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Sintering and Microwave Dielectric Characteristics of $ZnTa_{2-x}Nb_xO_6$ Ceramics

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Abstract. The effects of Nb_2O_5 content upon the microwave characteristics of $ZnTa_{2-x}Nb_xO_6$ ceramics are investigated. The appropriate sintering temperatures of $ZnTa_{2-x}Nb_xO_6$ ceramics slightly decrease with the increase of Nb_2O_5 content, and the densities and dielectric constants of $ZnTa_{2-x}Nb_xO_6$ ceramics linearly decrease with the increase of Nb_2O_5 content. As the Nb_2O_5 content increases, the Q×f value of $ZnTa_{2-x}Nb_xO_6$ ceramic first decreases, reaches a minimum value at x=1.0, then increases and reaches a maximum value at x=2.0. The τ_f values of $ZnTa_{2-x}Nb_xO_6$ ceramics are positive for $x \leq 0.3$, and change to negative ones as $x \geq 0.6$.

Introduction

Materials with a high dielectric constant (ε_r), a high quality value (Q×f), and a low temperature coefficient of resonant frequency (τ_f) are required for the miniaturization of microwave components in communications [1-3]. In general, a dielectric material with a high dielectric constant has a large τ_f value [4, 5]. To adjust τ_f value of microwave dielectric resonators to be close to zero, two or more compounds having negative and positive τ_f values are employed to form a solid solution or mixed phases. Chen et al. reported that small τ_f value could be achieved in CaO-Li_2O-Sm_2O_3-TiO_2 (CLST) system [5], in which the $Li_{1/2}Sm_{1/2}TiO_3$ (ε_r=52, Q×f=2280 GHz, and τ_f=−260 ppm/^oC) and $CaTiO_3$ (ε_r=170, Q×f=3600 GHz, and τ_f=800 ppm/^oC) were combined [6]. In the $BiNbO_4$ system, Choi et al. used Nd_2O_3 to substitute for Bi_2O_3 to form $(Bi_{1-x}Nd_x)NbO_4$ compositions [7], and Chen et al. used Sm_2O_3 to substitute for Bi_2O_3 to form $(Bi_{1-x}Sm_x)NbO_4$ compositions [8], and both possessed high Q values and low τ_f values. In the past, the microwave dielectric characteristics of ATa_2O_6 and ANb_2O_6 ceramics (A=Ca, Mg, Mn, Co, Ni, and Zn) were developed by Lee [9]. The ANb_2O_6 ceramics exist the lower sintering temperature and higher quality value (Q×f) than those of ATa_2O_6 ceramics, but the ATa_2O_6 ceramics reveal the τ_f value of much closer to 0 ppm/^oC than the ANb_2O_6 ceramics. However, there are no reports about the sintering and microwave dielectric characteristics of $ATa_{2-x}Nb_xO_6$ ceramics. For that, the sintering and microwave dielectric properties of $ZnTa_{2-x}Nb_xO_6$ ceramics were investigated in this study, and the relationships between the crystalline phases and the microwave properties were also discussed.

Experimental

Proportional amounts of reagent-grade starting materials of ZnO, Ta_2O_5, and Nb_2O_5 were mixed according to the composition $ZnTa_{2-x}Nb_xO_6$, (x=0, 0.3, 0.6, 1.0, 1.4, 1.7, and 2.0, respectively), and ball-milled for 5h with deionized water. After drying, the powder was ground and calcined at 1000°C for 2h. After mixing with polyvinyl alcohol (PVA) as binder, the mixed powder was pressed into pellets in a steel die. After debindering, sintering of these pellets was carried out at temperature between 1200^{o}C and 1350^{o}C under ambient conditions for 4h.

The crystal structures were analyzed by X-ray powder diffraction method using CuK_α radiation. The densities of the sintered specimens, as a function of Nb_2O_5 content, were measured by the liquid

displacement method using deionized water as the liquid (Archimedes's method). Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method [10], which was improved by Courtney [11]. An HP8720ET network analyzer was used for the measurements of microwave characteristics. The dielectric constant can be accurately determined by measuring the resonant frequency of the TE_{011} mode and verified by the $TE_{01\delta}$ resonant modes. The temperature dependence of resonant frequency $\Delta f_o/f_o$ and temperature coefficient of resonant frequency τ_f are defined as:

$$\Delta f_o / f_o = (f_T - f_o) / f_o \quad (1)$$

and

$$\tau_f = \Delta f_o / (f_o \times \Delta T) \quad (2)$$

where f_T and f_o are the resonant frequencies at T°C and 20°C, respectively.

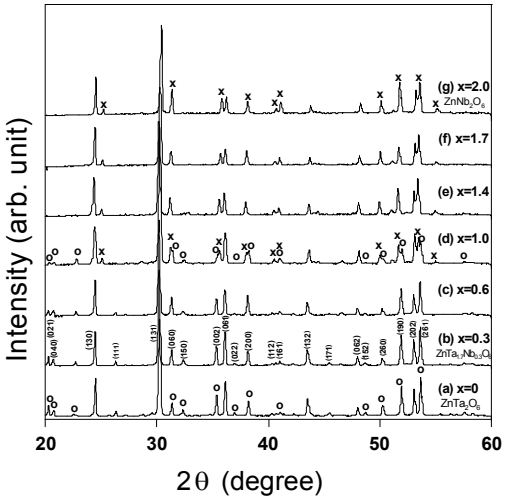

Fig. 1 The XRD patterns of $ZnTa_{2-x}Nb_xO_6$ ceramics under appropriate sintering temperature (a) x=0, S_T=1300°C, (b) x=0.3, S_T=1250°C, (c) x=0.6, S_T=1250°C, (d) x=1, S_T=1250°C, (e) x=1.4, S_T=1250°C, (f) x=1.7, S_T=1200°C, and (g) x=2.0, S_T=1200°C (**o**: $ZnTa_2O_6$-typed orthorhombic structure, **x**: $ZnNb_2O_6$-typed orthorhombic structure)

Results and Discussion

Fig. 1 shows the XRD patterns of $ZnTa_{2-x}Nb_xO_6$ ceramics sintered at appropriate temperatures (the uniform grain growth sintering temperatures) for 4h in air, respectively. The crystal structure of $ZnTa_2O_6$ ceramic has a space group Pnab(60), with a=5.0682 Å, b=17.0787 Å, and c=4.7003 Å, as reported by Shannon [14]. In this study, $ZnTa_2O_6$ (x=0) ceramics sintered at 1300°C reveal a single phase which belongs to orthorhombic structure with space group Pnab(60) and a=5.065 Å, b=17.078 Å, and c=4.694 Å. $ZnNb_2O_6$ (x=2) ceramics sintered at 1200°C also reveal a single phase which belongs to orthorhombic structure with space group Pnab(60) and a=5.720 Å, b=14.178 Å, and c=5.306 Å. Both the $ZnTa_2O_6$ and $ZnNb_2O_6$ ceramics have orthorhombic structures, but the crystalline peaks of these two ceramics have some differences, as shown in Figs. 1(a) and 1(g). As shown in Fig. 1, the 2θ shifts to higher values as the Nb_2O_5 content increases, which cause the variations of lattice constants and unit volume. However, the $ZnTa_2O_6$ and $ZnNb_2O_6$ ceramics exactly form a solid solution.

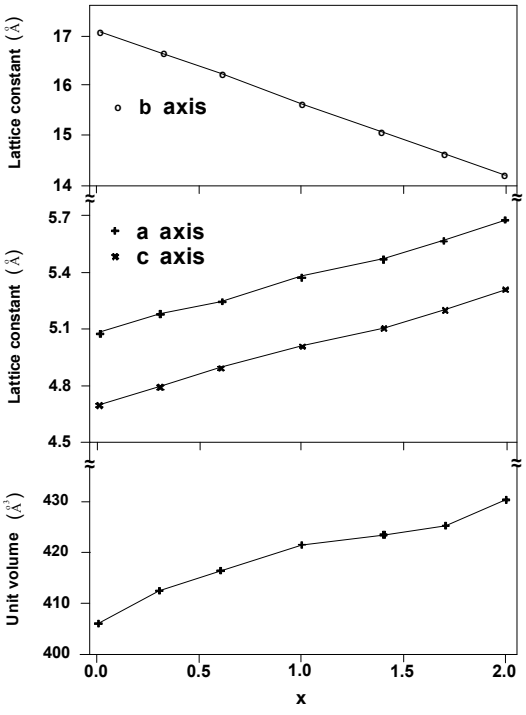

Fig. 2 The lattice constant and unit volume of $ZnTa_{2-x}Nb_xO_6$ ceramic as a function of Nb content.

Fig. 2 shows the lattice constants a, b, c and the unit volume (a×b×c) of $ZnTa_{2-x}Nb_xO_6$ system, respectively. As shown, the lattice constants a and c of $ZnTa_{2-x}Nb_xO_6$ ceramics linearly increase but b linearly decreases with the increase of Nb_2O_5 content. Whereas, the unit volume of $ZnTa_{2-x}Nb_xO_6$ ceramics increases with the increase of Nb_2O_5 content. For that the influence of Nb_2O_5 content on the densities of $ZnTa_{2-x}Nb_xO_6$ ceramics will be predicted.

The densities and dielectric constants of $ZnTa_{2-x}Nb_xO_6$ ceramics are shown in Fig. 3. The theoretical and measured densities of $ZnTa_2O_6$

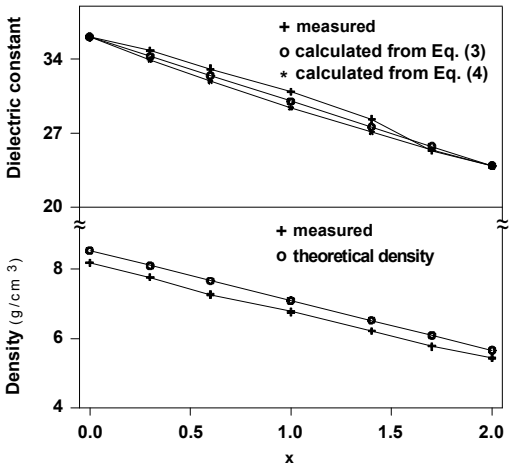

Fig. 3 The densities and dielectric constants of $ZnTa_{2-x}Nb_xO_6$ ceramics as a function of Nb content

ceramic sintered at 1300°C are 8.529 g/cm^3 [12] and 8.184 g/cm^3, while those of $ZnNb_2O_6$ ceramic sintered at 1200°C are 5.624 g/cm^3 [13] and 5.436 g/cm^3. The theoretical densities of $ZnTa_{2-x}Nb_xO_6$ ceramics (calculated by using 8.529 g/cm^3 for $ZnTa_2O_6$ and 5.624 g/cm^3 for $ZnNb_2O_6$) and the measured densities are shown in Fig. 4, in which the measured densities of $ZnTa_{2-x}Nb_xO_6$ ceramics exhibit values higher than 96.8 % theoretical densities. Figure 4 also shows that the theoretical densities and measured densities of $ZnTa_{2-x}Nb_xO_6$ ceramics decrease with the increase of Nb_2O_5 content. This phenomenon will be caused by two reasons, the first is the substitution of heavier Ta atoms by lighter Nb atoms, and the second is the increase of unit volume of $ZnTa_{2-x}Nb_xO_6$ ceramics with the increased Nb_2O_5 content.

According to the ionic polarizabilities reported by Shannon [14], the ionic polarizabilities of Ta^{5+}, Nb^{5+}, Zn^{2+}, and O^{2+} are 4.73, 3.97, 2.04, and 2.01DÅ^3, respectively. The molar polarizabilities of $ZnTa_{2-x}Nb_xO_6$ ceramics can be estimated by summing up those of the constitute ions, and the equation is:

$$\alpha(AB_2O_6) = \alpha(A^{2+}) + 2\alpha(B^{5+}) + 6\alpha(O^{2-}) \quad (3)$$

where A represents Zn, B represents Ta and Nb, $\alpha(AB_2O_6)$ represents the molecular polarizability, $\alpha(A^{2+})$, $\alpha(B^{5+})$, and $\alpha(O^{2-})$ represents the ionic polarizability of Zn^{2+}, Ta^{5+} (or Nb^{5+}), and O^{2-} ions, respectively. By estimating the molecular polarizability from Eq. (3), it is recognized that the molecular polarizabilities of $ZnTa_{2-x}Nb_xO_6$ ceramics will linearly decrease with the increase of Nb^{5+} ion content, which will account for the decrease in dielectric constant in $ZnTa_{2-x}Nb_xO_6$ ceramics, as shown in Fig. 3. Thus, it is clarified that the variation in composition has a reveal influence on the dielectric constant of $ZnTa_{2-x}Nb_xO_6$ ceramics.

If the $ZnTa_2O_6$ and $ZnNb_2O_6$ ceramics are considered to be heterogeneous phases in the $ZnTa_{2-x}Nb_xO_6$ ceramics, the microwave dielectric properties of $ZnTa_{2-x}Nb_xO_6$ ceramics can be predicted by the empirical model [15]:

$$V \ln(\varepsilon_r) = V_i \ln(\varepsilon_{ri}) \quad (4)$$

$$1/Q = V_i / Q_i \quad (5)$$

$$\tau_f = V_i \tau_{fi} \quad (6)$$

where V_i, ε_{ri}, τ_{fi} and Q_i (i = 1 and 2) are the volume fraction, the dielectric constant, the temperature coefficient of resonant frequency and the quality value of each-phase, respectively; while V, ε_r, τ_f, and Q are the volume, the dielectric constant, the temperature coefficient of resonant frequency and the quality value of the multi-phase component, respectively. To develop the microwave dielectric properties of $ZnTa_{2-x}Nb_xO_6$ ceramics, the parameters of 1300°C-sintered $ZnTa_2O_6$ ceramics (τ_f=9.24 ppm/°C, ε_r=36.1, Q×f=60180 GHz, and d=8.184 g/cm^3) and 1200°C-sintered $ZnNb_2O_6$ ceramics (τ_f=−58.2 ppm/°C, ε_r =23.9, Q×f=77270 GHz, and d=5.436 g/cm^3) are used as the reference data. By estimating the dielectric constant from Eq. (4), it is also recognized that the dielectric constant of $ZnTa_{2-x}Nb_xO_6$

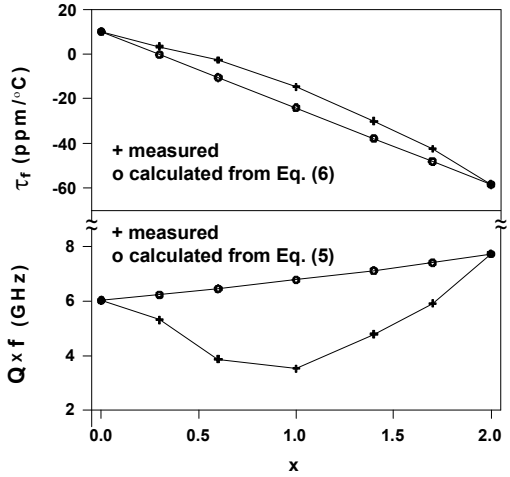

Fig. 4 The densities and dielectric constants of $ZnTa_{2-x}Nb_xO_6$ ceramics as a function of Nb content

ceramics decreases with the increase of Nb^{5+} ion content, as shown in Fig. 3. The measured dielectric constants exist some degree of difference as compared with both the estimated values from Eq. (3) and Eq. (4).

Figure 4 shows the estimated (by using Eq. (5) and Q×f=60180 GHz for $ZnTa_2O_6$ ceramic, and Q×f=77270 for $ZnNb_2O_6$ ceramic) and measured Q×f values of $ZnTa_{2-x}Nb_xO_6$ ceramics. The estimated Q×f values of $ZnTa_{2-x}Nb_xO_6$ ceramics exhibit a linear increase with the increase of Nb_2O_5 content, however, the measured ones exist a relatively different behavior. Comparing the morphologies of $ZnTa_{2-x}Nb_xO_6$ ceramics, the $ZnTa_{2-x}Nb_xO_6$ ceramics exist both bar-typed and disk-typed grains as $0.6 \le x \le 1.4$, and the results are shown in Table I. Thus, the measured values reveal a large difference with the estimated ones. As the Nb_2O_5 content of $ZnTa_{2-x}Nb_xO_6$ ceramics increases, the Q×f values first critically decreases, reaches a minimum value of 35200 GHz at x=1.0, then critically increases and reaches a maximum at x=0.2.

Figure 4 also shows the estimated (by using Eq. (6) and τ_f=+9.24 ppm/^oC for $ZnTa_2O_6$ ceramic, and τ_f=−58.2 ppm/^oC for $ZnNb_2O_6$ ceramic) and measured τ_f values of $ZnTa_{2-x}Nb_xO_6$ ceramics. Both the estimated and measured values linearly vary from positive values ($x \le 0.3$) to negative ones ($x \ge 0.7$) as the Nb_2O_5 content increases. However, the measured values are slightly larger than the estimated ones.

Conclusion

Even the crystalline phases of $ZnTa_{2-x}Nb_xO_6$ ceramics include the phases of $ZnTa_2O_6$ and $ZnNb_2O_6$ ceramics, the mixing rules can not be used to predict the Q×f value. However, except the Q×f values, the measured densities, dielectric constants and τ_f values of $ZnTa_{2-x}Nb_xO_6$ ceramics are much closed to the estimated values. When the Nb_2O_5 content increases, the dielectric constant and density decrease, and the τ_f value changes from +9.24ppm/^oC (x=0) to −58.2 ppm/^oC (x=2). In this study, the $ZnTa_{2-x}Nb_xO_6$ (x=0.3) ceramics sintered at 1250^oC exhibited the optimum microwave dielectric characteristics of ε_r=35.2, Q×f=53100 GHz, and τ_f=3.0 ppm/^oC.

References

[1] R. Christoffersen, P. K. Davies and X. Wei: J. Am. Ceram. Soc. Vol. 77 (1994), p. 1441.
[2] S. B. Desu and H. M. O'Bryan: J. Am. Ceram. Soc. Vol. 68 (1985), p. 546.
[3] T. Negas, G. Yeager, S. Bell and N. Coats: Am. Ceram. Soc. Bull. Vol. 72 (1993), p. 80.
[4] S. Kucheiko, J. W. Choi, H. J. Kim and H. J. Jung: J. Am. Ceram. Soc. Vol. 79 (1996), p. 2739.
[5] Y. C. Chen, P. S. Cheng, C. F. Yang and W. C. Tzou: J. Mater. Sci. Let. Vol. 20 (2001), p. 863.
[6] K. Ezaki, Y. Baba, H. Takhashi, *et al.*: Jpn. J. Appl. Phys. Vol. 32 (1993), p. 4319.
[7] W. Choi and K. Y. Kim: J. Mater. Res. Vol. 13 (1998), p. 2945.
[8] Y. C. Chen, W. C. Tzou, C. F. Yang and P. S. Cheng: Jpn. J. Appl. Phys. Vol. 40 (2001), p. 3252.
[9] H. J. Lee, I. T. Kim and K. S. Hong: Jpn. J. Appl. Phys. Let. Vol. 36 (1997), p. 1318.
[10] B. W. Hakki and P. D. Coleman: IEEE. Trans. MTT. Vol. 8 (1960), p. 402.
[11] W. E. Courtney: IEEE. Trans. MTT. Vol. 18 (1985), p. 476.
[12] JCPDS card No. 76-1826, 1997 JCPDS International Center for Diffraction Data Formerly by the Joint Committee on Power Diffraction Standards.
[13] JCPDS card No. 76-1827, 1997 JCPDS International Center for Diffraction Data Formerly by the Joint Committee on Power Diffraction Standards.
[14] R. D. Shannon: J. Appl. Phys. Vol. 73 (1993), p. 348.
[15] U. D. Kingery, H. K. Bowen and D. R. Uhlmann: Introduction to Ceramics (Wiley, New York, 1976), pp. 948.