the susceptor, the values of densities would be identical to those for the conventional heating method. In addition, a "microwave field effect" was found in microwave sintered Al_2O_3 or ZrO_2 ceramics by many researchers [14-17]. The "microwave field effect" shows that the same soaking time and sintering temperature in the microwave field give higher densities and finer microstructures. Meanwhile, enhanced densification in the microwave field is also observed. Even though there is still much to explain in microwave field assisted densification, the effect appears real and significant.

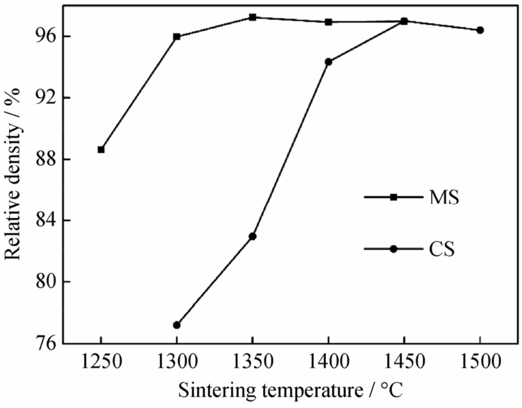

Fig. 2. Relative densities of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared by conventional and microwave sintering techniques as a function of sintering temperature.

The XRD patterns of some samples prepared by conventional and microwave sintering techniques are shown in Fig. 3. All the peaks in the XRD patterns are in good agreement with JCPDF card 89-0058 ($(CaTiO_3)_{0.6}(La_{0.3333}Nd_{0.3333}TiO_3)_{0.4}$), only accompanying with a shift of all the peaks to the lower angles. This is because that La^{3+} ions with a larger ionic radius (0.136 nm) are substituted for Nd^{3+} ions with a smaller ionic radius (0.127 nm). Obviously, the resultant XRD patterns mean that $Ca_{0.6}La_{0.2667}TiO_3$ phase with an orthorhombic perovskite structure can be obtained without detectable secondary phase formation. It may be deduced that the two sintering techniques have no distinct effect on the crystalline structure.

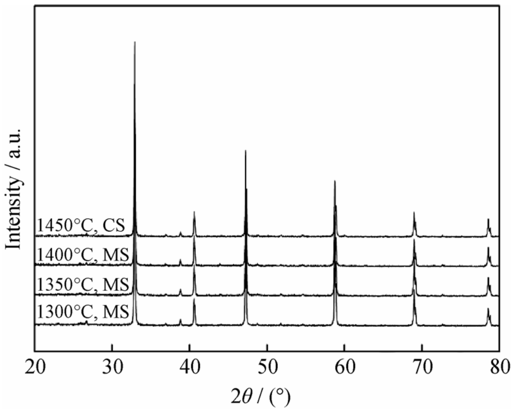

Fig. 3. XRD patterns of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared by conventional and microwave sintering techniques.

There are no significant differences in microstructural characteristics of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics at different sintering temperatures. The typical scanning electron micrographs (SEM) of the surfaces of microwave and conventionally sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics with the highest density are demonstrated in Fig. 4. It can be observed that well densified ceramics are obtained, and almost no porosity is observed, regardless of sintering methods used, but the microstructures of the $Ca_{0.6}La_{0.2667}TiO_3$ ceramics change significantly with different sintering techniques. As far as the macroscopical characteristics are concerned, the grains are relatively larger for the conventionally sintered ceramics (~40 μm, Fig. 4(b)) than those for the microwave sintered materials (~5 μm, Fig. 4(a)) due to a higher sintering temperature and a longer soaking time. As is well known, experimental parameters such as sintering temperature, sintering time, and heating rate must be optimized in order to control microstructural development. In microwave sintering, rapid heating has produced beneficial effects such as high final sintered density for a given grain size or fine microstructure compared with slow heating for similar densities, but conventional fast heating possesses some difficulties. Differential sintering that causes differential densification is one of the problems most often encountered in conventional fast heating. Therefore, microstructural development, a much finer average grain size, and a higher density obtained in the $Ca_{0.6}La_{0.2667}TiO_3$ system by microwave sintering result in improved dielectric properties. It has also been observed that the microwave sintered ceramics possess pronouncedly smaller grains than the conventionally sintered ones in other materials system [10, 18]. A probable explanation for this phenomenon is that different sintering methods lead to the difference of diffusion mechanisms in sintering. According to the sintering theory, the densification of ceramics depends on mass transport, which includes surface transport and bulk transport. In case of microwave sintering, grain boundary diffusion and bulk diffusion are more important than surface diffusion, which plays a dominant role in the conventional sintering process. Surface diffusion that leads to a coarse-graining process in low temperature can be effectively avoided in microwave sintering due to the rapid heating rate of 20°C/min. Therefore, bulk diffusion will directly be conducted to densify the sintering materials. In the grain growth process, the densification results from interdiffusion between the vacancies and the adjacent cations or anions. Such a process is markedly enhanced in the presence of the microwave, since the vacancy-cation (or vacancy-anion) pairs are polar in nature. To reiterate, the microwave sintering process can preferentially improve the densification process without inducing grain growth, resulting in a fine grain microstructure [19].

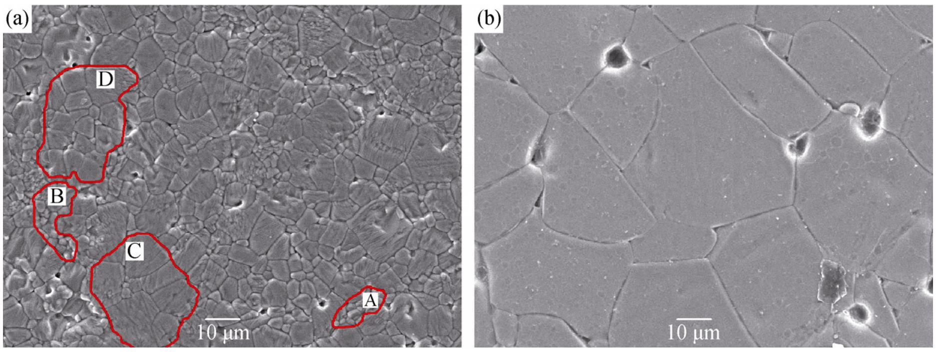

Fig. 4. SEM images of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics with the highest densities for different sintering techniques: (a) microwave sintering; (b) conventional sintering.

On the other hand, in case of microscopical characteristics, there is a remarkable difference in the microstructures of microwave and conventionally sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics. It can be found from Fig. 4 that the grain size distribution of conventionally sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics is more homogeneous than that of the microwave sintered. Moreover, a trend is found that some larger grains (grain size range: 8-10 μm) incline to assemble in one area (such as areas C and D in Fig. 4(a)) but some smaller ones (grain size range: 2-4 μm) incline to gather in another area (such as areas A and B in Fig. 4(a)) in microwave sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics. This difference in the microstructure may be caused by different heating mechanisms in different sintering processes. It is well known that energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material in conventional sintering. In contrast, microwave energy is transferred directly to materials by an interaction of the electromagnetic field at the molecular level in microwave sintering. In other words, the sintering effect is achieved by materials absorbing microwave energy itself in the electromagnetic field. The degree to absorption of microwave energy will be different if the composition in the sintered ceramics is inhomogeneous, which commonly appears in the materials prepared by the solid state reaction method. Once the composition of the microarea absorbs readily microwave energy, the temperature of this area will rise and then the grains grow.

Variations of microwave dielectric properties for $Ca_{0.6}La_{0.2667}TiO_3$ ceramics prepared by conventional and microwave sintering at different sintering temperatures are shown in Fig. 5. The microwave dielectric properties are significantly influenced by sintering temperature, regardless of sintering techniques. The curves of ε_r and Qf have similar trends. The values of ε_r and Qf first increase with the increase of sintering temperature, reach a maximum at 1350°C for microwave sintering and 1450ºC for conventional sintering, and then decrease continuously, which are in good agreement with change of density as a function of sintering temperature. This is because the microwave dielectric properties of the ceramics are generally known to be strongly influenced by relative density. O'Bryan *et al.* [20] reported that all of the dielectric properties are improved after increasing the sintering density. The same result is confirmed by the relationship between the microwave dielectric properties and relative density of the ceramics prepared by microwave sintering that is widely considered as one of new ceramic sintering techniques.

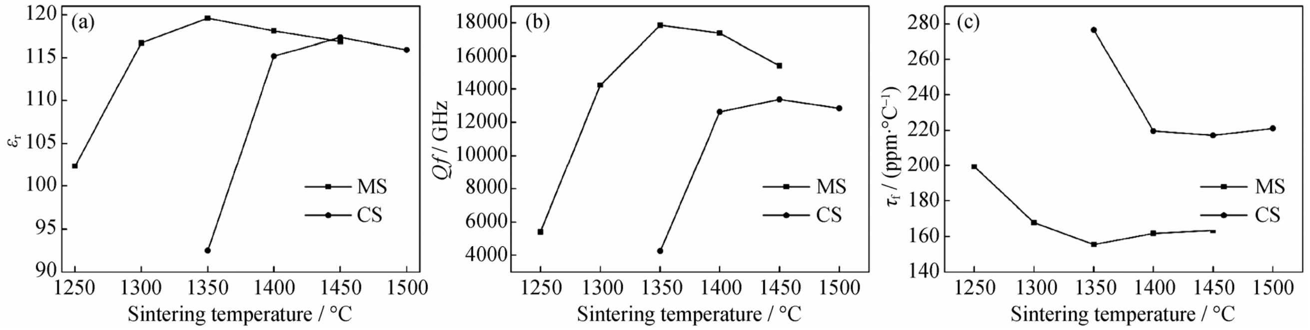

Fig. 5. Microwave dielectric properties of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics as a function of sintering temperature: (a) ε_r; (b) Qf; (c) τ_f.

However, there are some differences in microwave dielectric properties of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics for the two sintering techniques. Firstly, as shown in Fig. 5(a), the microwave sintered sample possesses a larger ε_r value at the same sintering temperature compared with the conventionally sintered one. The result can be explained by the difference in the microstructures of the microwave sintered ceramics and the conventionally sintered ceramics. In general, the dielectric constant depends on crystalline phase and preparation processing. The secondary phase is not detected in the microwave sintered samples or conventionally sintered samples, as confirmed in Fig. 3. Therefore, the dielectric constant of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics is closely related to preparation processing. From the above results of relative densities and microstructures of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics as shown in Fig. 2 and Fig. 4, microwave sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics exhibit a finer grain size and higher relative density compared with the conventionally sintered ones, which lead to a larger dielectric constant. Earlier studies reported that the dielectric constant of microwave ceramics such as $BaTiO_3$ [21-22] is affected by grain size, showing the maximum at an appropriate grain size (about 1 μm for the $BaTiO_3$ system) and then decreasing with increasing grain size, which is called "grain size effect". However, the grain sizes of the microwave and conventionally sintered samples are about 5 and 40 μm, respectively. In the light of these results, a conclusion may be drawn that the grain size effect is available in the $Ca_{0.6}La_{0.267}TiO_3$ system, but the critical grain size must be far smaller than 5 μm. Therefore, the ε_r value of the microwave sintered sample is slightly higher than that of the conventionally sintered sample. The maximum value of dielectric constant (ε_r = 119.6) is obtained at 1350ºC for microwave sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics, whereas the maximum value of dielectric constant (ε_r = 117.4) appears at 1450ºC for conventionally sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics. Thus, it can be concluded that better microwave properties and energy saving can be obtained by microwave sintering because of the lower sintering temperature.

Secondly, as shown in Fig. 5(b), microwave sintered $Ca_{0.6}La_{0.2667}TiO_3$ ceramics possess a remarkably larger Qf value compared with the conventionally sintered ones at the same sintering temperature. In general, there are many factors to influence the Q value, such as sintered density, crystal defects, microstructure, and secondary phase. The lower Qf value may be partly due to the lower relative density of $Ca_{0.6}La_{0.2667}TiO_3$ ceramics by conventional sintering at 1350-1500ºC. In addition, it was reported that the lattice imperfections and dielectric losses of the samples depend on fine grain size [23]. As observed in Fig. 4, the grain size of the conventionally sintered sample is obviously larger than that of the microwave sintered sample. Over-large grains in dielectric ceramics usually contain more defects, such as dislocations, planar defects, and even dislocation networks, which lead to the decrease of Qf values to some extent [24-25]. On the other hand, there are two basic kinds of crystal defects in the present ceramics. One is derived from La^{3+} ion substitution for Ca^{2+} ions in $CaTiO_3$, and the defect reaction is given by the following equation:

$$La_{2/3}TiO_3 \rightarrow \frac{2}{3}La_{Ca}^{\bullet} + \frac{1}{3}V_{Ca}'' + Ti_{Ti}^{x} + 3O_{O}^{x} \quad (1)$$

The other is the familiar oxygen vacancy formation reaction given by

$$2\mathrm{Ti}_{\mathrm{Ti}}^{x} + \mathrm{O}_{\mathrm{O}}^{x} \rightarrow 2\mathrm{Ti}'_{\mathrm{Ti}} + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O}_2 \qquad (2)$$

The increase in grain size generally results in more oxygen vacancies in titanate ceramics [26], because the reoxidation process during cooling penetrates little to the larger grains, and this leads to the increase of dielectric loss with increasing sintering temperature. In addition, all unit cell volumes for the microwave and conventionally sintered samples are calculated and the value is 0.22625 nm^3 for the microwave samples sintered at 1350 °C, which is markedly lower than the value of 0.22637 nm^3 for the conventional sample sintered at 1450°C. In general, a decrease in lattice parameter means a decrease in defects concentration. This decreasing defects concentration will also result in the increasing of quality factor. It is obvious that the *Qf* values of the samples by conventional sintering at 1450 and 1500°C (13375 GHz and 12846.9 GHz, respectively) are lower than those of the microwave samples sintered at 1350 and 1400°C (17858.5 GHz and 17379.5 GHz, respectively), although their relative densities are similar to those of the microwave samples (relative density > 95%).

The τ_f values of $\mathrm{Ca_{0.6}La_{0.2667}TiO_3}$ ceramics prepared by conventional and microwave sintering techniques are illuminated in Fig. 5(c). It is well known that τ_f is related to the composition and the secondary phase of a material. As the composition remained unchanged and no secondary phase is detected, no significant change in the τ_f value is observed as expected for a fixed sintering technique. The measured τ_f values range from 155.5 to 199.3 ppm/°C for microwave sintered $\mathrm{Ca_{0.6}La_{0.2667}TiO_3}$ ceramics, which are remarkably lower than those of conventionally sintered $\mathrm{Ca_{0.6}La_{0.2667}TiO_3}$ ceramics in this paper (τ_f= 217.2 ppm/°C) and the published literatures (τ_f= 213 and 304.4 ppm/°C) [5, 27]. It is amazing that the τ_f value is suppressed by microwave sintering. Unfortunately, it is unclear whether the relationship is a coincidence between τ_f and grain size or not. However, a conclusion may be drawn that the decrease in τ_f of the microwave sintered sample results from changes in crystal structure with grain size reduction. To our knowledge, no related research on this aspect has been reported. Therefore, an elaborate investigation must be carried out to make the suppressed mechanism of microwave sintering on the τ_f of dielectric ceramics clear. Now this corresponding work is ongoing in our lab.

4. Conclusions

$\mathrm{Ca_{0.6}La_{0.2667}TiO_3}$ dielectric ceramics have been prepared by conventional and microwave sintering techniques at different sintering temperatures. A comparative investigation on their sinterability, microstructure, and microwave dielectric properties has also been performed. The results show that microwave sintering can reduce the sintering temperature and shorten the sintering time due to a microwave effect. Compared with the conventionally sintered ceramics, microwave sintered $\mathrm{Ca_{0.6}La_{0.2667}TiO_3}$ ceramics possess a finer and inhomogeneous microstructure. At the same time, they exhibit the slightly higher ε_r, improved *Qf* value, and suppressed τ_f. The microwave dielectric properties for the samples prepared by microwave sintering at 1350°C are ε_r = 119.6, *Qf* = 17858.5 GHz, and τ_f = 155.5 ppm/°C. In contrast, the dielectric properties for the samples prepared by conventional sintering at 1450°C are ε_r= 117.4, *Qf* = 13375 GHz, and τ_f = 217.2 ppm/°C. The improvement in *Qf* values is attributed to a higher densification and fewer oxygen vacancies in the microwave sintered ceramics, whereas the reason that the τ_f values of microwave sintered ceramics are suppressed is still unclear but is worthy of further study.

References

[1] H. Takahashi, Y. Baba, K. Ezaki, Y. Okamoto, and K. Shibaba, K. Kuroki, and S. Nakano, Dielectric characteristics of $(\mathrm{A}_{1/2}^{1+}\mathrm{A}_{1/2}^{3+})\mathrm{TiO_3}$ ceramics at microwave frequencies, *Jpn. J. Appl. Phys.*, 30(1991), p.2339.

[2] J.P. Mercurio, M. Manier, and B. Frit, Dielectric properties of ceramics within the $\mathrm{BaO\text{-}Ln_2O_3\text{-}TiO_2}$ system, *Ferroelectrics*, 127(1992), p.35.

[3] K. Ezaki, Y. Baba, H. Takahashi, K. Shibata, and S. Nakano, Microwave dielectric properties of $\mathrm{CaO\text{-}Li_2O\text{-}Ln_2O_3\text{-}TiO_2}$ ceramics, *Jpn. J. Appl. Phys.* 1, 32(1993), p.4319.

[4] J. Kato, H. Kagata, and K. Nishimoto, Dielectric properties of lead alkaline-earth zirconate at microwave frequencies, *Jpn. J. Appl. Phys.*, 30(1991), p.2343.

[5] C.L. Huang, J.S. Tsai, and Y.B. Chen, Dielectric properties of $(1-y)\mathrm{Ca}_{1-x}\mathrm{La}_{2x/3}\mathrm{TiO_3}\text{-}y(\mathrm{Li,Nd})_{1/2}\mathrm{TiO_3}$ ceramic system at microwave frequency, *Mater. Res. Bull.*, 36(2001), No.3-4, p.547.

[6] P. Yadoji, R. Peelamedu, D. Agrawal, and R. Roy, Microwave sintering of Ni-Zn ferrites: comparison with conventional sintering, *Mater. Sci. Eng. B*, 98(2003), No.3, p.269.

[7] I. Teoreanu, E. Andronescu, and A. Folea, Microwave processing of $\mathrm{Ba_2Ti_9O_{20}}$ ceramics, *Ceram. Int.*, 22(1996) No.4, p.305.

[8] B. Vaidhyanathan, D.K. Agrawal, T.R. Shrout, and Y. Fang, Microwave synthesis and sintering of $\mathrm{Ba(Mg_{1/3}Ta_{2/3})O_3}$, *Mater. Lett.*, 42(2000), No.3, p.207.

[9] S.D. Hutagalung, M.I.M. Ibrahim, and Z.A. Ahmad, Microwave assisted sintering of $\mathrm{CaCu_3Ti_4O_{12}}$, *Ceram. Int.*,

34(2008), No.4, p.939.

[10] H.X. Geng, A. Mei, C. Dong, Y.H. Lin, and C.W. Nan, Investigation of structure and electrical properties of $Li_{0.5}La_{0.5}TiO_3$ ceramics via microwave sintering, *J. Alloys Compd.*, 481(2009), No.1-2, p.555.

[11] R.L. Fullman, Measurement of particle size in opaque bodies, *J. Met.*, 5(1953), No.3, p.447.

[12] B.W. Hakki and P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, *IRE Trans. Microwave Theory Tech.*, 8(1960), p.402.

[13] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators, *IEEE Trans. Microwave Theory Tech.*, 18(1970), p.476.

[14] M.A. Janney and H.D. Kimrey, Microwave sintering of alumina at 28 GHz, [in] *Ceramic Powder Science IIB*, Westerville, 1988, p.919.

[15] Y. Fang, D.K. Agrawal, D.M. Roy, and R. Roy, Microwave sintering of hydroxyapatite ceramics, *J. Mater. Res.*, 9(1994), No.1, p.180.

[16] A.Dé, I. Ahmad, E.D. Whitney, and D.E. Clark, Effect of green microstructure on microwave processing of alumina: effect of particle size, *Ceram. Eng. Sci. Proc.*, 11(1990), No.9-10, p.1743.

[17] S.A. Nightingale, D.P. Dunne, and H.K. Worner, Sintering and grain growth of 3 mol% yttria zirconia in a microwave field, *J. Mater. Sci.*, 31(1996), No.19, p.5039.

[18] H.Y. Chang, H.W. Chen, C.T. Hu, and I. Lin, High T_c positive temperature coefficient resistivity $(Pb_{0.6}Sr_{0.3}Ba_{0.1})TiO_3$ materials prepared by microwave sintering, *Ferroelectrics*, 195(1997), No.1, p.65.

[19] C.Y. Tsay, K.S. Liu, and I. Lin, Microwave sintering of $(Bi_{0.75}Ca_{1.2}Y_{1.05})(V_{0.6}Fe_{4.4})O_{12}$ microwave magnetic materials, *J. Eur. Ceram. Soc.*, 24(2004), No.6, p.1057.

[20] H.M. O'Bryan Jr., J. Thomson Jr., and J.K. Ploude, New $BaO\text{-}TiO_2$ compound with temperature stable high permittivity and low microwave loss, *J. Am. Ceram. Soc.*, 57(1974), No.10, p.450.

[21] G. Arlt, D. Hennings, and G. De With, Dielectric properties of fine-grained barium titanate ceramics, *J. Appl. Phys.*, 58(1985), No.4, p.1619.

[22] M.H. Frey, Z. Xu, P. Han, and D.A. Payne, The role of interfaces on an apparent grain size effect on the dielectric properties for ferroelectric barium titanate ceramics, *Ferroelectrics*, 206(1998), No.1, p.337.

[23] S. Kucheiko, J.W. Choi, H.J. Kim, and H.J. Jung, Microwave dielectric properties of $CaTiO_3\text{-}Ca(Al_{1/2}Ta_{1/2})O_3$ ceramics, *J. Am. Ceram. Soc.*, 79(1996), No.10, p.2739.

[24] M.H. Liang, C.T. Hu, H.F. Cheng, I.N. Lin, and J. Steeds, Effect of sintering process on microstructure characteristics of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics and their microwave dielectric properties, *J. Eur. Ceram. Soc.* 21(2001), No.15, p.2759.

[25] C.C. Chou, D.S. Tsai, I.N. Lin, and J. Steeds, Microstructural defects in $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave dielectric materials, *Mater. Chem. Phys.*, 79(2003), No.2-3, p.218.

[26] M.S. Fu, X.Q. Liu, and X.M. Chen, Structure and dielectric characteristics of $Ca_{1\text{-}x}Nd_{2x/3}TiO_3$ ceramics, *J. Eur. Ceram. Soc.*, 28(2008), No.3, p.585.

[27] B.L. Liang, X.H. Zheng, W.Q. Ni, and D.P. Tang, $Ca_{1-3x}Ln_{2x}TiO_3$ (x = 0.13, 0.2; Ln = La, Nd, Sm): high ε microwave dielectric ceramics, *Rare Met. Mater. Eng.*, 36(2007), Suppl.1, p.418.