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Magnesium doped ($Zr_{0.8}$, $Sn_{0.2}$)TiO_4 ceramics for microwave devices

L. NEDELCU*, A. IOACHIM, M. I. TOACSĂN, M. G. BANCIU,
C. A. DUŢU, F. LIFEI, F. VASILIU, G. STOICA[a]
National Institute of Materials Physics, P.O. Box MG-7, RO 077125, Bucharest-Magurele, Romania
[a] S.C. Armtech S.A., Curtea de Argeş, Romania

Magnesium doped ($Zr_{0.8}Sn_{0.2}$)TiO_4 material has been prepared by solid state reaction and characterized. The samples were sintered in the temperature range of 1270 ÷ 1315 °C for 2 hours. The effect of sintering temperature on structural and dielectric properties was investigated. The 0.2 wt.% MgO addition improves the sintering process and well sintered samples with a high value of bulk density were achieved. The material exhibits a dielectric constant $\varepsilon_r \sim 36.6$ and high values of the $Q\times f$ product, greater than 61000 at microwave frequencies. The dielectric properties make the magnesium doped ($Zr_{0.8}Sn_{0.2}$)TiO_4 material very attractive for such microwave applications as dielectric resonators, filters, dielectric antennas, substrates for hybrid microwave integrated circuits, etc.

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1. Introduction

With the current worldwide explosion in the development of microwave-based communications technologies, the production of dielectric materials has emerged as one of the most rapid growth areas in electronic ceramic manufacturing. For the application of dielectric ceramics to microwave devices, a high dielectric constant, low losses and high temperature stability are required [1, 2].

Zirconium tin titanate solid solutions, especially the ($Zr_{0.8}$ $Sn_{0.2}$)TiO_4 composition (ZST), are some of the most utilized ceramic materials for such microwave application as frequency discriminators [3], low phase-noise dielectric resonator oscillators (DROs) [4], duplexers and filters [1, 5]. The ZST solid solution is usually obtained for sintering temperature around 1400 °C [6, 7]. Nevertheless, at these temperatures, the SnO_2 volatilization can be happen. Therefore, extensive research has focused on doping the ZST materials in order to lower the sintering temperature without degrading significantly the dielectric properties [8-12].

As a result of our previous investigations, ZST materials with attractive microwave and millimeter wave characteristics were achieved by La_2O_3 and ZnO additions, which lowered the sintering temperature down to 1330°C [12,13]. The aim of this work was a further decrease of the sintering temperature by using a 0.2 wt.% MgO supplementary addition.

2. Experimental

The ($Zr_{0.8}Sn_{0.2}$)TiO_4 compounds based on the $ZrO_2 - SnO_2 - TiO_2$ ternary system were prepared by solid-state reaction. Powder oxides ZrO_2, SnO_2 and TiO_2 with purity higher than 99 % were mixed according to the ($Zr_{0.8}Sn_{0.2}$)TiO_4 stoichiometry, equivalent to a weight ratio of 47:15:38. In order to reduce the sintering temperature, 2 wt % La_2O_3 and 1 wt % ZnO was added. The powders were ground in 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. Next, 0.2 wt % MgO was added to the calcined powder. After the biaxial pressing at 5 MPa and sintering at temperatures of 1270÷1315 °C for 2 h, pellets of 12 mm diameter and 6 mm height were obtained.

The bulk density of the sintered pellets was measured using a water immersion technique. The crystalline phases were identified by X-ray diffraction (XRD) patterns. A Seifert Debye Flex 2002 diffractometer, provided with copper target X-ray tube with $\lambda(CuK_\alpha) = 0.1541$ nm was used in order to investigate the ZST structure. The morphology and microstructure of the sintered ceramics were analyzed by using scanning electron microscopy (SEM).

At microwaves, the ZST cylindrical samples exhibit very low dielectric loss, high dielectric constant, and a very good stability with temperature. Therefore, the dielectric parameters of ZST samples were investigated by using the Hakki-Coleman method [14]. A computer-aided measurement system, which combines a HP 8757C network analyzer and a HP 8350B sweep oscillator, was used for the microwave measurements. The temperature coefficient of the resonant frequency τ_f in the microwave range was measured by heating the samples from +20 °C to +90 °C.

3. Results and discussion

Following the sintering process, ceramic materials with a good compactness were obtained for all sintering temperatures. The bulk density and porosity of the sintered samples is shown in Fig. 1. All samples exhibit porosity less than 3.1 %, which is sufficient for the optimum dielectric loss. The dielectric loss due to the pores does not vary with the sample compactness for such small values of the porosity [8].

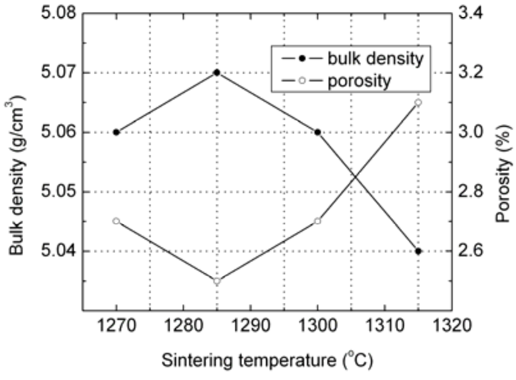


Fig. 1. The bulk density and porosity versus sintering temperature for Mg doped ZST samples.

XRD patterns showed that the $(Zr_{0.8}Sn_{0.2})TiO_4$ samples are single-phase, with crystalline structure of the α-PbO_2 type, i.e. orthorhombic unit cell. This corresponds to the standard crystallographic data [15]. The X-ray diffraction pattern of MgO doped ZST samples for sintering temperatures between 1270 ÷ 1315 °C are presented in Fig. 2. The unit cell parameters (a_o, b_o, c_o, V_o) of the orthorhombic compounds were determined by using the peaks (022), (202) and (220), which showed either splittings or even isolated doublets.

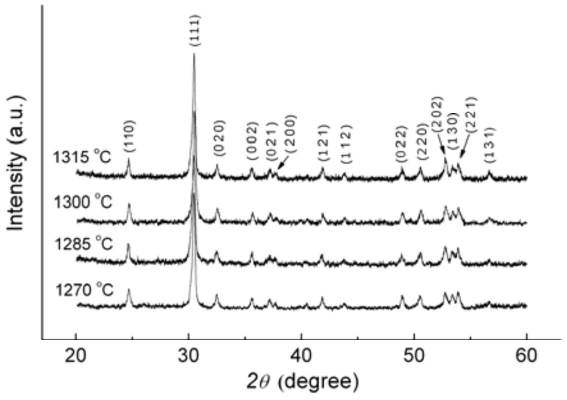


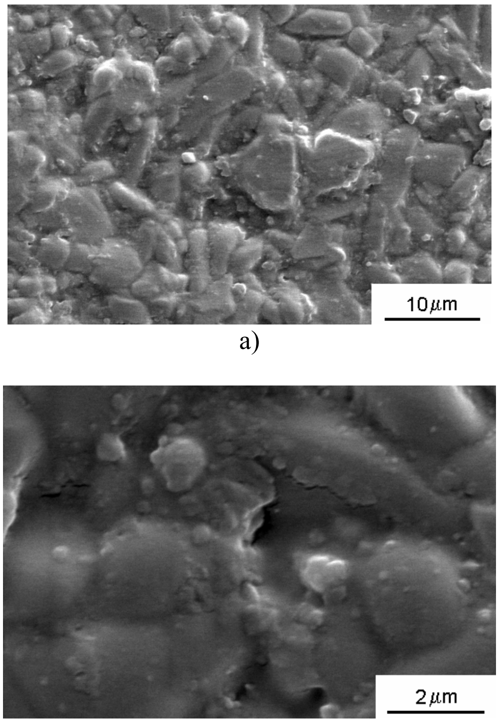
Fig. 2. X-ray diffraction patterns of MgO doped ZST samples with the increase of sintering temperature T_s from 1270 °C to 1315 °C.

The values of the lattice constants a_o, b_o, c_o and the unit cell volume V_o are given in Table 1. Even though, these parameters present only a small variation on the sintering temperature interval, the cell volume V_o exhibits a minimum value for samples sintered at 1285 °C/2h. In the ZST unit cell, the Sn cations can substitute to a certain degree for either Zr or Ti, or for both cations. The decrease of the unit cell volume V_o with the increase of sintering time, suggests the preferential replacement of Zr cations by the smaller Sn ions, corresponding to a better short-range ordered structure.

Table 1. Calculated unit cell parameters for Mg doped ZST samples.

Sample	Sintering temperature T_s (°C)	Unit cell parameters			Unit cell volume V_o (Å^3)
		a_o (Å)	b_o (Å)	c_o (Å)	
1	1270	4.778	5.508	5.035	132.51
2	1285	4.760	5.495	5.029	131.54
3	1300	4.761	5.505	5.037	132.02
4	1315	4.775	5.499	5.044	132.44

The microstructure of ZST ceramics sintered at 1270 °C/ 2h was investigated by using SEM. The images are presented in Fig. 3. The needlelike grains with size up to 10 μm and the polyhedral ones with rounded corners can be observed in Fig. 3a. Submicronic grains with spherical shape are located on the grain surfaces (Fig. 3b). The porous structure is reduced; only few small spherical pores with size up to 1 μm are located between grains.



a)

b)

Fig. 3. SEM micrographs of ZST sample sintered at 1270 °C: a) magnification 1000 x*; b) magnification 5000* x.

Microwave measurements of the dielectric constant and losses of the ZST samples were also performed. The experimental data for Mg doped ZST samples measured around 6.7 GHz are listed in Table 2. The product *Q x f* of the intrinsic quality factor Q and the frequency f of samples are ranging from 53000 to 61000 GHz. Moreover, the ZST samples exhibit a temperature coefficient τ_f in the $2 \div 6$ ppm/ °C range. The maximum values of electric permittivity and quality factor were achieved for Mg:ZST samples sintered at 1285°C for 2h, that is for the same samples, which exhibit the greatest bulk density and the minimum unit cell volume.

Table 2. 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 Qxf (GHz)
1	1270	6.76	36.6	1.15	8700	58812
2	1285	6.64	36.7	1.09	9200	61088
3	1300	6.77	36.6	1.19	8400	56868
4	1315	6.65	36.5	1.23	8100	53865

For ZST samples doped with only 0.2 wt % MgO, the grain growth and the distortion of shape of the grains were suppressed. If the Mg^{2+} ions diffuse into the grains, the quality factor Q is strongly deteriorated, due to the disordered charge distribution created by the oxygen vacancies [16]. For 1 at % MgO doped ZST samples, the Mg^{2+} ions diffuse into the grains and the Q is decreased to 800 at 5 GHz [17]. The magnesium doped ZST samples presented in this paper exhibit very high values of the quality factor ($Q \sim 8500$ at 6.5 GHz), so we can assume that the Mg^{2+} ions do not diffuse into the grains. It is possible that, Mg and Zn ions are located at the boundary phase and form a (Zn, Mg)$_2$TiO$_4$ spinel structure like in the case of samples doped with NiO and ZnO [6]. The outcome of the MgO addition is to enhance the Sn role of stabilization the interface between Zr-rich and Ti-rich domains, which appear during the cation-ordering transformation.

4. Conclusions

The dielectric parameters and the morpho-structural properties of Mg doped ($Zr_{0.8}Sn_{0.2}$)TiO_4 ceramic materials were studied. The ZST samples were prepared by solid-state reaction and sintered at temperatures in the range $1270 \div 1315$ °C for 2 h.

Investigations have revealed a very good densification of the ZST:Mg ceramics. XRD patterns showed that the ($Zr_{0.8}Sn_{0.2}$)TiO_4 compound is single-phase, with an orthorhombic unit cell. The SEM investigations revealed polyhedral grains with rounded corners. The porous structure is reduced; only few small spherical pores are present between grains.

Microwave measurements revealed ZST:Mg samples with the dielectric constant $\varepsilon_r \sim 36.6$, an intrinsic quality factor of $Q \sim 9000$ at 6.7 GHz and a temperature coefficient τ_f in the $2 \div 6$ ppm/ °C range.

Mg doped ($Zr_{0.8}Sn_{0.2}$)TiO_4 ceramics sintered at 1285 °C for 2h, which exhibit a high dielectric constant (≈36), a good thermal stability and characterized by a $Q\,x\,f$ product up to 61000 GHz represent a cost effective solution for microwave compact devices.

Acknowledgements

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[*] Corresponding author: nedelcu@infim.ro