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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

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Abstract

Li_2O–Nb_2O_5–TiO_2 based ceramic systems have been the candidate materials for LTCC application, due to their high dielectric constant and $Q \times f$ value and controllable temperature coefficient in the microwave region. However, the sintering temperature was relatively higher (above 1100 °C) for practical application. In this study, dielectric properties of $Li_{(1+x-y)}Nb_{(1-x-3y)}Ti_{(x+4y)}O_3$ solid solution were studied with different x and y contents and among them, the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ composition ($x = 0.1$, $y = 0.1$) was selected, due to its reasonable dielectric properties to determine the possibility of low temperature sintering. The effects of $0.17Li_2O$–$0.83V_2O_5$, as a sintering agent, on sinterability and microwave dielectric properties of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics were investigated as a function of the sintering agent content and sintering temperature. With addition of $0.17Li_2O$–$0.83V_2O_5$ above 0.5 wt%, the specimens were well densified at a relatively lower temperature of 850 °C. Only slight decrease in apparent density was observed with increasing $0.17Li_2O$–$0.83V_2O_5$ content above 0.75 wt%. In the case of 0.5 wt% $0.17Li_2O$–$0.83V_2O_5$ addition, the values of dielectric constant and $Q \times f$ reached maximum. Further addition caused inferior microstructure, resulting in degraded dielectric properties. For the specimens with 0.5 wt% $0.17Li_2O$–$0.83V_2O_5$ sintered at 850 °C, dielectric constant, $Q \times f$ and TCF values were 64.7, 5933 GHz and 9.4 ppm per °C, respectively.

Keywords: Sintering; Microstucture-final; Dielectric properties; Niobates; Li_2O–V_2O_5 flux

1. Introduction

The rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. Many materials have been developed and modified, according to the needs of the specific applications.[1] Recently, low temperature co-fired ceramics (LTCC) for microwave application represent a key position in the development of future electronic products in a high frequency application for IC packaging and wireless technologies.[2] LTCC components were high electrical performance by using highly conductive and inexpensive internal electrode metals, such as silver, copper and their alloys, where their low melting temperature limits the sintering temperature of co-fired ceramics in a multi-layer device.[3] So, dielectric materials are continuing to play a very important role in the LTCC technologies. Using high dielectric constant materials that enable miniaturization since the effective wavelength in the substrate is inversely proportional to the square root of the dielectric constant. However, most of the known commercial LTCC dielectric substrate materials (Dupont 951, CT2000 etc.) show relatively lower dielectric constant (7–10) for integrated compact passive devices, such as resonator and filter.[4] Furthermore, various high dielectric ceramic materials such as $BiNbO_4$ and (PbCa)(MeNb)O_3 systems have been introduced and applied for LTCC process.[2,5]

In the case of $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ systems, Villafuerte-Castrejon et al.[6] have first described that a series of so-called M-phase solid solutions, which form an extended phase field in the center of the ternary section (Li_2O–Nb_2O_5–TiO_2), have structures related to $LiNbO_3$. Since their microwave dielectric properties have been reported by Alvina Borisevich et al.[7], $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x = 0.1$, $y = 0.05$–0.175) solid solution was known as potential candidate materials for LTCC application with high dielectric constant, low loss and stable temperature coefficient of resonance frequency. However, volatile Li^{2+} has a deleterious effect on dielectric properties in Li-based ceramics due to the decrease of density and the lattice defects resulting from the deficiency of lithium. Thus, it is known to be very difficult to synthesize reliable crystal phase.

In this study, physical properties, including dielectric properties, of $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x = 0.1$, $y = 0.05$–0.175)

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ceramics were first represented and then optimizing composition ($Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$, $x=0.1$, $y=0.1$) was selected from resulting dielectric characteristics. Also, for liquid phase sintering, $0.17Li_2O–0.83V_2O_5$ composition with eutectic melting point of 620 °C[8] was used as a flux, which may compensate the possible Li^{2+} evaporation in the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ system. The effects of $0.17Li_2O–0.83V_2O_5$ flux on sinterability and microwave dielectric properties of the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ were investigated in terms of microstructure and XRD analysis.

2. Experimental

The powders of this study were synthesized by the conventional mixed oxide method. Reagent-grade Li_2CO_3, Nb_2O_5, TiO_2 and V_2O_5 (all Aldrich Chemical Co., 99.9% purity) were used as starting raw materials. They were weighed according to the compositions $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x=0.1$, $y=0.05–0.175$) and then milled for 24 h in ethyl alcohol. The mixtures were dried and calcined at 1150 °C for 10 h. The calcined powder was re-milled with different amounts of $0.17Li_2O–0.83V_2O_5$ and after drying, pressed into pellets with 12 mm diameter and 6 mm thick. These pellets were sintered at 800–1150 °C for 10 h. The densities of the sintered pellets were determined by the Archimedes method. X-ray diffraction was carried out on powders obtained by crushing the sintered specimens for phase identification. Pure silicon powder was utilized as an internal standard for calibration. The well-polished and etched surfaces of the specimens were investigated by a scanning electron microscopy with energy dispersive X-ray spectroscopy (JSM-5600). The dielectric constant and the unloaded Q value were measured at 5–6 GHz using the parallel-plate method (Hakki and Colemann method) in the TE_{011} mode interfaced with a network analyzer (HP 8720ES).[9] The temperature coefficient of resonant frequency was measured in the temperature ranges of +25 to +85 °C.

3. Results and discussion

Table 1 represents the experimental composition and measured microwave dielectric properties for the fully-sintered $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ceramic systems without $0.17Li_2O–0.83V_2O_5$ flux at 1150 °C for 10 h. Dielectric constant exhibits a well-defined compositional dependency and generally decreases in the y direction, which indicates that these systematic changes in dielectric properties may be induced by variation in Li–Ti–Nb ratio within the phase field rather than by more complicated structural effect.[7] This conjecture is reinforced by the behavior of the temperature coefficient of the relative permittivity (τ_ε), therefore temperature coefficients exhibit high tunability.

Table 1
Apparent densities and microwave dielectric properties of $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ system

x	y	Apparent density (g/cm^3)	Dielectric constant	$Q\times f$ (GHz)	TCF (ppm/°C)
0.1	0.05	4.11	62.4	1621	−43.5
	0.075	4.07	60.9	4255	−35.7
	0.1	3.98	56.5	4578	−6.7
	0.125	3.92	54.8	4859	15.6
	0.175	3.84	53.3	8515	29.1

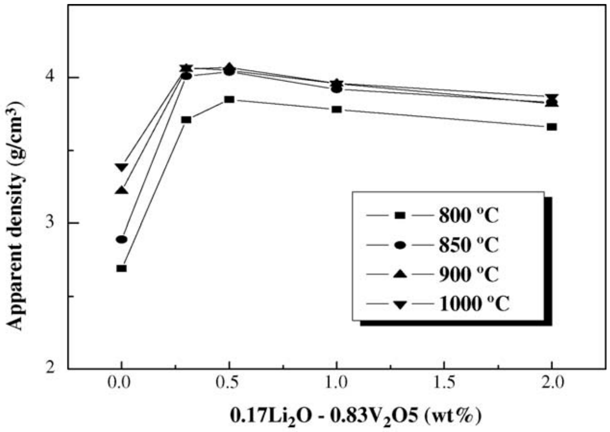

Fig. 1. Effect of sintering temperature on apparent densities of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimens as a function of $0.17Li_2O–0.83V_2O_5$ content.

Fig. 1 shows the apparent densities of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics with various $0.17Li_2O–0.83V_2O_5$ contents at different sintering temperatures from 800 to 1000 °C. The variations in density represent typical liquid phase sintering character, where the rapid densification (about 20–40% improvement) occurred due to the liquid phase effect of $0.17Li_2O–0.83V_2O_5$. It reached maximum value at the $0.17Li_2O–0.83V_2O_5$ contents of 0.3–0.5 wt% and then slightly decreased as shown in Fig. 1. The effect of flux addition on crystal structure was investigated by XRD analysis. In Fig. 2, the XRD patterns of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic containing selected contents of $0.17Li_2O–0.83V_2O_5$ at

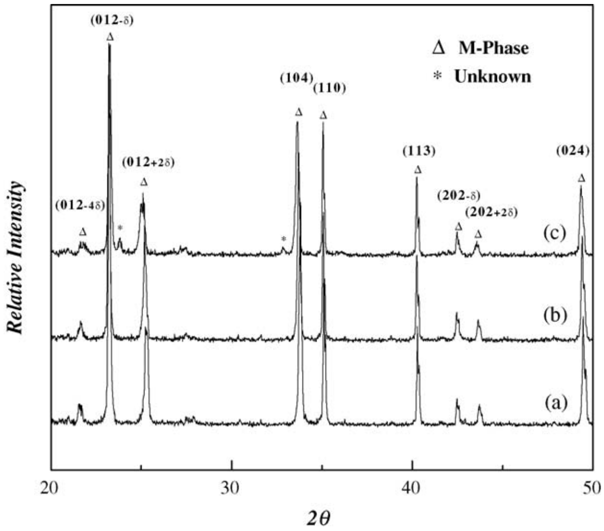

Fig. 2. X-ray diffraction patterns of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimen sintered at 850 °C for 10 h as a function of $0.17Li_2O–0.83V_2O_5$: (a) 0 wt%; (b) 0.5 wt% and (c) 2 wt%.

the sintering temperature of 850 °C, which was considered as the optimum temperature for its LTCC process as confirmed by the densification data of this study shown in Fig. 1. In case of no flux added specimen, XRD pattern was obtained at the sintering temperature of 1000 °C. A single phase (M-phase) presented at no flux added specimen was maintained below 2.0 wt% $0.17Li_2O–0.83V_2O_5$ addition. However, for the specimens containing 2 wt% $0.17Li_2O–0.83V_2O_5$, unknown phase was detected weakly as a secondary phase (Fig. 2c). Changes in crystallity of specimens due to lower sintering temperature was hardly observed. And it was detected that 2θ angles of polycrystalline peaks slightly shifted to lower angle with increasing $0.17Li_2O–0.83V_2O_5$ content.

The SEM photographs of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic with various $0.17Li_2O–0.83V_2O_5$ contents sintered at 850 °C for 10 h are illustrated in Fig. 3(a–e). The $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics with no $0.17Li_2O–0.83V_2O_5$ addition (Fig. 3a) was hardly sintered at 850 °C. As $0.17Li_2O–0.83V_2O_5$ content increased, the specimen became well-densified as well as rapid grain growth. The liquid phase sintering effect was clearly observed considering the grain morphology containing above 0.3 wt% flux. For the specimen with 0.5 wt% $0.17Li_2O–0.83V_2O_5$, optimum microstructure with densely connected grains were obtained and further addition of flux resulted in inferior microstructure as shown in Fig. 3d and e. Although the grain morphology of the specimen with 2 wt% $0.17Li_2O–0.83V_2O_5$ addition (Fig. 3e) exhibited different-typed grains, the same composition was confirmed by EDS analysis. Fig. 3f shows the SEM photograph of the 2 wt% flux added specimen sintered at 1000 °C for 10 h, which indicate that more uniform grain morphology and size were formed, rather than 850 °C (Fig. 3e).

Fig. 4 shows the microwave dielectric properties (ε_r, $Q \times f$, TCF) of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic with $0.17Li_2O–0.83V_2O_5$ addition at different sintering temperatures. The dielectric constant was saturated at 64–65 for the well-sintered $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics at 850–900 °C with 0.5 wt% $0.17Li_2O–0.83V_2O_5$ addition. Further addition of the flux led to the slight decrease in dielectric constant. The dielectric con-

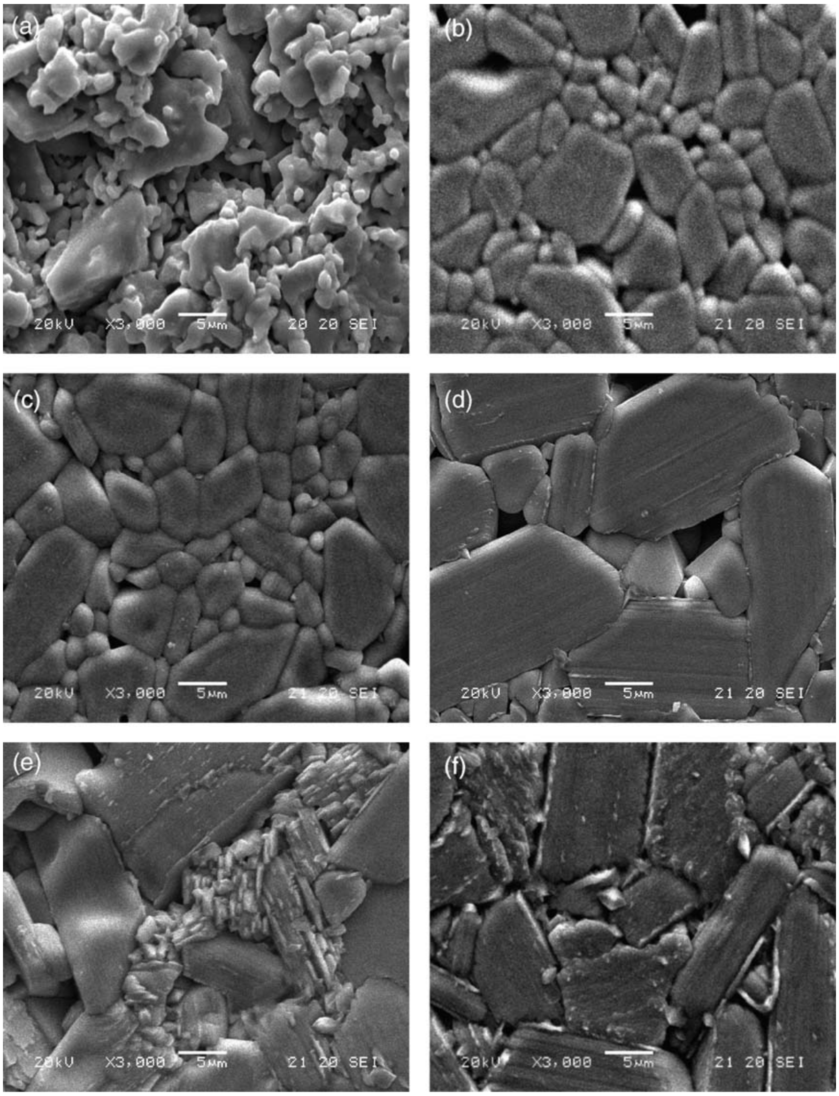

Fig. 3. SEM photographs of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimens containing: $0.17Li_2O–0.83V_2O_5$ of (a) 0 wt%; (b) 0.3 wt%; (c) 0.5 wt%; (d) 1.0 wt%; (e) 2.0 wt%, sintered at 850 °C and (f) 2.0 wt%, sintered at 1000 °C for 10 h, respectively.

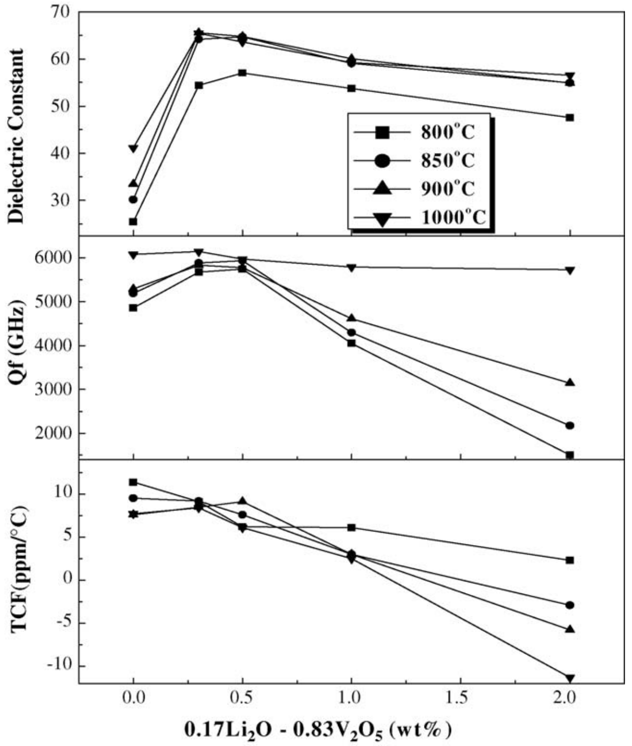

Fig. 4. Microwave dielectric properties of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimens as a function of $0.17Li_2O–0.83V_2O_5$ content.

stant variation in Fig. 4a revealed so similar tendency with the apparent density as shown in Fig. 1. For $Q \times f$ value, higher sintering temperatures of 900 and 1000 °C exhibited higher value for the flux addition up to 0.5 wt%, where its higher $Q \times f$ value was nearly maintained in the case of 1000 °C. But the specimens sintered at 800 and 850 °C, respectively showed maximum $Q \times f$ of 5933 when 0.5 wt% flux was added and further addition abruptly decreased its value as shown in Fig. 4. Considering the microstructure of the 2 wt% flux added specimen sintered at 1000 °C in Fig. 4f, it is though that relatively superior microstructure uniformity compared to other specimens containing same content of flux sintered at 800–900 °C may attributed to the improved $Q \times f$ value, which implies that $Q \times f$ value depends strongly on extrinsic loss factor such as microstructure, as well as intrinsic loss factor.[10] Maximum ε_r and $Q \times f$ values measured were about 64.7 and 5933 GHz, which is superior to that of pure $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimen sintered at 1150 °C for 10 h.

Also Fig. 4 shows the temperature coefficient of resonance frequency (TCF) of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramics with $0.17Li_2O–0.83V_2O_5$ content at different sintering temperatures. As increasing $0.17Li_2O–0.83V_2O_5$ content, TCF tends to be shifted to negative region linearly. It seems to be so difficult to explain the result. However, it probably may be understood by considering the tendency of XRD peak shift in $0.17Li_2O–0.83V_2O_5$ added ceramics and LNT based ceramics with M-phase. In Fig. 5, the change of (1 0 4) and (1 1 0) peaks with flux content in $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ and y content in $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x = 0.1$) was presented. Based on the result of Table 1 and Fig. 5b, as (1 0 4) and (1 1 0) peaks shifted to lower angle, TCF was shifted to negative direction possibly due to reinforced $LiNbO_3$ phase in M-phase systems because $LiNbO_3$ ceramic at room temperature has a large negative TCF.[11] Probably, the slightly lowered 2θ angles of (1 0 4) and (1 1 0) peak with $0.17Li_2O–0.83V_2O_5$ flux addition may be related to the negatively shifting effect of TCF of the specimens sintered with flux. The optimum values of $\varepsilon_r = 64.7$, $Q \times f = 5933$ GHz and TCF = 9.4 ppm per °C were obtained for the 0.5 wt% $0.17Li_2O–0.83V_2O_5$ added specimen sintered at 850 °C for 10 h.

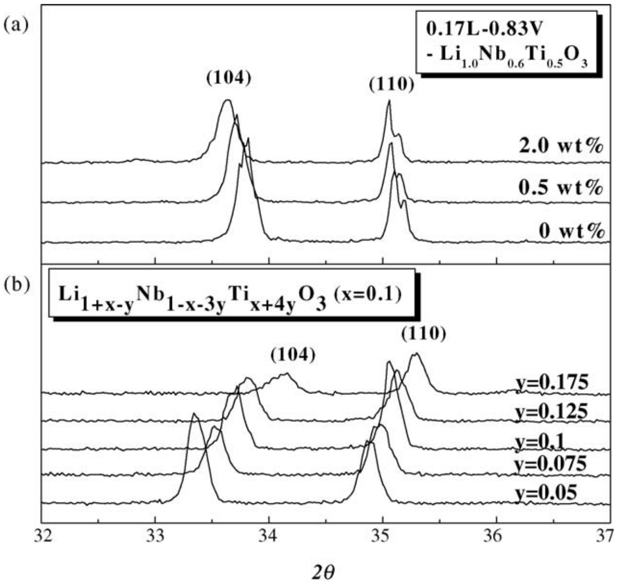

Fig. 5. (1 0 4) and (1 1 0) peaks variation for the (a) $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x = 0.1$, $y = 0.05\sim0.175$) specimens sintered at 1150 °C, (b) $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ specimens containing $0.17Li_2O–0.83V_2O_5$, sintered at 850 °C.

4. Conclusions

In $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ system, $0.17Li_2O–0.83V_2O_5$ was acted as an effective flux to lower sintering temperature up to 850°C without degradation in dielectric properties. The addition of $0.17Li_2O–0.83V_2O_5$ significantly enhanced the sinterability and also the M single phase was maintained until the flux added below 2.0 wt%. When the specimen was sintered at 850 °C, by adding 0.5 wt% $0.17Li_2O–0.83V_2O_5$, the values of apparent density, dielectric constant and $Q \times f$ reached maximum. Further addition caused inferior sinterability and microstructure, resulting in degraded dielectric properties. However, in case of sintering at relatively higher temperature, 1000 °C, degrading effect of $Q \times f$ values were rarely observed with increasing $0.17Li_2O–0.83V_2O_5$ content, possibly due to the superior uniformity in microstructure. As increasing $0.17Li_2O–0.83V_2O_5$ content, TCF is shifted to negative region linearly.

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