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Phases in La_2O_3 and NiO Doped (Zr,Sn)TiO_4 Microwave Dielectric Ceramics

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Abstract

Dielectric ceramics with composition in the ZrO_2–SnO_2–TiO_2 system containing La_2O_3 and NiO as sintering aids were prepared and investigated by XRD, XPS, SEM, EDS, and microwave dielectric measurements. Ceramics prepared with deflocculed slurry using a Dyno-Mill®, and sintered at 1370°C exhibit very good microwave dielectric characteristics: $\varepsilon = 37$ and QF up to 62 000 at 4 GHz. We have observed a matrix phase with at least two or three different secondary phases in function of the employed grinding media (balls of zircon or magnesium stabilised zirconia). So, we have synthesised and characterised these phases. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: microwave resonators, milling, mixing, powders: solid state reaction, dielectric properties.

1 Introduction

Zirconium tin titanate ceramics have been developed for microwave applications in communication networks. One main characteristics of these components is the loss factor, the inverse being expressed as the QF factor, that has to be as high as possible, together with a resonance frequency temperature coefficient (τ_f) as close to zero as possible. These ceramics are prepared either by attrition, raw materials were ball-milled for long time,[1,2] or by a sol–gel method.[3] Depending on sintering aids, different phases have been observed.[1–12] This paper reports on an investigation of phases, by XRD, XPS, SEM and EDS, on ZST ceramics, doped with La_2O_3 and NiO as sintering aids and prepared by an attrition method using a Dyno-Mill®.

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2 Experimental Procedure

2.1 Materials preparation

Zirconium tin titanate ceramics were prepared by solid state reactions from relatively pure oxides (upper to 99%). Compositions close to 51 mol% TiO_2, 32 mol% ZrO_2, 17 mol% SnO_2 with 1 wt% NiO and 2 wt% La_2O_3 additions were mixed in deionized water at pH 11·5 adjusted with NH_4OH, in order to obtain a defloculated slurry[4] with a load of 50 wt% of powders. The slurry was milled in a Dyno-mill®, an industrial horizontal attrition mill, for a short period.[5] Two kinds of balls were used as grinding media, the first one was Mg-stabilised zirconia balls (with 10 at% of Mg) and the other was zircon balls ($ZrSiO_4$). The abrasion of balls during the grinding process involve unintentional additions respectively of 2·75 wt% of Mg-zirconia balls in specimens A and B, and 0·28 wt% of zircon balls in specimens C and D. Slurries were dried, calcined or not, 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.

2.2 Materials characterisation

X-ray diffractometer Siemens D5005 was used to identify crystalline phases in calcined powders and sintered pellets. The microstructure was observed on polished surfaces into 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. Fragments of pellets, mechanically ground and ion milled using argon at ultra-vacuum pressure, were investigated by XPS (Escalab 220i–xl). Dielectric properties at microwave frequency were measured

Table 1. Characteristics of sintered pellets, dielectric properties are measured at 4 GHz

Ref.	*Grinding media*	*Calcination*	*Density*	*Dielect. constant* ε	*Dielect. loss* Q	*QF (GHz)*	τ_f *(ppm)*	*Number of secondary phases*
A	Zircon	No	5·29	37·4	12 600	50 500	−1	3
B	Zircon	1200°C	5·27	37·2	12 550	50 200	1	3
C	Mg zirc.	1200°C	5·27	36·9	13 950	55 800	−9	2
D	Mg zirc.	No	5·29	37·2	15 450	61 900	−9	2

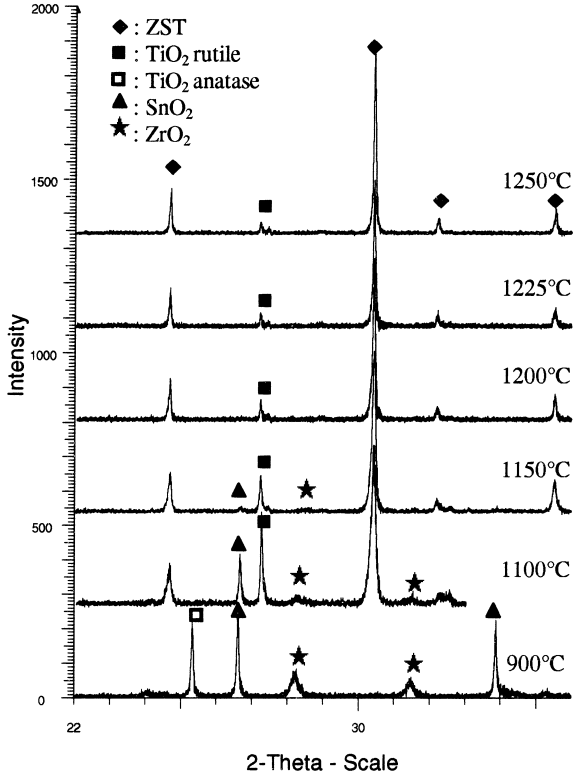

Fig. 1. XRD patterns of calcined powders of ZST mixed with zircon balls, temperature ranging from 900 to 1250°C for 5 h.

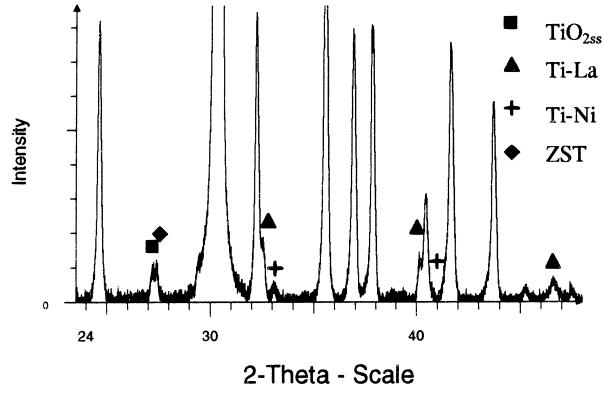

Fig. 2. XRD pattern of sintered ceramics A.

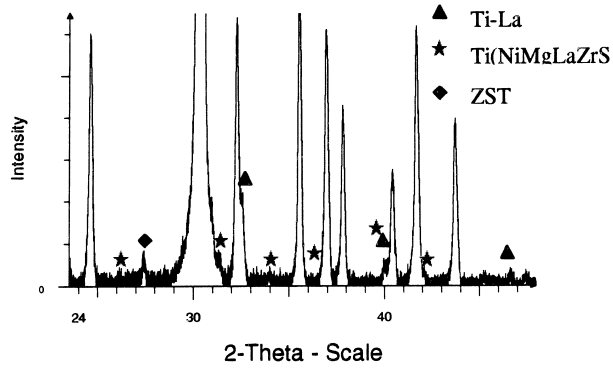

Fig. 3. XRD pattern of sintered ceramics D.

using Hakki and Coleman's method[6] by Tekelec Temex. The density of sintered specimens was measured with an helium pycnometer (Micromeritics accupyc 1330) and their porosity with a mercury porosimeter (micromeritics autopore III) covering the pore diameter range from 360 to 0.003 μm.

3 Results and Discussion

We have mainly studied four specimens, which present very good microwave properties (Table 1). The dielectric constants ε are close to 37 that are normal values for this composition. These ceramics own very low dielectric losses, QF ranges from 50 000 to 62 000 GHz for specimen D at a resonant frequency of 4 GHz. Specimens A and B have a τ_f near zero. A small addition of Mg seems to grow τ_f into negative values, with a τ_f of −9 ppm for specimens C and D. Those dielectric properties are one of the best in literature for this diagram whatever the preparation method may be, by classical solid state reaction[7] or sol–gel method.[3,8,9] These ceramics are dense and present no detectable external porosity (< 0·1%).

The mixed ZST powder was calcined at various temperatures ranging from 900 to 1250°C for 5 h. The existing phases at each temperature are shown in the XRD patterns (Fig. 1). With increasing calcination temperature, we observe the progressive disappearance of the starting materials and the formation of the orthorombic phase ZST. Between 900 and 1100°C TiO_2 anatase is transformed into the rutile phase. After 1150°C ZrO_2 and SnO_2 totally disappeared, yet, up to 1250°C, TiO_2 is remaining. This is contrary to the results presented by Yoon *et al.*[10] and by Han[9] who noticed the presence of TiO_2 in $(Zr_{0.8}Sn_{0.2})TiO_4$ calcined powders compositions

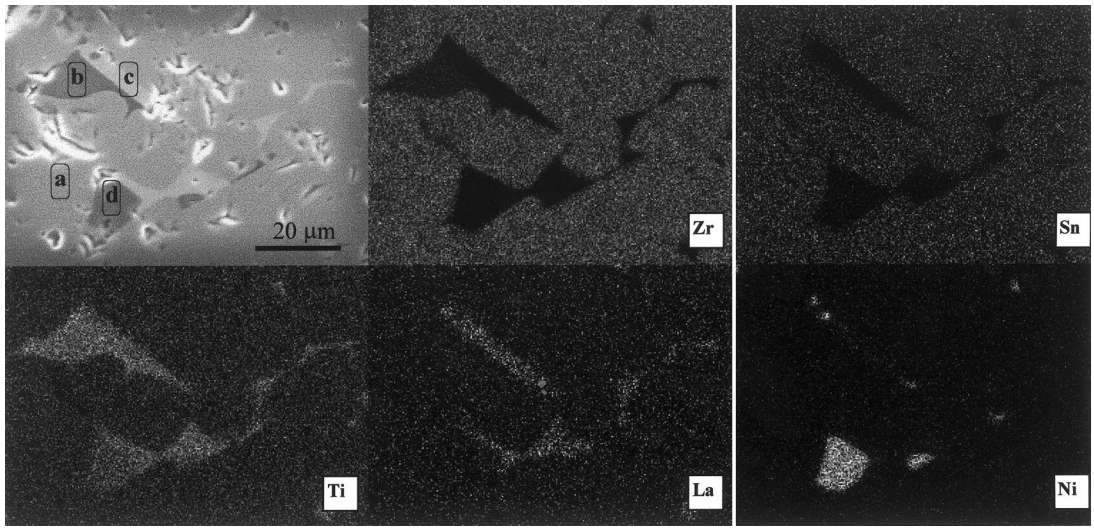

Fig. 4. SEM micrographs and its corresponding EDS element maps for specimen A.

up to 1100°C, and they have obtained a single ZST phase at 1150°C. In contrast, Andronescu *et al.*[11] have observed a TiO_{2ss} phase up to 1450°C in $(Zr_{0.45}Sn_{0.6}Ti_{0.85})O_4$ compositions.

The studied sintered ceramics were multiphased. XRD patterns of specimens A and D are shown in Figs 2 and 3. We observe a major phase which could be indexed in terms of an orthorombic unit cell ZST (ASTM 34-0033). However, minor phases are detected. In order to verify the presence of these minor phases, SEM and EDS analysis were carried out on sintered pellets. Figures 4 and 5 present SEM micrographs on polished surfaces of the bulk of specimens A and D. Polished surfaces have been observed, without acid treatment or thermal etching, in order to not affect the composition of phases at the surface. Tables 2 and 3 present the EDS average compositions of bulk, surface and different phases observed in specimens A and D. We notice here that SEM, EDS, and XRD observations are the same for respectively specimens A and B, and specimens C and D.

Samples A and B exhibit four distinct phases: the major phase ZST; a 'Ti–La' rich phase close to the composition '$Ti_3La_2O_9$' with a small amount of Ni (3·5 at%); a 'Ti–Ni' phase close to the composition $TiNiO_3$ with a small amount of Sn (3 at%) and Zr (2 at%), a similar phase has been observed by Lee *et al.*;[12] and a Ti rich phase with Zr (11 at%) and Sn (11 at%) that we notice 'TiO_{2ss}'.

Samples C and D exhibit different minor phases due to the presence of Mg that is a not negligible addition coming from balls abrasion. In this case, the same 'Ti–La' rich phase is present, but 'Ti–Ni' and 'TiO_{2ss}' phases are not detected. A Ti rich phase with Ni, Mg, La, Zr and Sn has been detected in bulk, principally at the surface. In fact, this phase is inclined to migrate at the surface of the ceramic, that explains the difference between bulk and surface EDS analysis in Table 3.

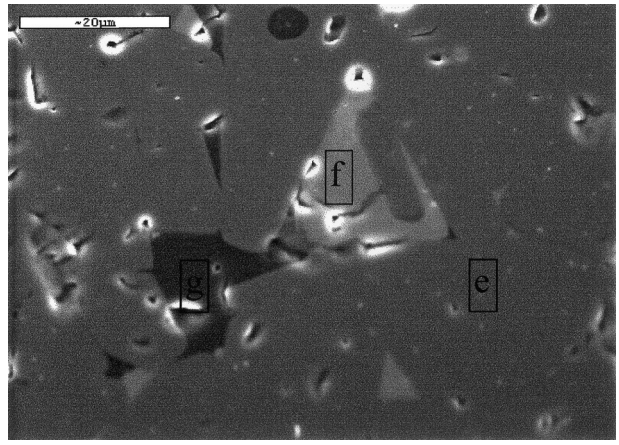

Fig. 5. SEM micrographs for specimen D.

Table 2. EDS concentration values for component elements (at%) for specimen A

	Ti	*Zr*	*Sn*	*Ni*	*La*
Bulk	48·3	32·8	17·0	1·5	0·5
Surface	48·2	31·5	18·3	1·0	0·9
Plot a	46·9	34·6	18·0	0·5	—
Plot b	77·9	10·7	11·4	—	—
Plot c	57·4	—	—	3·5	39·1
Plot d	47·9	2·2	2·8	47·2	—

Preliminary XPS investigations have been conducted for specimen D. XPS spectra of Ti (2p) and Sn (3d) of a bulk fragment point out that there are three different Ti and two different Sn which are related to different environments or different oxidation degrees. This is in accordance with the different phases observed in this specimen, there are three phases including Ti and two phases with Sn.

Table 3. EDS concentration values for component elements (at%) for specimen D

	Ti	*Zr*	*Sn*	*Ni*	*La*	*Mg*
Bulk	47·0	34·7	16·3	1·2	0·5	0·4
Surf.	54·2	21·2	9·1	8·5	4·5	2·5
Plot e	46·1	36·4	17·1	0·4	—	—
Plot f	57·5	—	—	3·2	39·3	—
Plot g	62·7	6·0	3·5	17·8	4·6	5·4

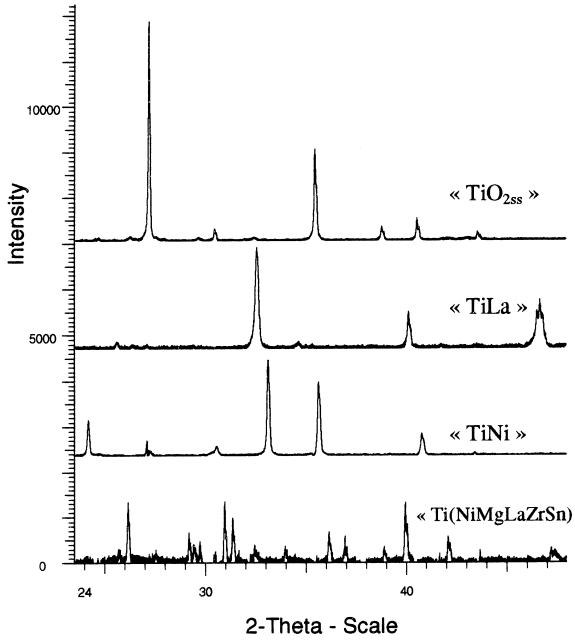

Fig. 6. XRD patterns of the synthesised second phases.

In the main ZST phase, La was not detected. A very small amount of Ni was detected ($\approx$0·5 at%), in opposition with the observations of Lee *et al.*[12] Small amounts of La are difficult to quantify because of the overlap of Ti and La energy pics. About 0·5 at% of La is quantified in opposition to the 1·3 at% expected. Quantification of Ni is correct with 1·4 at%. So, Ni and La prefer to gather with Ti in minor phases at the grain boundaries.

To confirm the above analysis, we have prepared all the minor phases detected, according to EDS compositions, by sintering at 1370°C. XRD patterns of these phases have been recorded in Fig. 6 and their dielectric properties are Table 4. All these minor phases have more dielectric losses than the ZST phase. The XRD patterns have confirmed the formation of the tetragonal $NiTiO_3$ phase (ASTM 33-0960) with small amount of ZST and TiO_2 phases. The 'Ti–La' phase seem to be close to the orthorhombic $La_{2/3}TiO_3$ phase (ASTM 26-0827). The 'TiO_{2ss}' phase is close to the tetragonal rutile TiO_2 (ASTM 21-1276). A similar TiO_2-based solid solution $(Ti,Sn,Zr)_2O_{4ss}$ has been observed by McHale *et al.*[2] The 'TiNiMgLaZrSnO' phase could not be identified with a known phase. So major peaks of each minor phase have been reported on the XRD patterns of specimens A and D (Fig. 2 and Fig. 3), which confirm the presence of these phases in ceramics in accordance with the SEM observations. Further investigations will be required in order to understand the roles of these phases on the dielectric properties.

Table 4. Dielectric properties of the synthesised minor phases

	Diel. Const. ε	*Diel. Loss* Q	*Freq. (GHz)*	*QF (GHz)*	τ_f *(ppm)*	*Density*
'TiO_{2ss}'	26·3	1440	4·3	6200	15·6	4·48
'Ti–Ni'	19·2	1200	5·6	6700	−24·4	5·02
'Ti–La'	64·6	4770	3·3	15 700	—	5·40
'TNMLZS'	42·4	900	5·7	5100	—	4·58

4 Conclusion

$(Zr,Sn)TiO_4$ dielectric resonators, La_2O_3 and NiO doped, prepared by solid state reaction using a Dyno-Mill®, exhibit very good dielectric properties: $\varepsilon = 37$, QF close to 50 000 GHz at 4 GHz and τ_f near zero. A small amount of Mg increases QF up to 62 000 GHz at 4 GHz, and also increases τ_f.

According to SEM and XRD data, in specimens without Mg, a major ZST solid solution is formed with at least three minor phases:

- a tetragonal $TiNiO_3$ phase with small amounts of Zr and Sn;
- a orthorhombic $La_{2/3}TiO_3$ phase with 3% of Ni;
- a $(Ti_{0·8}Zr_{0·1}Sn_{0·1})O_{2ss}$ phase TiO_2-basis solid solution.

Specimens with a small amount of Mg have shown the presence of two minor phases: the same 'Ti–La' phase and a $Ti_{0·6}(Ni,Mg,La,Zr,Sn)_{0·4}O_x$ phase, the latter phase is inclined to migrate at the surface. So further investigations will be required in order to understand the roles of these phases on the dielectric properties.

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