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Microwave properties and microstructures of $La_{2/3}TiO_3$ stabilized with NiO

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Abstract

$(1–x)La_{2/3}TiO_3–xTiNiO_3$ ceramics with x ranging from 0.01 to 0.2, were elaborated by conventional solid-state reaction starting from TiO_2, La_2O_3, and NiO powders. These compositions have been identified as secondary phases detected in $(Zr,Sn)TiO_4$ ceramics sintered with La_2O_3 and NiO. Microwave resonators were sintered at temperatures ranging from 1340 to 1380°C. These sintering temperatures have been determined taking into account thermodilatometric data. Microwave dielectric properties and microstructures were investigated. Perovskite phase $La_{2/3}TiO_3$ was identified by XRD, SEM and EDS together with minor phases. Dielectric constants are in the 50–70 range and QF values, measured at 3 GHz, are close to 20 000 GHz. One significant composition is characterized by $k=69$ and $QF=17{,}000$ GHz at 3 GHz. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Lanthanum titanate; Microwave resonators

1. Introduction

Five main ceramic materials families are classically used for the fabrication of microwave resonators. The first four are: complex perovskites such as $Ba(Mg_{1/3}Ti_{2/3})O_3$ or $Ba(Zn_{1/3}Ta_{2/3})O_3$; $(Zr,Sn)TiO_4$; $Ba_2Ti_9O_{20}$–$BaTi_4O_9$; materials belonging to the diagram CaO–TiO_2–Al_2O_3-rare earth oxides; permit the obtaining of high quality factor Q ranging from 4000 to more than 30 000 at 10 GHz, together with dielectric constants k ranging from 20 to 47. The fifth one, belonging to the diagram BaO-TiO_2-rare earth oxides, has much higher dielectric constants k ranging from 78 to 80 but together with only lower Q values minor to 12 000 at 1 GHz. One need is to obtain new materials with a dielectric constant k ranging from 50 to 70, quality factors higher than 4000 at 10 GHz, and a temperature coefficient of the dielectric τ_f either close to 0 or adjustable.

Trying to aim for this goal, we, therefore, investigated the microwave dielectric properties of the perovskite phase $La_{2/3}TiO_3$ stabilized with some amounts of nickel. We observed this compound for the first time when investigating secondary phases present in (Zr,Sn) TiO_4 ceramics sintered with La_2O_3 and NiO.[1] We tried then to synthesize it alone in order to evaluate its influence on the characteristics of the ZST ceramics. The measured characteristics prompted us to investigate further this promising compound.

Pure $La_{2/3}TiO_3$ is an ‘‘unstable’’ perovskite phase. Its instability is due to the high amount of vacancies in the ‘‘A’’ cationic sublatice. This compound does not appear in the binary phase diagram TiO_2–La_2O_3, (Fig. 1), established by MacChesney and Saueur.[2] Abe et al. pointed out for the first time the existence of phases with the composition $La_{2/3}TiO_{3-\delta}$, $0.007<\delta<0.079$, that they sintered in a low oxygen partial pressure.[3] Their studies permitted the establishment of the JCPDF card no. 26-0827 that we shall use as a reference. They showed that there exists an order in the A cationic sublattice of the perovskite between the La^{3+} cations and the vacancies, leading to the substructure of the lattice that is doubled along the c direction. Yet, the presence of Ti^{3+} ions in the lattice leads to conductive properties of the ceramic. Belous et al. succeeded in stabilizing the structure with sodium and lithium doping.[4] Ceramics are then good ionic conductors.[5]

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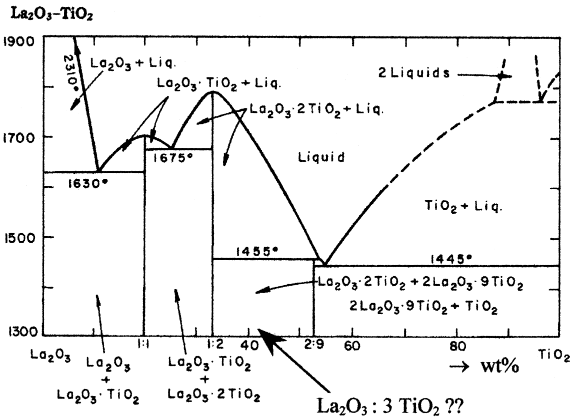

Fig. 1. Binary phase diagram La_2O_3–TiO_2 (from MacChesney and Saueu).[2]

Other dopants have been used that permit the stabilization of the $La_{2/3}TiO_3$ phase into ceramics owning useful dielectric characteristics, such as Ca, Sr, Pb[6], Sc, Cr, Al[7] or Nb.[8] The system $(1–x)La_{2/3}TiO_3–xLaAlO_3$ is the most popular for dielectric microwave applications.[9–11]

Stabilization of $La_{2/3}TiO_3$ with nickel has not been studied up until now. We shall present here our last results concerning the determination of the optimum amount of nickel leading to a high performance dielectric material for microwaves.

2. Experimental

We mixed together reagent grade TiO_2, La_2O_3 and NiO powders for 1 h by attrition milling, using 0.8–1.25 mm zircon balls. pH of the 30 wt.% aqueous slurries was adjusted to 11 with ammonia in order to get well dispersed and stabilized mixing conditions.[12] The different batches owned the stoechiometric compositions $(1-x)La_{2/3}TiO_3–xNiTiO_3$ with $x=0.01$, 0.02, 0.03, 0.05, 0.075, 0.1, 0.15 and 0.2. After drying, the mixed powders were calcined 5 h at 1160°C. After addition of 1 wt.% of organic binder (Optapix®), they were pressed into 15 mm diameter and 7.5 mm high cylinders. The resonators were sintered for 10 h in an oxygen flux at a temperature, ranging from 1340 to 1380°C depending on the composition, determined by dilatometry. Microwave characterizations were made with the post-resonator method proposed by Hakki and Coleman.[13] Microstructure observations and elementary analysis were made with a SEM Hitachi S 2460 N coupled with an EDX analysis system "Link Isis" from Oxford. Grain boundaries were revealed by thermal annealing of polished surfaces. X ray analyses were made using a D5005 Siemens diffractometer.

3. Experimental results

3.1. Microwave properties of ceramics

Table 1 resumes the microwave properties of the sintered ceramics. Dielectric constant k (Fig. 2) ranges from 50 to 70. It climbs up versus x for low nickel amounts, attains a maximum value ($k=70$) for $x=0.03$, and owns lower values for higher nickel amounts. The quality factor (or the $Q \times F$ value) (see Fig. 3), shows the same behavior: its value climbs up to 17,000 GHz for $x=0.03$, and decreases for higher x values. The value of the temperature coefficient of the dielectric τ_f seems less sensitive to the composition, as shown in Fig. 2. All coefficients range between 18 and 25 ppm °C^{-1}. It slows down with x for the low nickel amounts and reaches a minimum value equal to 18 ppm°C^{-1} for $x=0.03$. For higher nickel amounts, it seems to be constant and close to 22 ppm °C^{-1}.

It is noteworthy that the composition with x = 0.03 has maximum values for k and QxF and a minimum value for τ_f. The ceramics made with this particular composition, that we can write $La_{0.647}Ni_{0.03}TiO_3$, are characterized by highly interesting microwave properties : $k=69.4$, $Q=5500$ at 3.1 GHz and $\tau_f=18$ ppm °C^{-1} although not any optimization of their elaboration has been made yet.

3.2. Structure and microstructure

X ray diffraction patterns made on the bulk of the different ceramics are gathered in Fig. 4. By comparison to the JCPDF card no. 26-0827, we can see that a phase isomorphic to $La_{2/3}TiO_3$ is observed for every x value. For $x=0.01$, it is present together with $La_2Ti_2O_7$ (28-0517 card) and $La_4Ti_9O_{24}$ (36-0137 card). $La_2Ti_2O_7$ is not present for x values >0.02, while $La_4Ti_9O_{24}$ is always present. We can also point out a surstructure peak for $2\theta=11.4°$, leading to the evidence of an order in the A cationic sublattice of the perovskite between the La^{3+} cations and the vacancies.

Both SEM observations (Fig. 5) and EDX analysis made on x = 0.03 ceramics confirm the presence of these two phases. $La_{2/3}TiO_3$ appears as light gray grains and $La_4Ti_9O_{24}$ as dark grains well dispersed into the ceramic. Both phases grains show a similar size, ranging from 2 to 5 μm. The EDX analysis of the ceramic is equivalent to the one expected, that is to say not any sublimation or evolution of the global composition occurs during the sintering cycle. Nickel seems to be only present in the $La_{2/3}TiO_3$ phase with an amount of 2.2% (0.5% measured into $La_4Ti_9O_{24}$ is at the limit of detection). Nickel seems, therefore, to allow the stabilization of this phase.

We expected when synthesizing our compositions as $(1–x)La_{2/3}TiO_3–xNiTiO_3$ to permit a decrease in the

Table 1
Microwave properties of $(1-x)La_{2/3}TiO_3$–$xNiTiO_3$ resonators

x	Sintering temperature (°C)	Density	Dielectric constant (k)	Quality factor (Q)	Resonance frequency (GHz)	$Q \times F$ (GHz)	Temperature coefficient τ_f (ppm. °C^{-1})
0.01	1380	5.31	51.4	440	3.55	1563	24.7
0.02	1377	5.30	63.3	1884	3.30	6212	21.8
0.03	1375	5.30	69.4	5503	3.08	16966	18.4
0.05	1360	5.28	59.6	4574	3.25	14866	21.5
0.075	1350	5.28	58.0	4479	3.36	15049	22.6
0.15	1340	5.26	53.3	3762	3.44	12956	21.3
0.2	1340	5.18	50.7	3896	3.57	13893	23.5

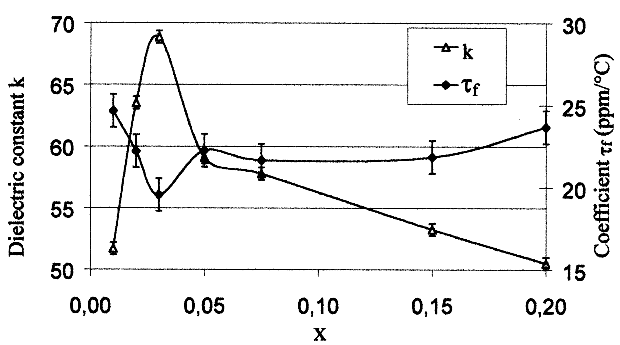

Fig. 2. Dielectric constant k and temperature coefficient of the dielectric τ_f versus x.

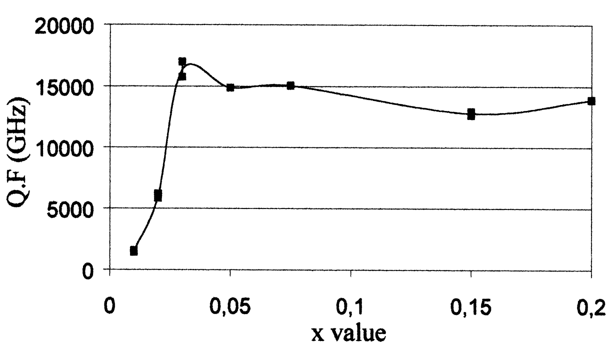

Fig. 3. QxF (GHz) value versus x.

number of vacancies into the A cationic sites with the increase of the nickel amount with the consequence of a stabilization of the structure. EDX analysis of the light gray grains (Table 2) allow one to write the $x=0.03$ composition as $La_{0.689}Ni_{0.038}Ti_{0.964}O_3$ with $Ni+Ti=1.002$, these two cations filling all the B sites of the perovskite. As a consequence, the number of vacancies in the A sites decreases from 1/3 ($x=0$) to 0.302. Considering the realized composition, titanium is, therefore, in excess, leading to the formation of $La_4Ti_9O_{24}$ that owns, according to Takashi et al.[14] a lower dielectric constant than the $x=0.03$ ceramic. Table 3 resumes the microwave properties of both $La_4Ti_9O_{24}$ and $La_2Ti_2O_7$ according to this last author. We can, therefore, explain the evolution Fig. 2 of k versus x. For low x values, up to 0.03, nickel addition helps $La_{2/3}TiO_3$ to be stabilized

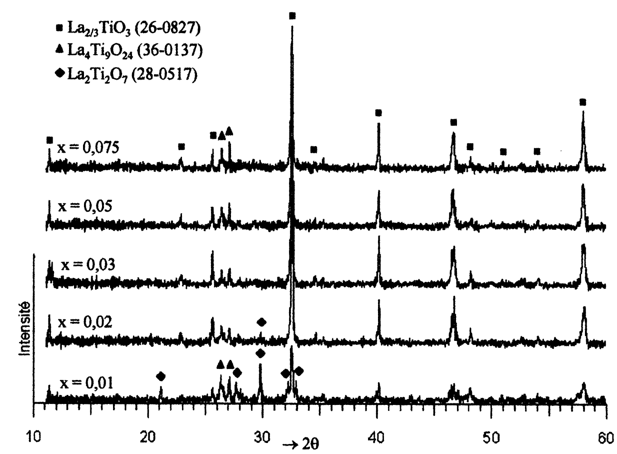

Fig. 4. X ray diffraction patterns of the different sintered ceramics.

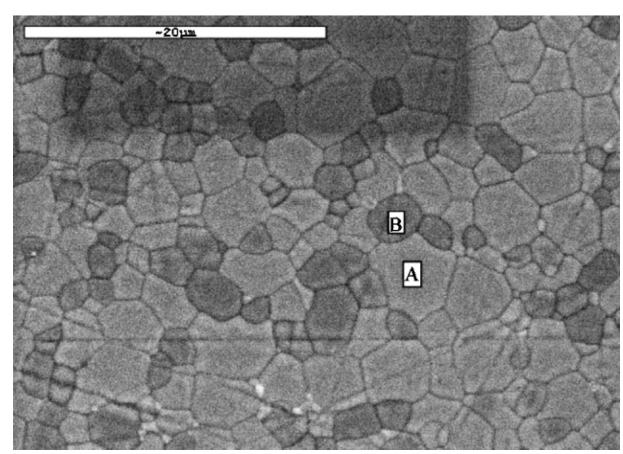

Fig. 5. SEM picture of a ceramic with $x=0.03$, (A): $La_{2/3}TiO_3$; (B): $La_4Ti_9O_{24}$.

with the presence of decreasing amounts of $La_4Ti_9O_{24}$ and $La_2Ti_2O_7$ phases when x increases. As a consequence, k value of the ceramic increases as these two phases own lower k. The more x increases with values higher than 0.03, the more titanium is in excess and the higher the amount of $La_4Ti_9O_{24}$, leading to a decrease of the value of the dielectric constant.

Further work will consist of an attempt to directly synthesize and sinter $La_{0.689}Ni_{0.038}Ti_{0.964}$ in order to obtain a single-phase ceramic.

Table 2
EDX analysis of 1/ the whole ceramic, 2/[A] light grey grains and 3/[B] dark grains

		Ti	La	Ni	Ti/La	Phase
Realized composition	%	59.64	38.57	1.79	1.55	
Whole ceramic	%	59.40	38.62	1.98	1.54	
	σ	0.55	0.35	0.42	0.02	
Dark grains [B]	%	67.41	32.05	0.54	2.10	$La_4Ti_9O_{24}$
	σ	0.94	0.69	0.32	0.07	
Light gray grains [A]	%	57.01	40.76	2.23	1.40	$\ll La_{2/3}TiO_3 \gg$
	σ	0.62	0.35	0.39	0.03	

Table 3
Microwave dielectric properties of $La_2Ti_2O_7$ and $La_4Ti_9O_{24}$ (after Takashi et al.)[14]

	ε_r	Q	F (GHz)	QF (GHz)	τ_f (ppm/°C)
$La_2Ti_2O_7$	47	1090	7.8	8500	−10
$La_4Ti_9O_{24}$	37	3060	8.1	24800	15

4. Conclusions

The work we presented here must be considered only as a first approach of a more extensive study of $La_{2/3}TiO_3$ whose microwave properties seem of all the more interest. Structural and microstructural analysis allowed us to show that nickel seems to get a 6 coordinance permitting the stabilization of an isomorphic phase to $La_{2/3}TiO_3$. Yet, it has not been possible up to now to get this isomorphic phase pure. However, the obtained microwave dielectric characteristics point out the potential relevance of this system for further microwave resonators developments.

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