Structure and Dielectric Properties of (Sr$_{0.2}$Ca$_{0.488}$Nd$_{0.208}$)TiO$_3$-Li$_3$NbO$_4$ Ceramic Composites

C C Xia$^1$ and G H Chen$^2$

School of Materials Science and Engineering, Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, P.R. China

$^1$2324514656@qq.com; $^2$chengh@guet.edu.cn

Abstract. The new ceramic composites of (1-x) Li$_3$NbO$_4$-(Sr$_{0.2}$Ca$_{0.488}$Nd$_{0.208}$)TiO$_3$ were prepared by the conventional solid state reaction method. The sintering behavior, phase composition, microstructure and microwave dielectric properties of the ceramics were investigated specially. The SEM and XRD results show that (1-x) Li$_3$NbO$_4$-(Sr$_{0.2}$Ca$_{0.488}$Nd$_{0.208}$) TiO$_3$ (0.35≤x≤0.5) composites were composed of two phase, i.e. perovskite and Li$_3$NbO$_4$. With the increase of x, the $\varepsilon_r$ increases from 27.1 to 38.7, $Q\times f$ decreases from 55000 GHz to 16770 GHz, and the $\tau_f$ increases from -49 ppm/°C to 226.7 ppm/°C. The optimized dielectric properties with $\varepsilon_r$~31.4, $Q\times f$~16770GHz and $\tau_f$~−8.1ppm/°C could be obtained as x=0.4 sintered at 1100°C for 4h. The as-prepared ceramic is expected to be used in resonators, filters, and other microwave devices.

1. Introduction
With the rapid development of microwave communication technology, the widespread usage of several different wireless systems has required the development of materials and process technologies that can provide the rapid production of low-cost, lightweight, small, multifunctional and highly reliable devices[1]. As the development direction of high performance microwave dielectric materials, perovskite structure materials with high $\varepsilon_r$, high $Q\times f$ value and low $\tau_f$ quickly become the research focus. It is well known that an effective way to achieve near-zero $\tau_f$ is to mix two compounds, one with a positive and the other with a negative $\tau_f$ to form a solid solution or composite.

Recently, CaTiO$_3$ with the perovskite structure and SrTiO$_3$ materials, are widely employed as dielectric resonators because of their higher dielectric constant ($\varepsilon_r$)[2,3]. In theory, CaTiO$_3$-Li$_{0.5}$RE$_{0.5}$TiO$_3$ (RE=Sm, Nd), Ca$_{1-x}$Re$_{2x/3}$TiO$_3$-Li$_{1/2}$Ln$_{1/2}$TiO$_3$ (RE=Sm, Nd, La; Ln = Sm, Nd) system showed a higher dielectric constant[4]. Unfortunately, although the resonant frequency temperature coefficient of the material ($\tau_f$) close to zero, but the $Q\times f$ reduced rapidly (2000~7500 GHZ), it is difficult to meet the high demand of high-end communication electronic components on the properties of microwave dielectric ceramic dielectric. Therefore, domestic and foreign scholars have studied not only reduce device size, but also has low loss performance of high $Q$ value, high dielectric of microwave dielectric ceramics. These ceramic materials meet the requirements of thermal stability and have high $Q\times f$ value at the same time. In the past few years, F. Liu et al reported that (Sr$_{0.2}$Ca$_{0.488}$Nd$_{0.208}$)TiO$_3$ ceramic showed following dielectric properties: $\varepsilon_r$=130.4, $Q\times f$ =9500 GHz, and $\tau_f$ =332.5 ppm/°C[5]. D. Zhou et al reported that Li$_3$NbO$_4$ exhibited an excellent dielectric properties sintered at 930 °C/2h: $\varepsilon_r$ = 15.8, a high $Q\times f$=55,009 GHz and $\tau_f$ = -49 ppm/°C [6]. H. F. Zhou et al found that CaTiO$_3$-Li$_3$NbO$_4$ ceramic composites sintered at 1020°C/2h possessed...
outstanding dielectric properties of $\varepsilon_r=21.9$, $Q\times f=24,900$ GHz, and $\tau_f=5.6$ ppm/°C [7]. However, its sintering temperature ($\geq1400$ °C) and $\tau_f$ is too high to use practically. The purpose of the present study is to achieve near-zero $\tau_f$ along with a high $\varepsilon_r$ and high $Q\times f$ by incorporating $(\text{Sr}_{0.2}\text{Ca}_{0.488}\text{Nd}_{0.208})\text{TiO}_3$ into $\text{Li}_3\text{NbO}_4$, and to investigate the effects of $(\text{Sr}_{0.2}\text{Ca}_{0.488}\text{Nd}_{0.208})\text{TiO}_3$ addition into the $\text{Li}_3\text{NbO}_4$ on the structure and microwave dielectric properties of the ceramics.

2. Experimental

2.1. Sample preparation
Analytical reagent $\text{Sr}_2\text{CO}_3$, $\text{CaCO}_3$, $\text{TiO}_2$, $\text{Nd}_2\text{O}_3$, $\text{Li}_2\text{CO}_3$ and $\text{Nb}_2\text{O}_5$ ($>99.0\%$) were used as raw materials. The suppliers of the raw materials are Guangdong Shantou West Long Chemical Company. The $\text{Li}_3\text{NbO}_4$ (LN) and $(\text{Sr}_{0.2}\text{Ca}_{0.488}\text{Nd}_{0.208})\text{TiO}_3$ (SCNT) were prepared according to the stoichiometric ratio and ball milled in ethanol medium for 24 h in nylon jars using yttria stabilized zirconia balls. After drying, the LN and SCNT mixtures were calcined at 900 °C and 1150 °C in air for 4 h, respectively. Samples of $(1-x)$ LN-$x$SCNT with $x=0.35$, 0.4, 0.45, 0.5 were prepared from pure calcined LN and SCNT powders by weight ratio. The mixtures were ball-milled in alcohol for 12 h and dried. The slurries were dried, then mixed with 5wt% polyvinyl alcohol (PVA) as binder and granulated. The granulated powders were pressed into disks of 12 mm diameter and 6 mm in thickness. The specimens obtained were then heat-treated at 600°C for 3 h to eliminate PVA, followed by sintering at 1060-1160°C in air for 4 h at a heating and cooling rate of 4°C/min.

2.2. Performance measuring
The bulk density was measured by using the Archimedes method. The crystal structure and phase purity of the powdered samples were analyzed by using X-ray diffraction (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) with CuKa radiation. The microstructure observation of the samples was performed by using scanning electron microscopy (FE-SEM; Quanta FEG450, America). The microwave dielectric properties were measured by a Vector Network Analyzer (N5230C, Agilent Technologies, Palo Alto, CA). The temperature coefficient of resonant frequency ($\tau_f$) was measured in the temperature range of 25°C to 75°C using the following equation [8]:

$$\tau_f = \frac{(f_{75} - f_{25}) \times 10^6}{50 \times f_{25}} \text{ ppm/°C}$$

where $f_{75}$ and $f_{25}$ are the resonant frequencies at 75°C and 25°C, respectively.

3. Results and discussion

3.1. Phase analysis
Figure 1 shows the XRD patterns of $(1-x)$ LN-$x$SCNT $(0.35 \leq x \leq 0.5)$ composites sintered at optimum sintering temperature for 4h. From the XRD results, it is seen that all samples show two phase coexistence state, i.e. LN and perovskite phase. With the increase of x value, the diffraction peaks of perovskite phase obviously enhance.
Figure 1. XRD patterns of (1-x) LN-xSCNT specimens

3.2. Microstructure

Figure 2. SEM micrographs of 0.6LN-0.4SCNT specimens sintered at different temperatures: (a)1060 °C, (b)1080 °C, (c)1100 °C, (d)1120 °C, (e)1140 °C

Figure 2 shows the SEM micrographs of the 0.6LN-0.4SCNT ceramic sintered at different temperatures. At 1060°C, the ceramic sample has a few of porosity shown in Figure 2a. With the increase of sintering temperature, the ceramic sample gets compact and the grain size is increased. When the sintering temperature reaches 1100°C, the grains grow up quickly, the uniform and densest microstructure is obtained, as shown in Figure 2c. With further increase of the sintering temperature, the grain boundaries become blurred and the porosity gradually is increased, the asymmetrical microstructure is formed, which may be due to excessive sintering. The crystal structure of SCNT and LN have big difference, good stability and easy to form a composite ceramics.
3.3. Sintering characteristics

Figure 3 shows the relative densities of (1-x) N-xSCNT (0.35≤x≤0.5) ceramic composite as a function of sintering temperature. Firstly, the relative densities of samples display a similar variation trend with the increment of temperature and reach a maximum value, then decrease with the further increase of temperature. Raising sintering temperature is beneficial to improving sintering densification of the ceramic materials. The different sample has various optimal sintering temperatures, as shown in Figure 3. At x = 0.4, the optimal sintering temperature is 1100°C and the relative density of the ceramic sample can reach 99.7%. With x increasing, optimal sintering temperature increases, which is due to that the sintering temperature of SCNT (1400 °C) is higher than that of LN (930 °C).

Figure 4 shows the $\varepsilon_r$ of (1-x) LN-xSCNT (0.35≤x≤0.5) ceramics sintered at different temperatures. For fixed x value, the $\varepsilon_r$ of ceramics first increases and then decreases. This change trend is consistent with that of relative density seen in Figure 3. At their optimum temperatures, the $\varepsilon_r$ value is 27.13, 31.38, 34.75, 38.71 for x=0.35, 0.4, 0.45, 0.5 sample, respectively. When x value is increased from 0.35 to 0.5, the dielectric constant is increased from 27.1 to 38.71. We know that the dielectric constant of SCNT (~130.4) is higher than that of Li$_3$NbO$_4$. According to compound rule, the higher the content of compound with high $\varepsilon_r$, the bigger the $\varepsilon_r$ of the composite.
Figure 5 shows the $Q \times f$ values of (1-x)LN-xSCNT (0.35≤x≤0.5) ceramics as a function of sintering temperature. The change of $Q \times f$ value is associated with the relative density of samples. As the composition keeps unchanged, the $Q \times f$ values show first increase and then decrease with an increase in sintering temperature. For different compositions, the $Q \times f$ value is distinctly decreased with the increase of x. This is owing to the quality factor of SCNT is lower than LN. Therefore, the $Q \times f$ value is related to not only the densification but also the composition.

Figure 6 shows the $\tau_f$ of the composites as a function of x value. It is observed that the $\tau_f$ increases from negative to positive with increasing x. One knows that the $\tau_f$ of LN is negative (~49 ppm/°C) and the $\tau_f$ of SCNT is positive (~332.5 ppm/°C). Therefore, the $\tau_f$ of the ceramic composites can be easily adjusted within a certain range. When x=0.4, the $\tau_f$ value is -8.1 ppm/°C.

4. Conclusions
The crystal structures and microwave dielectric properties of (1-x)LN-xSCNT (0.35≤x≤0.5) ceramics were investigated in this paper. The ceramic composites have been synthesized by the solid state reaction route. The research results show that the dielectric constant, relative density and quality factor of the composites firstly increase and then decrease with the increase of sintering temperature, but the temperature coefficient of resonant frequency ($\tau_f$) change from negative to positive with the increase of x. At 1100 °C, the 0.6 LN-0.4 SCNT ceramic composite has the best microwave dielectric properties: $\varepsilon_r=31.4, Q\times f=16,770$ GHz, $\tau_f=-8.1$ ppm/°C. The as-prepared ceramic is expected to be used in resonators, filters, and other microwave devices.

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