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Microwave dielectric properties of ceramics with compositions along the $La_{2/3}TiO_{3(STAB)}$–$LaAlO_3$ tie line

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The stabilization of $La_{2/3}TiO_3$ in the perovskite structure by 4 mol% $LaAlO_3$ resulted in maximum values for the relative permittivity ($k' \approx 72$) and temperature coefficient of resonant frequency ($\tau_f = 123$ ppm K^{-1}). The *Q*-value (quality factor) of these ceramics were over 5300 measured at 4.5 GHz. Higher contents of $LaAlO_3$ cause a decrease in both the permittivity and τ_f values, accompanied by an increase in the *Q*-value. Typical values measured at 6.0 GHz for ceramics with the composition 70 mol% $La_{2/3}TiO_3$ – 30 mol% $LaAlO_3$ are $k' > 44$, $\tau_f = +7$ ppm K^{-1} and $Q > 5500$. The results depend on the processing parameters. The sintering temperature increases with increasing $LaAlO_3$ content. An oxidizing sintering atmosphere improves the *Q*-value, whereas the permittivity and τ_f are not significantly affected.

1. Introduction

Compounds in the La_2O_3–TiO_2 system have interesting dielectric and ferroelectric properties. In particular, $La_{2/3}TiO_3$ is noted for its exceptionally high dielectric constant of 130 at 1 MHz [1]. However, this high dielectric constant is accompanied by a high dielectric loss. It is generally accepted that $La_{2/3}TiO_3$ is unstable in its pure form due to the high content of vacant La sites in the perovskite structure. The compound may be prepared with a slight oxygen deficiency [1–3] and trapped electrons on oxygen vacancies give rise to detrimentally high dielectric losses.

$La_{2/3}TiO_3$ may be stabilized by incorporation of (2+) and (1+) ions onto the "A sites" of the perovskite structure [3–7]. It has recently been shown that $La_{2/3}TiO_3$ can also be stabilized by the substitution of $LaAlO_3$ [8]. Preliminary examination of the dielectric properties of that system indicated a lowering of the dielectric constant of $LaAlO_3$ addition, with considerably improved dielectric losses [9, 10]. A more detailed examination of the dielectric properties at microwave frequencies has been reported [11].

In this paper we describe the influence of the composition and sintering parameters on the microwave dielectric properties of the $La_{2/3}TiO_3$–$LaAlO_3$ solid solution series.

2. Experimental procedure

Samples were prepared using the standard solid-state reaction technique from La_2O_3 (99.9%, Johnson Matthey), TiO_2 (99.8%, Ventron), and Al_2O_3 (99.99%, Johnson Matthey). The starting powders were weighed out according to the scheme (1-x) $La_{2/3}TiO_3$ (x) $LaAlO_3$, where (x) varied between 0.02–0.50. Powders were homogenized using ethanol as the solvent contained in plastic containers, dried, pressed into pellets and calcined at 1300 °C for 15 h. After the first stage of calcination the pellets were milled and the powder was pressed and calcined again for an additional 15 h at 1350 °C to obtain homogeneity. Before the final heating the calcined material was milled with ZrO_2 balls for 1 h. The average grain size of the powder after milling was below 1 μm. These powders combined with a binder (4% acetone solution of camphor) were uniaxially pressed into disks 4 mm high and 10 mm in diameter that were about 55% of the theoretical density. These disks were then fired at different temperatures (from 1300 to 1450 °C) in different atmospheres (air and oxygen) for 33 h.

Routine checking of the calcined powders was carried out using a Guinier-type focusing camera (Enraf-Nonius, Model FR590, Delft, Netherlands) whereas final analysis of the powders and surfaces of the ceramic samples were performed using an X-ray diffractometer (Philips, Model PW 1710, Bedrijven, The Netherlands). The microstructures of polished specimens were examined by electron microscopy (JEOL, Model JXA 840A, Tokyo, Japan).

The microwave dielectric properties were measured using a network analyser (HP, Model HP 8719 C, Santa Rose, USA). We used the closed resonant cavity method using the $TE_{01\delta}$ mode. The silver coated resonant cavity was 40 mm high and had a diameter of 50 mm. In order to determine the unloaded *Q*-value (quality factor), the reflection coefficients (S_{11}) were analysed as proposed by Kajfez and Hwan [12]. The permittivity was calculated using the variational improvement of the Itoh–Rudokas model [13]. Systematic error in the microwave properties measurements was minimized by the use of an improved approach to the measurements, described elsewhere [14]. The temperature

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coefficients of the resonant frequency were measured in the temperature range from 20 to 60 °C.

To detect any possible reduction of the ceramics their low frequency permittivity behaviour was followed by an impedance analyser (HP, Model HP 4192A. LF, Santa Rose, USA). Both surfaces of the ceramic disks were metallized and connected to the impedance bridge. The capacitance was measured in the frequency range from 1 MHz to 0.1 kHz [15].

3. Results and discussion

3.1. Sintering and microstructural evolution

Calcined and milled $La_{2/3}TiO_3$–$LaAlO_3$ solid solution powders are easily sintered in the temperature region 1325–1400 °C. It was established using dilatometric analysis that sintering starts at ≈ 900 °C. The compacts achieved a high density, 96.5–99.4% of the theoretical value (5.47 $g\,cm^{-3}$) in 33 h at the sintering temperature. With increasing $LaAlO_3$ content the sintering temperature required to achieve high density increased, as shown in Table I.

The microstructures of the sintered specimens, shown in Fig. 1(a–f) are in accordance with the phase equilibrium data reported in reference by Škapin *et al.* [8]. In the sintered ceramic containing, 2 mol % $LaAlO_3$ three phases can be distinguished, identified by energy dispersive spectroscopy as $La_4Ti_9O_{24}$, $La_{2/3}TiO_{3(STAB)}$ and $La_2Ti_2O_7$ (Fig. 1a). The full stabilization of the perovskite $La_{2/3}TiO_3$ solid solution is accomplished by the incorporation of 4 mol % $LaAlO_3$. Such a ceramic, after sintering at 1325 °C for 33 h, exhibits a single phase microstructure with a grain size of up to 10 μm (Fig. 1b). The microstructure does not significantly change in the entire region of the orthorhombic modification of $La_{2/3}TiO_{3(STAB)}$–$LaAlO_3$ solid solution. In ceramics containing 10 mol % of $LaAlO_3$, where the orthorhombic structure is transformed into a tetragonal one, a considerable increase in the grain size was noted (Fig. 1c). The grain size distribution becomes less homogeneous with the grain size reaching ~ 30 μm. With a further increase in the $LaAlO_3$ content the average grain size slowly decreases (Fig. 1d), and in ceramics containing 50 mol % $LaAlO_3$ the grains reach a size of less than 5 μm (Fig. 1e). The reason for the extensive grain growth in the sample containing 10 mol % $LaAlO_3$ is not clear at present, although it may be connected with the appearance of a liquid phase above 1400 °C.

3.2. Microwave dielectric properties along the $La_{2/3}TiO_{3(STAB)}$–$LaAlO_3$ tie line

The microwave dielectric property measurements of the samples (Table I) revealed a high degree of correlation between the dielectric properties and the crystal structure of the stabilized $La_{2/3}TiO_3$ [8, 9] and $La_{2/3}TiO_{3(STAB)}$–$LaAlO_3$ solid solutions.

In the samples containing 2 mol % $LaAlO_3$ three phases are present: La_2TiO_7, $La_4Ti_9O_{24}$ and $La_{2/3}TiO_{3(STAB)}$. The $La_2Ti_2O_7$ and $La_4Ti_9O_{24}$ are low-permittivity phases and cause a significant permittivity reduction in these multiphase samples. As can be noticed from the measured data plotted in Fig. 2a, the permittivity reaches its maximum value in the sample containing 4 mol % $LaAlO_3$ ($k' = 71.9$), which is consistent with the previously described observation [8] that for complete perovskite stabilization of $La_{2/3}TiO_3$ at least 4 mol % $LaAlO_3$ is required. By increasing the $LaAlO_3$ content above 4 mol % the permittivity is decreased and it approaches the permittivity value of single phase $LaAlO_3$ [16, 17]. The same tendency can be observed on measuring τ_f (Fig. 2b). The rather high τ_f of the sample containing 4 mol % $LaAlO_3$ ($+123$ ppm K^{-1}) is suppressed in the samples with a higher $LaAlO_3$ content. In fact, τ_f even reaches a negative value in samples containing 40 mol % (-15 ppm K^{-1}) and 50 mol % $LaAlO_3$ (-23 ppm K^{-1}).

The negative influence of the low-permittivity phases can be seen from the measured *Q*-values (Fig. 2c) of the sample containing 2 mol % $LaAlO_3$. A sharp increase of $Q \times f_r$-value from 12 930 to 23 900 is accompanied by complete stabilization of the perovskite structured $La_{2/3}TiO_3$. In general further increases in $LaAlO_3$ content cause an increase in the *Q*-value. The only discontinuity in this tendency appears in samples containing between 8 to 12.5 mol % $LaAlO_3$, where a decrease of the $Q \times f_r$-value was observed (from 28 530 to 23 200). The reason for such behaviour is not fully understood at present. X-ray analysis shows that the decrease in the *Q*-value coincides with a crystal structure change from

TABLE I Microwave dielectric properties of ceramics with various compositions along the $La_{2/3}TiO_3$–$LaAlO_3$ tie line (sintering time: 33 h)

$LaAlO_3$	f_r	Air				O_2			
(mol%)	(GHz)	T_s (°C)	k'	Oxf_r	τ_f (ppm K^{-1})	T_s (°C)	k'	Oxf_r	τ_f (ppm K^{-1})
2	5.2	1350	56.7	12930	101	1375	57.0	12000	94
4	4.5	1325	71.9	23900	123	1350	70.4	25200	124
6	4.7	1325	67.6	28500	93	1325	68.0	29510	96
8	4.8	1350	66.9	28350	85	1375	66.7	29000	85
10	4.9	1350	62.6	26100	82	1350	65.3	26200	79
12.5	5.1	1350	60.7	23200	69	1350	60.8	23400	69
15	5.2	1375	57.7	27900	65	1375	54.4	28500	64
20	5.4	1400	53.9	29000	35	1400	53.1	30250	36
30	6.0	1425	44.9	33320	7	1400	46.3	34700	8
40	6.3	1400	39.6	42200	− 15	1400	40.0	50800	− 15
50	6.7	1425	34.4	45000	− 23	1425	36.6	54410	− 24

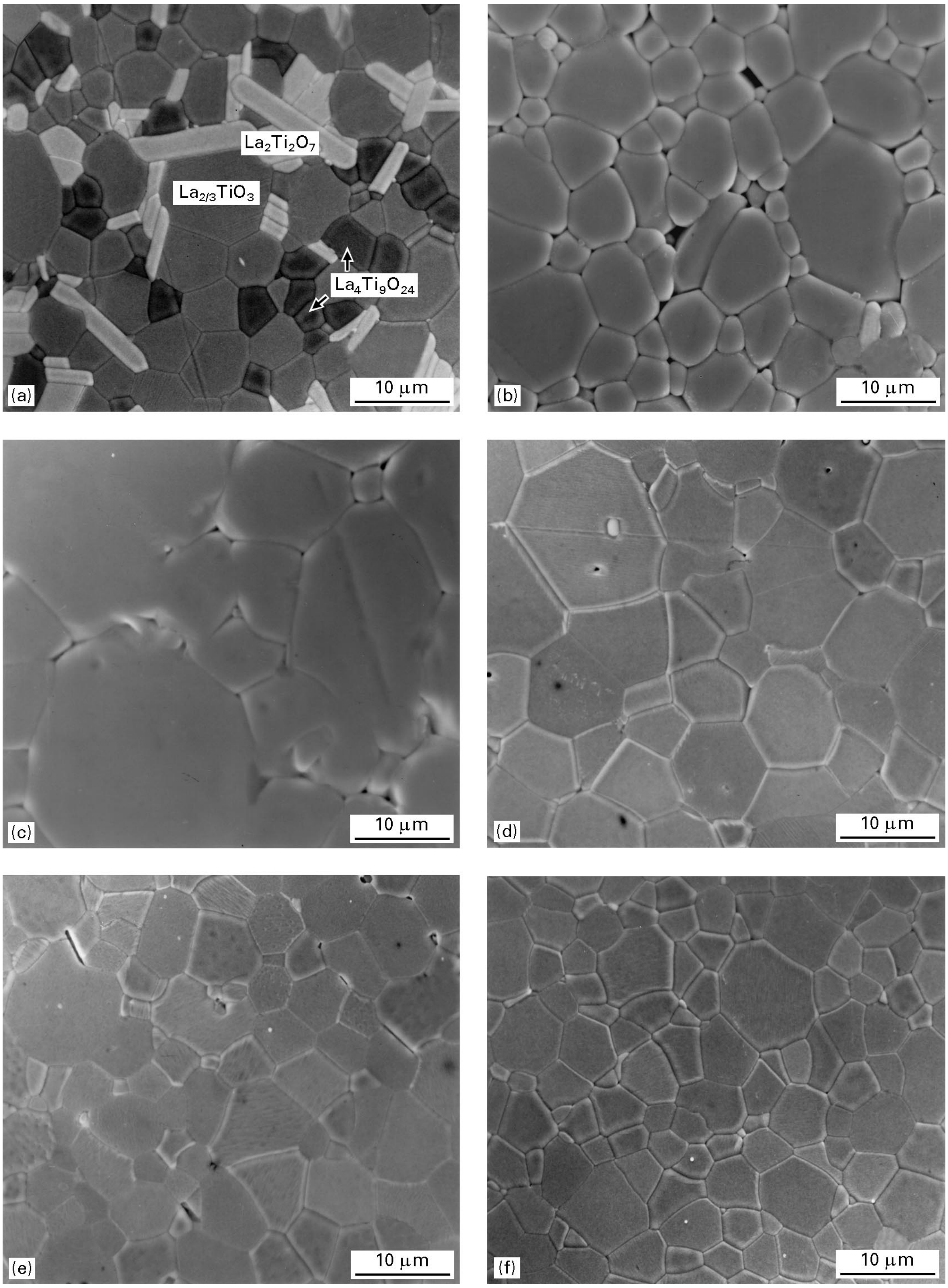

Figure 1 Microstructures of etched ceramic samples with the compositions of (a) 98 mol % $La_{2/3}TiO_3$ – 2 mol % $LaAlO_3$, (b) 96 mol % $La_{2/3}TiO_3$ – 4 mol % $LaAlO_3$, (c) 90 mol % $La_{2/3}TiO_3$ –10 mol % $LaAlO_3$, (d) 70 mol % $La_{2/3}TiO_3$ – 30 mol % $LaAlO_3$, (e) 60 mol % $La_{2/3}TiO_3$ – 40 mol % $LaAlO_3$, and (f) 50 mol % $La_{2/3}TiO_3$ – 50 mol % $LaAlO_3$, sintered at the temperatures listed in Table I.

orthorhombic to tetragonal-symmetry, as has been described by Škapin *et al.* [8].

From the measured microwave dielectric properties we can note that the composition containing 30 mol % $LaAlO_3$ is particularly interesting due to the nearly suppressed τ_f. The permittivity of such ceramics is higher than 44 and the Q-value is over 5500 (measured at 6 GHz). τ_f is slightly positive ($\tau_f = +7$ ppm K^{-1}); however, with small shifts in the composition towards higher $LaAlO_3$ contents it could be tuned to zero.

3.3. Influence of the processing parameters on the microwave dielectric properties

The microwave dielectric properties are highly dependent on the sintering temperature and atmosphere. The data listed in Table II for the 60 mol % $La_{2/3}TiO_3$ composition reveal the importance of the optimal sintering temperature. Although a difference in the sintering temperature of 50 °C does not appreciably increase the sintered density, it strongly influences the dielectric constant and Q-value of the ceramic (Fig. 3).

The measured permittivities of samples with various compositions sintered at $T_{S'}$ (the optimal sintering temperature) revealed no particular dependence on the sintering atmosphere (Fig. 2a). Also, τ_f is not affected by the sintering temperature or atmosphere (Fig. 2b). In contrast, a strong dependence of the Q-value on both sintering parameters was observed.

We can distinguish three different effects of the sintering atmosphere on the Q-value of samples with compositions on the $La_{2/3}TiO_{3(STAB)}$–$LaAlO_3$ tie line. In the region between 4 and 8 mol % $LaAlO_3$ the Q-value of the samples sintered in an oxygen atmosphere is higher than the Q-value of the samples sintered in air (Figs 2c and 4). The Q-values of samples containing 10, 12.5 and 15 mol % $LaAlO_3$ show no significant differences whether they are sintered in an oxygen or an air atmosphere. A significant difference can again be observed in samples with higher $LaAlO_3$ contents (Fig. 2c).

To follow the reduction of single phase samples (>4 mol % $LaAlO_3$) we measured the permittivity in the frequency range from 1 MHz to 0.1 kHz. In the case of samples sintered in air with a $LaAlO_3$ concentration between 4–8 mol %, an enormous increase in permittivity was observed as the measurement frequency was decreased (Fig. 4). This could be ascribed to space-charge polarization due to the existence of movable charge carriers in the reduced sample. The

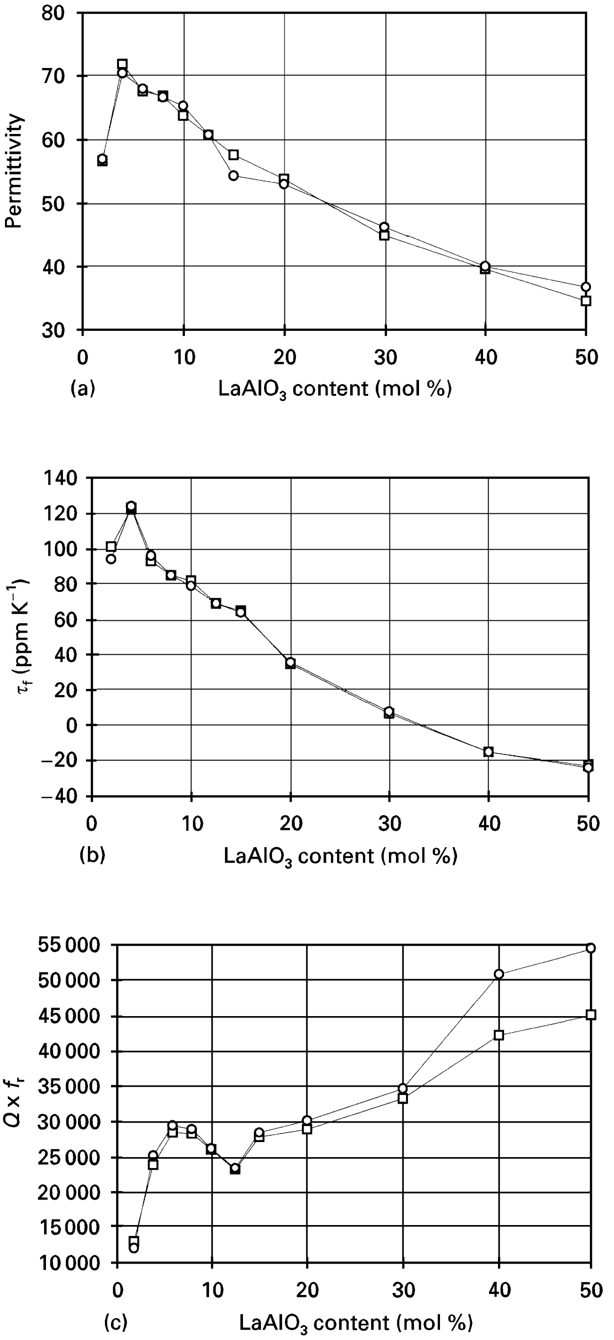

Figure 2 (a) Permittivity k', (b) temperature coefficient of resonant frequency τ_f, and (c) Q-value, of ceramic samples as a function of composition along the $La_{2/3}TiO_3$ – $LaAlO_3$ tie line, sintered at the optimal sintering temperatures T_S for 33 h (Table I). The data sintering occurred in: (□) air and (◇) oxygen.

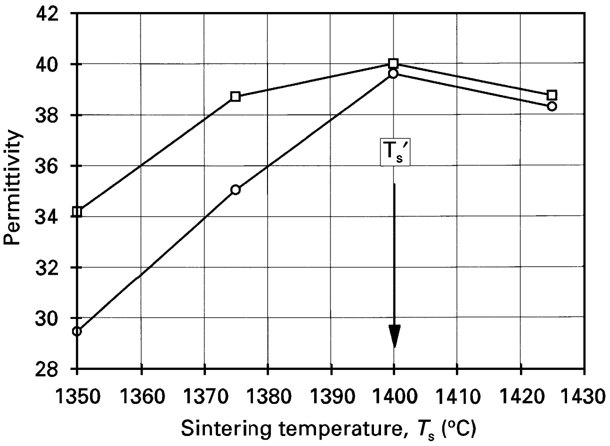

Figure 3 Permittivity k' of ceramics with the composition 60 mol % $La_{2/3}TiO_3$ – 40 mol % $LAlO_3$ as a function of sintering temperature in (○) air and (□) in O_2 atmosphere.

TABLE II Microwave dielectric properties of ceramics with the composition 60 mol % $La_{2/3}TiO_3$ – 40 mol % $LaAlO_3$ versus sintering conditions (sintering time: 33 h)

T (°C)	Atm	k'	Oxf_r	τ_f (ppm K^{-1})	ρ (% ρ_{th})
1350	Air	29.4	9900	– 15	96.5
	Oxygen	34.2	26 600	– 15	
1375	Air	35.1	28 200	– 15	98.6
	Oxygen	38.7	48 700	– 15	
1400	Air	39.6	42 200	– 15	99.4
	Oxygen	40.0	50 800	– 15	
1425[a]	Air	38.3	25 800	– 13	98.9
	Oxygen	38.7	34 500	– 13	

[a] Sample deformed

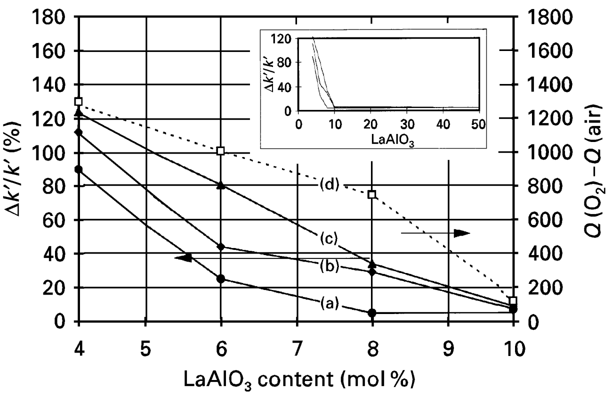

Figure 4 Relative increase of the permittivity ($\Delta k'/k'$) in the frequency range from 1 MHz to 0.1 kHz as a function of composition and sintering temperature of (a) 1360 °C, (b) 1375 °C and (c) 1400 °C and (d) the difference in the Q-values of samples sintered in either air or in oxygen atmosphere.

amplitude of the relative change in permittivity ($\Delta k'/k'$) is affected by at least two parameters, the sintering temperature and $LaAlO_3$ concentration. $\Delta k'/k'$ has its highest value in samples containing 4 mol % $LaAlO_3$. An increase in $LaAlO_3$ concentration produces a decrease in $\Delta k'/k'$ and in samples with 10 mol % $LaAlO_3$ it has a negligible value. These observations could be correlated with the Q-value measurements. The difference between the measured Q-value of samples sintered in the different atmospheres has its greatest value for sample containing 4 mol % $LaAlO_3$. On increasing the $LaAlO_3$ content, the difference decreased, which is accompanied by a decrease in $\Delta k'/k'$. In the case of the sample containing 10 mol % $LaAlO_3$, where measurements of $\Delta k'/k'$ revealed almost no reduction, we could observe a difference between the Q-value of the sample sintered in air and the one sintered in oxygen.

In the region between 10 and 15 mol % $LaAlO_3$ no significant effect of the sintering atmosphere on the Q-value was found. The sintering atmosphere became important again in samples with higher $LaAlO_3$ contents. In spite of a negligible $\Delta k'/k'$, we noticed considerably higher Q-values in samples sintered in oxygen (Fig. 2c). X-ray diffraction analyses of these samples did not reveal any differences between the samples sintered in oxygen or in an air atmosphere.

Possible anisotropic behaviour of the dielectric properties of the ceramic samples was also examined. For this purpose cubes with an edge of 4.5 mm were machined out of the disks sintered in different atmospheres [9]. In all the cases examined the measured properties were independent of the orientation of the cubes. These measurements, together with X-ray analysis, eliminated the possibility of grain orientation associated with dielectric anisotropy.

4. Conclusions

Microstructural investigations on the ceramics with compositions along the $La_{2/3}TiO_3$–$LaAlO_3$ tie line confirmed that complete stabilization of the perovskite structure for $La_{2/3}TiO_3$ occurs when 4 mol % $LaAlO_3$ is added. Complete solid solution exist between $La_{2/3}TiO_{3(STAB)}$ and $LaAlO_3$. In such ceramics the optimal sintering temperature increases with the $LaAlO_3$ content.

A maximum permittivity of 72 was achieved with these stabilized $La_{2/3}TiO_3$ ceramics. An increase in the $LaAlO_3$ content from 4 to 50 mol %, resulted in a gradual decrease of the permittivity and temperature coefficient of resonant frequency ($72 > k' > 34$ and $123\ \text{ppm K}^{-1} > \tau_f > -23\ \text{ppm K}^{-1}$), while the $Q \times f_r$-value increased ($12\,900 < Q \times f_r < 45\,000$). The sintering atmosphere has no significant influence on the permittivity and τ_f, but it does however strong influence on the Q-value. Up to 20% higher Q-values were achieved by sintering the ceramics in an oxygen atmosphere.

Especially interesting microwave dielectric properties were obtained for ceramics with the composition 70 mol % $La_{2/3}TiO_3$–30 mol % $LaAlO_3$. The permittivity of these ceramics sintered at 1400 °C for 33 h in air is 44.9 and $Q \times f_r$ is higher than 33 000 (measured at 6 GHz). τ_f is $+7\ \text{ppm K}^{-1}$ and can be controlled in this range simply by shifting the composition along the tie line. Further improvements in the microwave dielectric properties can be achieved by using an oxygen atmosphere during sintering: $k' = 46.3$. $Q \times f_r = 34\,700$ (measured at 6.0 GHz) and $\tau_f = +8\ \text{ppm K}^{-1}$.

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