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High-*k* Mg-doped ZST for microwave applications

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Abstract

The $(Zr_{0.8}Sn_{0.2})TiO_4$ material (ZST), has been prepared by solid state reaction and characterized. The samples were sintered in the temperature range of 1260–1320 °C for 2 h. The effects of sintering parameters like sintering temperature (T_s) and MgO addition (0.2 wt.%) on structural and dielectric properties were investigated. Bulk density increases from 4900 to 5050 kg/m^3 with the increase of sintering temperature. The effect of MgO addition is to lower the sintering temperature in order to obtain well sintered samples with high value of bulk density. The material exhibits a dielectric constant $\varepsilon_r \sim 37$ and high values of the $Q \times f$ product, greater than 45,000, at microwave frequencies. The dielectric properties make the ZST material very attractive for microwave applications such as dielectric resonators, filters, dielectric antennas, substrates for hybrid microwave integrated circuits, etc.

Keywords: High-*k* dielectrics; Mg-doped ZST; Dielectric resonators; Microwaves

1. Introduction

High-*k* dielectric materials have a determinant influence on the electronic engineering and communications. Due to their high dielectric constant, they offer a high degree of miniaturization. Ceramic materials provide cost-effective solutions for high frequency applications [1–3].

The development of materials based on the ZrO_2–SnO_2–TiO_2 ternary system was motivated by the achievement of very low loss and high dielectric constant and a controlled temperature coefficient of the permittivity [4,5]. Remarkable temperature stability can be achieved by using the compound $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) [6,7]. The resonators made of ZST exhibit an almost zero temperature coefficient of the resonance frequency. Therefore, the ZST materials have been successfully applied for microwave devices like low phase-noise dielectric resonator oscillators (DRO), duplexers, filters, frequency discriminators, etc. [8,9].

The preparation of ZST materials at low sintering temperatures without additives is difficult. The La_2O_3 addition promotes the grain growth [10]. Such additives as La_2O_3, ZnO, increase the sinterability, but no mechanisms have been proposed for the improved densification kinetics or for their effect on the dielectric loss.

The ZST:Mg materials have been insufficiently investigated until now. The effect of MgO addition on crystalline structure, bulk density and dielectric properties, as well as on the sintering temperature, is presented in this paper.

2. Experimental

Ceramic materials based on the ZrO_2–SnO_2–TiO_2 ternary system were prepared by solid-state reaction according to the $(Zr_{0.8}Sn_{0.2})TiO_4$ composition. The raw materials were powder oxides ZrO_2, SnO_2 and TiO_2 with purity higher than 99%. In order to reduce the sintering temperature, 2 wt.% La_2O_3 and 1 wt.% ZnO were added. The powders were milled in the distilled water for 24 h in a mill with agate balls. All mixtures were dried and treated at 1200 °C for 2 h. The calcined powders were then milled again for 2 h. For some samples, 0.2 wt.% MgO was added to the calcined powders, in order to investigate the effect on ZST properties. Cylindrical samples of 10 mm diameter and 5 mm height were formed by uniaxial pressing and then sintered at 1230–1325 °C for 2 h.

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Table 1
Measured bulk density ρ of Mg-doped ZST samples

Sample	Sintering temperature (°C)	Bulk density	
		$\rho \times 10^{-3}$ (kg/m^3)	ρ_r (% theory)
1	1260	4.90	94.41
2	1280	5.05	97.30
3	1300	5.03	96.92
4	1320	5.04	97.11

The crystalline phases were identified by X-ray diffraction (XRD) patterns. A Seifert Debye Flex 2002 diffractometer, provided with copper target X-ray tube ((Cu Kα) λ = 0.1541 nm) was used in order to investigate the ZST structure. The bulk densities (ρ) of the sintered pellets were measured using a water immersion technique.

Measurements of the temperature dependence of the dielectric constant at 1 kHz were performed on a test setup, which includes a Hioki 3511-50 LCR HiTester in the range of −150 to +150 °C.

A computer-aided measurement system combining a HP 8757C network analyzer and a HP 8350B sweep oscillator was employed for the microwave measurements. The dielectric parameters of ZST samples were investigated by using the Hakki–Coleman method [11].

3. Results and discussions

The effects of MgO addition and the sintering temperature on the structural and dielectric characteristics of the ZST samples were investigated. The bulk density ρ and the fraction ρ_r versus the theoretical X-ray density are presented in Table 1. Following the sintering process, samples with a good compactness were obtained with the exception of the sample sintered at the lowest temperature T_s = 1260 °C.

The dependence of bulk density on the sintering temperatures is shown in Fig. 1. A better densification of the Mg-doped ZST samples comparatively with the undoped samples follows

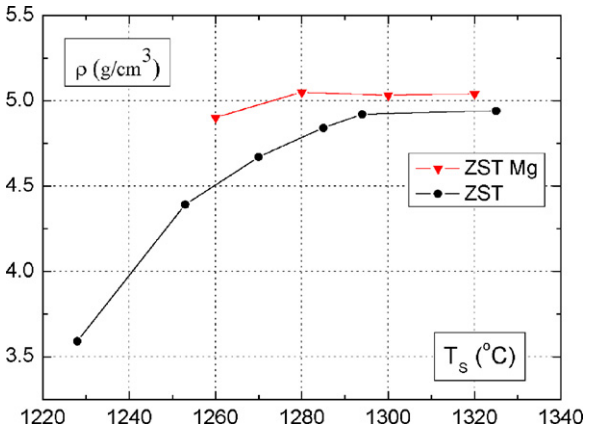

Fig. 1. The bulk density vs. sintering temperature for Mg-doped and undoped ZST samples.

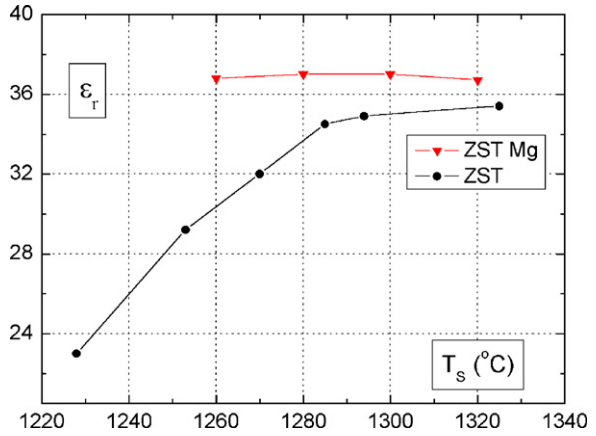

Fig. 2. The dielectric constant vs. sintering temperature for Mg-doped and undoped ZST samples.

from the data presented in Fig. 1 and Table 1. The density ρ_r given in Table 1 was computed as the ratio between the measured bulk density ρ and the theoretical X-ray density of 5190 kg/m^3, which was estimated by using the unit cell volume [12].

The doped samples exhibit higher bulk density (Fig. 1) and higher dielectric constant (Fig. 2) than the undoped samples. The purpose of this work was to achieve high values for the bulk density and the dielectric constant, therefore the ZST:Mg samples were sintered only at temperatures $T_s \geq 1260$ °C.

It can be observed that, the MgO addition has the effect of reducing the sintering temperature required for high-density samples. A temperature as low as T_s = 1280 °C is sufficient to prepare ZST:Mg samples with better characteristics than the undoped ZST samples sintered at a temperature around T_s = 1320 °C.

The X-ray diffraction pattern of MgO-doped ZST samples for sintering temperatures between 1260 and 1320 °C are presented in Fig. 3. XRD patterns showed that the $(Zr_{0.8}Sn_{0.2})TiO_4$ compound is single phase, with crystalline structure of the α-PbO_2 type, i.e. orthorhombic unit cell. This corresponds to the standard crystallographic data [12].

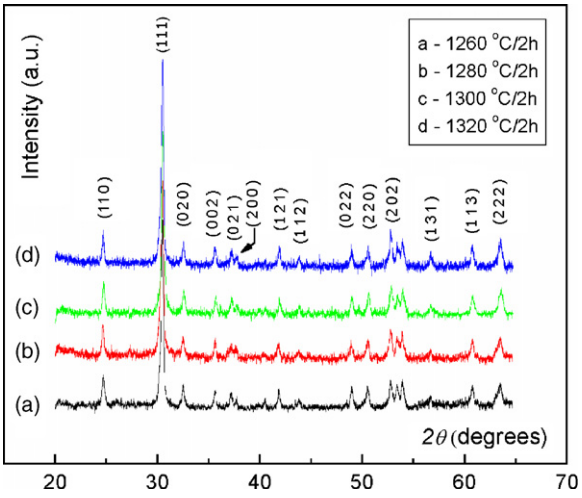

Fig. 3. X-ray diffraction patterns of Mg-doped ZST samples.

Table 2
Crystallite mean dimension of Mg-doped ZST samples

Samples	Sintering temperature, T_s (°C)	Bragg angle, θ (°)	Linewidth, β (rad)	Crystallite mean dimension, D (nm)
1	1260	15.233	0.00433	44.28
2	1280	15.218	0.00531	36.11
3	1300	15.260	0.00441	43.48
4	1320	15.242	0.00439	43.67

Table 3
Calculated unit cell parameters for Mg-doped ZST samples

Sample	Unit cell parameters			Unit cell volume, $V_0 \times 10^3$ (nm^3)
	a_0 (nm)	b_0 (nm)	c_0 (nm)	
1	0.4761	0.5505	0.5037	132.02
2	0.4778	0.5508	0.5035	132.51
3	0.4760	0.5495	0.5029	131.54
4	0.4775	0.5499	0.5044	132.44

The mean dimension (D) of the crystallites was calculated from the Scherrer formula, D (Å) = $k\lambda$ (Å)/$\beta \cos\theta$, where $\lambda = 0.1541$ nm, β the angular line width at half maximum intensity (rad), θ the Bragg angle and k is a constant depending on the crystallites shape. In a spherical coordinate system, $k = 1.2009$ for crystalline planes with Miller indices ($h\,k\,l$) greater than (1 1 0). The Mg-doped ZST samples presents crystallite mean size values less than 45 nm (Table 2) for all sintering temperatures.

The lattice constants a_0, b_0, c_0 and unit cell volume V_0 values are presented in Table 3. The lattice constants and the unit cell volume of doped samples present only a small variation on the sintering temperature interval 1260–1320 °C.

The complex dielectric constant of Mg-doped ZST samples was measured at 1 kHz and in the temperature interval from −150 °C to +150 °C. The dependence of the dielectric constant and loss, as a function of temperature, at 1 kHz is shown in Figs. 4 and 5 for the samples sintered at T_s = 1300 and 1320 °C, respectively. An excellent thermal stability of the dielectric constant in the −150 to +150 °C temperature range can be observed. Furthermore, the measured dielectric loss, tan θ, is constantly low in the investigated temperature range.

Microwave measurements of the complex dielectric constant of Mg-doped ZST samples were also performed. Plot of the dielectric constant of doped and undoped ZST samples versus sintering temperature is presented in Fig. 2. The dielectric constant of doped samples is higher than for undoped ZST samples at the same sintering temperature. The experimental data for ZST:Mg samples measured around 6.5 GHz are listed in Table 4. It can be noticed the decrease of the dielectric loss with the increase of the sintering temperature. The product $Q \times f$ between the intrinsic quality factor Q of the samples and the measurement frequency f are ranging from 45,000 to 60,000. These values of $Q \times f$ product recommend this material for dielectric resonators used for several microwave applications [2].

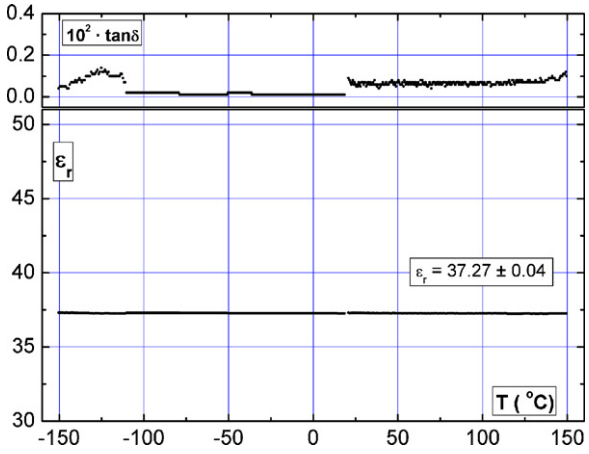

Fig. 4. The dielectric characteristics vs. temperature for the Mg-doped ZST sample sintered at 1300 °C.

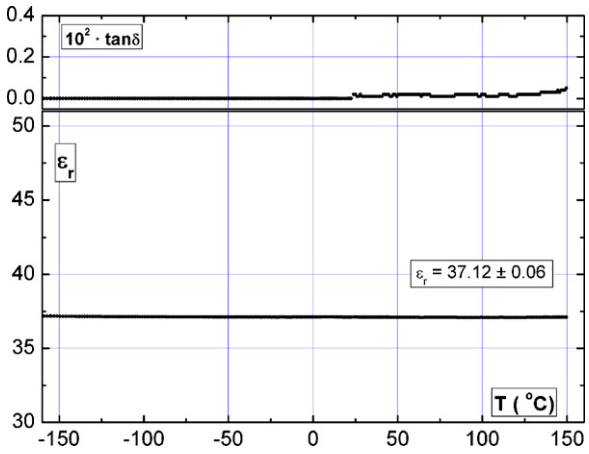

Fig. 5. The dielectric characteristics vs. temperature for the Mg-doped ZST sample sintered at 1320 °C.

Table 4
Dependence of the microwave dielectric parameters on the sintering temperature

Sample	Sintering temperature, T_s (°C)	Resonance frequency, f (GHz)	Dielectric constant, ε_r	Dielectric loss, tan $\delta \times 10^4$	Quality factor, Q	Product, $Q \times f$ (GHz)
1	1260	6.60	36.8	1.46	6855	45243
2	1280	6.52	37	1.16	8616	56176
3	1300	6.41	37	1.24	8087	51838
4	1320	6.50	36.7	1.08	9230	59995

4. Conclusions

The dielectric constant and the structural properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ undoped and Mg-doped samples were studied. Investigations have revealed a better densification of the Mg-doped ZST samples compared to the undoped ones.

The dielectric constant was substantially improved when 0.2 wt.% MgO was added. It was obtained samples with the dielectric constant $\varepsilon_r \sim 37$ and the intrinsic quality factor of $Q \sim 9000$ at 6.5 GHz.

The ZST:Mg samples show an insignificant decrease of the dielectric constant from 1 kHz to 6.5 GHz of less than 1 %. Moreover, there is also an exceptional thermal stability of the dielectric constant, in the temperature range −150 to +150 °C, of 6–7 ppm/°C.

Mg-doped ZST ceramic materials having high dielectric constant, stable with frequency from 1 kHz to 6.5 GHz and stable on a large temperature interval, characterized by a $Q \times f$ product of up to ∼60,000 GHz, are recommended for microwave applications, which require very low dielectric loss at very high frequencies.

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