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ZST TYPE MATERIAL FOR DIELECTRIC RESONATORS AND SUBSTRATES FOR HYBRID INTEGRATED CIRCUITS

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$(Zr_{0.8}Sn_{0.2})TiO_4$ ceramic (ZST) has been prepared and characterized. The effects of sintering parameters such as sintering temperature, sintering time and NiO addition on structural and dielectric properties were investigated. The material has a dielectric constant $\varepsilon_r \sim 36.0$ and high values of the $Q \cdot f$ product from 32,170 to 50,000 at microwave frequencies. The *tan* δ values are decreased by low level doping of NiO, while the temperature coefficient of the resonance frequency τ_f takes values in the range (-2÷+4) ppm/^{o}C. Investigations on whispering gallery modes revealed low dielectric losses in millimeter wave domain. An intrinsic quality factor of 480 was measured at 136.3 GHz. Dielectric resonators and substrates of ZST material were manufactured. The dielectric properties make the ZST material very attractive to microwave and millimeter wave applications such as filters, hybrid microwave integrated circuits, etc.

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1. Introduction

Modern wireless communications technologies require new materials with special properties at microwaves frequencies [1-4]. Dielectric materials with low loss and high dielectric constant can offer a high degree of miniaturization. Moreover, the ZST materials such as $(Zr_{0.8}Sn_{0.2})TiO_4$ provide an increased stability with the temperature and a low temperature coefficient τ_f [2], which can be controlled by preparation.

2. Experimental

Samples of $(Zr_{0.8}Sn_{0.2})TiO_4$, were synthesized by conventional solid-state reaction from oxide powders with purity higher than 99.9%. The starting materials were mixed according to the desired stoichiometry of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics, equivalent to a molar ratio of 47:15:38, with 2 wt % La_2O_3 and 1 wt % ZnO as sintering additives. The powders were ground in distilled water for 24 h in a mill with agate balls. All mixtures were dried and treated at 1200 ^{o}C for 2 h. The calcined powders were then remilled for 2 h. For some samples, 0.2 wt % NiO was added to the calcined powders, in order to investigate the effect of NiO sintering additive on ZST properties. Pellets of 10 mm diameter and 5.3 mm thick were formed by uniaxial pressing and sintered at temperatures of (1330÷1400) ^{o}C for (2÷4) h.

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The morphology, phase-composition and microstructure of the sintered ceramics were analyzed by means of scanning electron microscopy (SEM), and energy-disperse X-ray spectrometry (EDX). The crystalline phases were identified by X-ray diffraction (XRD) patterns. The bulk densities (ρ_r) of the sintered pellets were measured by the Archimede's method.

The dielectric constant ε_r and the quality factor Q values at microwave frequencies were measured by using the Hakki-Coleman dielectric resonator method [5]. A computer aided measurement system combining a HP 8757C network analyzer and a HP 8350B sweep oscillator was employed in microwave measurements. The temperature coefficient τ_f of the resonant frequency in microwave range was measured by heating the samples from 18 ^{o}C to 90 ^{o}C.

The investigation of the whispering gallery modes (WGM) [6,7] of the ZST disks allowed for dielectric measurements in the millimeter wave range due to the very low radiation loss of these modes. The WGMs were excited by using a dielectric waveguide as shown in Fig. 1.

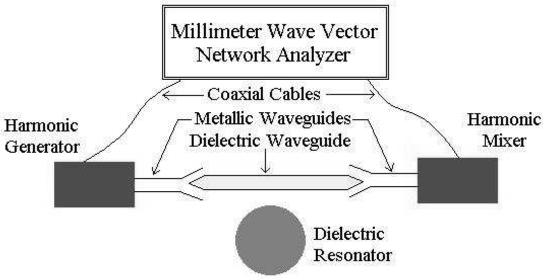


Fig. 1. Experimental setup for ZST disk characterization in the millimeter wave range.

3. Results and discussions

The investigated samples are generally multiphase. The compositions contain typically two solid solutions $(Zr_{0.8}Sn_{0.2})TiO_4$ and $ZrTiO_4$ and, at lower sintering temperatures (T_s), very small amount of unreacted TiO_2.. For sintering temperatures T_s equal or higher than 1330 ^{o}C, the $ZrTiO_4$ phase and TiO_2 tend to disappear and the crystalline lattice becomes more ordered.

The Sn ions stabilize the structure at high-temperature, so the XRD analyses revealed $(Zr_{0.8}Sn_{0.2})TiO_4$ solid solution coexisting with $ZrTiO_4$. The dielectric measurements and EDX compositional data on ZST cylindrical resonators are presented in Table 1. Samples 1 and 2 in Table 1 are rich in Zr compared to the initial molar composition ratio. For sintering temperatures $T_s \geq 1400$ ^{o}C, the XRD patterns indicate the disappearance of the unreacted TiO_2 [2].

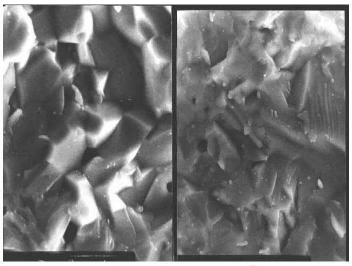
The X-ray data show the decrease of the volume V_o of the unit cell with the increase of the sintering temperature T_s [8, 9]. Sn ions substitute to a certain degree Zr ions or Ti ions. The decrease of the unit cell volume V_o while the sintering temperature T_s increases suggests the preferential replacement of Zr ions by the smaller Sn ions, corresponding to a better short-range ordered structure [10].

Table 1. Dependence on sintering temperature T_s of the unit cell volume V_0, EDX compositional data and microwave dielectric parameters of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics.

Sam-ple	Sintering temperature	Zr (at %)	Sn (at %)	Ti (at %)	Resonance frequency f_0 (GHz)	Dielectric constant ε_r	Quality factor Q
1	1330	54.61	15.50	29.89	6.09	35.3	2000
2	1360	54.24	14.85	30.91	6.03	33.9	3000
3	1400	45.80	16.80	37.40	6.78	35.3	5200

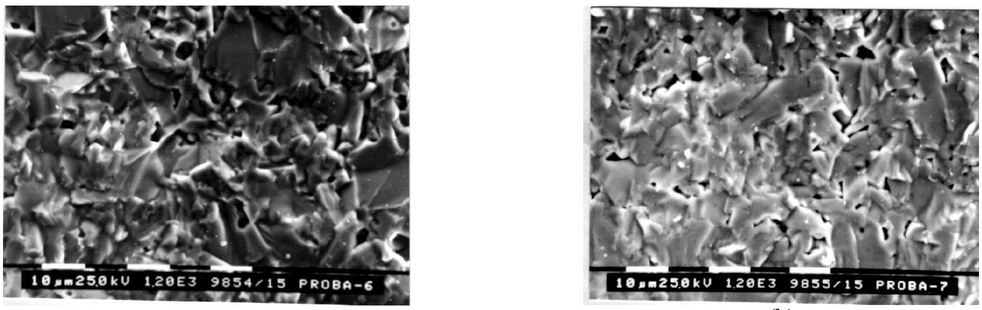
SEM images revealed an increase of grain size with the increase of the sintering temperature. Moreover, when T_s increases, the grains become more faceted as shown in Fig. 2a-b. For sintering temperatures $T_s \geq 1400$ ^{o}C, some intergranular pores with polyhedral facets appear. They can be attributed to SnO_2 segregation at grain boundaries followed by a vaporization at high temperatures. The presence of very little, spherical, light colored grains ($d = \leq 1$ μm) in these ceramics can be attributed to SnO_2 recrystallization produced during furnace cooling.

For samples with NiO sintering additive, the Ni ions, like Zn ions, do not diffuse into the grains, but remain at the boundary phase and form a spinel structure $(Zn, Ni)_2TiO_4$ [3]. The SEM images in Fig. 3-a, b reveal that Ni-doped samples exhibit more facets than undoped samples.



(a) (b)

Fig. 2. SEM image of ZST ceramics, a) T_s=1330 °C/4h, b) T_s=1360 °C/4h.



(a) (b)

Fig. 3. SEM image of ZST fracture; (a) ZST without NiO, (b) ZST with NiO.

It is believed that Sn ions stabilize the interface between Zr-rich and Ti-rich domains, which occur by cation-ordering transformation during sintering treatment [10]. The substitution of Sn for Zr in ZT leads to a gradual decrease in the length scale of cation correlation induced by slow-cooling. All these structural variations results in a modification of spatial charge [11], which contributes to the changes of the microwave dielectric parameters (ε_r, Q, *tan* δ) shown in Table 2.

Table 2. Microwave dielectric properties of ZST ceramics sintered at 1330 °C as a function of the NiO concentration and of the sintering time (t_p).

Sample	NiO (%wt)	Sintering time t_p(h)	Resonance frequency f (GHz)	Dielectric constant ε_r	Loss tangent *tan* δ ($x10^{-4}$)	Quality factor Q	$Q.f$ (GHz)	Bulk density (g/cm^3)
4	0	2.0	6.653	36.8	2.14	4,672	31,082	5.02
5	0	2.25	6.624	36.6	2.91	3,436	22,762	5.05
6	0	2.50	6.690	36.2	2.62	3,816	25,529	5.00
7	0.2	2.0	6.740	36.3	1.45	6,896	46,482	5.03
8	0.2	2.25	6.710	36.8	1.32	7,575	50,833	5.01
9	0.2	2.50	6.820	36.1	2.12	4,716	32,170	4.995

The addition 0.2 wt % NiO induces significant modifications of the microwave dielectric parameters. The EDX data confirm the presence of a thin $(Zn, Ni)_2TiO_4$ layer on grain surfaces inhibiting the Sn ions segregation at the grain boundaries [3]. We believe that this effect induces changes in the spatial charge and consequently reduces the Sn contribution to the dielectric loss.

The EDX data show for the sample 4 of Table 2 a Zr:Sn:Ti molar ratio of 58:12:30 and for the sample 9 a ratio of 50:17:33. Therefore, the composition ratio in the presence of Ni ions is closer of the standard initial ratio 47:15:38.

The experimental data show a decrease of the ZST dielectric loss in microwaves in the presence of Ni ions. The high values of $Q \cdot f$ ranging from 32,170 to 50,000 suggests that the role played by Ni is to enhance the Sn capability to stabilize the interface between Zr-rich and Ti-rich domains, which appear during the cation-ordering transformations during the sintering treatment. The *tan* δ values are decreased in ZST-Ni ceramics compared to the undoped ceramics and the temperature coefficient τ_f takes values in the range (-2 ÷ +4)ppm/^{o}C.

Table 3. Quality factor measurements on a ZST sample in millimeter waves domain.

Frequency *f* (GHz)	*Quality factor (Q)*	$Q \cdot f$
40.64	1300	52,832
62.86	900	56,574
87.07	600	52,242
88.08	600	52,848
115.6	440	50,864
136.3	480	65,424

The whispering gallery modes of ZST disks were investigated by using an experimental setup depicted in Fig. 1. The whispering gallery modes have the advantage of very low radiation losses, and, therefore, the intrinsic unloaded quality factor corresponds only to the dielectric loss [6,7]. The measured values of the quality factor *Q* are listed in Table 3 for frequencies up to 136.3 GHz for ZST disks sintered for two hours at 1330 ^{o}C with 0.2 wt% NiO addition. The measurements revealed low dielectric loss for the ZST samples in millimeter wave domain.

4. Conclusions

The investigations on $(Zr_{0.8}Sn_{0.2})TiO_4$ revealed that the increase of sintering temperature does not essentially affect the dielectric constant, but it results in a decrease of the dielectric loss. Moreover, the dielectric loss is further decreased by sintering addition (0.2 wt %) of NiO, while the other dielectric parameters, such as the dielectric constant ε_r and the temperature coefficient τ_f, do not show significant changes.

The investigations in millimeter wave range showed the decrease of the quality factor from Q = 1300 at 40.64 GHz to Q = 480 at 136.3 GHz. The high dielectric constant, low dielectric loss and controllable temperature coefficient recommend the ZST materials for microwave and millimeter wave applications.

References

[1] S. J. Fiedziuszko, I. C. Hunter, T. Itoh, Y. Kaobayashi, T. Nishikawa, S. N. Stitzer, K. Wakino, IEEE Trans. Microw. Theory Techn. Telecoms. Res. Inst., Warsaw, Poland **MTT-50**, 706 (2002).
[2] M. I. Toacsan, A. Ioachim, R. Coca, G. Stoica, Proc. Internat. Conf. Microwave Ferrites ICMF 2000, Rokosowo, Poland, p. 104 (2000).
[3] K. Wakino, K. Minai, H. Tamura, J. Am. Cer. Soc. **67**, 278 (1984).
[4] F. Vasiliu, D. Grozea, C. Bunescu, S. Moisa, J. Mat. Sci. **29**, 3337 (1994).
[5] B. W. Hakki, P. D. Coleman, IRE Trans. on **MTT-8**, (7), 402-410 (1960).
[6] G. Annino, M. Cassetari, I. Longo, M. Martinelli, IEEE Trans. Microw. Theory Techn., **MTT-45**, 2025 (1997).
[7] G. Annino, D. Bertolini, M. Cassettari, M. Fittipaldi, I. Longo, M. Martinelli, J. Chem. Phys. **112**, 2308 (2000).
[8] S. Hirano, I. Hayashi, A. Hattori, J. Am. Cer. Soc. **74**, 1320 (1991).
[9] G. Wolfram, H. E. Gobel, Mater. Res. Bull. **16**, 1455 (1991)
[10] R. Christoffersen, P. K. Davies, X. Wei, J. Am. Cer. Soc. **77**, 1441 (1994).
[11] H. Tamura, Amer. Ceram. Soc. Bull. **73**, 92 (1994).