Journal of the Korean Ceramic Society
Vol. 40, No. 4, pp. 346~349, 2003.

Influence of ZnO-Nb_2O_5 Substitution on Microwave Dielectric Properties of the $ZrTiO_4$ System

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(Received March 19, 2003; Accepted March 31, 2003)

ABSTRACT

Microwave dielectric characteristics and physical properties of the new $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($0.2 \le x \le 1.0$) system have been investigated as a function of the amount of $Zn_{1/3}Nb_{2/3}O_2$ substitution. With increasing $Zn_{1/3}Nb_{2/3}O_2$ content (x), two phase regions were observed: α-PbO_2 solid solution ($x<0.4$), mixture of the rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ and the α-PbO_2 solid solution ($x \ge 0.4$). In the α-PbO_2 solid solution region below $x<0.4$, the $Q \cdot f_0$ value sharply increased and the Temperature Coefficient of the Resonant Frequency(TCF) decreased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents while dielectric constant (K) showed nearly same value. In the mixture region above $x \ge 0.4$, the dielectric constant and TCF increased with increasing $Zn_{1/3}Nb_{2/3}O_2$ content. $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ materials have excellent microwave dielectric properties with K=44.0, $Q \cdot f_0$ = 41000 GHz and TCF = −3.0 ppm/°C at x=0.35.

Key words : ZnO-Nb_2O_5, Microwave dielectric, $ZrTiO_4$

1. Introduction

Microwave dielectric materials have been utilized for filters and for stabilizer of the frequency of oscillation in microwave integrated circuits. The dielectric resonators or duplexer are required small size, low insertion loss and temperature stability in the microwave frequencies. Therefore, the materials for use in the microwave components are required to have a high dielectric constant (K), high Q ($\cong 1/\tan\delta$) and small Temperature Coefficient of the Resonant Frequency (TCF).

Many types of microwave dielectric materials have been investigated to meet the requirements of the microwave applications.[1-3] $Zr_xSn_yTi_zO_4$ (x+y+z=2) systems are widely investigated because of their superior microwave dielectric properties, nearly zero TCF value, and high $Q \cdot f_0$ value.[4] $Zr_xSn_yTi_zO_4$ (x+y+z=2) materials are $ZrTiO_4$ based solid solutions with α-PbO_2 type structure.[5] It has been found that zirconium tin titanate powders do not readily sinter by solid state diffusion, therefore sintering agents, such as ZnO, have been added to achieve good densification at temperatures between 1300~1400°C.[6] There are numerous reports on the role of sintering agent, additives such as ZnO, Nb_2O_5, La_2O_3, Ta_2O_5, Sb_2O_5, in $Zr_xSn_yTi_zO_4$ ceramics.[6-8] Sintering agent or additives used for zirconium tin titanate ceramics are added as a single or a combination of two or more oxides from ZnO, Nb_2O_5, La_2O_3, Ta_2O_5, and Sb_2O_5.

The substitution of Zr^{+4} ions of $ZrTiO_4$ by other ions would affect the microwave dielectric properties and the densification of the specimens. The ionic sizes of the Zn^{+2} ion (0.74 Å, coordination number=6) and Nb^{+5} ion (0.64 Å, C.N.=6) were similar to that of Zr^{+4} ion (0.72 Å, C.N.=6).[9] Therefore, tetravalent Zr^{+4} ion could be substituted by one third of Zn^{+2} ion and two thirds of Nb^{+5} ions in the $ZrTiO_4$. In this study, the microwave dielectric properties of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($0.2 \le x \le 1.0$) system have been investigated with the substitution of ZrO_2 by $Zn_{1/3}Nb_{2/3}O_2$.

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2. Experimental Procedures

ZrO_2 (Millennium Co., Henderson, Australia), ZnO (Hayashi Pure Chemical Co., Tokyo, Japan), Nb_2O_5 (Aldrich Chemical Co., Milwaukee, WI) and TiO_2 (Fuji-Titan, Tokyo, Japan) with >99.5% purity were used as starting materials. The powders were weighed according to the composition $Zr_{1-x}(Zn_{1/3}Nb_{2/3})TiO_4$ ($0.2 \le x \le 1.0$) and milled with ZrO_2 balls for 24 h in deionized water and then dried. The dried powders were calcined at 1000°C for 2 h and milled for 1h with 2.0 mm diameter zirconia balls in polyethylene jars using a planetary mill. The milled powders were dried and granulated with PVA binder and pressed into a 14 mm diameter disk. These pellets were sintered at 1250°C for 3 h. The heating rate was 5°C/min and the cooling rate was 3°C/min down to 900°C. X-Ray Powder Diffraction(XRD) analysis was used to identify the phases of the samples. The reflectivity spectra were measured using a Fourier transform infrared spectrometer (Model DA-8.12, Bomen Inc., Canada) from 50 to 4000 cm^{-1}. Dielectric constant and $Q \cdot f_0$ value at microwave frequencies were measured by the post resonant method developed by Hakki and Coleman,[10] which consisted of parallel conducting plates and coaxial probes on

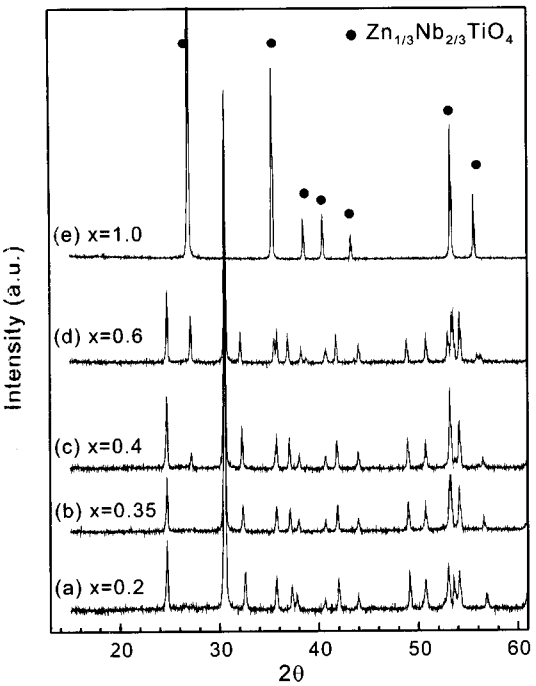

Fig. 1. X-ray diffraction patterns of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ powders sintered at 1250°C for 3 h; (a) x=0.2, (b) x=0.35, (c) x=0.4, (d) x=0.6, and (e) x=1.0.

the TE_{011} mode (where TE_{011} is transverse electric waves in y and z direction) at 5 GHz. And the TCF was measured using a cavity in the temperature range from 20°C to 85°C at 4 GHz.

3. Results and Discussion

Fig. 1 shows the X-ray powder diffraction patterns of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens sintered at 1250°C for 3 h with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. Orthorhombic α-PbO_2 type solid solutions[5] were obtained from x=0.2 to x=0.35 and there was no secondary phase. With further substitution of $Zn_{1/3}Nb_{2/3}O_2$ above x=0.4, rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ phase was detected. The solid solution range of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ system was similar to that of the $Zr_{1-x}Sn_xTiO_4$ systems.[5] And the amount of the secondary phase $Zn_{1/3}Nb_{2/3}TiO_4$ was increased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. At x=1.0 only $Zn_{1/3}Nb_{2/3}TiO_4$ phase was observed. From the XRD results as shown on Fig. 1, two regions were observed in the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ system with increasing amount of $Zn_{1/3}Nb_{2/3}O_2$: α-PbO_2 type solid solutions below x=0.4, mixture of the rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ and the α-PbO_2 type solid solutions, above x=0.4. The relative density of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens was over 96% in the whole composition range. For the specimen sintered at 1250°C for 3 h, the relative density of $ZrTiO_4$ was about 70% of theoretical density. Therefore, the sinterability of the specimens was enhanced by the substitution of $Zn_{1/3}Nb_{2/3}O_2$ to ZrO_2 in the $ZrTiO_4$.

In order to obtain the calculated dielectric constant and intrinsic loss, far infrared reflectivity spectrum was measured. Fig. 2 shows the measured and calculated reflectivity spectra of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ (x=0.35) solid solution system. The measured spectrum was very similar to the $ZrTiO_4$ specimen.[12] The calculated reflectivity spectrum was well fitted with the measured one. Table 1 shows the dispersion parameters of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimen (x=0.35) obtained from the best fit to the reflectivity data. ω_j, γ_j, and $\Delta\varepsilon_j$ is the resonant frequency, damping constant and modes contribution to the dielectric constant of the jth mode, respectively, and ε_∞ is the dielectric constant caused by the electronic polarization at higher frequencies.[2,3] The calculated dielectric constant and $Q\cdot f_0$ value were 43.8 and 41444 GHz from Table 1.

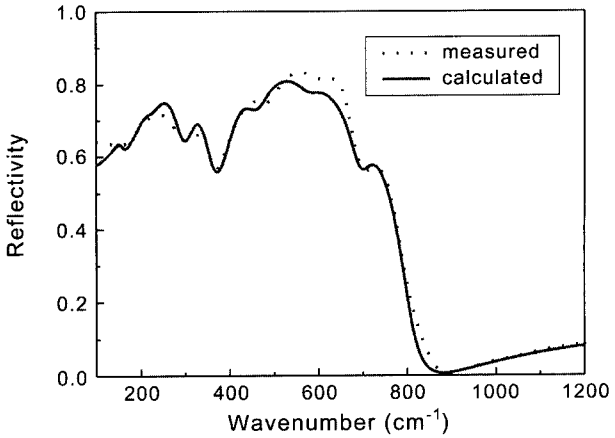

Fig. 2. Infrared reflectivity spectrum of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ (x=0.35) specimen.

Table 1. Dispersion Parameters of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ Specimen (x=0.35) Obtained from the Best Fit to the Reflectivity Data

	$Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ (x=0.35)				$ZrTiO_4$[12]		
j	ω_j (cm^{-1})	γ_j (cm^{-1})	$\Delta\varepsilon_j$	tan δ_j ($\times10^{-5}$)	ω_j (cm^{-1})	γ_j (cm^{-1})	$\Delta\varepsilon_j$
1	155	28	3.5	2.1778	145	043.5	5.0
2	210	42	11.0	5.5859			
3	245	53	15.1	7.0885	240	72	11.5
4	316	50	3.5	9.3361	318	47.7	2.6
5	406	65	4.4	9.2571	422	92.8	13.6
6	470	70	1.0	1.6936	500	30	1.6
7	580	65	0.06	5.7731			
8	699	60	0.05	3.3722	705	28.2	0.03
	ε_∞=5.2				ε_∞=8.0		

Fig. 3 shows the dielectric constant of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. In the solid solution region, dielectric constant slightly increased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. In the microwave frequency region, dielectric constant is sum of ionic and electronic polarization.[10] Therefore, the change of the dielectric constant in the solid solution region might be due to the change of the sum of the ionic and electronic polarization. In the mixed phase region above x=0.4, dielectric constant

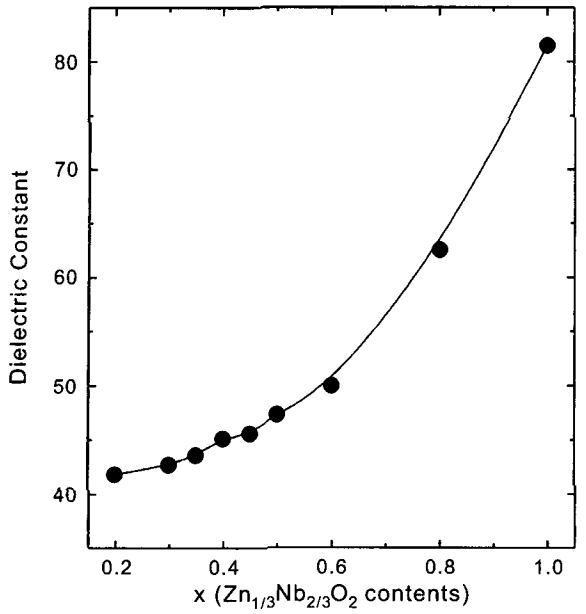

Fig. 3. Dielectric constant of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens with variation of x sintered at 1250°C for 3 h.

sharply increased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. The dependence of the dielectric constant on the relative amount of the phases present in the sintered specimens can be explained by the logarithmic mixing rule,[11]

$$\ln k = \sum v_i \ln k_i' \quad (1)$$

where, k_i' is the dielectric constant of the i phase and v_i is the volume fraction of the i phase. The increase in the dielectric constant is due to the increase of $Zn_{1/3}Nb_{2/3}TiO_4$ phase with higher dielectric constant (K=83) than that of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ solid solutions.

Fig. 4 shows the $Q{\cdot}f_0$ values of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. The $Q{\cdot}f_0$ value increased with increasing up to x=0.35, reaching as high as 41,000 GHz. The $Q{\cdot}f_0$ values of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens in the solid solution range were much higher values than that of the $ZrTiO_4$ specimen ($Q{\cdot}f_0$= 21,000~30,000 GHz).[12] The $Q{\cdot}f_0$ value depends on the extrinsic factors such as microstructure, secondary phases and sintering density and intrinsic ones representing the minimum loss related with lattice anharmonicity that can be expected for a particular materials composition and crystal structure.[7,13] The effects of density and secondary phase on the $Q{\cdot}f_0$ value of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens could be neglected because the relative density was higher than 96%[7] and there was no secondary phase in the solid solution range as shown in Fig. 1. Therefore, the increase of the $Q{\cdot}f_0$ value of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens was related to the decrease of the anharmonicity of the ions in the solid solution limit as confirmed by Table 1. In the mixed phase region, further substitution of $Zn_{1/3}Nb_{2/3}O_2$ over x=0.4 caused the decrease of the $Q{\cdot}f_0$ value due to the formation of a secondary phase. $Zn_{1/3}Nb_{2/3}TiO_4$ secondary phase has a lower $Q{\cdot}f_0$ value ($Q{\cdot}f_0$=7500 GHz) value than that of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ solid solutions.

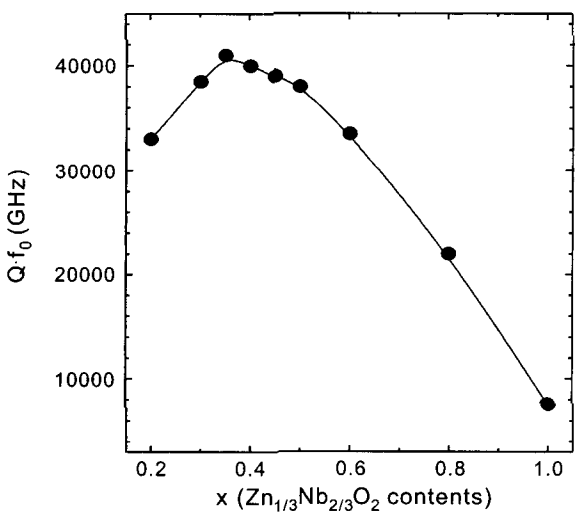

Fig. 4. $Q{\cdot}f_0$ of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens with variation of x sintered at 1250°C for 3 h.

Fig. 5 shows the Temperature Coefficient of the Resonant Frequency (TCF) as a function of the amount of $Zn_{1/3}Nb_{2/3}O_2$. It is reported that the Temperature Coefficient of the Resonant Frequency (TCF) value of $ZrTiO_4$ phase is about 59 ppm/°C.[12] In the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ systems, the substitution of ZrO_2 by $Zn_{1/3}Nb_{2/3}O_2$ led to decrease TCF value up to x=0.35. At x=0.3, nearly zero TCF value was obtained. In the mixed phase region, mixture of the α-PbO_2 type solid solutions and rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ phase, TCF value increased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. The dependence of the TCF in the mixed phase region with increasing

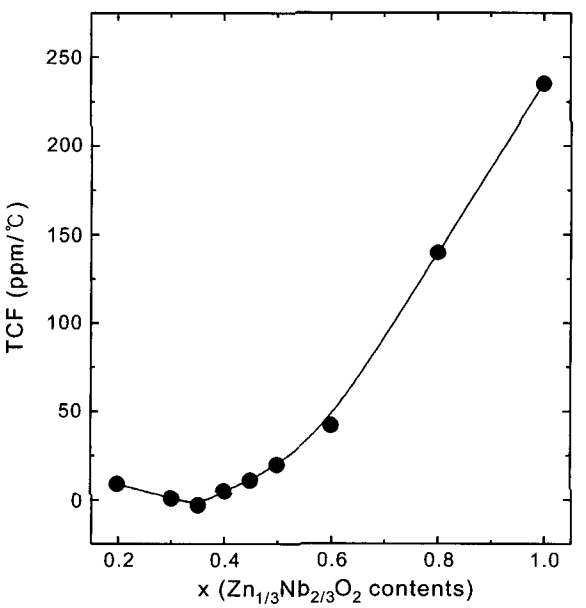

Fig. 5. TCF of $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ specimens with variation of x sintered at 1250°C for 3 h.

$Zn_{1/3}Nb_{2/3}O_2$ contents could be explained by the volume mixing rule[11] of the constituent phases. Excellent microwave dielectric properties was obtained at around x=0.35 in the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ system: K of 44, $Q{\cdot}f_0$ of 41,000 GHz, and TCF of −3.0 ppm/°C at x=0.35.

4. Conclusions

In the new $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ $(0.2 \le x \le 1.0)$ system, microwave dielectric properties could be controlled by the substitution of ZrO_2 by $Zn_{1/3}Nb_{2/3}O_2$. With increasing $Zn_{1/3}Nb_{2/3}O_2$ content (x), the α-PbO_2 solid solution were observed for the specimens below x=0.4, while the mixture of the rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ and the α-PbO_2 solid solutions were observed above x=0.4. In the α-PbO_2 solid solution region, the $Q{\cdot}f_0$ value sharply increased and the Temperature Coefficient of the Resonant Frequency (TCF) decreased with increasing $Zn_{1/3}Nb_{2/3}O_2$ contents. The specimens with x=0.35 showed excellent microwave dielectric properties: a dielectric constant of 44, $Q{\cdot}f_0$=41,000 GHz, and TCF=−3.0 ppm/°C. In the mixture phase region, the variation of the dielectric constant and TCF was explained by mixing rule of the present phases between $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ solid solution and $Zn_{1/3}Nb_{2/3}TiO_4$ phase.

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