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Effect of annealing on the microwave properties of $(Zr,Sn)TiO_4$ ceramics

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Abstract

$(Zr,Sn)TiO_4$ dielectric ceramics containing La_2O_3 and NiO as sintering aids were prepared by the conventional solid-state reaction. Ceramics sintered at 1370°C for 20 h exhibit dielectric constants k around 37.1 and a QF value of 41,500 GHz, measured at 4 GHz. After annealing, k remains constant. However, the QF value is strongly affected by the annealing process. At 1300°C, annealing has no effect on the quality factor Q. Annealing at temperatures 1225 and 1200°C induce a ≈50% decrease of QF values. Intermediate annealing temperatures of 1275 and 1250°C induce a ≈25% improvement of QF values. These ceramics were investigated by XRD, SEM and EDS. The matrix phase ZST was observed together with three different secondary phases: TiO_{2ss}, $La_{2/3}TiO_3$ and $TiNiO_3$. Appearance and following diffusion of these secondary phases and other impurities to the ceramic surfaces during annealing can explain the QF behaviour.

Keywords: Processing; Microwave resonators; Sintering

1. Introduction

Among the different materials for microwave ceramic resonators, $(Zr,Sn)TiO_4$ diagram is of particular importance as it has dielectric properties making it suitable for wireless communications. Its dielectric constant k is close to 37, and its quality factor Q can be higher than 5000 at 10 GHz with a stability coefficient of the resonance frequency τ_f adjustable at a value close to 0 ppm $°C^{-1}$. These compositions are classically prepared by solid state reaction, sintered at high temperature close to 1400°C and can be annealed at a lower temperature in order to increase the QF value. The role of this annealing thermal cycle has not up to now been fully understood.

The aim of this paper is to resume our observations concerning the effects of the annealing thermal cycle on the quality factor enhancement and on the microstructure of ceramics.

2. Experimental procedure

Zirconium tin titanate ceramics were prepared by solid state reactions from relatively pure oxides (upper to 99%). Formulation of our ceramics is close to $Zr_{0,648}Sn_{0,332}Ti_{1,02}O_4$ with some amounts of La_2O_3 and NiO as sintering aids. Powders were mixed in deionized water at pH 11.5 adjusted with ammonia, in order to obtain a defloculated slurry with a 50 wt.% solid load.[1,2] The slurry was milled in a Dyno-mill®, an industrial horizontal attrition mill, for a short period. Zircon balls ($ZrSiO_4$) were used as grinding media. The abrasion of these balls during the grinding process involves unintentional additions of 0.3 mol% silicon into the ceramics. Slurries were dried, mixed with an organic binder (PVA) and pressed into 15 mm diameter and 7.5 mm high discs under pressure of 2 T/cm^2. Pellets were sintered at 1370°C for 20 h in an oxygen flow. Some pellets were annealed at temperatures ranging from 1200 to 1300°C for 20 h after sintering.

X-ray diffractometer Siemens D5005 was used to identify crystalline phases in sintered pellets. The microstructure was observed both on ceramics surfaces and on

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polished surfaces in the bulk of samples, using a SEM (Hitachi S 2460 N) and phases compositions were investigated by EDX (Oxford Link Isis) operating at a 25 kV acceleration voltage. All microwave characterizations were made at 4 GHz resonance frequency by Tekelec Temex. The density of sintered specimens was measured with a helium pycnometer (Micromeritics accupyc 1330).

3. Effect of the annealing temperature

Just sintered ceramics get a dielectric constant $k=37.1$, a quality factor $QF=41{,}500$ GHz and a temperature coefficient close to zero. Ceramics have been then annealed for 20 h at a temperature ranging for 1200 to 1300°C. This annealing process at such a low temperature has no influence on the density of ceramics. Their dielectric constant and their temperature coefficient, as shown in Fig. 1, are only slightly affected, this last parameter lowering only slightly for annealing temperatures higher than 1275°C.

On the other hand, the annealing temperature strongly affects the value of the quality factor QF, as illustrated Fig. 1. Low temperature annealings, 1200 or 1225°C, lead to a strong decrease of QF value that can be less than 20,000 GHz. Higher annealing temperatures, 1250 or 1275°C, lead to an enhancement of the quality factor that can reach values higher than 50,000 GHz, that is to say a 25% increase. At higher temperatures, annealing thermal cycles lead to only slight changes. This 1250°C annealing temperature seems to be a border and leads to the obtaining of the best QF values with only little temperature coefficient variations.

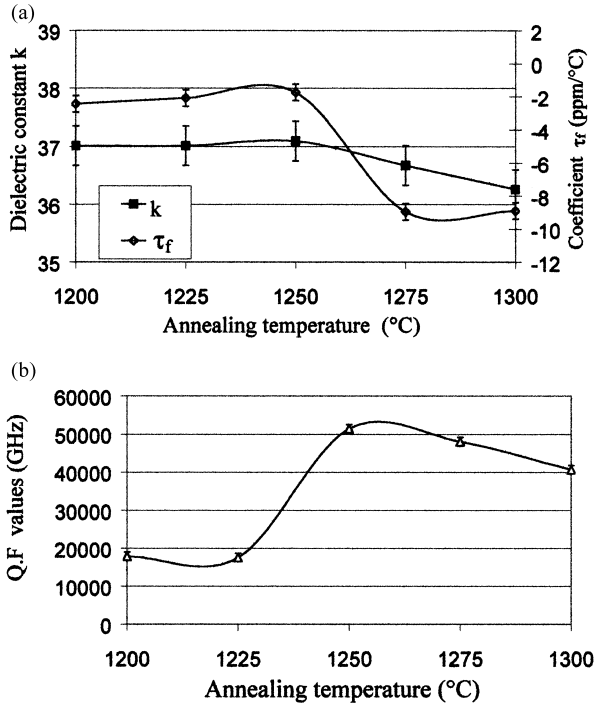

Fig. 1. (a) Dielectric constant and temperature coefficient τ_f and (b) quality factor $Q\times F$ versus the temperature of a 20 h annealing thermal cycle.

As a first comment, we can observe that it seems highly improbable that the effect of the annealing cycle is to enhance a structural reorganization of the ceramic and promote a better crystallization of the grains. Actually, if this assertion was right, the obtaining of a maximum value for the quality factor with a 1250°C intermediate annealing temperature together with the dramatic degradation of this parameter at lower temperatures and the only slight or null effect at higher temperatures would remain inexplicable. It has been earlier observed that these ceramics are multiphased.[3] So, we have made careful X-ray diffraction analysis and SEM observations together with elementary analysis of bulk and surface of ceramics correlated with the sintering and annealing schedules with the hope of finding some correlations.

4. Structure and microstructure of ceramics

4.1. After sintering at 1370°C

SEM observations and X ray diffraction analysis made into the bulk of the ceramic confirm that the ZST phase is observed together with the secondary phases earlier identified,[3] that is to say $La_{2/3}TiO_3$, $TiNiO_3$ and TiO_{2ss}. These secondary phases are in every case well dispersed into the bulk of the ceramic. Main phase ZST grain diameters range from 30 to 50 μm. These diameters are comparable to earlier observations made by Iddles et al.[4] Secondary phases are always formed of much smaller grains than the main ZST phase. EDS global composition is close to the expected one, as illustrated in Table 1.

SEM observations on the surface (Fig. 2a) show mainly large grains, with a size close to that of the main phase of the bulk. EDS analysis (Table 1) and X-ray diffraction (Fig. 3b) determine that they can be either composed of the ZST phase or of the TiO_{2ss} phase that is present in large amounts. In addition to these large grains, one or more secondary phases can be as well observed by SEM, one of them containing mainly Ti (37 mol%), Si (20%) and La (19%) together with some Zr (10%), Sn (5%) and Ni (9%). Although the ratio Si/La is always close to one, the amount of these two elements can range from 10 to 30%. Titanium is always the main element. Its amount can range from 30 to 50%. It is noteworthy that both $TiNiO_3$ and $La_{2/3}TiO_3$, previously detected in the bulk, are not present on the surface whatever the length of the plateau at 1370°C is. These observations are coherent with the fact that the global analysis of the surface is slightly different to the bulk one as reported in Table 1.

Table 1
EDS analysis on bulk and surface of ceramics sintered 1370°C 20 h without and with a 20 h annealing process at 1250°C

			Ti	Zr	Sn	Ni	La	Si
	Expected analysis of the ceramic	%	49.4	31.6	16.0	1.4	1.3	0.3
Bulk analysis	Sintered 1370°C 20 h	%	49.1	32.5	16.2	1.7	0.1	0.4
		σ	0.6	0.5	0.4	0.4	0.1	0.3
	Sintered 1370°C 20 h +	%	47.7	33.9	16.4	1.5	0.1	0.3
	annealed 1250°C 20 h	σ	0.4	0.3	0.2	0.2	0.1	0.1
Surface analysis	Sintered 1370°C 20 h	%	54.8	21.6	12.7	2.7	3.7	4.5
		σ	1.4	2.5	1.4	0.7	2.4	1.5
	Sintered 1370°C 20 h +	%	48.9	15.8	8.4	6.3	10.0	10.6
	annealed 1250°C 20 h	σ	1.2	2.5	1.4	1.0	1.8	2.0

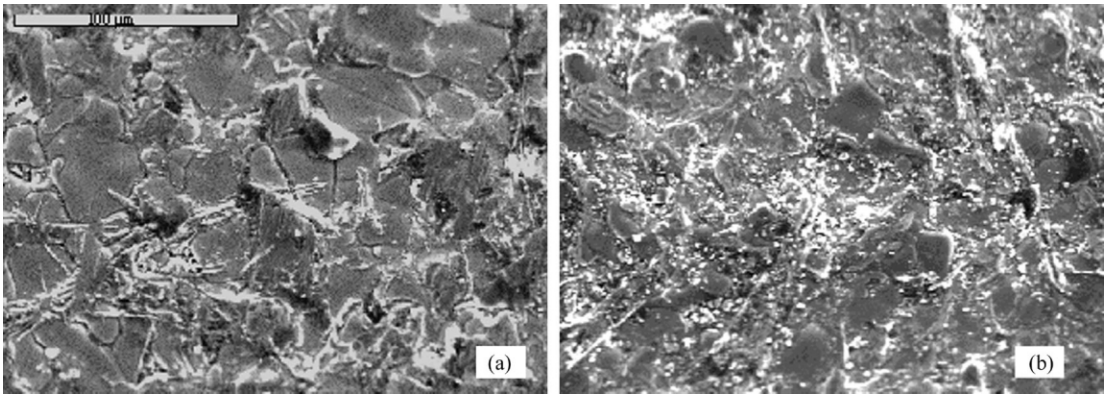

Fig. 2. SEM observation of the surface of ceramics sintered 20 h at 1370°C: (a) as sintered; (b) after annealing 20 h at 1250°C.

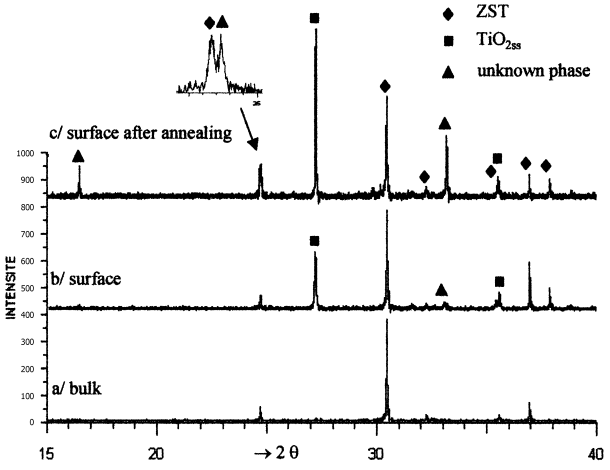

Fig. 3. X-ray diffraction patterns of ceramics sintered at 1370°C for 20 h. (a) bulk; (b) surface; (c) surface after annealing 20 h at 1250°C.

4.2. Effect of the annealing at 125O°C

Fig. 2 shows SEM observations of (a) the surface of a ceramic just sintered 20 h at 1370°C and of (b) the same ceramic after it has been annealed for 20 h at 1250°C. One can observe the grains and the grain boundaries on the surface of the just sintered ceramic. On the contrary, after annealing, main phase grains seem embedded under secondary phases that have diffused to the surface through the grain boundaries. The average composition of the surface, reported in Table 1, is quite different to the one of the just sintered ceramics: Si, La and Ni amounts are more than twice the one detected on the surface of just sintered ceramics. The composition of one of these phases is close to $Ti_{0.37}Si_{0.2}La_{0.19}Ni_{0.09}Zr_{0.1}Sn_{0.05}O_{1.8}$. It was already observed on the just sintered ceramics surface, but after annealing, it is present in a much larger amount.

This is confirmed, Fig. 3, by the comparison of the X-ray diffraction patterns of the surface of (b) just sintered and (c) sintered and annealed ceramics. It appears that, after annealing, TiO_{2ss} is in a larger amount, and a new unknown compound is present on the surface. This behavior can only be the consequence either of a modification of the composition of the phases present in the bulk or of an evolution of the amounts of the phases present in the bulk prior to the annealing process.

It is noteworthy that, when annealing polished sliced ceramics at 1250°C in order to thermally reveal the grain boundaries, little secondary phase grains appear and gather at tripled points. Analyses show that their composition is close to $Ti_{0.37}Si_{0.2}La_{0.19}Ni_{0.09}Zr_{0.1}Sn_{0.05}O_{1.8}$. Thus, one hypothesis suggests that this phase exudes from the bulk at the 1250°C annealing temperature.

Average composition analysis of the bulk before and after annealing show (Table 1) a significant evolution of the titanium amount that evolves from 49.1 to 47.7 while

Table 2
Image analysis quantification of the phases present into the bulk or close to the surface of ceramics sintered 20 h at 1370°C, without and with a 20 h annealing process at 1250°C

		Bulk			Close to surface		
		ZST	TiO_{2ss} + $TiNiO_3$	$La_{2/3}TiO_3$	ZST	TiO_{2ss} + $TiNiO_3$	$La_{2/3}TiO_3$
Just sintered	Vol.%	96.0	3.2	0.8	98.2	1.5	0.3
	σ	1.3	1.4	0.3	3.1	0.9	0.3
After annealing	Vol.%	96.0	2.8	1.2	94.4	3.4	2.1
	σ	2.6	1.1	0.5	2.1	0.8	0.9

the Zr and Sn amounts become slightly higher. That leads us to suppose that the TiO_{2ss} amount decreases in the bulk during the annealing process. The particular analysis of each phase present in the bulk shows no significant evolution: we can only assume a very slight evolution of the ZST composition, the titanium amount decreasing from 47.3 to 46.7%. Although this observation is at the limit of the accuracy of the analysis, it could explain the slight evolution of the temperature coefficient τ_f that is closely related to the exact composition of the ZST phase.

We have processed image analysis on many SEM pictures with the aim of quantifying the different phases present in the ceramics, before and after the annealing process, in the bulk or on the periphery of the ceramics (that is to say approximately 500 μm under the surface).[5] Table 2 resumes these observations.

The amounts of secondary phases are more important close to the surface after the annealing process. This is in accordance with the assumption that the annealing process helps migrations of some secondary phases from the bulk to the surface. This also supports the assumption of a correlation of this migration with an increase of the quality factor *QF*: the TiO_{2ss} phase that leads to a degradation of the quality factor will have only little influence when gathered close to the surface. This may also be the case for Si impurity, the presence of which is supposed to be detrimental to the quality factor. Si is included in both TiO_{2ss} and $Ti_{0.37}Si_{0.2}La_{0.19}Ni_{0.09}Zr_{0.1}Sn_{0.05}O_{1.8}$ phases that seem to be precipited from the ZST phase and then diffuse toward the surface during the annealing process.

5. Discussion

The effect of the annealing process on the microwave dielectric properties of the ceramics can be correlated to the evolution of their microstructure. All our observations are in accordance with the hypothesis that some cations that act as impurities harmful to high performances are soluble into the ceramic at 1370°C, temperature that has to be held for densification. The lower the temperature, the lower the solubility of these impurities. Annealing processed at a temperature as low as 1250°C leads to an exudation of these impurities into secondary phases that can diffuse toward the surface, thanks to the temperature high enough to allow this behavior. When annealing is processed at lower temperatures, the quality factor decreases. That can be thus explained by the formation of these secondary phases detrimental to the quality factor, but the temperature is then too low to permit their diffusion to the surface and therefore their elimination from the bulk.

6. Conclusion

After annealing, the dielectric constant *k* remains constant whatever the annealing temperature. On the contrary, *QF* values are strongly affected and effects depend on temperature. At 1300°C, annealing has no effect on the quality factor *Q*. At 1225 and 1200°C, annealing induces a strong decrease of *QF* values. And at 1275 and 1250°C annealing temperatures induce a *QF* value improvement of about 25%.

The effect of the annealing process on the microwave dielectric properties of the ceramics can be correlated to the evolution of their microstructure. Precipitation and diffusion toward the ceramic surfaces during annealing of some secondary phases, containing impurities and detrimental to the quality factor, can explain the QF enhancement.

References

1. Houivet, D., Haussonne, J.-M., Vallar, S. and Hemidy, J.-F., Comportement d'une barbotine d'oxydes lors d'un broyage par attrition. *L'Industrie Céramique*, 1996, **916**(6-7), 423–431.
2. Vallar, S., Houivet, D., Kervadec, D. and Haussonne, J.-M., Oxide slurries stability and powders dispersion: optimisation with zeta potential measurements and rheological measurements. *J. Eur. Ceram Soc.*, 1999, **19**, 1017–1021.
3. Houivet, D., El Fallah, J. and Haussonne, J.-M., Phases in La_2O_3 and NiO doped $(Zr,Sn)TiO_4$ microwave dielectric ceramics. *J. Eur. Ceram. Soc.*, 1999, **19**, 1095–1099.
4. Iddles, D. M., Bell, A. J. and Moulson, A. J., Relationships between dopants, microstructure and the microwave dielectric properties of ZrO_2–TiO_2–SnO_2 ceramics. *J. Mater. Sci.*, 1992, **27**(23), 6303–6310.
5. Belhomme, P., Houivet, D., Lecluse, W. and Haussonne, J.M., Image analysis of multiphased ceramics. *ELECTROCERAMICS VII*, Portoroz (Slovenia), September 2000.