Effect of V$_2$O$_5$ on the aqueous tape casting of Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ microwave ceramic

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Abstract

The effect of V$_2$O$_5$ addition on the aqueous tape casting of Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ microwave ceramics has been investigated. The isoelectric point of the ceramic particles moved slightly toward more acid region after the dispersant absorbed on the particles, while the zeta potential increased significantly. The rheological test indicated that the ceramic slurry exhibited a typical pseudoplastic behavior without thixotropy and the addition of V$_2$O$_5$ increased the viscosity of the slurries. It is found that doping of V$_2$O$_5$ can improve the densification of Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ green tapes. Due to the liquid phase effect of V$_2$O$_5$ addition, Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramic could be sintered at 900°C. A secondary phase was observed at the level of 3 wt% V$_2$O$_5$ addition. The addition of V$_2$O$_5$ does not induce much degradation on the microwave dielectric properties. In the case of 2 wt% V$_2$O$_5$ addition, the ceramics show good microwave dielectric properties of $\varepsilon_r = 65$, $Q\times f = 6350$ GHz. It represents that the ceramics could be promising for multilayer low-temperature co-fired ceramics (LTCC) application.

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Keywords: Aqueous tape casting; V$_2$O$_5$; rheology; dielectric properties

1. Introduction

The rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. Recent studies have demonstrated that the solid solution Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$, also referred to as the “M-Phase”, exhibit chemically tunable dielectric properties of interest for use in wireless communication systems. Therefore, LNT was known as potential candidate materials for low temperature co-fired ceramics (LTCC) application with high dielectric constant, low loss and stable...
temperature coefficient of resonance frequency[1-5]. Generally, LTCC can be realized through using sintering additives to lower ceramic sintering temperature. \( \text{V}_2\text{O}_5 \) has been reported as a good flux former to lower the sintering temperature for many materials[6,7]. In the present work, \( \text{V}_2\text{O}_5 \) was added to the \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) ceramics to decrease the sintering temperature for LTCC applications. The effect of \( \text{V}_2\text{O}_5 \) addition on the aqueous tape casting of \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) microwave ceramics has been investigated.

Tape casting process is the best method for creating large, thin and flat ceramic or metallic parts by now. Traditionally, tape casting is based on a non-aqueous solvent as the liquid medium. Non-aqueous solvents have low boiling points and prevent the ceramic powder from hydration, but require special precautions concerning toxicity and flammability.

In recent years, the environmental and health aspects of the tape casting process have received comprehensive attention. There is now a trend to move away from organic solvents and an expected transition towards water-based sytems[8-10]. However, in comparison with organic solvent-based tape casting slurries, aqueous tape casting systems have a smaller tolerance to minor changes in processing parameters. It is important to understand and control the rheology of aqueous tape casting slurries. The slurry should exhibit pseudoplastic behavior and time dependent behavior is undesired[11,12]. So far, aqueous tape casting has been successfully applied to many advanced ceramics such as Al2O3, BaTiO3, Si3N4, AlN, etc., which used for preparation of ceramic substrates, multilayer structures and special components comprised of several materials for quite different applications.

In this work, we discuss the effect of \( \text{V}_2\text{O}_5 \) on the rheological properties of the tape casting slurries. Microstructure, green density and microwave dielectric properties of low-fired \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) ceramics with \( \text{V}_2\text{O}_5 \) additions were also investigated.

2. Experimental procedure

The \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) powders were synthesized by mixed oxide method. Reagent-grade dried \( \text{Li}_2\text{CO}_3, \text{Nb}_2\text{O}_5, \text{TiO}_2 \) powders were used as starting materials. Stoichiometric proportions of the above raw materials (1.72:1:1.44 by mole) were ball-milled in ethanol using \( \text{ZrO}_2 \) balls for 24h. The mixtures were then calcined at 900 °C for 8 h. Different amounts of \( \text{V}_2\text{O}_5 \) were individually added in the calcined powder and remilled for 24 h. The amount of \( \text{V}_2\text{O}_5 \) doped content is expressed on a dry weight of \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) powder basis. In aqueous tape casting process, a solution of 10 wt% polyvinyl alcohol (PVA) and ethylene glycol (EG) were used as binder and plasticizer, respectively. The dispersant was a commercial ammonium polyacrylate (NH4 PA) solution with molecular weight was 5000 g/mol.

The optimal composition of tape casting slurry was listed in Table 1. \( \text{Li}_{1.075}\text{Nb}_{0.625}\text{Ti}_{0.45} \) powders, \( \text{V}_2\text{O}_5 \) and de ionized water, with the dispersant were first mixed in polyethylene jar with \( \text{ZrO}_2 \) ball for 12h. The binder and plasticizer were added, and then, the slurry was mixed for another 12 h. Tape casting was performed on a table top tape caster with a moving blade on a glass slab. Drying was conducted at 80 °C.

Zeta potential of the co-fired particles was determined by Zeta-Probe Analyzer (Colloidal Dynamics Corp., USA). The rheological behavior of the slurries was characterized using a controlled stress rheometer (Haake VT550, Germany) at 25°C. The tensile strength and the strain to failure of the green tapes were measured using an Instron universal testing instrument (AG-1 Instron tensile tester, Japan) at a constant load speed of 2.5 mm/min. The tapes were weighted and measured to determine the green density. The tapes were sintered at 900 °C. Microwave dielectric constants \( \varepsilon_r \) and the quality values \( Q\times f \) at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using an Agilent 8719ET (50 MHz to 13.5 GHz) Network Analyzer. Microstructure of the green and sintered tapes was observed using SEM (Hitachi S-570, Japan).
Table 1. Slurry formulation of aqueous tape casting Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$.

| Materials                  | Function      | Content (wt %) |
|----------------------------|---------------|----------------|
| Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ | Ceramic powders | 50, 49, 48, 47 |
| V$_2$O$_5$                  | Sintering aid | 0, 1, 2, 3     |
| Water                      | Solvent       | 34.2           |
| NH$_4$PA                    | Dispersant    | 0.8            |
| PVA solution (10 wt%)       | Binder        | 10             |
| Ethylene glycol            | Plasticizer   | 5              |

3. Results and discussion

Figure 1 shows the zeta potential of co-fired particles with and without the dispersant. For the pure particles, the isoelectric point (IEP) is around pH 3. A shift of IEP occurs when the NH$_4$PA dispersant was added to the suspension. The zeta potential became more negative and the IEP was displaced towards acidic values, reaching around pH 2.4. For the suspensions containing dispersant, the maximum zeta potential (absolute value) was ca. 70 mV at pH 10. Obviously, the NH$_4$PA dispersant greatly influenced the interaction between colloidal particles in the aqueous suspensions. Distinct changes in surface charge were due to the adsorption of dispersant onto the surface of the particles, inducing a more negative charge to the particle double layer, since this kind of dispersant can dissociate in aqueous solution with higher pH value according to the following reaction:

\[
\text{RCOO-NH}_4^+ + \text{H}_2\text{O} \rightarrow \text{RCOO}^- + \text{NH}_4^+ \quad (1)
\]

With such an enhanced negative surface charge, the suspension can be stabilized more easily.

Figure 2 shows the rheological properties of the tape casting slurries with different V$_2$O$_5$ content. From the Fig. 2(a), it can be seen that the slurries showed shear-thinning behavior. This kind of “shear thinning” behavior had been interpreted as a result of the gradual breaking of the structures formed while the fluid was in repose, indicating that a high shear stress was necessary to break them. At low shear rates, the suspension structure was close to equilibrium, and thermal motion dominated over viscous forces. At higher shear rates, the viscous forces affected the suspension structure more, causing the suspension structure to become distorted, hence leading to shear thinning. The shear thinning behavior is desired for
the tape casting process. This enables structure decomposition when the slurry passes under the blade and its level out, and the structure regeneration after padding the blade, avoiding particles sedimentation and unwanted post-casting flows. Moreover, an increasing trend of viscosity was observed with increasing added amount of V$_2$O$_5$. From the Fig.2(b), it can be seen that the slurries showed no time dependent behavior over the applied shear-rate since the increasing and decreasing shear stress curves coincided fairly well.

![Fig.2 Rheological properties of the slurries with different V$_2$O$_5$ contents: (a) shear rate vs. viscosity curves; (b) shear rate vs. shear stress curves.](image)

Table 2 presents the results of tensile strength, strain-to-failure, absolute density of the green tapes with different V$_2$O$_5$ doped content. It can be seen that there were no obvious difference on mechanism properties among these tapes. The mechanism properties of the green tapes were mainly depending on the binder and plasticizer used in tape casting process. However, with the increase of the V$_2$O$_5$ doped content, the green density of the tapes increased.

Table 2. Mechanical properties and green density of the tapes with different V$_2$O$_5$ doped contents.

| Properties       | V$_2$O$_5$ doped contents |
|------------------|---------------------------|
|                  | 0 wt% | 2 wt% | 3 wt% |
| Tensile strength (MPa) | 1.73  | 1.76  | 1.75  |
| Strain to failure (%)  | 24    | 22    | 23    |
| Green density (g/cm$^3$) | 2.00  | 2.23  | 2.51  |

Table 3. Relatively density and microwave dielectric properties of the tapes sintered at 900 °C with different V$_2$O$_5$ doped contents.

| Properties       | V$_2$O$_5$ doped contents |
|------------------|---------------------------|
|                  | 0 wt% | 2 wt% | 3 wt% |
| Relatively density | 85%   | 95.2% | 95.3% |
| $\varepsilon_r$   | 42    | 65    | 63    |
| $Q\times f$ (GHz) | 3500  | 6350  | 6100  |

The relatively density and microwave dielectric properties of the tapes sintered at 900 °C with different V$_2$O$_5$ content are illustrated in Table 3. When the V$_2$O$_5$ content was over 2 wt%, the tapes could reach higher densities (>95% theoretical density). The results show that V$_2$O$_5$ was effective in enhancing
the sintering ability of the Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramic. The relationship between the $\varepsilon_r$ values and V$_2$O$_5$ contents presents a trend similar to that between densities and V$_2$O$_5$ contents. Owing to the higher densities, the $\varepsilon_r$ values of the Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramics with 2-3 wt% V$_2$O$_5$ addition are higher than the pure Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramic. It could be observed that the $Q\times f$ values of the V$_2$O$_5$-doped Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramics increased when the V$_2$O$_5$ content increased to 2 wt%, and then decreased with further increase in the addition amount. Maximum $\varepsilon_r$ and $Q\times f$ values measured were about 65 and 6350 GHz for 2 wt% V$_2$O$_5$-doped ceramics.

Figure 3 (a) shows the SEM images of the green tapes. The picture illustrates that the tapes achieved by aqueous process show a smooth and well-packed surface morphology. The average particle size was 0.5~1$\mu$m. There is no apparent agglomerate in the tape. The presence of small pores was due to the evaporation of the water. Normally with the evaporation of water in tape, the slurry contracted slowly and organic additives, such as binder and plasticizer, linked to a net and formed an organic membrane. Fig. 3 (b) shows the SEM micrograph of the tapes sintered at 900 °C with 2 wt% V$_2$O$_5$ content. It can be seen that the sintered tape had a uniform and regular microstructure. The average grain size in diameter was about 2~4$\mu$m.

Fig. 3 SEM images of the tapes surface: (a) green body; (b) sintered at 900°C for 2 h tape with 2 wt% V$_2$O$_5$ content.

The X-ray diffraction patterns of the samples with different amounts of V$_2$O$_5$ additive are shown in Figure 4, where the undoped ceramic was sintered at 1100 °C, and the V$_2$O$_5$–doped ceramics were sintered at 900 °C with (b) 1 wt%, (c) 2 wt%, and (d) 3 wt% V$_2$O$_5$ addition.

Fig. 4 X-ray diffraction patterns of (a) the undoped Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramic sintered at 1100 °C, and the ceramics sintered at 900 °C with (b) 1 wt%, (c) 2 wt%, and (d) 3 wt% V$_2$O$_5$ addition.

The X-ray diffraction patterns of the samples with different amounts of V$_2$O$_5$ additive are shown in Figure 4, where the undoped ceramic was sintered at 1100 °C, and the V$_2$O$_5$–doped ceramics were sintered at 900 °C. It is observed that all the compounds below 3 wt% V$_2$O$_5$ exhibited a single Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ phase, and only for the specimens containing 3 wt% V$_2$O$_5$, the secondary phase is detected in the ceramics. In addition, it is found the diffraction peak position of the V$_2$O$_5$–doped ceramics
have small shift compared with the pure Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ ceramic. With the V$_2$O$_5$ content increasing from 0 to 2 wt%, the peak position shift to low 2θ angles. However, the peak position shift towards higher diffraction angles when 3 wt% V$_2$O$_5$ added.

4. Conclusions

In Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ system, V$_2$O$_5$ acted as an effective sintering agent to lower sintering temperature up to 900 °C. The aqueous tape casting V$_2$O$_5$-doped Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ slurries were prepared. In the presence of dispersant, a higher density surface charge was achieved in a large range of pH value through zeta potential measurement. The aqueous slurries showed a typical shear-thinning behavior and no time dependent behavior, which is desirable in aqueous tape casting process. The addition of V$_2$O$_5$ significantly increased the viscosity of the casting slurries and the density of the green tapes. At a low addition level (< 3 wt%), the V$_2$O$_5$-doped ceramics remain single phase and present a secondary phase only when 3 wt% V$_2$O$_5$ is added. For the 2 wt% V$_2$O$_5$-doped tapes, excellent microwave dielectric properties of $\varepsilon_r = 65$, $Q\times f = 6350$ GHz could be obtained at 900 °C. Further addition caused inferior dielectric properties. This result shows that the Li$_{1.075}$Nb$_{0.625}$Ti$_{0.45}$O$_3$ dielectric ceramic is a good candidate for LTCC application.

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