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Effect of cooling rate on loss quality of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics with additives

Yil Seok Ahn[a], Ki Hyun Yoon[a,*], Eung Soo Kim[b]

[a]*Department of Ceramic Engineering, Yonsei University, Seoul 120-749, South Korea*
[b]*Department of Materials Engineering, Kyonggi University, Suwon 442-760, South Korea*

Abstract

Microwave dielectric properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics with Sb_2O_5 or WO_3 were investigated as a function of cooling rate. For the lattice parameters of $(Zr_{0.8}Sn_{0.2})TiO_4$, *c*-axis decreased with the decrease of cooling rate and reached to a minimum value at the cooling rate of 1 °C/min. The lattice parameters of the specimens with 1.0 mol% Sb_2O_5 or WO_3 showed the similar tendency. The relative density and Q_f were minimum at the specimen quenched in air, and increased with the decrease of the cooling rate. The increase of Q_f values could be explained by ordering of the cations caused by the transformation at high-temperature. These results could be contributed by not only the extrinsic effect such as grain size and density but also the intrinsic effect such as the structural change with cooling rate, which could be confirmed by the IR reflectivity spectra.

Keywords: Additives; Cooling rate; IR reflectivity; Loss quality; $(Zr_{0.8}Sn_{0.2})TiO_4$

1. Introduction

With advances in communication technology at microwave frequencies, various kinds of microwave dielectric materials have been investigated to meet the demand of the microwave application.

Especially $(Zr,Sn)TiO_4$ (ZST) ceramics have been investigated due to their high loss quality (Q_f) among many types of microwave dielectrics. The microwave dielectric properties of ZST ceramics largely depended on the crystal structures as well as the raw materials and the additives.[1,2] The crystal structure of ZST is known to be a high-temperature phase of pure $ZrTiO_4$, which is a orthorhombic and isomorphous phases with α-PbO_2 (space group P*bcn*, number 60), and the coordination octahedral of the Zn^{+4} are highly distorted due to the random distribution of Zr^{+4} and Ti^{+4} ions.[3,4] A random distribution of the cations in available octahedral cation sites could be controlled by the proceeding variables such as sintering temperature, cooling rate and so on. Therefore, the relationship between the dielectric properties and the crystal structure should be addressed to predict and control the microwave dielectric properties of ZST ceramics. Also, it is well known that Q_f of the microwave dielectrics depend not only the intrinsic properties related with the lattice vibrational modes, but also the extrinsic such as impurities, pores and grian boundary.[2]

The intrinsic properties of low loss materials were successfully estimated for the some kinds of microwave characteristics by the far–infrared reflectivity spectra.[5–7] Far–infrared spectra could be analyzed by the Kramers–Kronig relation[8] and the classical dispersion theory. Dielectric losses at microwave frequencies could be estimated by the dispersion parameters obtained by the classical dispersion theory.

In this study, the effect of the cooling rate on the lattice parameters and microstructure, and the microwave dielectric properties of the ZST with 1.0 mol% Sb_2O_5 or WO_3 were investigated The far–infrared reflectivity spectra of ZST ceramics also have been investigated to elucidate the factors affecting the change in the intrinsic loss of ZST ceramics.

2. Experimental procedure

The starting materials of high purity (>99.0%) ZrO_2, SnO_2, TiO_2, Sb_2O_5, and WO_3 powders were weighed

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* Corresponding author. Tel.: +82-2-2123-2847; fax: +82-2-392-1680.

E-mail address: khyoon@yonsei.ac.kr (K.H. Yoon).

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and mixed according to the composition of $(Zr_{0.8}Sn_{0.2})TiO_4$ with 1.0 mol% Sb_2O_5 or WO_3, respectively. The mixtures were milled with zirconia balls for 48 h in ethyl alcohol and calcined at 1150 °C for 5 h in air. And then 0.35 wt.% of (B_2O_3 Li_2O) as a sintering agent was added to the calcined powders and sieved using an 80-mesh screen. The sieved powders were uniaxially pressed into a 12 mm diameter disk at 700 kg/cm^2 and cold isostatically pressed at 1500 kg/cm^2. These pellets were sintered at 1300 °C for 5 h in air, and then cooled with various rates such as air quenching, 6 °C/min, and 1 °C/min.

X-ray powder diffraction analysis was done to observe the crystalline phases and the lattice parameters were calculated by the least square method.[9] The polished surface was observed and analyzed by a scanning electron microscope (JSM820, Jeol, Tokyo, Japan) and energy dispersive X-ray spectrometer (AN-10000, Link, High Wycombe, England). Microwave dielectric properties were measured using the post resonant method[10,11] at 7 GHz.

The infrared reflectivity spectra were obtained using a Fourier transform infrared spectrometer (model DA-8.12, Bomen Inc., Canada) from 50 to 4000 cm^{-1}. The spectra were recorded with the resolution of 4 cm^{-1}. The incident angle of radiation was 7°. The reflectivity spectra were evaluated by the Kramers–Kronig analysis and classical oscillator model.

3. Results and discussion

From the X-ray diffraction patterns of the specimens sintered at 1300 °C for 5 h, a single phase of the ZST was detected in all specimens regardless of the cooling rates and the kind of additive, Sb_2O_5 or WO_3.

Fig. 1 shows the lattice parameters of the ZST specimens sintered at 1300 °C for 5 h with various cooling rates. Lattice parameters of *a*-axis and *b*-axis were not changed significantly, but that of *c*-axis was decreased with the decrease of the cooling rate and reached a minimum value at the rate of 1 °C/min. ZST has similar structure with $ZrTiO_4$, and it had been reported that its *c*-axis length was decreased with the phase transformation from a high-temperature structure to a low-temperature structure.[12] Therefore, it could be explained that the high-temperature structure was maintained[13] at the specimen quenched in air so that its *c*-axis length was longer than that of the specimens cooled at the rate of 1 °C/min. This is consistent with the results by Hirano et al.[14] that the transformation from a high-temperature structure with a random distribution of cations to a low-temperature structure was accompanied by a continuous decrease of the *c*-axis length, probably because of partial ordering of the cations. The lattice parameters of the ZST specimens doped with 1.0 mol% Sb_2O_5 or WO_3 with various cooling rates showed similar tendencies.

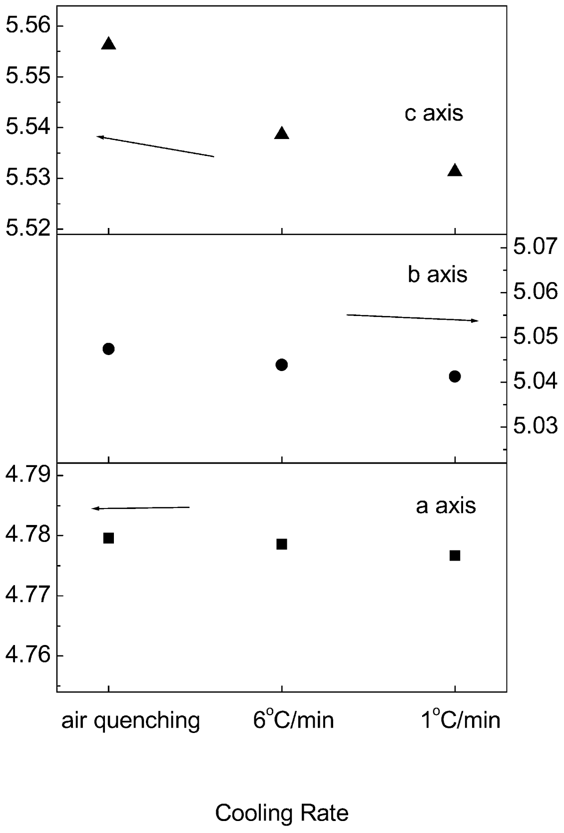

Fig. 1. Lattice parameters of $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens sintered at 1300 °C for 5 h with various cooling rates.

Microstructures of the ZST specimens with 1 mol% of Sb_2O_5 or WO_3 are shown in Fig. 2. The specimen quenched in air showed the smallest grain size, and the grain size increased with a decrease of the cooling rate. The grain size of doped specimens was larger than that of pure specimen, and it was also increased with the decrease of cooling rate.

Fig. 3 shows the relative density, dielectric constant, and $Q\times f$ values of the ZST specimens with 1 mol% of Sb_2O_5 or WO_3. The relative density showed a minimum value at the specimen quenched in air, and increased with the decrease of the cooling rate. This increase of the relative density was due to an increase of the grain size as in Fig. 2. However, the dielectric constant decreased with the decrease of the cooling rate. According to Hirano et al.[14] and Wang et al.,[15] the dielectric constant could be affected by the relative density and the lattice parameters. The increase of the *c*-axis length by quenching in air caused an increase of dielectric constant due to the enhancement of ionic polarization. Therefore, the dielectric constant seemed to be more depended on the lattice parameters rather than the relative density in this study.

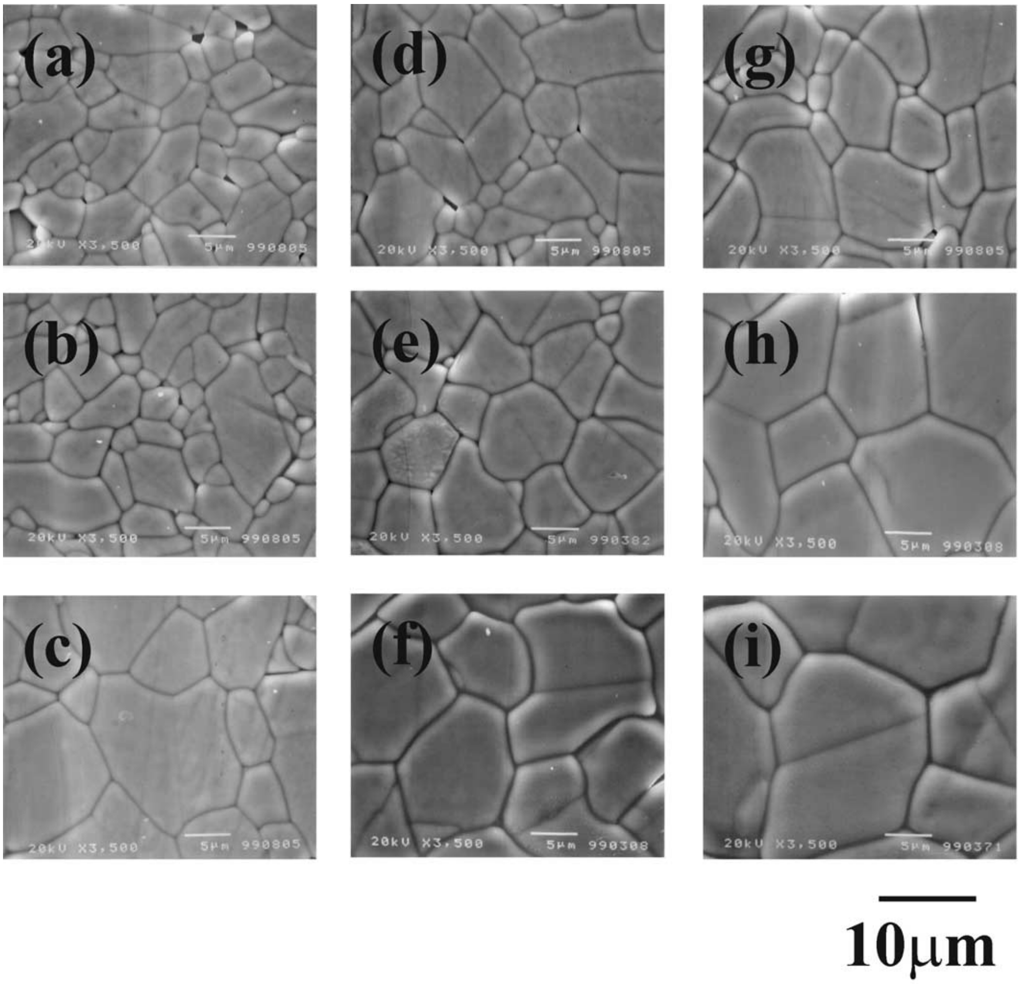

Fig. 2. Scanning electron micrograph of $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens sintered at 1300 °C for 5 h with various cooling rate; (a) air quenching, (b) 6 °C/min, (c) 1 °C/min; with 1.0 mol% Sb_2O_5, (d) air quenching, (e) 6 °C/min, (f) 1 °C/min; with 1.0 mol% WO_3 (g) air quenching, (h) 6 °C/min, (i) 1 °C/min.

The $Q\times f$ value was minimum in the specimen quenched in air, and increased with the decrease of the cooling rate. The increase of $Q\times f$ could be explained by ordering of the cations caused by the transformation from a high-temperature structure to a low-temperature structure with the decrease of the cooling rate.[12] That is also consistent with the results by Petzelt et al.[7] and Wang et al.[15] that the dielectric loss could be decreased by annealing and slow cooling. The $Q\times f$ values of the ZST specimens doped with 1.0 mol% Sb_2O_5 or WO_3 showed similar tendency but had higher values than those of pure specimen due to the decrease of the oxygen vacancy concentration as the following defect Eqs. (1) and (2).[8]

$$Sb_2O_5 + V_O^{\bullet\bullet} \xrightarrow{TiO_2} 2Sb_{Ti}^{\bullet} + 5O_O \qquad (1)$$

$$WO_3 + V_O^{\bullet\bullet} \xrightarrow{TiO_2} W_{Ti}^{\bullet} + 3O_O \qquad (2)$$

As reported by Wakino,[6] the intrinsic dielectric loss of microwave dielectrics is a function of the lattice vibrational modes. The infrared reflectivity data were transformed to the complex dielectric function by the Kramers–Kronig analysis,[8] and then trial and adjustment processes were done to simulate the experimental reflectivity data with the classical dispersion theory.

Fig. 4 shows the measured (dotted line) and simulated (solid line) infrared reflectivity spectra of ZST specimens as a function of the cooling rate. The reflectivity spectra showed similar shapes as reported by Kudesia et al.[5] and Kim et al.,[16] and the specimens with 1.0 mol% Sb_2O_5 or WO_3 also showed similar patterns as the pure specimens. In the real and imaginary parts of the complex dielectric function of ZST specimens calculated by the Kramers–Kronig analysis, the strongest band was located around 200–300 cm^{-1} were obtained.

The dispersion parameters corresponding to the best simulated spectra of the ZST specimens doped with 1.0 mol% Sb_2O_5 or WO_3 determined by the Kramers–Kronig analysis and classical oscillator model were listed in Table 1. The first mode contributed to the dielectric

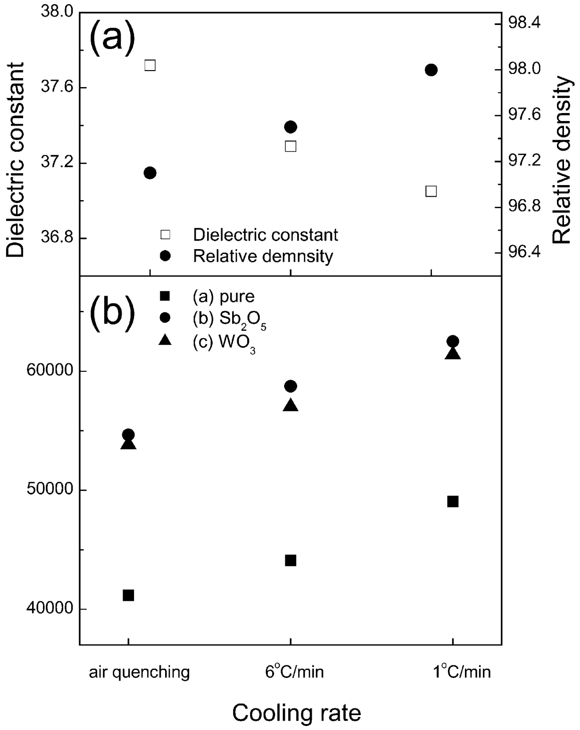

Fig. 3. (a) Dielectric constant and relative density of $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens sintered at 1300 °C for 5 h with various cooling rates, and (b) $Q{\times}f$ values of pure and doped $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens sintered at 1300 °C for 5 h with various cooling rate.

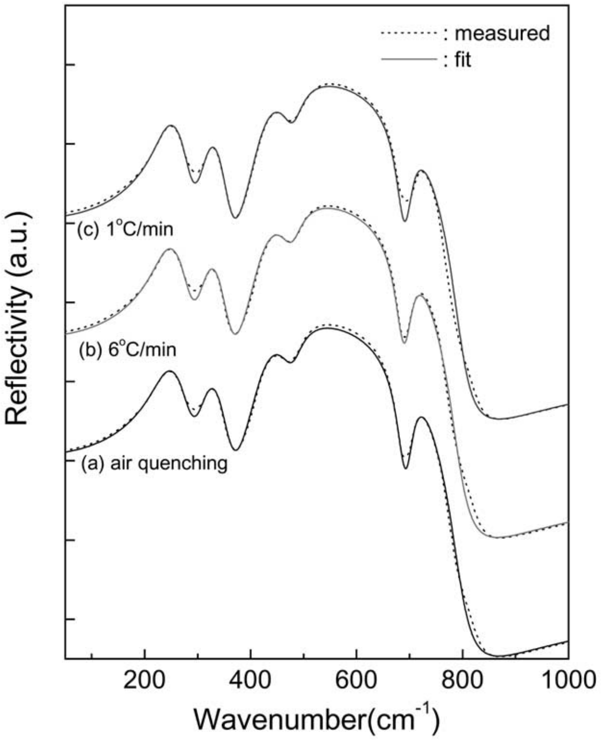

Fig. 4. Infrared reflectivity spectra of $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens sintered at 1300 °C for 5 h with various cooling rates; (a) air quenching, (b) 6 °C /min, and (c) 1 °C/min (—: measured, - - -: fit).

Table 1
Dispersion parameters of $(Zr_{0.8}Sn_{0.2})TiO_4$ specimens with various cooling rate obtained by the classical oscillator model

Air quenching				6 °C/min				1 °C/min			
ω_j (cm^{-1})	γ_j (cm^{-1})	$\Delta\varepsilon j'$	tan δj ($\times10^{-4}$)	ω_j (cm^{-1})	γ_j (cm^{-1})	$\Delta\varepsilon j'$	tan δj ($\times10^{-4}$)	ω_j (cm^{-1})	γ_j (cm^{-1})	$\Delta\varepsilon j'$	tan δj ($\times10^{-4}$)
Pure											
237	58	21.05	1.3580	237	54	20.70	1.2600	238	50	20.61	1.1158
316	48	4.57	0.1373	316	46	4.48	0.1308	317	43	4.39	0.1197
413	59	5.57	0.1204	413	58	5.55	0.1194	413	55	5.59	0.1148
484	50	0.65	0.0087	483	50	0.64	0.0087	485	48	0.63	0.0082
698	32	0.05	0.0002	695	33	0.049	0.0002	696	33	0.05	0.0002
	$\varepsilon_\infty = 5.47$				$\varepsilon_\infty = 5.46$				$\varepsilon_\infty = 5.41$		
Doped with 1.0 mol% Sb_2O_5											
239	43	21.41	0.9870	239	41	21.19	0.9400	237	38	21.02	0.8877
316	41	4.80	0.1207	315	37	4.70	0.1083	313	36	4.62	0.1061
411	54	5.72	0.1119	411	52	5.69	0.1083	411	52	5.63	0.1082
483	47	0.66	0.0082	483	45	0.67	0.0080	484	43	0.67	0.0076
692	30	0.047	0.0002	694	30	0.047	0.0002	696	30	0.045	0.0002
	$\varepsilon_\infty = 5.49$				$\varepsilon_\infty = 5.48$				$\varepsilon_\infty = 5.42$		
Doped with 1.0 mol% WO_3											
241	46	19.69	0.9397	241	43	19.27	0.8801	240	40	19.12	0.8247
322	44	5.12	0.1331	320	42	5.05	0.1279	318	40	5.01	0.1230
417	66	6.65	0.1544	418	65	6.56	0.1506	415	63	6.54	0.1487
492	63	1.45	0.0023	491	62	1.43	0.0023	493	62	1.43	0.0023
697	28	0.028	0.0001	701	28	0.028	0.0001	695	28	0.028	0.0001
	$\varepsilon_\infty = 5.52$				$\varepsilon_\infty = 5.51$				$\varepsilon_\infty = 5.46$		

constant and loss much higher than other modes. This is well agreed with the report by Zurmuhlen[17] that the microwave dielectric loss was mainly affected by the mode in the lowest frequency. The origin of damping constant (γ_j) can be explained by lattice anharmonic interaction and lattice imperfection such as impurities.[18] The damping constant (γ_j) showed a minimum value in the specimens cooled at 1 °C/min which was due to the decrease of the lattice anharmonic interaction resulting from the transformation to a low-temperature structure in which ordering of cations were occurred by slow cooling. The specimens quenched in air showed the highest damping constant due to the increased anharmonic interaction resulting from a high-temperature in which cations were randomly distributed. The $Q \times f$ values calculated from the dispersion parameters were higher than the measured ones by Hakki and Coleman's method because the calculated values represented intrinsic loss in which there was no effect of loss from the extrinsic factors such as pores or grain boundaries.

4. Conclusion

When ZST was treated with air quenching, cooling rate of 6 and 1 °C/min after sintering, the slower cooling resulted in the decrease of dielectric constant which was due to the decrease in ionic polarization resulting from the decrease of the *c*-axis length, and the increase of the $Q \times f$ value which was due to the ordering of cations resulting from the transformation of a high-temperature structure to a stable low-temperature structure. From the Far–infrared reflectivity spectra measurement, the specimens cooled at 1 °C/min. showed the lowest damping constant (γ_j) and consequently the highest $Q \times f$ value, which was due to the decrease of the lattice anharmonic interaction resulting from the transformation to a low-temperature structure in which the ordering of cations was occurred by slow cooling.

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