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Effects of CaF_2 addition on the microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics

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Abstract

The effects of CaF_2 additions on the microstructure and the microwave dielectric properties of $ZnNb_2O_6$ ceramics were investigated systematically. The sintering temperature of $ZnNb_2O_6$ ceramics with 0.5 wt.% CaF_2 additions can be effectively reduced from 1150 °C to 1080 °C. The secondary phase $CaNb_2O_6$ was observed in sintered samples with 1–5 wt.% CaF_2 additions. There was evidence of reaction between CaF_2 and $ZnNb_2O_6$ during sintering. The dielectric properties at microwave frequencies (6–8 GHz) in this system were strongly dependent on the relative density, sintering temperature and CaF_2 content. For 0.1–5 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics, The dielectric constants (ε_r) of densified samples range in 28–31 which is higher than that of undoped $ZnNb_2O_6$ ceramics, However, the Q×f values decreased and ranged from 39000 GHz to 68000 GHz. The τ_f values were shifted toward zero direction with the increase of CaF_2 addition. $ZnNb_2O_6$ ceramics with 0.5 wt.% CaF_2 addition sintered at 1080 °C have the optimum microwave dielectric properties: $\varepsilon_r = 32$, $Q\times f = 68\,000$ GHz and $\tau_f = -55$ ppm/°C.

Keywords: A. Sintering; B. Microstructure-final; C. Dielectric properties; $Z_nNb_2O_6$

1. Introduction

Recently, multilayer microwave devices had been received much attention due to the rapidly progress on the satellite and mobile communications such as cellular phone, phasers and GPS [1]. In multilayer structures, the dielectrics with low sintering temperature were needed to cofire with low loss conductors and melting-point electrode such as silver and copper [2,3]. Most of well-know commercial microwave dielectric materials exhibit high quality factor (Q), high dielectric constant (ε_r) values and small temperature coefficient of resonant frequency (τ_f), such as $BaTi_4O_9/BaTi_9O_{20}$, $(Zr,Sn)TiO_4$, $BaO–R_2O_3–TiO_2$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ systems [4–7]. However, they are not compatible with silver or copper electrodes because of their high sintering temperature. $ZnNb_2O_6$ have the excellent dielectric properties($Q\times f = 87\,300$ GHz, $\varepsilon_r = 25$ and $\tau_f = -56$ ppm/°C), and are promising candidates for low temperature sintering dielectrics, because they can be sintered at 1150 °C without sintering aids [8–10]. The dielectric properties of $ZnNb_2O_6$ ceramics have been initially reported by Maeda et al. [8], and Lee et al. have investigated the microwave dielectric properties of MNb_2O_6 compounds (where M = Ca, Co, Mn, Ti and Zn) [9,10], more recently, Kim et al. investigated the influence of CuO on the sintering temperature and microwave dielectric properties of $ZnNb_2O_6$ ceramics. They report that 5 wt.% CuO can lower the sintering temperature of $ZnNb_2O_6$ ceramics from 1150 °C to 900 °C [11]. However, the effects of other dopants on the microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics has not been thoroughly studied.

In the present work, CaF were added to lower the sintering temperature of $ZnNb_2O_6$ ceramics. The influences of CaF additions on the densification, microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics were investigated.

2. Experimental procedure

High-purity oxide powders (>99.99%) of ZnO, Nb_2O_5 were used as starting materials. They were mixed according to the composition $ZnNb_2O_6$, and ball-milled

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in a polyethlene bottle with agate balls using ethanol as a medium. The mixtures were then dried and calcined at 1000 °C for 2 h. The calcined powders were re-milled for 6 h with CaF_2 additions. After drying and sieving, the powders were uniaxially pressed into pellets with the size of 10 mm in diameter and 4 mm in thickness under the pressure of 100 MPa. The samples were sintered at 1050–1130 °C with a heating rate of 5 °C/min, and then cooled to room temperature.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structure of sintered samples were analyzed by X-ray diffractometry with a graphite monochromator, and CuK_α radiation with step scanning. The microstructures analysis and element analysis were observed by a scanning electron microscopy (SEM) and a energy dispersive spectra (EDS) The microwave dielectric properties of sintered samples were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Kobayashi and Courteny et al. by HP8720ES network analyzer in the frequency range of 6–8 GHz [12–14].

3. Results and discussion

The bulk density curves of $ZnNb_2O_6$ ceramics with various amount of CaF_2 additions as a function of sintering temperature are shown in Fig. 1. It can be seen that the densities of sample increase steady with increasing sintering temperature, after reaching a maximum at 1080–1100 °C, then decreased slightly. The densification temperature of $ZnNb_2O_6$ ceramics is 1150 °C, as CaF_2 was added as sintering aids, the saturation densities of $ZnNb_2O_6$ ceramics were obtained at a lower temperature which decreased with the increase amount of CaF_2 additions. However, the bulk densities of $ZnNb_2O_6$ ceramics decreased when the amount of CaF_2 additions is above 0.5 wt.%. It indicated that large amount of CaF_2 additions is not needed.

Fig. 2 shows the XRD patterns of $ZnNb_2O_6$ ceramics sintered at 1080 °C as a function of amount of CaF_2 additions. At the level of 0.1–1.0 wt.% additions, $ZnNb_2O_6$ ceramics exhibited single phase with columbite structure. However, a secondary phase (marked as C in XRD patterns) was detected in the samples with 1.5–5 wt.% CaF_2 additions. The intensity of the second phase peak increase with increasing amount of CaF_2 additions. The secondary phase is identified as $CaNb_2O_6$ in this study. It indicated that CaF_2 might be reacted with $ZnNb_2O_6$.

The SEM micrographs of $ZnNb_2O_6$ ceramics doped with different amount of CaF_2 additions sintered at different temperature are shown in Fig. 3. With the addition of CaF_2, a much easier densification of $ZnNb_2O_6$ ceramics is evident. For 0.1–0.3 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics some pores were easily observed, even after sintering at 1100 °C, as shown in Fig. 3a. For 0.5–3 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics, the grain are uniform in size, and almost no pores is observed (Fig. 3b,c,d). Further increasing amount of CaF_2 addition, such as 5 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics, some pores appear again. For all samples sintered at 1100 °C, no changes in grain size and shape is observed. Moreover, the secondary phase at the grain boundary was not observed for all samples. To clear the location of CaF_2, EDS of 5 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics sintered at 1100 °C was demonstrated in Fig. 4, It shows that Ca^{2+} appeared at grain phase but not the intergranular phase. And Zn^{2+} is not observed at where Ca^{2+} exists. It suggested that the Ca^{2+} has substituted for Zn^{2+}, and formed the new phase $CaNb_2O_6$. These results agree with those of XRD analysis. $ZnNb_2O_6$ ceramics with different amount of CaF_2 additions exhibit the same results.

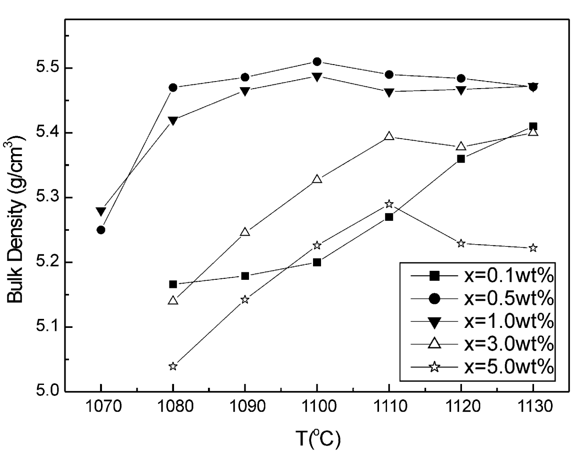

Fig. 1. The bulk densities of $ZnNb_2O_6$ ceramics with different amount of CaF_2 additions as a function of sintering temperature.

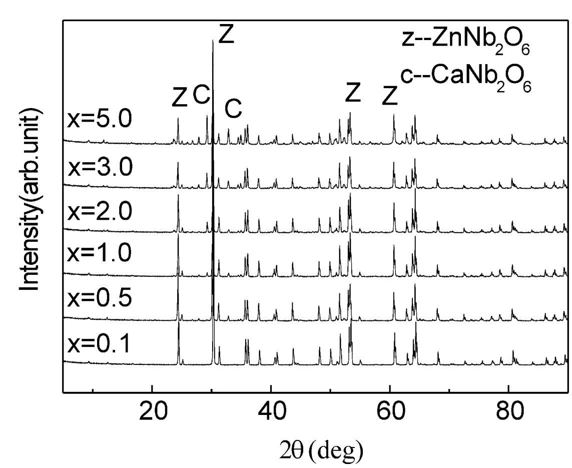

Fig. 2. The XRD patterns of the specimens doped with (x) wt.% CaF_2 additions sintered at 1080 °C for 2 h.

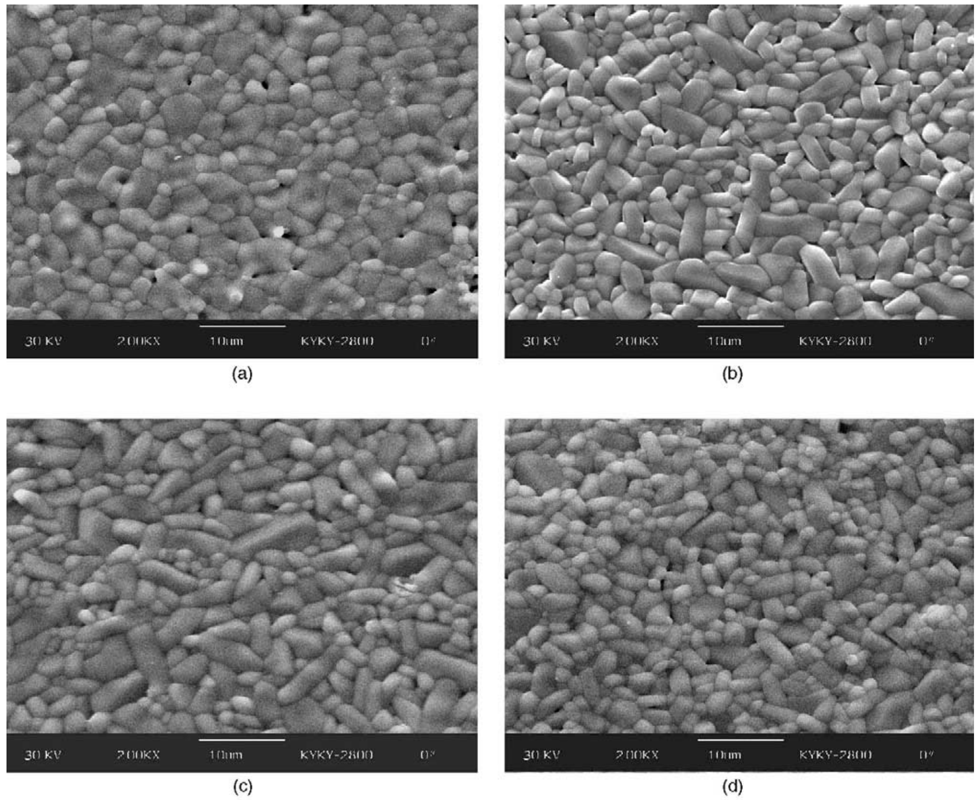

Fig. 3. SEM micrographs of CaF_2 doped $ZnNb_2O_6$ ceramics sintered at 1080 °C (a) 0.3 wt.% CaF_2, (b) 0.5 wt.% CaF_2, (c) 1.0 wt.% CaF_2, (d) 5.0 wt.% CaF_2.

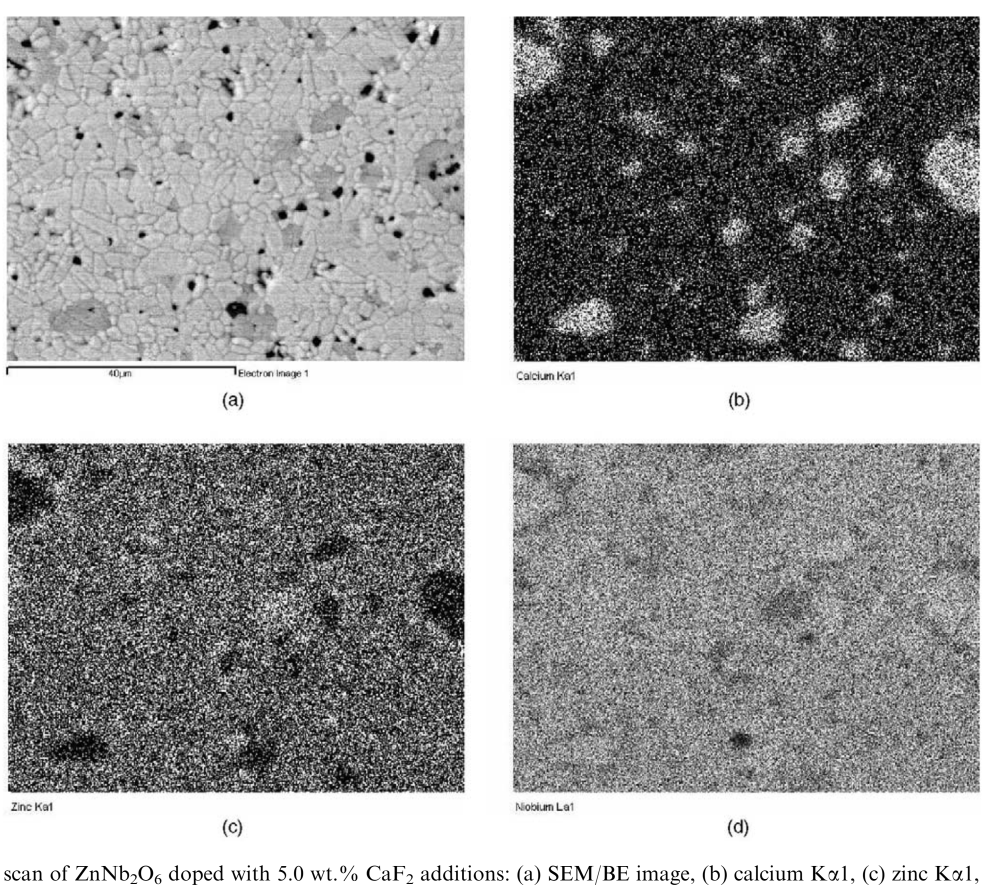

Fig. 4. EDS face scan of $ZnNb_2O_6$ doped with 5.0 wt.% CaF_2 additions: (a) SEM/BE image, (b) calcium Kα1, (c) zinc Kα1, (d) niobium Lα1.

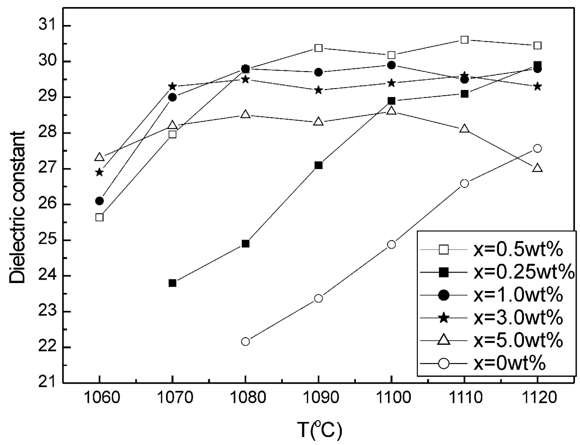

Fig. 5. ε_r Values of $ZnNb_2O_6$ ceramics doped with CaF_2 addition as a function of sintering temperature at 6–8 GHz.

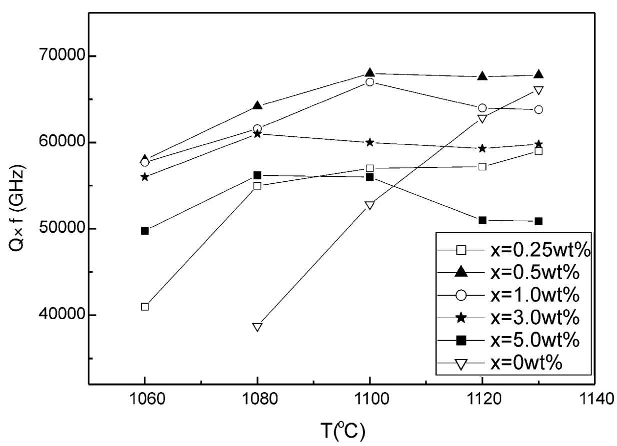

Fig. 6. $Q\times f$ values of $ZnNb_2O_6$ ceramics doped with CaF_2 addition as a function of sintering temperature at 6–8 GHz.

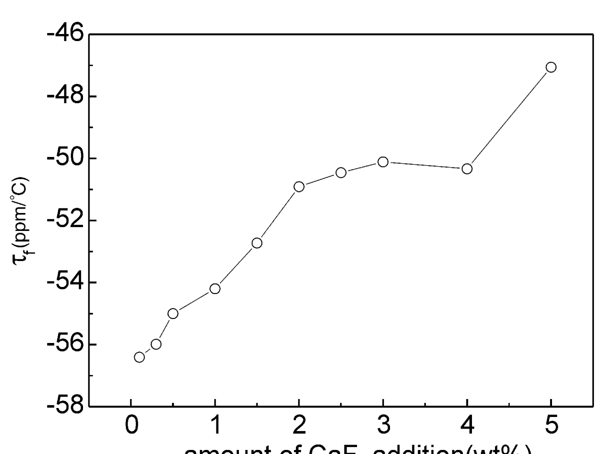

Fig. 7. τ_f Values of $ZnNb_2O_6$ ceramics doped with different amount CaF_2 addition sintered at 1100 °C.

The microwave dielectric properties of $ZnNb_2O_6$ ceramics doped with CaF_2 additions sintered at 1100 °C were demonstrated in Figs. 5–7. The relationships between ε_r values and sintering temperatures show the same trend with those between densities and sintering temperatures. As shown in Fig. 5. The ε_r values increased with increasing the sintering temperature, and then reached a saturation value, which shifts to lower temperature as the amount of CaF_2 additions increased. These results might be caused by the increasing of the sintered densities with the sintering temperature. However, the ε_r values of CaF_2-doped $ZnNb_2O_6$ ceramics are higher than those of undoped $ZnNb_2O_6$ ceramics. The reason may be the contribution of the second phase $CaNb_2O_6$.

Fig. 6 shows the $Q\times f$ values of CaF_2-doped $ZnNb_2O_6$ ceramics as a function of sintering temperature. The $Q\times f$ values of CaF_2-doped $ZnNb_2O_6$ ceramics are lower than those of undoped $ZnNb_2O_6$ ceramics and strongly dependent on the sintering temperature and amount of CaF_2 additions. As shown in Fig. 6, for all samples, the $Q\times f$ values increased with increasing sintering temperature, after reaching a maximum value, then decreased slightly. The maximum $Q\times f$ value is obtained at $x=0.5$ wt.%. These results are attributed to the presence of $CaNb_2O_6$ phase with low $Q\times f$ values.

Fig. 7 illustrates the τ_f values of samples with 0.1–5 wt.% CaF_2 additions. The τ_f values of $ZnNb_2O_6$ ceramics change from −56 ppm/°C at 0.1 wt.% CaF_2 addition to −47 ppm/°C at 5.0 wt.% CaF_2 addition. It implied that CaF_2 addition can adjust the τ_f values of $ZnNb_2O_6$ ceramics to small negative values The changes of τ_f values of $ZnNb_2O_6$ ceramics were attributed to the presence of $CaNb_2O_6$ grain phase which has a τ_f about +13 ppm/°C. In general, the $ZnNb_2O_6$ ceramics with small amount of additions, such as 0.5 wt.% CaF_2 additions have the good dielectric properties.

4. Conclusions

The sintering characteristics, microstructure and microwave dielectric properties of $ZnNb_2O_6$ ceramics with different CaF_2 additions were investigated systematically in this study. $ZnNb_2O_6$ ceramics with 0.5 wt.% CaF_2 additions can be well densified to approach 97% of theoretical density at 1080 °C. The formation of second phase $CaNb_2O_6$ was observed in $ZnNb_2O_6$ ceramics as CaF_2 content is above 1 wt.%. The presence of $CaNb_2O_6$ phase affected the dielectric properties of $ZnNb_2O_6$ ceramics. As CaF_2 addition increased, both ε_r values and $Q\times f$ values reveal a maximum at 0.5 wt.% CaF_2 content, and are 32 and 68 000 GHz respectively. However, τ_f values of $ZnNb_2O_6$ ceramics were shifted to small negative values with increasing amount of CaF_2 additions. 0.5 wt.%-CaF_2-doped $ZnNb_2O_6$ ceramics have the optimum dielectric properties: $\varepsilon_r = 32$, $Q \times f = 68\,000$ GHz and $\tau_f = -55$ppm/°C.

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References

[1] K. Wakino, T. Nishikawa, Y. Ishikawa, H. Tamura, Dielectric resonator materials and their applications for mobile communication systems, Br. Ceram. Trans. J. 89 (2) (1990) 39–43.
[2] H. Kagata, T. Inoue, J. Kato, I. Kameyama, Low-fired bismuth-based dielectric ceramics for microwave use, Jpn. J. Appl. Phys. 31 (Part1) (1992) 3152–3155.
[3] W. Choi, K.Y. Kim, Effects of Nd_2O_3 on the microwave dielectric properties of $BiNbO_4$ ceramics, J. Mater. Res. 13 (10) (1998) 2945–2949.
[4] H. Ohasato, S. Nishigaki, T. Okuda, Superlattice and dielectric properties of $BaO–R_2O_3–TiO_2$ (R = La, Nd and Sm) microwave dielectric compounds, Jpn. J. Appl. Phys. 31 (1992) 3136–3138.
[5] T. Negas, G. Yeager, S. Bell, N. Coats, I. Minis, $BaTi_4O_9$/$BaTi_9O_{20}$-based ceramics desurrected for mordern microwave applications, Am. Ceram. Soc. Bull. 72 (1) (1993) 80–89.
[6] S.I. Hirano, T. Hayashi, A. Hattori, Chemical processing and microwave characteristics of $(Zr,Sn)TiO_4$ microwave dielectrics, J. Am. Ceram. Soc. 74 (6) (1991) 1320–1324.
[7] K.H. Yoon, D.P. Kim, E.S. Kim, Effect of $BaWO_4$ on the microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics, J. Am. Ceram. Soc. 77 (4) (1994) 1062–1066.
[8] M. Maeda, T. Yamamura, T. Ikeda, Dielectric characteristics of several complex oxide ceramics at microwave frequencies, Jpn. Appl. Phys. Supp. 26 (Suppl. 2) (1987) 76–79.
[9] H.J. Lee, I.T. Kim, K.S. Hong, Dielectric properties of AB_2O_6 compounds at microwave frequencies (A = Ca, Mg, Mn, Co, Ni, Zn, and B = Nb, Ta), Jpn. J. Appl. Phys. 36 (Part 2) (1997) 1318–1320.
[10] H.J. Lee, K.S. Hong, S.J. Kim, Dielectric properties of MNb_2O_6 compounds (where M = Ca, Mn, Co, Ni, OR Zn), Mater. Res. Bull. 32 (7) (1997) 847–855.
[11] D.W. Kim, K.H. Ko, K.S. Hong, Influence of copper (II) oxide additions to zinc niobate microwave ceramics on sintering temperature and dielectric properties, J. Am. Ceram. Soc. 84 (6) (2001) 1286–1290.
[12] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE. Trans. Microwave Theory Tech. 8 (1960) 402–410.
[13] W.E. Courteny, Analysis and evaluation of a method of measuring the complex permitivity of microwave insulators, IEEE. Trans. Microwave Theory Tech. 18 (1985) 476–485.
[14] Y. Kobayashi, M. Katoh, Microwave measurement of dielectric properties of low-loss materials by the dielectric rod resonator method, IEEE. Trans. Microwave Theory Tech. 33 (1985) 586–592.