

## Microwave Dielectric Properties of Solid Solutions in the $ZrTiO_4$ - $Y_2O_3$ - $Nb_2O_5$ System

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With increasing contents of substituting ion pairs, the dependences of lattice constants to quench temperatures of the title system increased, while those of the  $ZrTiO_4$ - $In_2O_3$ - $Ta_2O_5$  system decreased. Similarities and differences of the two systems were made clear about changes in dielectric properties caused by substitutions including nonstoichiometric compositions

### 1. INTRODUCTION

The compound  $ZrTiO_4$  and its solid solutions exhibit abnormal behaviors. Ikawa et al reported those anomalies on the phase transformation, cell volume, thermal expansion, dielectricity, and crystal structure [1-6]. Further, they proposed a working hypothesis to explain those anomalies phenomenologically [1]. The hypothesis was verified effective [5] to design a composition which exhibited prescribed axial thermal expansions.

Meanwhile,  $Zr_{0.8}Sn_{0.2}TiO_4$  is a historical material as a ceramic dielectrics for microwave applications [7]. This study was planned as an extension of foregoing studies to find a composition having improved properties.

### 2. EXPERIMENTAL

The co-precipitated precursor mixing  $ZrO_2$  and  $TiO_2$  was prepared by adding ammonia water to a mixture of their respective sulfate solutions,

followed by firing at 900°C. The precursor was mixed with a pair of reagent oxides  $Y_2O_3$  and  $Nb_2O_5$  or a pair of  $In_2O_3$  and  $Ta_2O_5$  to make a compound with a nominal composition  $Zr_{1-x}Ti_{1-y}Y_zNb_wO_{4-v}$  or  $Zr_{1-x}Ti_{1-y}In_zTa_wO_{4-v}$  (here after abbreviated as ZTYN or ZTIT, and the same abbreviations are used as ZTS, ZHT, and ZT). The mixed powder was milled followed by a calcination at 1300°C or 1400°C for 5 h. The process was repeated before sieving and CIP shaping into a pellet under 100 MPa. Pellets were sintered, in most cases covered with powder of a same composition, at a temperature between 1500 and 1600 °C for 5 to 10 h and furnace cooled at a rate of 10°C/min (this is denoted as an original sample).

Original samples were heat treated under various conditions before measurements. Apparent and bulk densities were measured by an Archimedes method. Lattice constants were calculated from corrected data by Si internal standard.

Dielectric properties were measured for sintered pellets (1 to 5 pellets for each conditions)

about 7 mm in diameter. The thickness was 1.5 to 2 mm to measure at 1 kHz and was 3.5 to 4 mm to measure at a frequency from 7 to 10 GHz. A high precision capacitance bridge (Andeen Hagerling, 2500A) was used which operated at 1 kHz. The other experimental details were reported elsewhere [3,4] including the modified Hakki/Coleman method.

### 3.RESULTS AND DISCUSSION

Composition ranges were limited as listed in Table 1, especially for nonstoichiometric compositions, in which zirconium titanate solid solutions were the one only crystalline phase that appeared on XRD patterns. Moreover, for ZTYN with  $x+y$  0.2, super structure diffractions [1,2] ( $3x_0$  of the  $\alpha$ - $\text{PbO}_2$  structure) were seen in XRD of original specimens, and the compound with code 29 in Table 1 showed a sign of decomposition after it was cooled from 1200 to 1000°C at 1.2°C/h rate.

Cube root of unit cell volume ( $V^{1/3}$ ) of some compounds is shown in Fig. 1 as a function of quench temperature. A small crushed piece of a original sample was heated again for 5 h at a temperature higher than 1200°C before quenching into water, or an original piece was heated at 1200°C, 5 h and then cooled at 1.2°C/h rate to the quench temperature to hold at 1100°C for 5 h or at 1000°C for 24 h. The figure also shows data of cited compounds [1,5,8]. Increases in cell volumes of ZTS and ZTIT from that of ZT are notable. Further, those two show small change with quench temperatures. It is reminded that these compounds are less abnormal because the unit cell volume of a phase should not change by a quench temperature. These observations has been discussed [5] by considering the mean cation radius and the working hypothesis. That is, electron configurations of  $\text{Sn}^{4+}$  and  $\text{In}^{3+}$  ions are same to have the outermost shell of  $5d^{10}$ ; and the increasing content of these ions --decreasing

content of  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  ions-- works effectively to increase the cell volume, and further to decrease its dependence with quench temperatures. Small differences in cell volumes with quench temperatures of ZTS and ZTIT are reflected well for the limited differences in dielectric properties between HT1 and HT2 of related compounds in Table 1 and Fig. 2.

The  $V^{1/3}$  values of codes 29 and 10 change linearly with quench temperatures from 1100 to 1400°C. Those schema are different from that of ZT, and ZTS and ZTIT. Unit cell volumes of ZTYN's were plotted on the figure 4 of reference 5 --the figure of cell volume quenched from 1200°C vs mean radius of constituent cations-- to elucidate visually that cell volumes of ZTYN's were further smaller relatively than that of ZT which was contracted by itself. The electron configurations of  $\text{Y}^{3+}$  and  $\text{Nb}^{5+}$  ions are identical with that of  $\text{Zr}^{4+}$ ; this configuration, further to say, the excited 4d orbital of it was attributed to the clue of the mystery of ZT [1]. Accordingly, these results are consistent with the working hypothesis that cell volumes of ZTYN -- their values and dependence on a quench temperature-- become strange further with increasing content of  $\text{Y}^{3+}$  and  $\text{Nb}^{5+}$  ions.

Selected dielectric data on high dense ceramics are listed in Table 1 and illustrated in Fig. 2. Following observations are evident, although data are not available on nonstoichiometric compositions the mean valences of which are larger than 4.0. Relative permittivities,  $\epsilon_r$ , of HT1 specimens decrease almost linearly with  $x+y$ , although the dependences are different to each systems. On the other hand,  $\epsilon_r$ 's of HT2 specimens look like to take maximums at small values of  $x+y$ , which was noted for ZHT [3,4]. Dielectric properties of the two HT1 and HT2 samples of respective ZTS [8] and ZTIT show small differences with the increase of  $x+y$ . However, for the case of ZTYN significant differences are noted between HT1 and HT2

Table 1. Apparent density, dielectric data and standard deviation in parenthesis at 20°C, 1 kHz and at 25 °C, 7 to 10 kHz

Code	Composition			Parameter	Heat	$\epsilon_r$	Q/	TCCorTCF	d/%
	x	y	z	w	Treat		10 <sup>3</sup>	/10 <sup>-6</sup> K <sup>-1</sup>	
Zr <sub>1-x</sub> Ti <sub>1-y</sub> YzNb <sub>w</sub> O <sub>4-v</sub>									
1	0.000	0.000	0.000	0.000	HT1	46.0(1)	24(4)	-168(1)	97.8
2	0.000	0.000	0.000	0.000	HT2	43.2(4)	16(1)	-155(4)	97.0
3	0.050	0.050	0.050	0.050	HT1	44.9(1)	26(3)	-75(1)	97.0
4	0.050	0.050	0.050	0.050	HT1	44.3\$	2.8\$	32.4\$	97.0
5	0.050	0.050	0.050	0.050	HT2	43.6(9)	13(1)	-71(1)	96.7
6	0.050	0.050	0.050	0.050	HT2	42.5\$	2.9\$		96.7
7	0.075	0.075	0.075	0.075	HT1	43.5(3)	2(0)	-8(0)	97.4
8	0.075	0.075	0.075	0.075	HT1#	43.5(2)	18(2)	-61(3)	97.4
9	0.075	0.075	0.075	0.075	HT2	41.3(3)	16(2)	-55(4)	97.8
10	0.100	0.100	0.100	0.100	HT1	41.1(1)	0.5	-167(20)	97.4
11	0.100	0.100	0.100	0.100	HT1#	41.3(2)	25(4)	-57(3)	97.4
12	0.100	0.100	0.100	0.100	HT1#	42.0\$	2.4\$		97.4
13	0.100	0.100	0.100	0.100	HT2	39.3(4)	17(0)	-44(4)	96.7
14	0.100	0.100	0.100	0.100	HT2	39.4\$	2.7\$		96.7
15	0.150	0.150	0.150	0.150	HT1#	38.1	2.3(2)	62(7)	97.8
16	0.150	0.150	0.150	0.150	HT2	33.8(8)	9.0(1)	32(1)	98.0
17	0.075	0.075	0.0825	0.0675	HT1#	43.8(1)	5.8(1)	-41(1)	98.5
18	0.075	0.075	0.0825	0.0675	HT2	41.8(1)	6.4(1)	-41(1)	98.6
19	0.075	0.075	0.090	0.060	HT1	43.7(2)	3.2(3)	-30(2)	98.7
20	0.075	0.075	0.090	0.060	HT1#	43.2(3)	3.4(4)	-32(2)	98.7
21	0.075	0.075	0.090	0.060	HT2	41.6(2)	3.8(1)	-34(2)	98.6
Zr <sub>1-x</sub> Ti <sub>1-y</sub> YzNb <sub>w</sub> O <sub>4-v</sub>									
22	0.100	0.000	0.050	0.050	HT1#	44.4(1)	2.5(3)	-42(1)	97.8
23	0.100	0.000	0.050	0.050	HT1#	43.8\$	3.5(1)\$		97.8
24	0.100	0.000	0.050	0.050	HT1#	43.5\$	4.6\$	25\$	97.8
25	0.100	0.000	0.050	0.050	HT2	42.4(3)	6(2)	-50(0)	97.7
26	0.100	0.000	0.050	0.050	HT2	42.3\$	4.9\$	24\$	97.7
27	0.000	0.100	0.050	0.050	HT1#	43.6(1)	18(2)	-86(1)	98.0
28	0.000	0.100	0.050	0.050	HT2	40.0(8)	0.5(1)	-95(5)	97.1
29	0.000	0.200	0.100	0.100	HT1#	40.8(3)	11(2)	-79(2)	97.1
30	0.000	0.200	0.100	0.100	HT1#	42.7\$	2.6\$	42\$	97.1
31	0.000	0.200	0.100	0.100	HT2	38.3(4)	12(1)	-60(1)	97.0
Zr <sub>1-x</sub> Ti <sub>1-y</sub> YzNb <sub>w</sub> O <sub>4-v</sub>									
32	0.000	0.000	0.000	0.000	HT1	46.6(3)	21	-120(3)	98.4
33	0.000	0.000	0.000	0.000	HT2	39.9(2)	8	-98(1)	97.3
34	0.040	0.040	0.040	0.040	HT1	45.1(1)	11	-75(1)	97.4
35	0.040	0.040	0.040	0.040	HT1	44.6\$	1.8\$	39\$	97.4
36	0.040	0.040	0.040	0.040	HT2	42.9(4)	12	-82(3)	96.8
37	0.040	0.040	0.040	0.040	HT2	42.3\$	1.9\$	40\$	96.8
38	0.040	0.040	0.046	0.034	HT1	45.5(3)	5.5	-63(2)	96.8
39	0.040	0.040	0.046	0.034	HT1	44.3\$	1.1\$	33\$	96.8
40	0.040	0.040	0.046	0.034	HT2	43.3(3)	6.3	-71(3)	95.7
41	0.040	0.040	0.046	0.034	HT2	41.6\$	1.2\$	34\$	95.7
42	0.040	0.040	0.052	0.028	HT1	44.7(2)	4.2	-58(2)	98.1
43	0.040	0.040	0.052	0.028	HT2	42.7(3)	4	-58(6)	97.3
Zr <sub>1-x</sub> Ti <sub>1-y</sub> lnzTaw <sub>04-v</sub>									
44	0.050	0.050	0.0575	0.0425	HT1	43.7(2)	20	-54(1)	97.9
45	0.050	0.050	0.0575	0.0425	HT2	41.9(2)	21(4)	-73(1)	97.7
46	0.100	0.100	0.115	0.085	HT1	42.3	5.6	-9	97.8
47	0.100	0.100	0.115	0.085	HT2	40.9(0)	21(4)	-30(0)	97.7
48	0.050	0.050	0.065	0.035	HT1	43.8	9.1	-55	98.2
49	0.050	0.050	0.065	0.035	HT2	41.6(2)	11(2)	-72(0)	98.7

Comments and abbreviations: rows are gathered to each experiment operators, and the second crowds (22-31) were prepared from oxide reagents, HT1: heated at 1300°C, 5 h before quenching in air, HT2: heated at 1200°C, 2 h before cooling to 900°C at 0.5°C/min rate, #: oxidized in air at 700°C for 48 to 144 h, \$: data at GHz, TCC and TCF: temperature coefficient of capacity and resonance frequency at 20°C, 1 kHz and at 25°C, GHz.

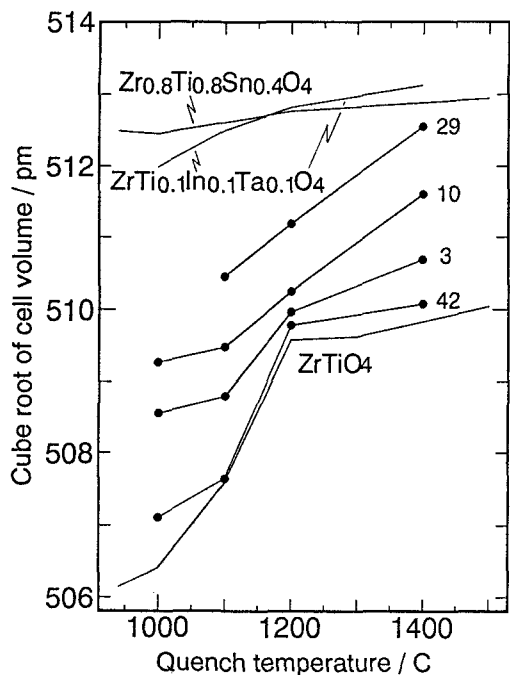


Figure 1. Cube root of cell volume at room temperature vs quench temperature. Code numbers are referred to compositions listed in Table 1.

specimens even for  $x+y=0.3$  (code 15, 16). Those differences in properties between the HT1 and HT2 samples are consistent with the differences in cell volumes mentioned above.

The values of  $\epsilon_r$  change in small ranges with  $z$  and  $w$  for fixed  $(x+y)$ 's, although limited data are available, however, with decreasing mean cation valences --decreasing oxygen content,  $4-v$  --  $Q$ 's decrease sharp and TCC's increase considerably. It may well reach a conclusive remark by referring to related data that it is impossible to improve 'considerably' the characteristic values of this established microwave dielectric material [7] even by searching the nonstoichiometric compositions.

#### REFERENCES

1. H. Ikawa, A. Iwai, H. Hiruta, H. Shimojima, K. Urabe and S. Udagawa, *J. Am. Ceram. Soc.*, 71 (1988) 120.
2. H. Ikawa, H. Shimojima, K. Urabe, T. Yamada

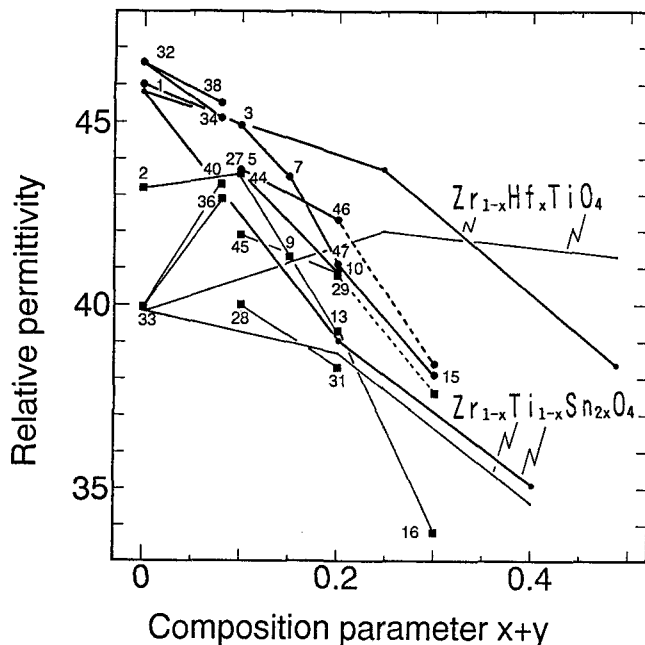


Figure 2. Relative permittivity vs composition. Code numbers,  $x$  and  $y$  are referred to Table 1. Thick and fine lines connect respective HT1 specimens (circle) and HT2 specimens (square) in the same system.

and S. Udagawa, *Science of Ceramics Vol. 14* (1988) 509.

3. H. Ikawa, H. Narita, O. Fukunaga and R. E. Newnham, *Ceramic Transactions Vol. 15* (1990) 143.
4. H. Ikawa, H. Narita and O. Fukunaga, *J. Ceram. Soc. Jpn.*, 98 (1990) 860.
5. H. Ikawa, H. Shimojima, K. Urabe and O. Fukunaga, *J. Am. Ceram. Soc.*, 74(1991)1899.
6. A. Yamamoto, T. Yamada, H. Ikawa, O. Fukunaga, K. Tanaka and F. Marumo, *Acta Cryst.*, C47 (1991) 1588.
7. K. Wakino, K. Minai and H. Tamura, *J. Am. Ceram. Soc.*, 67 (1984) 278.
8. H. Ikawa, H. Narita and O. Fukunaga, 94th ACerS Annual Meeting, 19-SIX-92.