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Short communication

Microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics with perovskite-like layered structure

Chunchun Li [a], Xiaoyong Wei [a,*], Haixue Yan [b], Michael J. Reece [b]

[a] *Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China*

[b] *School of Engineering and Material Science, Queen Mary University of London, London E1 4NS, UK*

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Abstract

The first characterization of the microwave dielectric properties of the $La_3Ti_2TaO_{11}$ ceramics is presented. An ordinarily sintered ceramic at 1560 °C exhibits good microwave dielectric properties with $\varepsilon_r = 46$, $Q \times f = 7500$ GHz and $\tau_f = -47$ ppm/°C. An alternative approach to tailor the temperature coefficient of resonate frequency of $La_3Ti_2TaO_{11}$ ceramics is also presented. Textured $La_3Ti_2TaO_{11}$ ceramics were fabricated using spark plasma sintering (SPS). By controlling the sintering temperature, orientation degree increased together with the steadily increase in ε_r and $Q \times f$. A noteworthy change in τ_f from −43.1 ppm/°C to −13.6 ppm/°C with increasing orientation degree was observed. These results suggest that grain-orientation control was an effective way to tailor the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics.

Keywords: Dielectric properties; Powders-solid state reaction; Sintering; X-ray methods; Perovskite-like structure

1. Introduction

Microwave dielectric ceramics have been widely used for several decades as dielectric resonators (DRs) and filters for reasons of cost, dimension, stability, efficiency and ease of use.[1] To qualify as a commercially viable microwave ceramic, three key properties need to be optimized: a high quality factor (Q) for the selectivity, a high relative permittivity (ε_r) to enable miniaturization and a near zero temperature coefficient of resonant frequency (τ_f) to satisfy thermal stability.[2,3] In spite of any of these requirements alone can be satisfied in a broad range of materials, their combination severely limits the number of available options. Therefore, further searching for new materials with desired properties and simple experimental procedure is still a hot issue of scientific research.

Recently, dielectrics in the system $A_nB_nO_{3n+2}$ with perovskite-like layered structure (PLS) have been considered to be promising materials for microwave applications since they exhibit relatively high dielectric constant, small temperature coefficient of permittivity (τ_ε) and low dielectric loss, such as $Ln_2Ti_2O_7$ (Ln = La, Nd)[4–7] and $A_2M_2O_7$ (A = Ca, Sr; M = Nb, Ta) systems.[8] $La_3Ti_2TaO_{11}$ is an $n = 3$ member of the serious $A_nB_nO_{3n+2}$.[9] The structure of $La_3Ti_2TaO_{11}$ was described as being built up of perovskite layers with $n = 2$ (orthorhombic $LaTaO_4$) and $n = 4$ (orthorhombic $La_2Ti_2O_7$) stacked in an ordered manner. In consideration of the low loss and temperature stability of $La_2Ti_2O_7$, it is reasonable to anticipate that $La_3Ti_2TaO_{11}$ can possess an intrinsic coexistence of a high Q and a low τ_f.

Moreover, it has been previously reported that texture in ceramics are available for enhancing the dielectric properties due to the large anisotropy in the textured structure. Wada et al.[10] reported that a desired τ_f value could be obtained by controlling the grain orientation in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics while maintaining high ε_r and $Q \times f$ values. More recently, highly grain-oriented $Ln_2Ti_2O_7$ (La = La, Nd)[6] and $A_2Nb_2O_7$ (A = Ca, Sr)[11] ceramics fabricated by spark plasma sintering (SPS) were obtained because of the typical plate-like grain morphology of these ceramics and the textured ceramics were characterized by enhanced dielectric and piezoelectric properties. It evoked our attention to investigate the texture effects on the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics.

* Corresponding author. Tel.: +86 29 82668679; fax: +86 29 82668794.
E-mail address: wdy@mail.xjtu.edu.cn (X. Wei).

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In the present work, we fabricated polycrystalline $La_3Ti_2TaO_{11}$ ceramics by conventional sintering and spark plasma sintering (SPS). The microwave dielectric properties of the present ceramics were characterized and reported for the first time. The grain orientation effects on the microwave properties were also measured and discussed.

2. Experimental procedure

2.1. Powder synthesis

$La_3Ti_2TaO_{11}$ powders were prepared by high temperature solid state reactions of high purity raw powders of La_2O_3 (99.9%), Ta_2O_5 (99.95%) and TiO_2 (99.9%). Prior to weighing, La_2O_3 and TiO_2 were dried at 900 °C to remove the moisture. Stoichiometric amounts of the raw powders were weighed and ball milled using zirconia balls for 4 h in plastic containers with ethanol as media. The powders were calcined at 1300–1450 °C for 4 h.

2.2. Ceramic fabrication

2.2.1. Conventional

The calcined powders were re-milled well and mixed with 5 wt.% solution of PVA as a binder. The resultant powders were then uniaxially pressed into cylindrical disks with 11 mm diameter and 7 mm height under a pressure of 150 MPa. The samples were fired at 600 °C for 2 h to remove the organic binder and then sintered in the range 1480–1560 °C for 4 h to approach the maximum densities. The samples were cooled at a rate of 2 °C/min to 1100 °C, and then naturally cooled to room temperature.

2.2.2. Spark plasma sintering (SPS)

Textured ceramics were prepared using a two-step SPS process. In the first step, the powders were sintered in a graphite die with a diameter of 20 mm for 3 min under a pressure of 75 MPa at 1350 °C. In the second step, these sintered ceramics were placed in a graphite die with a diameter of 30 mm for sintering at 1400–1475 °C for 5 min under a pressure of 80 MPa. The compressive stress of 75 MPa was applied within 1 min of reaching the target temperatures. Finally, the sintered ceramics were annealed at 100 °C below their sintering temperature for 10–20 h in an air furnace to remove any carbon contamination, which increased their DC resistivity and density.

2.3. Characterization

Both conventional sintered and SPS-ed $La_3Ti_2TaO_{11}$ disks were annealed at 1200 °C for 10 h. The densities of the compacts were measured by the Archimedes method. The phase constitution of the samples was examined using an X-ray diffractometer (Rigaku D/MAX-2400, Japan) using CuKa radiation ($\lambda = 0.15406$ nm) in a 2θ range from 15° to 55°. The degree of grain orientation was estimated using the Lotgering orientation factor, *f*, from the XRD peak intensities, $I.f = (P - P_o)/(1 - P_o)$, where $P = \sum I(h\,0\,0)/\sum I(h\,k\,l)$ over 15–50° of 2θ values; $P_o = P$ for a non-oriented sample. The microstructures were studied using a JEOL JSM-6390A scanning electron microscopy (SEM). The microwave dielectric properties were measured by the dielectric post resonator method using a network analyzer (Model N5230A, Agilent, USA) and a temperature chamber (DELTA 9039, Delta Design, USA). The τ_f values were measured by noting the variation of resonant frequency of the TE_{011} resonant mode over the temperature range of 25–85 °C.

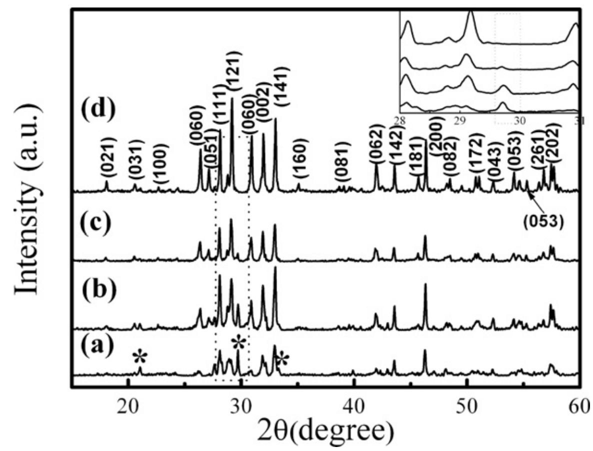

Fig. 1. Room-temperature XRD patterns of $La_3Ti_2TaO_{11}$ powders calcined at different temperatures: (a) 1300 °C, (b) 1350 °C, (c) 1400 °C, and (d) 1450 °C (peaks of second phases are marked with asterisks). Inset: detail with enlarged scale.

3. Results and discussion

3.1. Phase analysis and the microwave dielectric properties of ordinarily sintered $La_3Ti_2TaO_{11}$ ceramics

XRD patterns performed on the calcined $La_3Ti_2TaO_{11}$ powders at various temperatures are presented in Fig. 1. Within the sensibility of the XRD equipment, all the observed peaks of 1450 °C calcined powders are in good agreement with the diffraction data for pure $La_3Ti_2TaO_{11}$ (JCPDF No. 54-0632) with space group $Pmc2_1$. Nevertheless, when calcined at temperatures below 1450 °C, the trace amount of second phase can be detected in terms of appearance of some additional peaks (marked separately with asterisks in the patterns). The second phase is identified as Ta_2O_5 (JCPDF No. 54-0632). These results suggest that the minimum temperature for pure $La_3Ti_2TaO_{11}$ phase is limited to 1450 °C. Dense ceramics with relative densities above 90% were obtained when sintered above 1520 °C. Fig. 2(a)–(d) presents SEM imagines obtained for the thermally etched surface of $La_3Ti_2TaO_{11}$ ceramics sintered at different temperatures. A porous microstructure was observed for the 1480 °C sintered ceramic (Fig. 2(a)). With increasing sintering temperature, the grain size of the ceramics was slightly increased while the porosity decreased. When sintered at 1540 °C, a dense microstructure with an average grain size of 2–5 μm was formed (Fig. 2(d)).

The variation of the relative density, ε_r and $Q \times f$ values with the sintering temperature are shown in Fig. 3. The relative density increased with sintering temperature and reached a

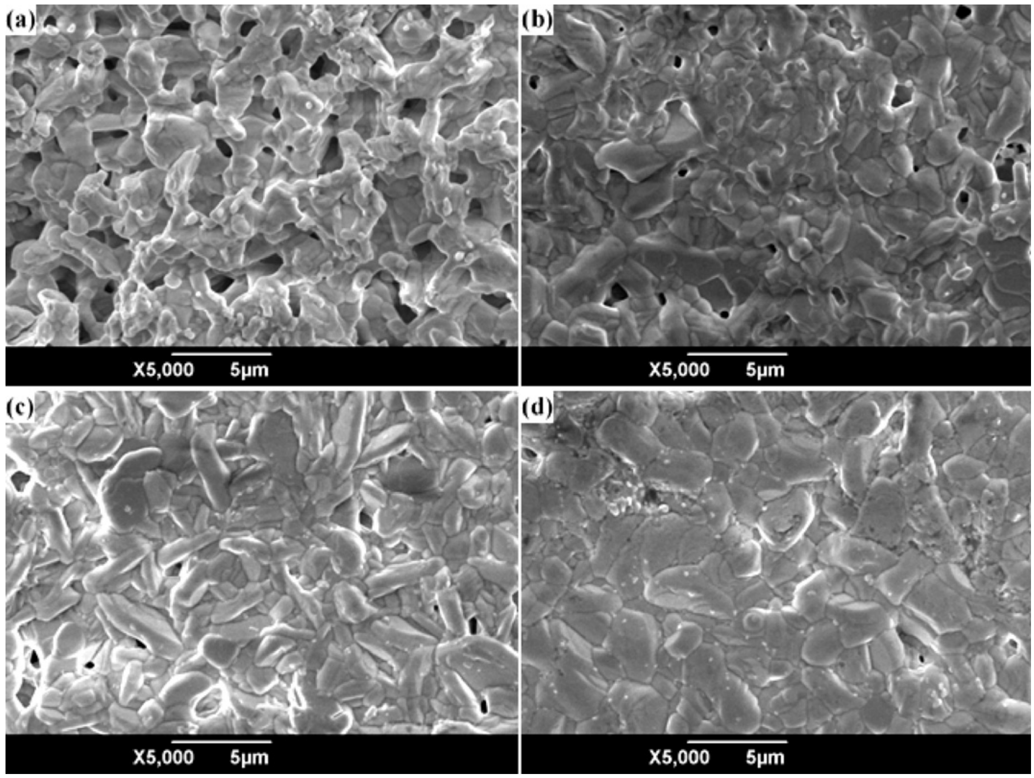

Fig. 2. SEM images of the surfaces of ordinarily sintered $La_3Ti_2TaO_{11}$ ceramics at (a) 1480 °C, (b) 1500 °C, (c) 1520 °C, and (d) 1540 °C.

maximum value of 97.3% of the theoretical density for samples sintered at 1560 °C. The relationship between relative permittivity and sintering temperature showed a tendency similar to that of relative density, indicating that the higher the density, the higher the permittivity. According to the SEM imagines shown in Fig. 2, the very low relative permittivity of the 1480 °C sintered samples can be ascribed to the porous microstructure.

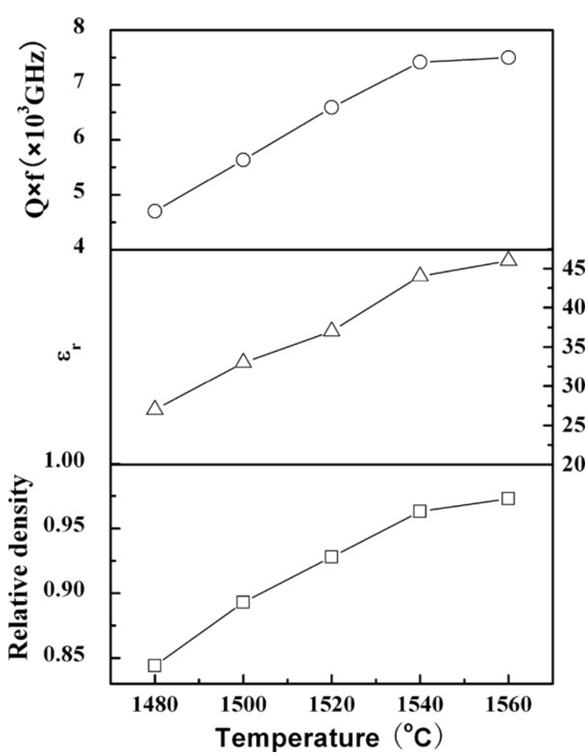

Fig. 3. The relative density, $Q \times f$, and ε_r values of the ordinarily sintered $La_3Ti_2TaO_{11}$ ceramics as a function of sintering temperature.

The variation of $Q \times f$ values with sintering temperature exhibited similar behavior to that of density and relative permittivity (Fig. 3), increasing remarkably from 4720 GHz to 7508 GHz. It is proposed that in the present work, the major factor that affected the quality factor were poor densification and the trapped porosity.[12] The temperature coefficient of resonant frequency of the 1560 °C sintered ceramic was calculated in temperature range 25–85 °C, to have a value of ∼−47 ppm/°C. Unfortunately, τ_f value is still too high for practical applications.

Table 1 summarizes the microwave dielectric properties (ε_r, $Q \times f$ and τ_f) of $La_3Ti_2TaO_{11}$ ceramics compared with those of other ceramics in $A_nB_nO_{3n+2}$ family. The relative permittivity of $La_3Ti_2TaO_{11}$ is competitive with that of $La_2Ti_2O_7$, whereas the $Q \times f$ value is much lower than those of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$. The dielectric properties of $La_3Ti_2TaO_{11}$ are competitive with

Table 1
Comparison of microwave properties of $La_3Ti_2TaO_{11}$ with other $A_nB_nO_{3n+2}$ microwave dielectric ceramics.

Composition	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Ref.
$Ca_2Nb_2O_7$	33.6	1300	−103	13
$Ca_2Ta_2O_7$	22.6	3300	235	13
$Ca_{1.4}Pb_{0.6}Nb_{0.5}Ta_{1.5}O_7$	39.2	3250	588	12
$La_2Ti_2O_7$	47	8500 (7.8 GHz)	−10	10,11
$Nd_2Ti_2O_7$	36	16,400 (9.1 GHz)	−118	10
$La_3Ti_2TaO_{11}$	46	7500 (4.56 GHz)	−47	This work

those of tungsten bronze-type $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R: rare earth) solid solutions ($Q \times f$ = 1800–10,000 GHz, small τ_f).[2,13] The τ_f value of $La_3Ti_2TaO_{11}$, however, is still too high for commercial applications. It is expected that upon optimization of the microwave properties, especially the τ_f value, the $La_3Ti_2TaO_{11}$ ceramics can be potentially useful for application in satellite communication and cell phone base stations, which requires the permittivity in the range of 25–50.

3.2. Effect of grain orientation on the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics

It is well known that the temperature stability of the materials is crucial for applications and should not exceed a few ppm/°C.[1,14,15] In the previous section, we found that τ_f value of $La_3Ti_2TaO_{11}$ is still high, which needs to be suppressed for commercial applications. Generally, two main approaches have been used to tune τ_f of microwave dielectric ceramics including partial cation substitution to form a solid solution and formation of composite materials with opposite sign of τ_f. However, these methods often give rise to the reduction in ε_r and/or $Q \times f$ values. Lastly, another effect method is reported to apparently tune τ_f values of microwave ceramics and films. Wada et al.[10] reported that grain-orientation control in $Ba_4Sm_{9.33}Ti_{18}O_{54}$ ceramics can tune τ_f to a desired value close to zero while maintaining ε_r and $Q \times f$ values. The present section discussed the effect of grain orientation on the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics.

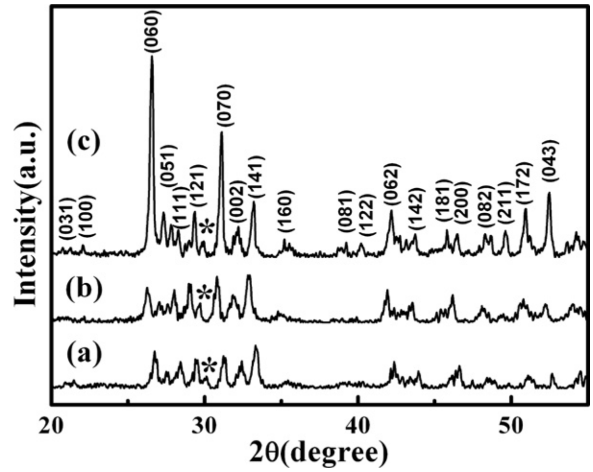

Fig. 4. XRD patterns performed on textured $La_3Ti_2TaO_{11}$ ceramics parallel to the pressing direction: (a) 1400 °C, (b) 1450 °C, and (c) 1475 °C (peaks of second phases are marked with asterisks).

Fig. 4 shows XRD patterns obtained for the textured $La_3Ti_2TaO_{11}$ ceramics sintered at 1400 °C, 1450 °C and 1475 °C, respectively. Broad peaks were observed in the XRD patterns which might be ascribed to the stressed induced during pressing and polishing. Despite of the high sintering temperature up to 1475 °C, the trace amount of second phase was detected with additional peak located at $2\theta \sim 30°$, similar to the XRD patterns of ordinarily sintered $La_3Ti_2TaO_{11}$ ceramics sintered below 1450 °C and the second phase was identified as

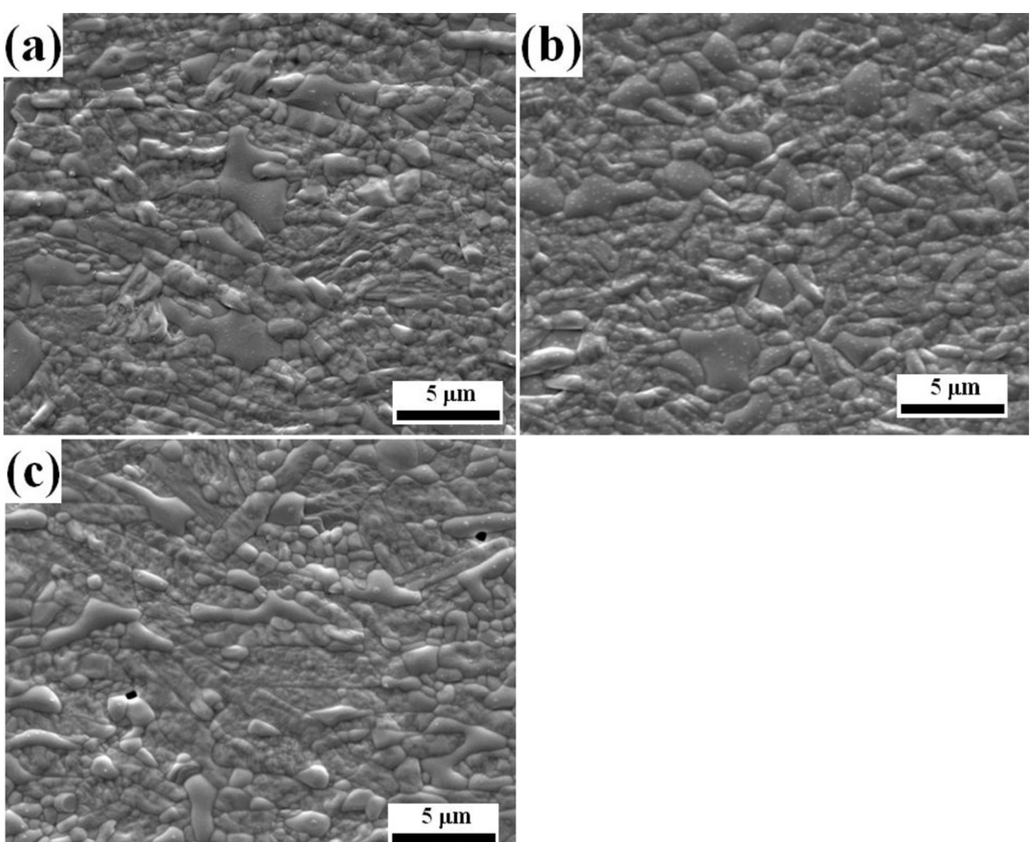

Fig. 5. SEM micrographs of the surface perpendicular to the pressing direction of textured $La_3Ti_2TaO_{11}$ ceramics: (a) 1400 °C, (b) 1450 °C, and (c) 1475 °C.

Table 2
The relative densities, the Lotgering orientation factor (*f*), and the microwave dielectric properties (ε_r, $Q\times f$ and τ_f) of SPS-ed $La_3Ti_2TaO_{11}$ ceramics sintered at different temperatures.

Sintering temperature	Relative densities	f	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
1400 °C	96.8%	0.32	48.2	8360	−43.1
1450 °C	97.5%	0.37	49.6	9842	−31.3
1475 °C	98.6%	0.63	52.3	11,026	−13.6

Ta_2O_5. The observed peaks except for the one at $2\theta\sim 30°$ could be indexed according to the orthorhombic $La_3Ti_2TaO_{11}$ with $Pmc2_1$ symmetry (JCPDF No. 54-0632) despite of the difference in relative intensity. There results suggested the formation of $La_3Ti_2TaO_{11}$ phase as the main crystalline phase with a second phase of Ta_2O_5. As expected, the XRD patterns from the surface perpendicular to the pressing direction exhibited stronger (0 *k* 0) reflections. As the temperature increased the degree of (0 *k* 0) orientation estimated using the Lotgering orientation factor increased distinctly, being maximized with a value of 0.63 for ceramics sintered at 1475 °C.

Dense ceramics with relative density above 96% could be obtained at relative lower temperature (∼1400 °C) with respect to that of ordinarily sintered samples (∼1560 °C), indicating that SPS effectively improved the sinterability of $La_3Ti_2TaO_{11}$ ceramics. SEM imagines of the polished and thermal etched surfaces perpendicular to the pressing direction of textured $La_3Ti_2TaO_{11}$ ceramics sintered at different temperature are depicted in Fig. 5. A very dense microstructure with only remaining porosity was clearly seen from these images for all the SPS-ed ceramics, accordance with the high relative densities. Elongated grains were observed in all the microstructures, but enhanced as the sintering temperature increases. Moreover, as the temperature increased obvious difference in terms of grain size, grains shape and the elongation of the grains were observed, indicating the strong dependence of the microstructures of textured ceramics on the sintering temperature.

The relative densities, the Lotgering orientation factor (*f*), and the microwave dielectric properties (ε_r, $Q\times f$ and τ_f) of SPS-ed $La_3Ti_2TaO_{11}$ ceramics are summarized in Table 2. As shown, the densification was enhanced and the grain orientation factor (*f*) obviously increased with increasing sintering temperature. Both relative permittivity (ε_r) and quality factor ($Q\times f$) showed a steadily increase as sintering temperature increased, which might be ascribed to the enhanced densification. The most noteworthy point is the change in the temperature coefficient of resonant frequency (τ_f) from −43.1 ppm/°C to −13.6 ppm/°C with the increase of sintering temperature from 1400 to 1475 °C, associated with the orientation factor (*f*) from 0.32 to 0.67. The observed relationship between τ_f and the orientation factor indicates that the change in τ_f may be related to the anisotropy changes in the morphology of textured $La_3Ti_2TaO_{11}$ ceramics. These results suggest that τ_f can be controlled to a desired value close to zero if sintered at the appropriate temperature. Similar effects were previous observed in textured $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = La, Nd and Sm) ceramics.[10,16] Additionally, the observed change in temperature coefficient of resonant frequency is partly due to the secondary phase, which needs to be further studied.

Compared with the ordinarily sintered $La_3Ti_2TaO_{11}$ ceramics, the SPS-ed ceramics show larger ε_r, higher $Q\times f$, and lower τ_f. The enhanced densification and texturing might be responsible for the improved dielectric properties. These results suggest that grain-orientation is an effective way to control the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics.

4. Conclusions

The first characterization of the microwave dielectric properties of the $La_3Ti_2TaO_{11}$ ceramics is presented. A ceramic with $\varepsilon_r = 46$, $Q\times f = 7500$ GHz and $\tau_f = -47$ ppm/°C was obtained when sintered at 1560 °C. Textured microstructure developed in $La_3Ti_2TaO_{11}$ ceramics fabricated by spark plasma sintering (SPS) and its impact on the microwave dielectric properties was studied. The orientation degree increased with increasing sintering temperature and approached 0.63 when sintered at 1475 °C. ε_r and $Q\times f$ showed a steadily increase as sintering temperature increased. A noteworthy change in τ_f from −43.1 ppm/°C to −13.6 ppm/°C with increasing orientation degree was observed. This result suggested that grain-orientation was an effective way to control the microwave dielectric properties of $La_3Ti_2TaO_{11}$ ceramics. Further work should be focused on the controlling of the sintering conditions to tailor τ_f to be a near-zero value.

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