A novel $LiNb_{0.6}Ti_{0.5}O_3$ microwave dielectric ceramic with Ca substitutions

Huaibao Sun, Enzhu Li, Hongyu Yang, Hongcheng Yang, Shuren Zhang

PII: S0167-577X(17)31378-2
DOI: http://dx.doi.org/10.1016/j.matlet.2017.09.042
Reference: MLBLUE 23156

To appear in: *Materials Letters*

Received Date: 29 June 2017
Revised Date: 19 August 2017
Accepted Date: 11 September 2017

Please cite this article as: H. Sun, E. Li, H. Yang, H. Yang, S. Zhang, A novel $LiNb_{0.6}Ti_{0.5}O_3$ microwave dielectric ceramic with Ca substitutions, *Materials Letters* (2017), doi: http://dx.doi.org/10.1016/j.matlet.2017.09.042

A novel $LiNb_{0.6}Ti_{0.5}O_3$ microwave dielectric ceramic with Ca substitutions

Huaibao Sun, Enzhu Li*, Hongyu Yang, Hongcheng Yang, Shuren Zhang

School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

Tel: 86-28-8320-6695 Email: lienzhu@uestc.edu.cn

Abstract

A novel microwave dielectric ceramic $LiNb_{0.6}Ti_{0.5}O_3$ (LNT) with Ca substitutions $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ was synthesized by solid-state method. It was found that with Ca substitutions, the temperature coefficient of resonant frequency τ_f could be adjusted to zero, due to the appearance of the second phase $Ca_5Nb_4Ti_3O_{21}$. The τ_f of the $Ca_5Nb_4Ti_3O_{21}$ phase is -144.3 ppm/℃ through the simulation and numerical value calculation. Furthermore, the $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic shows a higher dielectric constant ε_r and a denser microstructure. The $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic with x = 0.03 sintered at 1100℃ for 2 h shows excellent microwave dielectric properties: $\varepsilon_r = 76.89$, $Q \times f = 4064$ GHz, $\tau_f = 0.25$ ppm/℃.

Key words: $LiNb_{0.6}Ti_{0.5}O_3$, $CaCO_3$, Ceramics, Microwave dielectric properties, Microstructure

1. Introduction

Owing to the rapid development in the mobile telephone systems, 4G cellular, and wireless local-area networks, microwave dielectric ceramics are receiving increased attention in the research community. For microwave dielectric ceramics, an appropriate dielectric constant ε_r, a low dielectric loss (a high $Q \times f$ value), and a near zero temperature coefficient of resonant frequency τ_f is required in order to adapt the development of electronic industry [1-3]. The research about Li_2O–Nb_2O_5–TiO_2 (LNT) system dielectric ceramics attracts people intensely due to their superior microwave dielectric properties.

The so-called "M-phase" solid solution ($Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4-y}O_3$) ($0.05 \leq x \leq 0.3, 0 \leq y \leq 0.182$) reported by Villafuerte-Castrejon et al. firstly with excellent dielectric properties [4] (ε_r = 55-80, a tunable τ_f, and Q × f value up to 9000 (6 GHz)). As one of M-phase compounds, $LiNb_{0.6}Ti_{0.5}O_3$ (LNT) ceramics are known to have good microwave dielectric properties [5]. To improve ceramic properties, Kang et al. obtained dielectric properties of $\varepsilon_r = 64.5$, $Q \times f = 5{,}933$ GHz, and $\tau_f = 9.4$ ppm/℃ by adding 0.5 wt% of $0.17Li_2O–0.83V_2O_5$ [5]. Recently, Zeng et al. obtained dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5{,}400$ GHz, and $\tau_f = -6.39$ ppm/℃ by adding 1 wt% of B_2O_3 [6]. Although the $LiNb_{0.6}Ti_{0.5}O_3$ is reported to have a tunable τ_f [7], the τ_f is still difficult to regulate to zero. In our previous work, we found that the τ_f of the $LiNb_{0.6}Ti_{0.5}O_3$ is 30.6 ppm/℃. In this work, we found that the Ca substitutions could adjust the τ_f of LNT almost linearly from a positive value (30.6 ppm/℃) to a negative value (-78 ppm/℃). The influence of Ca substitutions on the phase structure development, microstructures and microwave dielectric properties of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ (x = 0.01-0.1) ceramics were investigated in detail, especially the reason of the adjustment of the τ_f is discussed in depth.

2. Experiment

High-purity Li_2CO_3 (>99%), Nb_2O_5 (>99%), TiO_2 (>99%) and $CaCO_3$ (>99%) powders were weighed according to the nonstoichiometric composition of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ (x = 0.01-0.1). The powders were ball-milled in a nylon jar with zirconia balls for 5 h using deionized water as a medium. The mixtures were dried and calcined at 870℃ for 4 h. Then, the calcined powders were ball-milled in deionized water for 5 h, and then dried and added with 3 wt% PVA to form pellets at 20 MPa (15 mm in diameter and 8 mm in height). The samples were sintered at 1100℃ for 2 h with a heating rate of 2 ℃/min in air.

The phase composition was analyzed by X-ray diffraction (XRD, DX-1000 CSC, Japan) using Cu

Kα radiation. The microstructures of the samples were examined using a scanning electron microscope (SEM, FEI Inspect F, the United Kingdom). Dielectric behaviors in microwave frequency were measured by the Hakki-Coleman dielectric resonator method in the TE011 mode using a network analyzer (HP83752A, the United States). The temperature coefficients of resonant frequencies τ_f were measured by using the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 (\text{ppm/℃}) \tag{1}$$

where f_{25} and f_{85} are the resonant frequencies at 25℃ and 85℃, respectively.

3. Result and discussion

Figure 1 shows the XRD patterns of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics with (a) x = 0, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04, (f) x = 0.05, (g) x=0.07 Ca content sintered at 1100℃ for 2 h. For x=0, the XRD pattern indicates that the M-phase ($Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ phase) is the unique crystallized phase (Fig. 1a). With the increasing content of Ca, a second phase of $Ca_5Nb_4Ti_3O_{21}$ (JCPDS #31-0291) (Fig. 1b-g) appears, and the X-ray diffraction peak intensity of the $Ca_5Nb_4Ti_3O_{21}$ phase enhances. As the $Ca_5Nb_4Ti_3O_{21}$ phase does not have detailed information, the rietveld refinement could not be obtained.

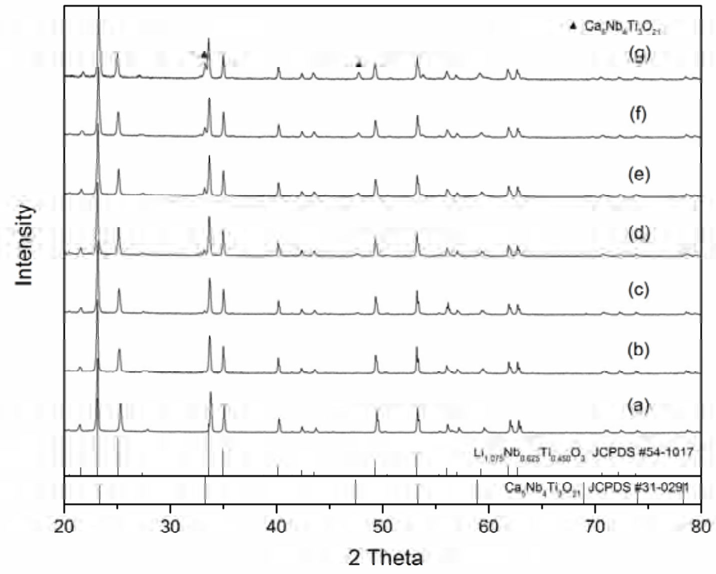


Table I shows the dielectric constant ε_r, the Q × f values and the temperature coefficient of resonant frequency τ_f values of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with increasing Ca substitutions sintered at 1100□ for 2 h. From Table I, it could be observed that the change in the dielectric constant ε_r and the Q × f values are attributed to the second phase content, as the second phase may have a higher permittivity and a lower Q value ($Ca_5Nb_4Ti_3O_{21}$ shows a high permittivity (ε_r = 134) and a low Q-value (360) at 4 GHz) [8]. However, the literature reported a positive τ_f value of $Ca_5Nb_4Ti_3O_{21}$, which is not agreed with our experiment data. As reported, the $Ca_5Nb_4Ti_3O_{21}$ phase always presents with other phases, and microwave dielectric properties of the pure $Ca_5Nb_4Ti_3O_{21}$ has not been reported. We have tried to synthesis the pure $Ca_5Nb_4Ti_3O_{21}$ but failed, so we tried to calculate the τ_f of the $Ca_5Nb_4Ti_3O_{21}$.

Sample		ε_r	Q × f (GHz)	τ_f (ppm/□)
$LiNb_{0.6}Ti_{0.5}O_3$		69	5446	30.6
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.01	69.25	4681	19.31
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.02	74.41	4583	13.40
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.03	76.89	4064	0.25
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.04	81.9	3649	-10.33
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.05	82.96	3078	-21.73
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.07	86.84	2666	-39.34
$LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$	x=0.1	94.5	1777	-78.26

The dielectric properties of the mixture composition can be predicted using the following empirical relationships [9]:

$$\ln \varepsilon = V_1 \ln \varepsilon_1 + V_2 \ln \varepsilon_2 \tag{2}$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2} \tag{3}$$

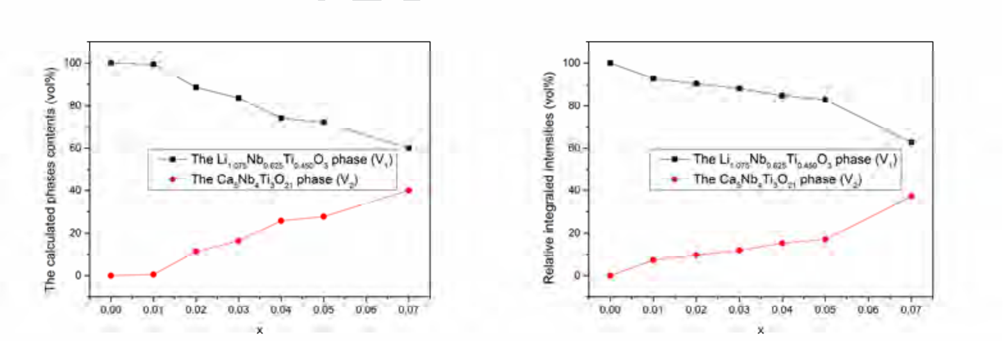
Equation (2) and (3) shows the experimental results as a function of vol% using the above equations. For convenience, V_1, ε_1, and τ_{f1} are the volume fraction, dielectric constant and temperature coefficient of resonant frequency of the main phase, and V_2, ε_2, τ_{f2} are the volume fraction, dielectric constant and temperature coefficient of resonant frequency of the second phase. With the data of Table I processed, the equation (4) could be obtained to calculate the results as a function of the main phase content:

$$\varepsilon = 134 * \exp[V_1 * \ln(69/134)] \tag{4}$$

Figure 2 shows the calculated phases contents of different $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics (a) and the relative integrated intensities of the $Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ (V_1) and $Ca_5Nb_4Ti_3O_{21}$ (V_2) phases highest peaks (at 23° and 33°, respectively) (b). The relative integrated intensities of phase peaks demonstrate the difference in amount of each phase more clearly [10]. The integrated intensities of the $Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ and $Ca_5Nb_4Ti_3O_{21}$ highest peaks are employed to assume that the relative intensities represent the amount of each phase present. From Fig. 2, the phase content of the $Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ and $Ca_5Nb_4Ti_3O_{21}$ could be obtained, and the two similar results could be used to simulate the τ_f as a function of the V_2 with exploiting equation (3):

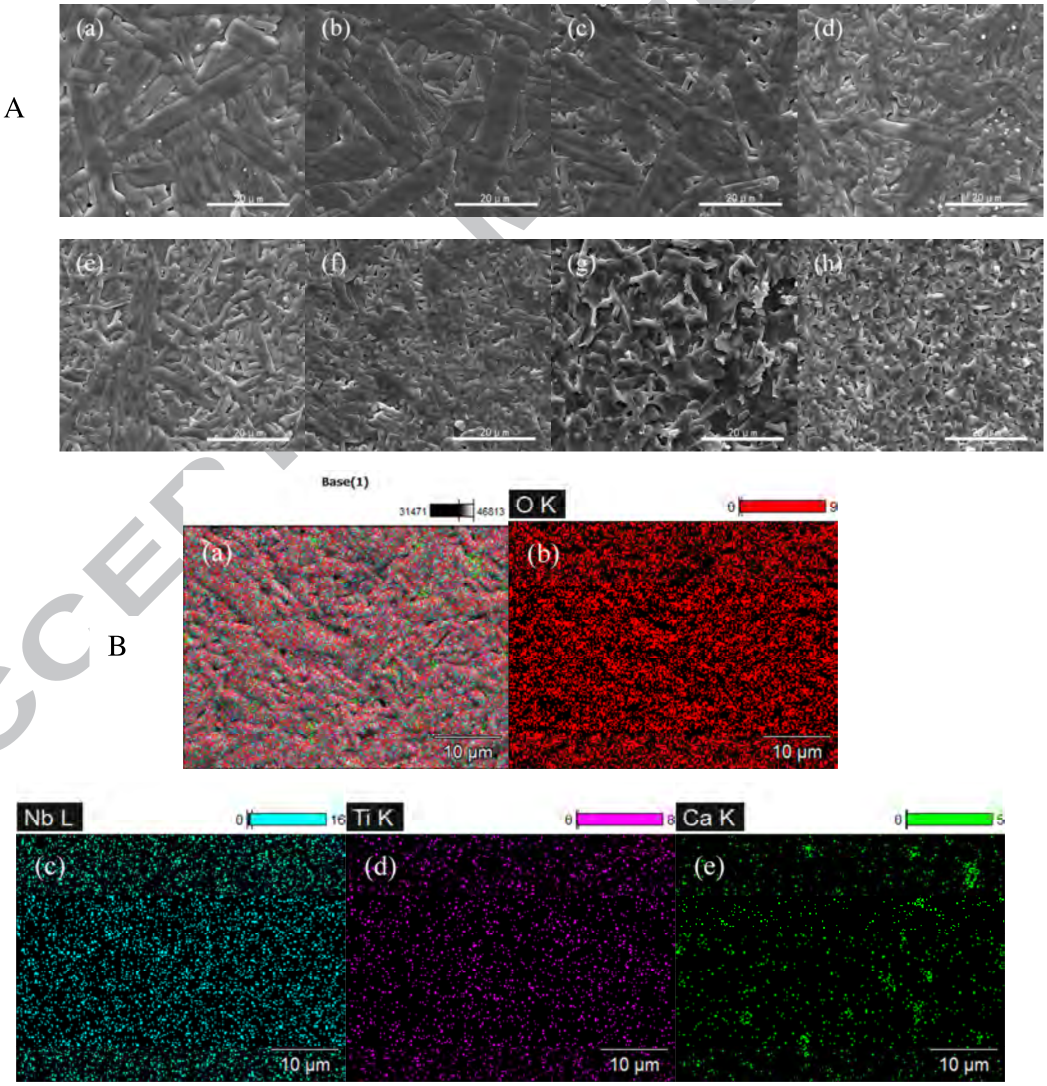
$$\tau_f = 30.6 - 174.9V_2 \tag{5}$$

Then, the result of τ_{f2} = -144.3 ppm/℃ could be obtained when V_2 = 1. These results indicate that the pure $Ca_5Nb_4Ti_3O_{21}$ should have a high permittivity, and also a negative τ_f value.



(a) (b)

Figure 3 shows the microstructures of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics prepared with the contents of Ca substitutions from x = 0 to x = 0.1 (A) and the mapping of the $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic with x = 0.04 Ca substitutions (B) sintered at 1100℃ for 2 h. Irregular platelet or strip shaped grains could be observed in all these micrographs. For $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with different contents of Ca substitutions, it can be observed that the grain size of these samples decreases with the increase of Ca substitutions, and the structure becomes denser. Meanwhile, it can be seen that the Nb ions, Ti ions and O ions are distributed in the sample uniformly, and the segregation of Ca ions at grain boundaries can be observed in all of the samples. The Ca located at the grain boundaries results in the decreasing of ions diffusion rate. Therefore, the move of grain boundary is hindered and the growth of grains is limited, which are corresponded with the observed SEM results. All these results show that the main phase ($Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ phase) is distributed in the sample uniformly, and the second phase ($Ca_5Nb_4Ti_3O_{21}$ phase) is present which adjusts the τ_f value of the LNT ceramic to near zero.



4. Conclusion

A new $LiNb_{0.6}Ti_{0.5}O_3$ (LNT) ceramic with Ca substitutions, composing of M-phase ($Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ phase) and $Ca_5Nb_4Ti_3O_{21}$ phase was investigated in detail. For $LiNb_{0.6}Ti_{0.5}O_3$ ceramics, a small amount of Ca substitutions can dramatically impact its microwave dielectric properties. Especially, the temperature coefficient of resonant frequency τ_f values of the ceramics could be effectively lowered from positive (30.6 ppm/℃) to negative (-78.26 ppm/℃). For the x = 0.03 Ca-doped $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic sintered at 1100℃ for 2 h, excellent microwave dielectric properties of $\varepsilon_r = 76.89$, $Q \times f = 4064$ GHz, $\tau_f = 0.25$ ppm/℃ could be obtained.

Acknowledgements

This work is partly supported by National Natural Science Foundation of China (51272035), Specialized Research Fund for the Doctoral Program of Higher Education of China (20110185120004) and Scientific Research Foundation for the Returned Overseas Chinese Scholars.

Reference

[1] E. Li, P. Zhang, S. Duan, J. Wang, Y. Yuan, B. Tang, Low temperature sintering of low-loss $ZnTiO_3$ microwave dielectric ceramics with Zn–B–Si glass, J. Alloys Compd. 647 (2015) 866-872.

[2] D. Zhou, D. Guo, W.B. Li, L.X. Pang, X. Yao, D.W. Wang, I.M. Reaney, Novel temperature stable high-ε_r microwave dielectrics in the Bi_2O_3–TiO_2–V_2O_5 system, J. Mater. Chem. C 4 (2016) 5357-5362.

[3] L.X. Pang, D. Zhou, Z.M. Qi, W.G. Liu, Z.X. Yue, I.M. Reaney, Structure–property relationships of low sintering temperature scheelite-structured $(1 - x)BiVO_4$–$xLaNbO_4$ microwave dielectric ceramics, J. Mater. Chem. C 5 (2017) 2695-2701.

[4] A.Y. Borisevich, P.K. Davies, Crystalline Structure and Dielectric Properties of $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ M-Phase Solid Solutions, J. Am. Ceram. Soc. 85 (2002) 573-578.

[5] D.H. Kang, K.C. Nam, H.J. Cha, Effect of $Li_2O–V_2O_5$ on the low temperature sintering and microwave dielectric properties of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics, J. Eur. Ceram. Soc. 26 (2006) 2117-2121.

[6] Q. Zeng, W. Li, J.L. Shi, J.K. Guo, H. Chen, M.L. Liu, Effect of B_2O_3 on the sintering and microwave dielectric properties of M-phase $LiNb_{0.6}Ti_{0.5}O_3$ ceramics, J. Eur. Ceram. Soc. 27 (2007) 261-265.

[7] S. Bahel, R. Singh, G. Kaur, S.B. Narang, Low fire M-phase lithium based dielectric ceramics for microwave applications: A review (I), Ferroelectrics 502 (2016) 49-56.

[8] M. Maeda, T. Yamamura, T. Ikeda, Dielectric Characteristics of Several Complex Oxide Ceramics at Microwave Frequencies, Jpn. J. Appl. Phys. 26 (1987) 76-79.

[9] M.T. Sebastian, Dielectric Materials for Wireless Communication, first ed., Elsevier, Amsterdam, 2008.

[10] D.W. Kim, J.H. Kim, J.R. Kim, K.S. Hong, Phase Constitutions and Microwave Dielectric Properties of $Zn_3Nb_2O_8$-TiO_2, Jpn. J. Appl. Phys. 40 (2001) 5994-5998.

Figure captions:

Fig. 1. The XRD patterns of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics with: (a) x = 0, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04, (f) x = 0.05, (g) x=0.07 Ca content sintered at 1100℃ for 2 h

Fig. 2. The calculated phase contents of different $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics (a) and the relative integrated intensities of the $Li_{1.075}Nb_{0.625}Ti_{0.450}O_3$ (V_1) and $Ca_5Nb_4Ti_3O_{21}$ (V_2) phases highest peaks (at 23° and 33°, respectively) (b)

Fig. 3. The microstructures of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics with: (a) x = 0, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04, (f) x = 0.05, (g) x = 0.07, (h) x = 0.1 Ca substitutions (A) and the mapping of the $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic with x = 0.04 Ca substitutions (B) sintered at 1100℃ for 2 h

Table I. Dielectric properties of $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramics sintered at 1100℃ for 2 h

- A novel $LiNb_{0.6}Ti_{(0.5-x)}Ca_{1.231x}O_3$ ceramic with near zero τ_f was synthesized.

- The Ca substitutions could lower the τ_f of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics effectively.

- $Ca_5Nb_4Ti_3O_{21}$ phase has a high ε_r and a negative τ_f by the mixture calculation.