Effects of LiF on microwave dielectric properties of $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ ceramics

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Abstract. The effects of LiF addition on sinterability, microstructure and microwave dielectric properties of $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ ceramics were investigated. The LiF addition enhanced the sintering temperature of $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ ceramics from 1200 to 1300°C, because the LiF addition could compensate the evaporation of Li during the sintering process. It was found that the bulk density and dielectric constant (ϵ_r) gradually decreased, the quality factor (Q_f) greatly increased and the temperature coefficient of resonant frequency (τ_f) shifted to a near-zero value with the increase in LiF addition. Obviously, excess Li addition could efficiently improve the microwave dielectric properties. In addition, $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3 + 4.0 \text{ wt}\%$ LiF ceramics sintered at 1350°C for 4 h exhibited good microwave dielectric properties of $\epsilon_r \sim 123.4$, $Q_f \sim 2209 \text{ GHz}$ (at 2.43 GHz) and $\tau_f \sim 12.3 \text{ ppm } ^\circ\text{C}^{-1}$.

Keywords. $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$; microwave dielectric properties; microstructures; LiF.

1. Introduction

Microwave dielectric materials with predictable dielectric properties of a high dielectric constant (ϵ_r), high quality factor (Q_f) and nearly zero temperature coefficient of the resonant frequency (τ_f) are indispensable for the rapid progress of microwave integrated circuits for wireless telecommunications. Generally, it is not easy to find materials which satisfy these three characteristics for microwave dielectric applications, because the materials with high dielectric constant have a high dielectric loss and large τ_f value. After the dielectric characteristics of the perovskite structure $\text{A}_{1-x}\text{A}'_x\text{BO}_3$ are reported,^{1–3} various dielectric ceramics with high dielectric constant based on the $(\text{Li}_{1/2}\text{Ln}_{1/2})\text{TiO}_3$ ($\text{Ln} = \text{Sm}, \text{Nd}$) system are investigated.^{4–8} Among these compositions, the $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ is an orthorhombic distorted perovskite-type microwave dielectric material with high relative dielectric constant ($\epsilon_r = 180$), the modest quality factor ($Q_f = 3000 \text{ GHz}$) and a very high positive temperature coefficient of resonant frequency ($\tau_f = +900 \text{ ppm } ^\circ\text{C}^{-1}$). In contrast, perovskite structure $(\text{Li}_{0.5}\text{RE}_{0.5})\text{TiO}_3$ ($\text{RE} = \text{Nd}, \text{Sm}$) exhibits large negative τ_f from -260 to $-310 \text{ ppm } ^\circ\text{C}^{-1}$ and high ϵ_r (~ 80). In theory, the high positive τ_f of $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ can be suppressed to nearly zero by the addition of

$\text{Li}_{0.5}\text{RE}_{0.5}\text{TiO}_3$, which makes it a potential suitable candidate for microwave telecommunication applications. Especially, it is reported that the $(1-x)\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3 - x\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ (CSLNTx, $0 \leq x \leq 1.0$) ceramics exhibit a single perovskite structure and a dense microstructure in the complete series. The optimum combination of microwave dielectric properties of $\epsilon_r \sim 111.6$, $Q_f \sim 2000 \text{ GHz}$ and $\tau_f \sim -27.5 \text{ ppm } ^\circ\text{C}^{-1}$ can be obtained at $x = 0.87$.⁹

In our previous work, the microwave dielectric ceramics based on $x\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}(1-x)\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ ($0.25 \leq x \leq 0.4$) system (not yet published) have been successfully produced. And also, the most excellent microwave dielectric properties can be obtained at $x = 0.25$ sample. Therefore, this study focuses on the microwave dielectric properties of the $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3\text{--}0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ (referred to hereafter as CSN25) ceramics sintered at different temperatures. Moreover, LiF was added to improve the microwave dielectric properties of CSN25 ceramics, which is in agreement with the results reported by Huang *et al.*¹⁰ It is well known that LiF addition often can lower the sintering temperature for perovskite materials.^{11,12} However, the sintering temperature gradually increases with increase in addition of LiF in the present work due to the fact that a certain amount of Li^+ addition can compensate the evaporation of Li during the sintering process. In addition, the effects of LiF on the densification, microstructures and microwave dielectric properties of CSN25 ceramics are investigated.

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2. Experimental

Specimen powders are prepared through the conventional solid-state reaction technique. High purity (99.9%) CaCO_3 , SrCO_3 , Li_2CO_3 , Nd_2O_3 and TiO_2 are used as raw materials. The powder mixtures are weighed according to the stoichiometric amount of CSN25 solid solution and ball milled for 24 h in ethanol and dried. After calcining at 1100°C for 2 h, the powders can be mixed with γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) and re-milled for additional 24 h, dried and then pressed into disks of 11 mm in diameter and 5 mm in thickness under a uniaxial pressure of 200 MPa using polyvinyl alcohol (PVA) as a binder. After burning off PVA at 600°C for 2 h. Then the CSN25 + γ wt% LiF ($\gamma = 0.5, 1.0, 2.0, 4.0, 8.0$) specimens are sintered at different temperatures (1200 – 1400°C) for 4 h.

The phase structure of the sintered specimens are identified by X-ray powder diffraction with Ni-filtered $\text{CuK}\alpha$ radiation. The densities of the ceramics are measured by the Archimedes method. The microstructures of the sintered samples are characterized by scanning electron microscopy. Moreover, the dielectric constant, unloaded Q value at frequencies of 2–4 GHz are measured by the post-resonant method developed by Hakki and Coleman¹³ and the temperature coefficient of the resonator frequency (τ_f) is measured using invar cavity at the temperature range from 25 to 75°C ,¹⁴ and calculated by the following equation

$$\tau_f = \frac{\Delta f_0}{f_0 \Delta T} = \frac{f_{75} - f_{25}}{f_{25} \times 50}, \quad (1)$$

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

3. Results and discussion

3.1 $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ – $0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ ceramics

Figure 1 shows the X-ray diffraction (XRD) patterns of CSN25 specimens sintered at 1200 – 1350°C for 4 h. A distorted perovskite phase similar to CaTiO_3 -based systems is formed from the XRD data. All the compositions can be indexed within the constraints of orthorhombic perovskite structure. This result is similar to those previous reports on CSLNTx ceramic systems without Li doped.⁹ And also, no second phase is detected at 1200 – 1350°C for 4 h, which is in agreement with that reported by Kim et al.¹⁵ Figure 1 also shows that the intensity of the (121) peak decreases and that of the (202) peak increases when the sintering temperature increases from 1200 to 1350°C for 4 h, which is considered as a part of Ti ions in the matrix dissolved into the liquid phase with an increase in the sintering temperatures. The changes of Ti ions content (as shown in figure 2 and table 1) lead to

Figure 1. X-ray diffraction patterns of CSN25 specimens sintered at 1200 – 1350°C for 4 h.

the formation of oxygen vacancy, maybe for this reason why the intensity of the (202) peak is higher than that of the (121) peak at 1350°C for 4 h.

The apparent density and microwave dielectric properties of CSN25 ceramics sintered at 1200 – 1350°C for 4 h in air are illustrated in figure 3. Generally, the ϵ_r is significantly dependent upon the densities and ionic polarizability at microwave frequencies. On the one hand, the ionic polarizability can be ignored in the same composition for CSN25 ceramics. On the other hand, as shown in figure 3, the maximum apparent density (4.69 g cm^{-3}) and ϵ_r (141) of CSN25 ceramics can be obtained after being sintered at 1250°C for 4 h. As a result, the observed change in ϵ_r is attributed to the improved densification process, as shown in figure 4a–c. Furthermore, the ϵ_r suddenly drop to 134 at 1350°C due to the appearance of liquid phases, which is attributed to the higher sintering temperature (as shown in figure 4d). And also, the Q_f value reaches a maximum ~ 1200 GHz (at 2.35 GHz) at 1250°C . It also means that, with regard to the ϵ_r , Q_f value of CSN25 ceramics, 1250°C is the optimal sintering temperature. Furthermore, the τ_f value shifts from 52.7 to $33.4 \text{ ppm } ^\circ\text{C}^{-1}$ when the sintering temperature increases up to 1350°C .

3.2 $0.25\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ – $0.75\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ + γ wt% LiF ceramics

Figure 5a shows the XRD patterns of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics sintered at different sintering temperatures for 4 h. As seen in the figure, no obvious secondary phase are observed, this result is similar to those samples without Li doping. It also shows that the CSN25 ceramics can form a single orthorhombic perovskite type with an increase in γ -value at different sintering temperatures for 4 h. Moreover, relative ionic sizes of Li^+ ($0.76 \text{ \AA}$) is smaller than that of Ca^{2+} ($1.34 \text{ \AA}$), Sr^{2+} ($1.44 \text{ \AA}$) and Nd^{3+} ($1.27 \text{ \AA}$) at the same coordination

Figure 2. EDS analysis of the CSN25 ceramics with sintering temperature at (a) 1200°C and (b) 1350°C for 4 h.

Table 1. EDS results of CSN25 ceramics sintered at 1200 and 1350°C for 4 h.

Element	1200°C		1350°C	
	Element (%)	Atomic (%)	Element (%)	Atomic (%)
Ti	30.79	22.08	23.43	14.52
O	29.88	64.15	35.65	70.26

Figure 3. The values of apparent density, ϵ_r , Q_f and τ_f of CSN25 ceramics as functions of the sintering temperatures for 4 h.

number.¹⁶ Generally, Li^+ substitutes into the lattice, the main reflection peaks such as the (202) face should shift to higher degree, but in the present work, Li is a volatile constituent at high temperatures. It illustrates that the LiF addition can compensate the evaporation of Li during the sintering process and it is also the reason why the sintering temperature increases with the increase in the LiF content. To confirm that the Li^+ has been compensated into $\text{Li}_{0.5}\text{Nd}_{0.5}\text{TiO}_3$ during the sintering processes, the lattice parameters of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics are determined, and the results are shown in figure 6. The lattice parameters of the a , b and c axes of CSN25 + γ wt% LiF ceramics slightly increase with the increase in γ -value in the range of 0.5–8.0, which means that such an increase in the lattice parameters is due to the compensation of Li^+ into the matrix. Thus, as shown

Figure 4. Microphotographs of the as-sintered surfaces of CSN25 ceramics at (a) 1200°C, (b) 1250°C, (c) 1300°C and (d) 1350°C for 4 h.

Figure 5. (a) X-ray diffraction patterns of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics sintered at different temperatures for 4 h and (b) the magnified figure of the (202) peak.

in figure 5b, the main (202) peak of CSN25 + γ wt% LiF ceramics shifts slightly towards the lower angle with increase in LiF content. Similar result is reported in the case of LiF addition in MgTiO₃ ceramics by Bernard *et al.*¹⁷

Typical grain surface microstructure photographs of the CSN25 + γ wt% LiF ceramics sintered at different temperatures for 4 h with $\gamma = 0.5, 1.0, 2.0, 4.0$ and 8.0 are illustrated in figure 7. The grain size increases with the increase in Li content and sintering temperature. When

Figure 6. Lattice parameters of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics with the variation of γ at different sintering temperatures for 4 h.

$\gamma = 8.0$, a heterogeneous microstructure with a small number of large grains occurs, which can increase dielectric loss for microwave dielectric materials, as seen in figure 7e.¹⁸ In addition, many pores can be found for the specimens with $\gamma = 0.5, 1.0$ (see figure 7a and b). It can be concluded that the LiF content has significant influence on the microstructure and sintering behaviour.

Figure 7. Microphotographs of the as-sintered surfaces of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics sintered at different temperatures for 4 h: (a) $\gamma = 0.5$, 1250°C; (b) $\gamma = 1.0$, 1270°C; (c) $\gamma = 2.0$, 1270°C; (d) $\gamma = 4.0$, 1350°C and (e) $\gamma = 8.0$, 1370°C.

The apparent density, ϵ_r , Q_f and τ_f of CSN25 + γ wt% LiF ($0.5 \leq \gamma \leq 8.0$) ceramics as functions of the sintering temperatures at 1200–1400°C for 4 h are shown in figure 8a–d. The relationship between ϵ_r and sintering temperature shows the same trend as that between apparent densities and sintering temperature. It also illustrates that the ϵ_r is significantly dependent upon the compactness at microwave frequencies. And also, according to figure 8b, the ϵ_r gradually decreases with the increase in LiF content, which can be attributed to the lower dielectric polarizability of Li^+ and F^- than that of Ti^{4+} and O^{2-} , respectively ($\alpha_D(\text{Li}^+) = 1.20 \text{ \AA}^3$, $\alpha_D(\text{Ti}^{4+}) = 2.93 \text{ \AA}^3$, $\alpha_D(\text{F}^-) = 1.62 \text{ \AA}^3$, $\alpha_D(\text{O}^{2-}) = 2.01 \text{ \AA}^3$).¹⁹ In figure 8c, the

Q_f value increases with the increment of the LiF content. Generally, the microwave dielectric loss (included intrinsic losses) is mainly caused by the lattice vibration modes and extrinsic losses are dominated by densification/porosity, secondary phases, grain sizes and oxygen vacancies, etc.²⁰ The improved Q_f values cannot be attributed to the densification because a dense microstructure has not been significantly observed by the LiF addition (see figures 4 and 7). In this work, we suggest that the addition of Li can cause the reduction of vacancies concentration due to a certain amount of LiF compensating the Li^+ evaporation during the sintering process, which results in the decrease in migration loss. Thus, the maximum Q_f value

Figure 8. The variations of (a) apparent density, (b) ϵ_r , (c) Q_f values and (d) τ_f values of CSN25 + γ wt% LiF (0.5 ≤ γ ≤ 8.0) ceramics at different sintering temperatures for 4 h.

~2300 GHz (at 2.63 GHz) can be obtained as γ = 8.0 after sintering at 1370°C for 4 h. It is therefore concluded that the LiF addition can improve Q_f values for CSN25 ceramics. Figure 8d shows the change of τ_f values of CSN25 + γ wt% LiF (0.5 ≤ γ ≤ 8.0) ceramics sintered at different temperatures for 4 h. The τ_f value decreases with the increase in the LiF content, and shifts from approximately 40 $\text{ppm } ^\circ\text{C}^{-1}$ (γ = 0.5) to 3.5 $\text{ppm } ^\circ\text{C}^{-1}$ (γ = 8.0).

4. Conclusions

Phase structure, sintering behaviour and microwave dielectric properties of CSN25 + γ wt% LiF (0.5 ≤ γ ≤ 8.0) ceramics have been studied in this work. An optimized microwave dielectric properties with ϵ_r ~ 141, Q_f ~ 1200 GHz (at 2.35 GHz) and τ_f ~ 47.5 $\text{ppm } ^\circ\text{C}^{-1}$ can be obtained for the CSN25 ceramics after sintering at

1250°C for 4 h. The CSN25 specimens can form solid solution with γ wt% LiF addition in the range of 0.5 ≤ γ ≤ 8.0 at different sintering temperatures for 4 h. Moreover, the sintering temperature increases with the LiF addition because it can compensate the evaporation of Li during the sintering process. To compare with undoped CSN25 specimen, the LiF addition can effectively improve Q_f values and slightly decrease τ_f values for the CSN25 ceramics. And the CSN25 + 4.0 wt% LiF ceramics sintered at 1350°C for 4 h exhibit good microwave dielectric properties of ϵ_r ~ 123.4, Q_f ~ 2209 GHz (at 2.43 GHz) and τ_f ~ 12.3 $\text{ppm } ^\circ\text{C}^{-1}$.

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