Ceramics-Silikáty 61 (4), 351-356 (2017)
www.ceramics-silikaty.cz doi: 10.13168/cs.2017.0034

MICROWAVE DIELECTRIC PROPERTIES AND CRYSTAL STRUCTURE OF CeO_2 DOPED $(Na_{1/2}Nd_{1/2})TiO_3$ CERAMICS

#BIN TANG, XIAOHUI LUO, ZIXUAN FANG, LAN ZHOU, SHUREN ZHANG

*State Key Laboratory of Electronic Thin Films and Integrated Devices,
University of electronic Science and Technology of China, Chengd, China*

#E-mail: tangbin@uestc.edu.cn

Submitted February 14, 2017; accepted June 15, 2017

Keywords: Microwave dielectric ceramics, CeO_2, $(Na_{1/2}Nd_{1/2})TiO_3$, Perovskite structure

The crystal structures and microwave dielectric properties of $(Na_{1/2}Nd_{1/2})TiO_3$ (NNT) ceramics with x wt. % CeO_2 dopants (x = 0; 0.15; 0.3; 0.45) were investigated in this paper. X-ray diffraction (XRD) results showed that all the samples fitted well with a single perovskite structure phase in a Pm-3m space group. The lattice parameters increased because of the replacement of Ce^{4+} at the B-site. The change of dielectric constant (ε_r) was similar to that of ionic polarizabilities. The temperature coefficient of resonant frequency (τ_f) value of samples displayed a decreasing tendency with increasing x. The quality factor ($Q \times f$) was found to have a maximum value of 8287 GHz at x = 0.3. As a result, when x = 0.3, the $(Na_{1/2}Nd_{1/2})TiO_3$ ceramics sintered at 1300°C for 2 h has good microwave dielectric properties of ε_r = 105.36, high $Q \times f$ = 8287 GHz, and τ_f = 246.3 ppm·°C^{-1}.

INTRODUCTION

Microwave dielectric materials play a key role in a wide variety of microwave applications, ranging from terrestrial and satellite communications to environmental monitoring via satellite. The microwave dielectric ceramics are frequently used for the production of passive microwave components like substrates for integrated circuits, mounting, dielectric filters, dielectric antennas and dielectric resonators [1, 2]. The important characteristics required for microwave dielectric ceramics used in microwave telecommunication systems are: (a) high ε_r for miniaturization; (b) high $Q \times f$ or low dielectric loss ($Q = 1/\tan \delta$) for better selectivity and (c) low τ_f for frequency stability [3]. It is tough to acquire microwave dielectric materials with high ε_r and high $Q \times f$ simultaneously because ε_r and $Q \times f$ has generally inverse correlation. Microwave dielectric ceramics with high dielectric constant are divided into two categories: $CaO–Li_2O–Ln_2O_3–TiO_2$ and $BaO–Ln_2O_3–TiO_2$ ($80 < \varepsilon_r < 100$) (Ln = lanthanide). It is difficult to meet the requirements of further miniaturization of microwave devices due to their relatively low dielectric constant [4-6]. For the Pb-based perovskite materials, they have a high quality factor and dielectric constant, but it is easy for PbO to volatilize from the ceramics, resulting in air pollution. Therefore, it is quite imperative to explore non-lead microwave dielectric ceramics with high dielectric constant to satisfy the demand of integrated wireless communication devices.

In addition to ceramic systems above, Takahashi et al. reported that microwave dielectric ceramics with $(A^{1+}_{1/2}\,A^{3+}_{1/2})TiO_3$ type have a high quality factor and a higher dielectric constant ($\varepsilon_r > 100$) [7]. The microwave dielectric properties of NNT ceramics has a combination of high dielectric constant ($\varepsilon_r = 108$) and moderate quality factor ($Q \times f = 8115$ GHz).

It is well known that CeO_2 is commonly used as an additive to improve the comprehensive properties of dielectric ceramics, such as $(PbCa)(FeNb)O_3$, $Bi_{0.5}(Na_{0.725}Li_{0.1}K_{0.175})_{0.5}TiO_3$, and $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$. For example, Zhou et al. [8] revealed that the $Q \times f$ values were increased from 3850 to 6770 GHz because of the improvement of relative density and elimination of oxygen vacancies in Ce modified $(PbCa)(FeNb)O_3$ ceramics. For the Ce added $Bi_{0.5}(Na_{0.725}Li_{0.1}K_{0.175})_{0.5}TiO_3$ ceramics. Liao et al. [9] reported that a small amount of CeO_2 enhanced the crystalline grain growth and decreased the dissipation factor of the ceramics. Furthermore, F. Azough et al. [10] found that the quality factor were significantly promoted to an extremely high value of 84000 GHz by adding 0.4 wt. % CeO_2 to $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ ceramics. However, ceria, as an effective aid for many ceramic systems, has not been researched in the NNT system. In this study, the microstructure and microwave dielectric properties of x wt. % (x = 0, 0.15, 0.3 and 0.45) CeO_2 doped NNT ceramics were systematically investigated.

EXPERIMENTAL

Sample of NNT microwave ceramics were synthesized by the conventional solid-state reaction technique. Na_2CO_3 (99.9 % purity), Nd_2O_3 (99.9 % purity), and TiO_2

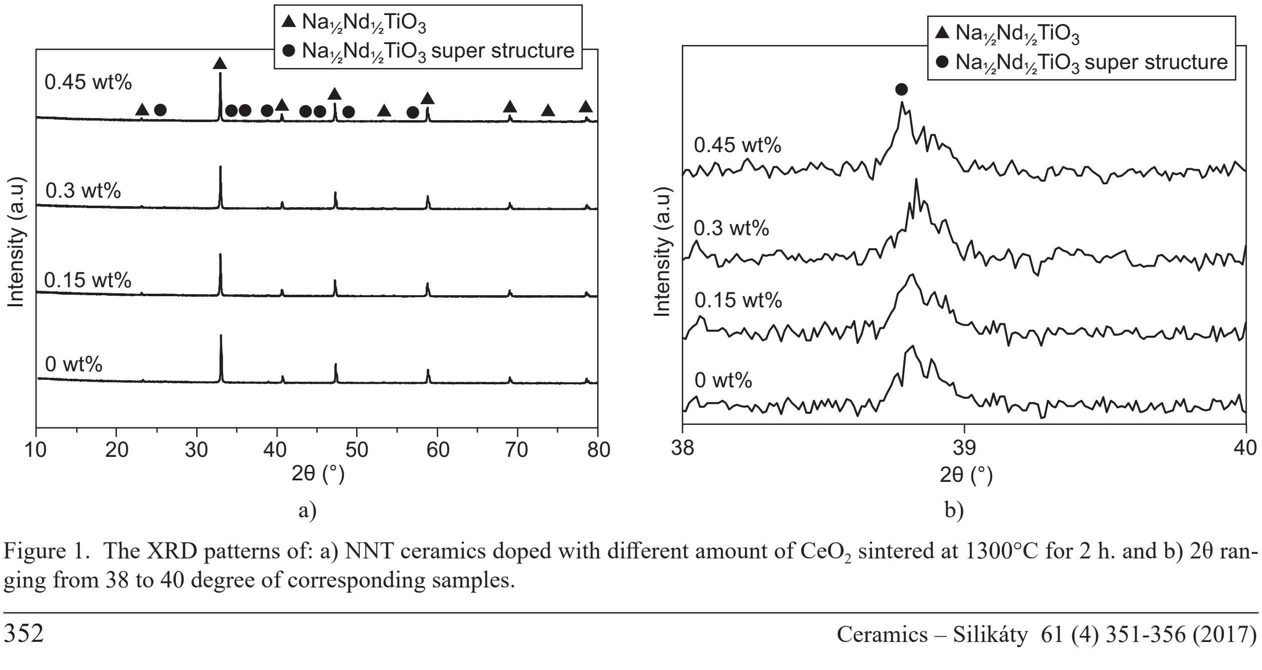
(99.9 % purity) were employed as starting raw materials. The starting materials were mixed in their stoichiometric ratio. The mixture of the starting materials was ball-milled in a nylon jar with zirconia balls and ethanol for 2 h. The mixed slurry was dried, passed through a 80-mesh sieve, and then calcined in air at 1000°C for 4 h. Thereafter x ($x = 0$; 0.15; 0.3 and 0.45) wt. % CeO_2 (99.9 % purity) powders were added into NNT powders. Then re-milled and dried as the first time. The fine powder with 7 wt. % of PVA as a binder was pressed into pellets with dimensions of 14.5 mm in diameter, 1 mm and 6 mm in thickness under the pressure of 200 kg·cm^{-2}. These samples were heated up to 600°C within 3 h and kept at 600°C for 4 h to remove binder. After heating up to 1300°C within 3.5 h, these specimens were sintered at 1300°C for 2 h, then cooled to natural temperature.

The bulk densities of the sintered pellets were measured by the Archimedes method in distilled water. X-ray diffraction method using Cu Kα radiation (XRD, Philips x'pert Pro MPD, Netherlands) were used to characterize the phase composition and the lattice parameters were determined from X-ray diffraction patterns with the least square method. Microstructures of the sintered surfaces were observed by scanning electron microscopy (SEM, FEI Inspect F, the United Kingdom). The dielectric characteristics at microwave frequencies were measured by the Hakki-Coleman dielectric resonator method in the TE011 mode using a network analyzer (Agilent Technologies E5071C, the United States) and a temperature chamber (DELTA 9023, Delta Design, the United States). The temperature coefficient of resonant frequency was determined from the difference between the resonant frequency obtained at 25°C and 85°C using the equation: $\tau_f = (f_{t_2} - f_{t_1})/[(f_{t_1} \times (t_2 - t_1)]$, where f_{t_1} and f_{t_2} are the resonant frequencies at $t_1 = 25$°C and $t_2 = 85$°C, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of NNT ceramics doped with different amount of CeO_2 sintered at 1300°C for 2 h. The powder X-ray diffraction profiles indicated that the main phase was NNT, which was confirmed as cubic perovskite structure in Pm-3m space group (JCPDS# 039-0880). And no Ce related secondary phases could be observed with the addition of CeO_2. This implied that CeO_2 had incorporated in the lattice of NNT ceramics. In this work, weak superlattice peaks were also observed, which was accordance to the reports of Takahashi's and Sun's studies [5, 7]. Furthermore, Glazer's [11, 12] investigation revealed that superlattice reflections also existed in $CaTiO_3$ with tiltings of oxygen octahedral. Figure 1b is a detailed XRD picture of 2 ranging from 38 to 40 degree, in which the superstructure peak could be seen clearly. It was evident that the diffraction peaks shifted towards the lower angles, indicating that there was a change in cell volume.

Figure 2 presents the lattice parameters of NNT ceramics doped with x wt. % ($x = 0$; 0.15; 0.3; 0.45) CeO_2 sintered at 1300°C for 2 h. With increasing Ce content, lattice parameters steadily increased from 3.8324 at $x = 0$ to 3.8441 at $x = 0.45$, and thus their corresponding unit cell volumes also expanded. This upward trend was mainly caused by the larger ionic radii of Ce^{4+} (0.114 nm) compared with that of Ti^{4+} (0.0605 nm) at B-site. The results confirmed that substitution of Ce for Ti happened at B-sites. Zhou et al. [8] and Fang et al. [13] reported that Ce first diffused into A-sites with a small amount of Ce dopants, later it incorporated into B-sites when an excessive amount of CeO_2 were added in (PbCa)(FeNb)O_3 and ($Na_{1/2}Sm_{1/2}$)TiO_3 ceramics, respectively. However, our results were different from the Zhou's and Fang's reports.



a)

b)

Figure 1. The XRD patterns of: a) NNT ceramics doped with different amount of CeO_2 sintered at 1300°C for 2 h. and b) 2θ ranging from 38 to 40 degree of corresponding samples.

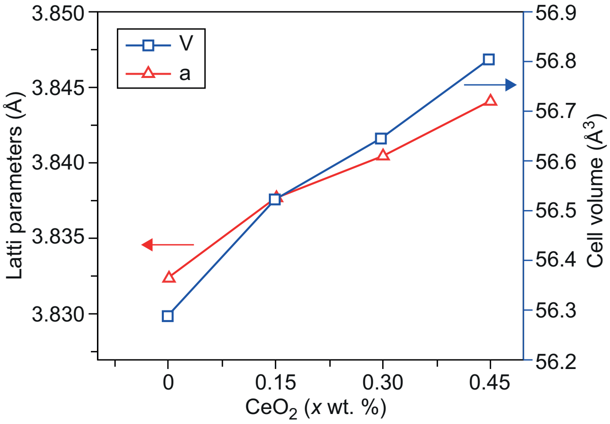
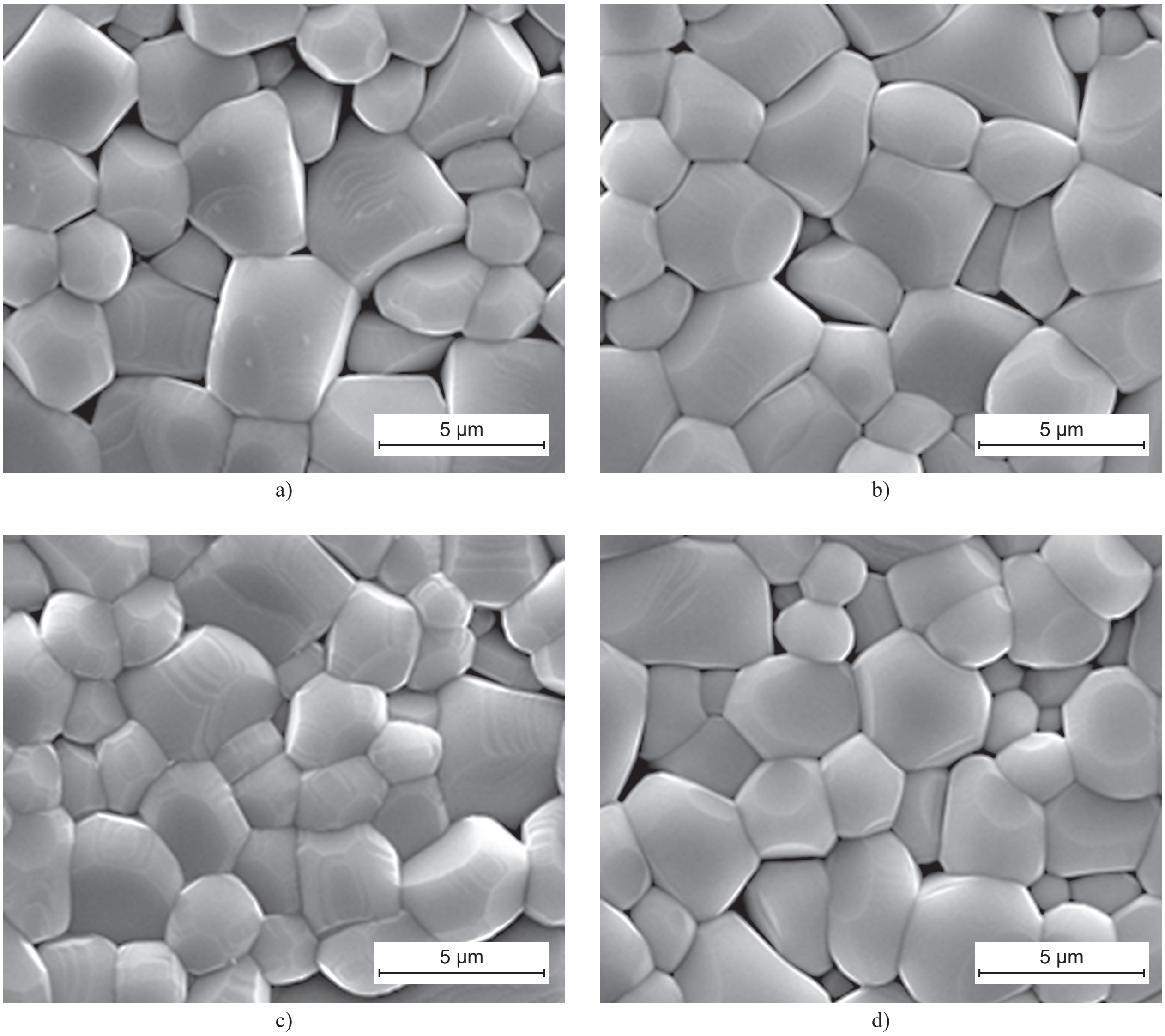


Figure 2. The lattice parameters and cell volumes of NNT ceramics doped with x wt. % CeO_2 sintered at 1300°C for 2 h.

Figure 3a-d displays the SEM photographs of NNT ceramics doped with different amount of CeO_2 sintered at 1300°C for 2 h: a) $x = 0$ wt. %, b) $x = 0.15$ wt. %, c) $x = 0.3$ wt. % and d) $x = 0.45$ wt. %. The results show that the addition of increasing amounts of CeO_2 content affected the microstructure. It was clear that the porous microstructure was observed with $x = 0$ wt. %. With the Ce content increasing from 0 wt. % to 0.3 wt. %, the grain growth was observed and the pores were gradually eliminated. The microstructure of the grain showed uniform and compact with $x = 0.3$ wt. %. The grain size increased because of the incorporation of Ce into the grains and Ce contents enhanced the mass transport rate as shown in Figure 3c. When superfluous Ce content ($x > 0.3$ wt. %) was added to NNT ceramics, it could be seen that a certain amount of pores appeared again. When $x > 0.3$ wt. %, the surface of the ceramics became more porous which will lead to a decline in the density of ceramics.



a) b) c) d)

Figure 3. The SEM photographs of NNT ceramics doped with different amount of CeO_2 sintered at 1300°C for 2 h: a) 0 wt. %; b) 0.15 wt. %; c) 0.3 wt. %; d) 0.45 wt. %.

Figure 4a depicts the apparent density and microwave dielectric properties of x wt. % (x = 0; 0.15; 0.3; 0.45) CeO_2 doped NNT ceramics sintered at 1300°C for 2 h. As demonstrated in Figure 4a, the apparent density showed a strongly dependent on CeO_2 content. The apparent density of NNT ceramics displayed an improved trend and increased from 5.12 g·cm^{-3} to 5.13 g·cm^{-3} with x from 0 wt. % to 0.3 wt. %, which primarily resulted from the elimination of pores. When the Ce concentration exceeded 0.3 wt. %, optional apparent density declined, and it was mainly due to the appearance of pores.

Figure 4b shows the permittivity of NNT ceramics with different amount of CeO_2 doped sintered at 1300°C for 2 h. The dependence of permittivity on the CeO_2 concentrations could be divided into two stages. The first stage was a continuous decrease of the permittivity from 108.68 to 105.36 with x from 0 wt. % to 0.3 wt. %, and the second stage was a slight increase of the permittivity to 105.83 at x = 0.45 wt. %. The permittivity is generally considered to be affected by relative densities, tilting of octahedron polarizabilities and secondary phases [14, 15]. Because of the single phase and high relative densities (higher than 96 %), the changing dielectric constant should be related to ionic polarizabilities. Shannon claims that the dielectric constant is directly proportional to the average ionic polarizability (α_D/V_m) according to the Clausius-Mosotti equation $\alpha_D = [V_m(\varepsilon_{rc} - 1)]/[b(\varepsilon_{rc} + 2)]$ [16], where ε_{rc} is the corrected dielectric constant, V_m is the molecular volume and b is 4π/3. And the corrected dielectric constant can be obtained by modifying experimental dielectric constant with porosity $(\varepsilon_r - \varepsilon_{rc})/3\varepsilon_{rc} = [P(\varepsilon_1 - \varepsilon_{rc})]/(2\varepsilon_{rc} - \varepsilon_1)$ [17], where ε_r experimentally measured dielectric constant, P is the fractional porosity and the relative permittivity of porosity ε_l is 1. It was clear that ε_r behaved similarly to variation of the average ionic polarizability (α_D/V_m) as shown in Table I. Thus, the varying dielectric constant should be mainly attributable to the change of average ionic polarizability.

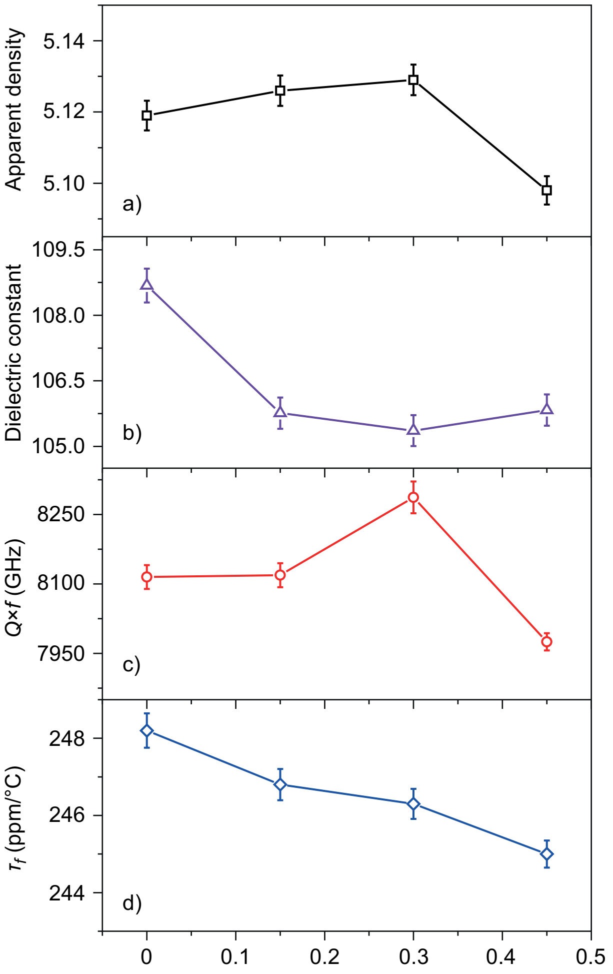


Figure 4. The apparent density and microwave dielectric properties of x wt. % CeO_2 doped NNT ceramics sintered at 1300°C for 2 h.

Figure 4c shows the $Q \times f$ values of NNT ceramics sintered at 1300°C for 2 h. The quality factor was found to increase initially and reach a saturation value of 8287 GHz at x = 0.3, and thereafter it decreased. In general, the quality factors are influenced by many factors, such as densification, pores, grain size and microstructure. The change in $Q \times f$ value and apparent density varied similarly. This is because both the $Q \times f$ value and apparent density are influenced by the same reason such as densification and pores [14, 18]. On the other hand, improvement of the quality factors may be related to the uniform microstructure and homogeneous grains, as shown in Figure 3. As a result, there is a significant increase of $Q \times f$ value due to the improvement of densification and uniform microstructure.

Figure 4d displays temperature coefficient of resonant frequency (τ_f) of NNT ceramics sintered at 1300°C as the function of different amounts of CeO_2. The τ_f is generally considered to be correlated with secondary phase[19] and B-site bond valence [20]. Apparently, the τ_f value did not change much and decreased slightly from 248.2 to 245 ppm/°C. Because of the small amount of addition of CeO_2 did not change the compositions and cause any noticeable secondary phase, the improvement of τ_f may be related to the changing B-site bond valence, especially for the ABO_3 type perovskites [21]. As previously reported, the increasing amounts of CeO_2 resulted in a decrease in τ_f in $(PbCa)(FeNb)O_3$ ceramics which was mainly attributable to the varying value of B-site bond valence . A similar effect that CeO_2 additions didn't intensively change the τ_f value was observed in $(Zr_{0.8},Sn_{0.2})TiO_4$ systems and $Na_{1/2}Sm_{1/2}TiO_3$ systems . As a result, it is reasonable that a slight decrease of τ_f was obtained when the NNT was doped with CeO_2 contents. In summary, the Ce^{4+} ions had incorporated into the lattice of NNT ceramics and take place of the Ti^{4+} at B-sites. When doped with 0.3 wt. % CeO_2, the NNT ceramics sintered at 1300°C for 2 h showed good comprehensive properties of $\varepsilon_{r=}$ 105.36, high $Q \times f$ = 8287 GHz, and relative low τ_f = 246.3 ppm/°C.

Table 1. Crystal parameters, relative densities (ρ) and average ionic polarizability (α_D/V_m) of *x* wt. % CeO_2 doped NNT microwave ceramics.

Sample	$x = 0.00$	$x = 0.15$	$x = 0.30$	$x = 0.45$
a (Å)	3.8324	3.8377	3.8405	3.8441
V_m (Å)	56.2876	56.5214	56.6452	56.8047
ρ (%)	96.64	97.09	97.28	96.89
ε_{rc}	114.092	110.32	109.59	110.70
α_D/V_m	0.2325632	0.2323560	0.2323143	0.2323775
$n(CeO_2) : n(NNT)$	0 : 1	0.157% : 1	0.314% : 1	0.472% : 1
M	179.498	179.645	179.784	179.931

CONCLUSION

The effects of *x* wt. % (x = 0; 0.15; 0.3; 0.45) CeO_2 addition on the density, microstructure, and the microwave dielectric properties of NNT ceramics were investigated. The powder XRD profiles indicated that the single phase was NNT, which was crystallized as cubic perovskite structure in Pm-3m space group. Weak superlattice peaks were observed in these samples. The SEM photographs of samples shows the compact and homogeneous microstructure with $x = 0.3$. With the increase of *x* value, the lattice parameters have shown a tendency of increasing. It was mainly a result of the larger ionic radii of Ce^{4+} compared with that of Ti^{4+}. The change of ε_r was similar to that of ionic polarizabilities. The τ_f value of samples displayed a decreasing tendency with increasing *x*. The $Q \times f$ was found to have a maximum value of 8287 GHz at $x = 0.3$. As a result, when $x = 0.3$ the NNT ceramics sintered at 1300°C for 2 h has good microwave dielectric properties of $\varepsilon_r = 105.36$, high $Q \times f = 8287$ GHz, and relative low $\tau_f = 246.3$ ppm/°C.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant No. 51402039).

REFERENCES

1. Fang Z., Tang B., Si F., Zhang S. (2017): Temperature stable and high-Q microwave dielectric ceramics in the $Li_2Mg_{3-x}Ca_xTiO_6$ system (x = 0.00 – 0.18). *Ceramics International*, *43*, 1682-1687. doi: 10.1016/j.ceramint.2016.08.055
2. Sebastian M.T., Ubic R., Jantunen H. (2015): Low-loss dielectric ceramic materials and their properties. *International Materials Reviews*, *60*, 392-412. doi:10.1179/1743280415Y.0000000007
3. Wang C., Zaki K.A. (2007): Dielectric resonators and filters. *IEEE Microwave Magazine*, *8*, 115-127. doi:10.1109/MMM.2007.903648
4. Tamura H., Konoike T., Sakabe Y., Wakino K. (1984): Improved High-Q Dielectric Resonator with Complex Perovskite Structure. *Journal of the American Ceramic Society*, *67*, c59-c61. doi:10.1111/j.1151-2916.1984.tb18828.x
5. Sun, Pai H., Nakamura T., Shan Y.-J., Inaguma Y., Itoh M. (1997): High temperature quantum paraelectricity in perovskite-type titanates $Ln_{1/2}$ $Na_{1/2}$ TiO_3 (Ln = La, Pr, Nd, Sm, Eu, Gd and Tb). *Ferroelectrics*, *200*, 93-107. doi:10.1080/00150199708008599
6. Kawashima S., Nishida M., Ueda I., Ouchi H. (1983): $Ba(Zn_{1/3}Ta_{2/3})O_3$ Ceramics with Low Dielectric Loss at Microwave Frequencies. *Journal of the American Ceramic Society*, *66*, 421-423. doi:10.1111/j.1151-2916.1983.tb10074.x
7. Hisakazu T., Yoko B., Kenichi E., Yasuhiko O., Kenichi S., Kazuhiko K., Shoichi N. (1991): Dielectric Characteristics of $(A_{1/2}^{1+} \cdot A_{1/2}^{3+})TiO_3$ Ceramics at Microwave Frequencies. *Japanese Journal of Applied Physics*, *30*, 2339.
8. Dong-xiang Z., Ming-zhe H., Sheng-lin J., Jing H. (2004): Microwave properties of CeO_2-modified (PbCa)(FeNb)O_3 dielectric ceramics. *Materials Letters*, *58*, 2684-2687. doi: 10.1016/j.matlet.2004.04.005
9. Liao Y., Xiao D., Lin D., Zhu J., Yu P., Wu L., Wang X. (2006): The effects of CeO2-doping on piezoelectric and dielectric properties of $Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$ piezoelectric ceramics. *Materials Science and Engineering: B*, *133*, 172-176. doi: 10.1016/j.mseb.2006.06.026
10. Azough F., Leach C., Freer R. (2006): Effect of CeO_2 on the sintering behaviour, cation order and properties of $Ba_3Co_{0.7}Zn_{0.3}Nb_2O_9$ ceramics. J*ournal of the European Ceramic Society*, *26*, 1883-1887. doi: 10.1016/j.jeurceramsoc.2005.09.016
11. Glazer A. (1975): Simple ways of determining perovskite structures. *Acta Crystallographica Section A*, *31*, 756-762. doi: 10.1107/S0567739475001635
12. Glazer A. (1972): The classification of tilted octahedra in perovskites. *Acta Crystallographica Section B*, *28*, 3384-3392. doi:10.1107/S0567740872007976
13. Fang Z.-x., Tang B., Si F., Zhang S.-r. (2016): Influence of CeO_2 on microstructure and microwave dielectric properties of $Na_{1/2}Sm_{1/2}TiO_3$ ceramics. *Journal of Materials Science: Materials in Electronics*, *27*, 1913-1919. doi:10.1007/s10854-015-3973-4

15. Fang L., Tang Y., Chu D., Zhou H., Zhang H., Chen X., Liu Q. (2012): Effect of B_2O_3 addition on the microstructure and microwave dielectric properties of $Li_2CoTi_3O_8$ ceramics. Journal of Materials Science: *Materials in Electronics*, *23*, 478-483. doi:10.1007/s10854-011-0421-y
15. Tseng C.-F., Wei T.-C., Lu S.-C. (2014): Influence of A-site Ba substitution on microwave dielectric properties of $(Ba_xMg_{1-x})(A_{0.05}Ti_{0.95})O_3$ (A=Zr, Sn) ceramics.

Ceramics International, *40*, 7081-7085. doi: 10.1016/j.ceramint.2013.12.040

16. Shannon R. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, *32*, 751-767. doi: 10.1107/S0567739476001551
17. Manu K.M., Karthik C., Ubic R., Sebastian M.T. (2013): Effect of Ca^{2+} Substitution on the Structure, Microstructure, and Microwave Dielectric Properties of $Sr_2Al_2SiO_7$ Ceramic. *Journal of the American Ceramic Society*, *96*, 3842-3848. doi:10.1111/jace.12598
18. Santha N.I., Sebastian M.T., Mohanan P., Alford N.M., Sarma K., Pullar R.C., Kamba S., Pashkin A., Samukhina P., Petzelt J. (2004): Effect of Doping on the Dielectric Properties of Cerium Oxide in the Microwave and Far-Infrared Frequency Range. *Journal of the American Ceramic Society*, *87*, 1233-1237. doi:10.1111/j.1151-2916.2004.tb07717_33.x
19. Li Y., Li H., Li J., Tang B., Zhang S., Chen H., Wei Y. (2014): Effect of TiO_2 Ratio on the Phase and Microwave Dielectric Properties of $Li_2ZnTi_{3+x}O_{8+2x}$ Ceramics. *Journal of Electronic Materials*, *43*, 1107-1111. doi:10.1007/s11664-014-3026-4
20. Chen G.-h., Yuan C.-l., Zhou C.-r., Yang Y. (2013): Low-firing high permittivity $Ca_{0.6}Sm_{0.8/3}TiO_3$–$(Li_{0.5}Nd_{0.5})TiO_3$ ceramics with $BaCu(B_2O_5)$ addition. *Ceramics International*, *39*, 9763-9766. doi: 10.1016/j.ceramint.2013.05.028
21. Fang Z., Tang B., Si F., Zhang S. (2017): Low temperature sintering of high permittivity Ca–Li–Nd–Ti microwave dielectric ceramics with $BaCu(B_2O_5)$ additives. *Journal of Alloys and Compounds*, *693*, 843-852. doi: 10.1016/j.jallcom.2016.09.292