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Synthesis and characterization of La_2O_3/BaO-doped $(Zr_{0.8}Sn_{0.2})TiO_4$ microwave ceramics

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Abstract

$(Zr_{0.8}Sn_{0.2})TiO_4$ microwave ceramics using La_2O_3 and BaO as sintering aids were prepared by the conventional mixed oxide route and investigated by XRD, SEM, EDS and dielectric measurements. The sintering temperature could be effectively lowered by using La_2O_3 and BaO additives. La_2O_3/BaO-doped ZST ceramics sintered at 1350 °C/4 h showed very good dielectric properties: $\varepsilon_r = 41$, $\tau_f = -3.79$ ppm/°C, and $Q = 9800$ at 1.8 GHz. In La_2O_3/BaO-doped ZST ceramics, a major ZST solid solution is formed with three minor phases: (i) $(Ti_{0.8}Zr_{0.1}Sn_{0.1})O_{2ss}$, a TiO_2-based solid solution, (ii) orthorhombic $La_{2/3}TiO_3$ containing 3.4 at.% Ba, (iii) orthorhombic Ba_2TiO_4 containing 2.2 at.% Zr and 2.8 at.% Sn. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: B. Microstructure; C. Dielectric properties; $(Zr_{0.8}Sn_{0.2})TiO_4$; Phase

1. Introduction

Zirconium tin titanate ceramics have attracted noticeable interest as microwave dielectric materials in communication networks. Among them, $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) has proved to be one of the most popular dielectric resonator materials, because of a high dielectric constant ε_r, a high quality factor Q, and a low temperature coefficient of resonant frequency τ_f [1]. ZST ceramics are prepared either by attrition milling [2] or by chemical processing methods [3]. Being difficult to fully densify ZST ceramics at a low temperature, a combination of two or more oxides are used as sintering aids, i.e. La_2O_3, ZnO, NiO, Fe_2O_3 and Co_2O_3, etc. [4–9].

Duk-Jun Kim and his co-workers [10] reported that all the alkaline earth metals were effective for densification of ZST ceramics, especially BaO. BaO additions did not affect the values of dielectric constant ε_r and temperature coefficient of resonant frequency τ_f, and can improve the quality factor Q. Although La_2O_3–BaO–TiO_2 has the ability to form eutectic liquids at temperature of 1350 °C or below [11], it has not yet been used as sintering aid in the ZST system. This paper reports an investigation on phase, microstructure and dielectric properties of ZST microwave ceramics doped with La_2O_3 and BaO.

2. Experimental procedures

The powders were prepared via the conventional mixed oxide route. The raw materials were high purity (>99.0%) ZrO_2, TiO_2, SnO_2, La_2O_3, and $BaCO_3$. To study the effects of different additives upon phase, microstructure and dielectric properties of ZST ceramics, four compositions were chosen:

(a) undoped $(Zr_{0.8}Sn_{0.2})TiO_4$
(b) $(Zr_{0.8}Sn_{0.2})TiO_4 + 1.0$ wt.% La_2O_3
(c) $(Zr_{0.8}Sn_{0.2})TiO_4 + 2.0$ wt.% BaO
(d) $(Zr_{0.8}Sn_{0.2})TiO_4 + 1.0$ wt.% $La_2O_3 + 2.0$ wt.% BaO

The above compositions were milled with ZrO_2 balls for 24 h in deionized water, dried, calcined at 1150 °C for 2 h, remilled with an organic dispersant and binder,

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molded into disks 10 mm in diameter and ~2 mm thick under a pressure of 100 MPa, then sintered in air at 1550 and 1350 °C for 4 h for undoped ZST and doped ZST, respectively. The heating rate was 300 °C/h. The cooling rate was 600 °C/h down to 800 °C, then furnace cooling to room temperature.

The bulk densities of the sintered bodies were measured by the Archimedes method. X-ray diffraction (XRD) analysis (D/Max-IIIB, Rigaku, Japan) was used to identify the crystalline phases of the sintered samples. For microstructural analysis samples were studied by scanning microscopy (SEM) (JSM-6301F, Jeol, Japan) in the as-sintered condition and polished, thermally etched condition. The phase composition was investigated by EDS (Link ISIS-300, UK).

Dielectric properties of sintered samples were measured at 1.8 GHz with a HP 4291B RF Impedance/Material analyzer. Silver paste was used for the electrodes. The temperature coefficient of dielectric constant τ_ε was determined at 1 MHz with a precision LCR meter (HP 4284A) equipped with a thermostat in the temperature 20–85 °C. The temperature coefficient of resonant frequency τ_f was calculated as follows,

$$\tau_f = -1/2\tau_\varepsilon - \alpha$$

where τ_ε is the temperature coefficient of dielectric constant and α is the linear thermal expansion coefficient of the material [8].

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the sintered specimens. A major phase indexed in terms of an orthorhombic unit cell $ZrTiO_4$ (JCPDS 34-415) could be observed. In undoped ZST and in La_2O_3-doped ZST, there were no secondary phases, whereas Ba_2TiO_4 was detected in the BaO-doped specimen; TiO_2, $La_{2/3}TiO_3$, Ba_2TiO_4 and an unknown phase were detected in the specimen doped with La_2O_3/BaO. These results are due to the differences of the ionic sizes between the substitution ions and the tetravalent ions in $(Zr_{0.8}Sn_{0.2})TiO_4$. The La^{3+} and Ba^{2+} could not be substituted for the tetravalent element of $(Zr_{0.8}Sn_{0.2})TiO_4$ being the ionic radii of La^{3+} (1.061 Å) and Ba^{2+} (1.35 Å) much larger than for Zr^{4+} (0.72 Å), Sn^{4+} (0.69 Å) and Ti^{4+} (0.605 Å) ions. Thus, with additions of La_2O_3 and/or BaO, La_2O_3 and BaO react with $(Zr_{0.8}Sn_{0.2})TiO_4$ and second phases are formed. Although La_2O_3 is well known to form a boundary phase, a secondary phase was not observed with addition of only 1 wt.% La_2O_3, due to the fact that detection of a minor phase by XRD is extremely difficult.

SEM micrographs of the as sintered specimens surfaces are shown in Fig. 2. Major differences between the microstructures are apparent. As shown in Fig. 2(a), the undoped ZST ceramics are dense at 1550 °C. The grains are rounded and uniform in shape. With La_2O_3 and/or BaO additions, a much easier densification of ZST ceramics at a lower temperature occurs, as shown in Fig. 2(b)–(d), grain sizes are larger than for the undoped sample and abnormal grain growth occurs. La_2O_3/BaO doped ZST consists of the largest grains and is characterized by round and bar shaped grains, the fraction of the bar grains being much lower than for round shaped grains. Different grain shape indicates that some second phases possibly formed. A similar abnormal grain growth was observed by Kudesia et al. [4] on addition of La_2O_3/ZnO, and by Huang et al. [12] on addition of CuO/ZnO.

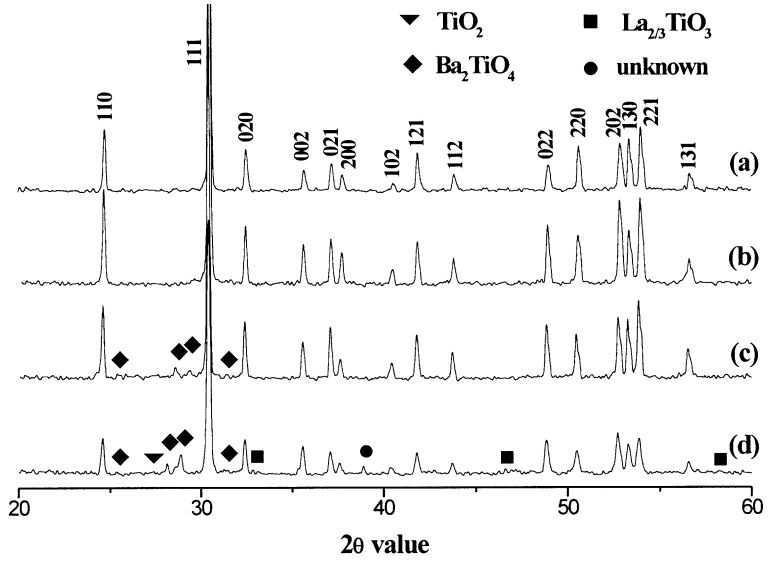
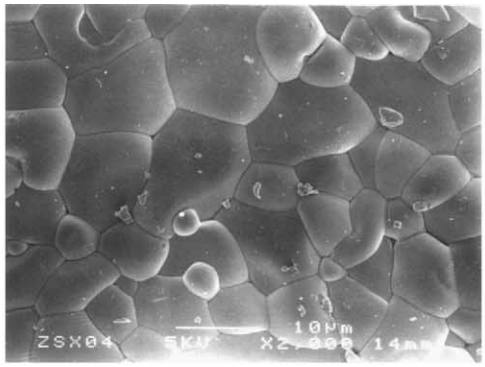
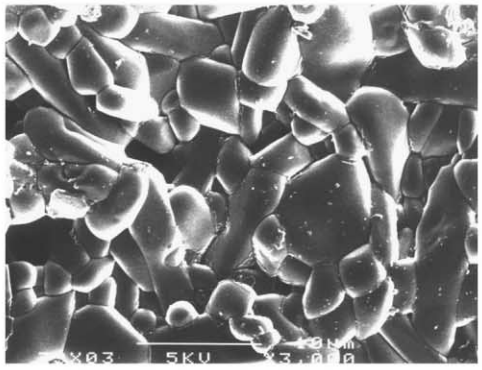


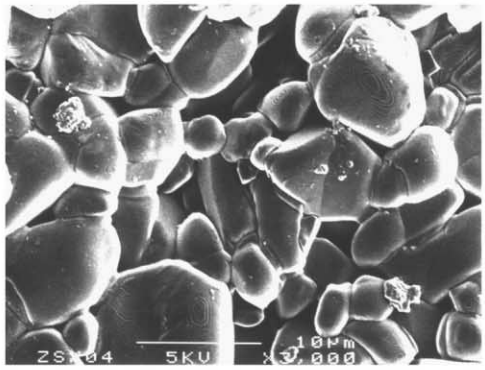
Fig. 1. X-ray diffraction patterns of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics. (a) 1550 °C, undoped; (b) 1350 °C, with 1 wt.% La_2O_3; (c) 1350 °C, with 2 wt.% BaO; (d) 1350 °C, with 1 wt.% La_2O_3 + 2 wt.% BaO.



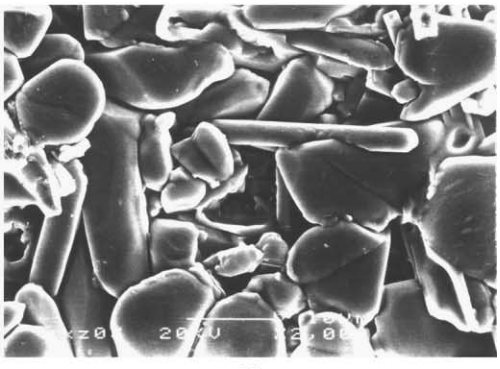
(a)



(b)



(c)



(d)

Fig. 2. SEM micrographs of the surfaces of as sintered ($Zr_{0.8}Sn_{0.2}$)TiO_4 ceramics. (a) 1550 °C, undoped; (b) 1350 °C, with 1 wt.% La_2O_3; (c) 1350 °C, with 2 wt.% BaO; (d) 1350 °C, with 1 wt.% La_2O_3 + 2 wt% BaO.

Such discontinuous-type grain growth is frequently encountered in titanate systems that contain a transient liquid phase [13].

In order to verify the presence of minor phases, SEM and EDS analyses were carried out on polished and etched surfaces. In the undoped ZST and La_2O_3-doped ZST, no second phases were observed, whereas minor second phases were found in BaO-doped ZST and La_2O_3/BaO-doped ZST. In BaO-doped ZST, a 'Ti-Ba' rich phase was present, whereas a phase rich only in 'Ti' was not detected. In La_2O_3/BaO-doped ZST, three minor second phases were found out, i.e. a 'Ti' rich phase, a 'Ti-La' rich phase and a 'Ti-Ba' rich phase.

Fig. 3 shows SEM micrographs and EDS maps of a polished and etched surface of La_2O_3/BaO-doped ZST, whereas Table 1 collects average elementary composition. The sample exhibits four distinct phases: the major phase ZST; a 'Ti' rich phase with Zr (10.8 at.%) and Sn (10.7 at.%) that we notice '$(Ti_{0.8}Zr_{0.1}Sn_{0.1})O_{2ss}$'; a 'Ti–La' rich phase close to the composition '$La_{2/3}TiO_3$' with a small amount of Ba (3.4 at.%), a similar phase has been observed by D. Houivet et al. [6]; a 'Ti–Ba' phase close to the composition 'Ba_2TiO_4' with a small amount of Zr (2.2 at.%) and Sn (2.8 at.%). In the main ZST phase, La and Ba were not detected. Small amounts of La and Ba are difficult to quantify because of the overlap of Ti and La, Ba energy peaks. About 0.2 at.% of La and 1.6 at.% of Ba are quantified in opposition to the 0.6 and 2.7 at.% expected, respectively. So, La and Ba prefer to gather with Ti in minor phases at the grain boundaries.

Dielectric properties of the almost fully densified ZST ceramics containing different additives are listed in Table 2. Except for the comparatively high τ_f value of the La_2O_3/BaO-doped specimen, the additives do not affect substaintially the values of ε_r and τ_f. However, Q is very sensitive to the additives. Namely, La_2O_3- and/or BaO-doped specimens exhibit Q values higher than undoped specimen. The changes in the values of ε_r, Q and τ_f can be explained by the effects of secondary phases. The high Q value of La_2O_3/BaO-doped ZST ceramics are caused by the high densification and the existence of second phases TiO_2 ($\varepsilon_r \sim 104$, $Q \sim 14{,}000$ at 3 GHz) [14] and $La_{2/3}TiO_3$ ($\varepsilon_r \sim 64.6$, $Q \sim 4770$ at 3.3 GHz) [6,15].

Table 1
EDS concentration values (at.%) for La_2O_3/BaO-doped ZST

	Ti	Zr	Sn	Ba	La
Bulk	48.4	32.7	17.1	1.6	0.2
Surface	48.3	31.6	18.4	1.1	0.6
Plot a	47.1	34.7	18.2	–	–
Plot b	78.5	10.8	10.7	–	–
Plot c	58.0	–	–	3.4	38.6
Plot d	31.6	2.2	2.8	63.4	–

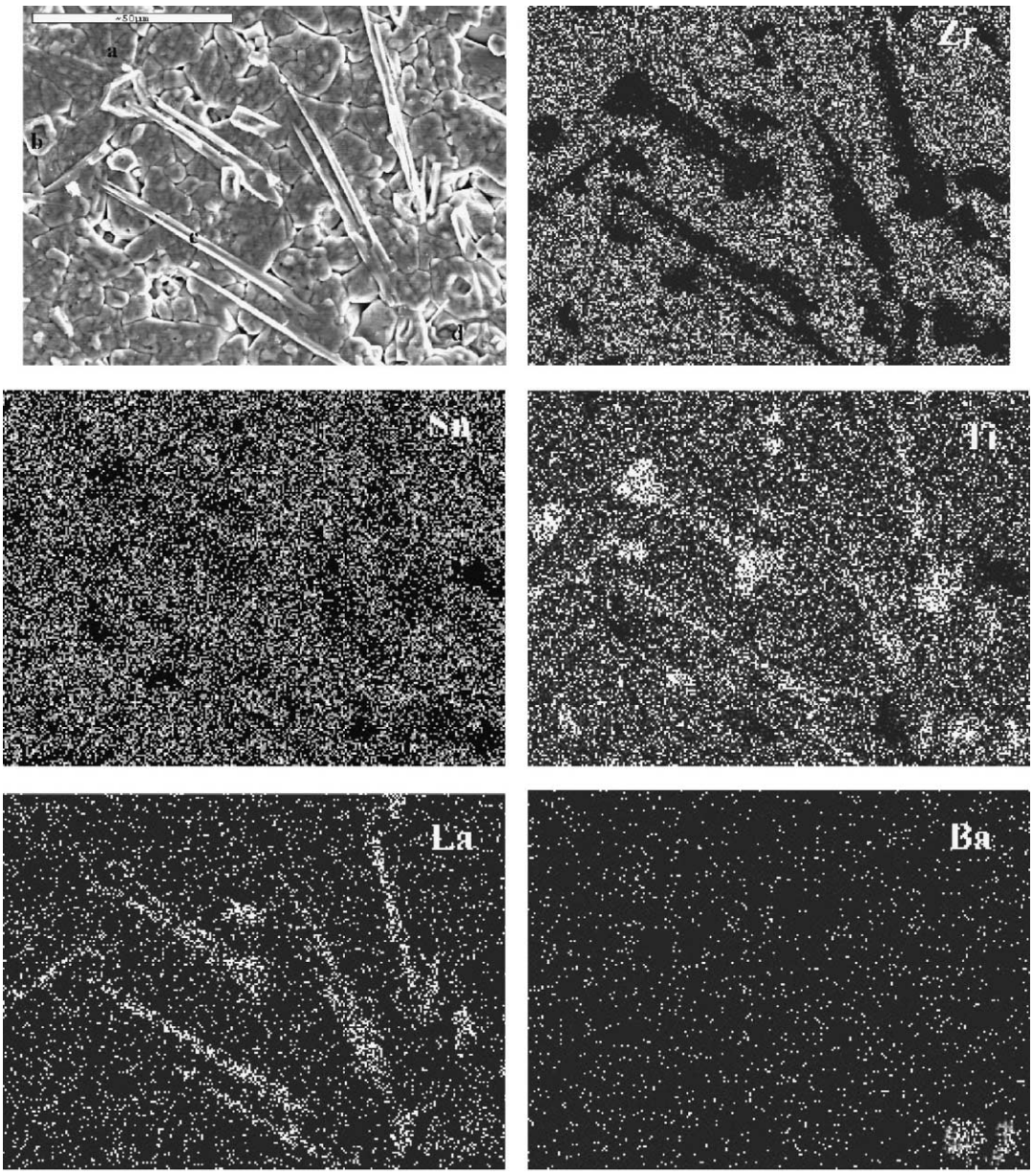


Fig. 3. SEM micrographs and EDS maps of a polished and etched surface of La_2O_3/BaO-doped ZST.

Table 2
Dielectric properties of ZST ceramics with different additives

Sample	Additives (wt.%)	Sintering temperature (°C)	Density (g/cm^3)	ε_r	Q	τ_f(ppm/°C)
(a)	Undoped	1550	4.968	37	6900	0
(b)	1 wt.%La_2O_3,	1350	4.776	38	8100	2.61
(c)	2 wt.% BaO	1350	5.000	39	8600	−0.37
(d)	1 wt.%La_2O_3, 2 wt.% BaO	1350	5.101	41	9800	−3.79

4. Conclusions

The effects of La_2O_3 and/or BaO additions on the phase, microstructure and dielectric properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ microwave ceramics were investigated. La_2O_3/BaO-doped ZST can be sintered to high density at 1350 °C, and exhibit very good dielectric properties: $\varepsilon_r = 41$, $Q = 9800$, $\tau_f = -3.79$ ppm/°C at 1.8 GHz. According to SEM and XRD analysis, in La_2O_3/BaO-doped ZST, a major ZST solid solution is formed

accompanied by three minor phases: (i) $(Ti_{0.8}Zr_{0.1}Sn_{0.1})O_{2ss}$, a TiO_2-based solid solution, (ii) orthorhombic $La_{2/3}TiO_3$ phase containing 3.4 at.% Ba, (iii) orthorhombic Ba_2TiO_4 phase containing 2.2 at.% Zr and 2.8 at.% Sn.

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