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Aqueous processing of $Li_{1.075}Nb_{0.625}Ti_{0.45}O_3$ green tapes

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An aqueous tape casting of $Li_{1.075}Nb_{0.625}Ti_{0.45}O_3$ (LNT) ceramics was developed using PCA-NH_4 as dispersant, PVA as binder and EG as plasticizer. Flexible, defect-free and smooth tapes of LNT were successfully produced. The study focused on obtaining the optimum slurry formulations and on the effects of the processing parameters such as the stability, the rheology on the properties on the tape characteristics. Surface properties of LNT powders in the aqueous suspensions are distinctly influenced by PCA-NH_4. The zeta potential measurement showed that the isoelectric point (IEP) of LNT powders in the absence of dispersant corresponds to a pH value of 3.7. The zeta potential values (absolute values) increased with the amount of dispersant and up to its maximum near pH 9-10. The rheology measurements of all the slurries investigated showed the desired shear thinning behavior, indicating that the LNT slurry was homogenous and well stabilized. An optimum formulation for the tape was investigated and it was shown that a high solid loading (50 wt%) would lead to a high relative green density (46.7%). Homogenous, smooth, and defect-free green tapes were successfully obtained by an appropriate slurry formula.

Key words: Aqueous tape casting, $Li_{1.075}Nb_{0.625}Ti_{0.45}O_3$, Zeta potential, Rheology.

Introduction

For the development of microwave dielectric ceramic components used in telecommunication and satellite broadcasting, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ is recognized as a potential material [1, 2]. Recent studies have demonstrated that the solid solution $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$, also referred to as the "*M*-Phase", exhibits chemically-tunable dielectric properties of interest for use in wireless communication systems. Moreover, the relatively low sintering temperatures of these ceramics render them attractive candidates for low-temperature co-fired ceramic (LTCC) technology [3-5].

Tape casting is a well known colloidal casting technique for thin ceramic products, that is used for the production of ceramic substrates or components e.g. the multilayered ceramic package (MLCP), multilayered ceramic capacitors (MLCC), solid-oxide fuel cells (SOFC's), sensors and transducers [6-8]. Colloidal processing consists of the preparation of slurries by mixing the ceramic powder, a solvent, and organic agents used as a dispersant, binder and plasticizer. Traditionally, tape casting was done using organic solvents. From a process point-of-view, solvent based tape cast processes are considered to be superior over aqueous tape cast processes. However, from both an environmental and health point-of-view, aqueous tape casting processes are preferred over solvent-based processing. So, the efforts spent on aqueous casting processes, using water and natural products as constituents, replacing toxic solvents and binders, have increased. Generally, colloidally stable suspensions are preferred in a tape casting process, since they usually produce higher average packing densities than flocculated suspensions. However, the interaction between the powder, water and the organic agents can be rather complicated. So far, aqueous tape casting has been successfully applied to prepare single- or multi-layer structure materials such as Al_2O_3 [9, 10], $BaTiO_3$ [11], Si_3N_4 [12], AlN [13], HA [14] etc., for quite different applications. However, the best of our knowledge, scant literature on $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ microwave ceramic prepared by aqueous tape casting process has been reported yet.

In this paper we discuss the preparation of aqueous $Li_{1.075}Nb_{0.625}Ti_{0.45}O_3$ (LNT) suspensions with high solids contents and viscosities suitable for aqueous tape casting. The fabrication of LNT substrates has also been investigated.

Experimental

Materials

LNT powders were synthesized by a conventional mixed oxide method [15]. Reagent-grade dried Li_2CO_3, Nb_2O_5, TiO_2 powders were used as starting materials. The raw materials were ball-milled in ethanol using ZrO_2 balls for 24 h. The mixture was dried and annealed at 900 °C. Distilled water was used as the solvent in this study. An ammonium polycarboxylate (PCA-NH_4, a 50 concentrated solution of average molecular weight 3000 g/mol) was used as dispersant in order to obtain stable LNT slurries with high solids content. Polyvinyl alcohol (PVA 1750, 10 wt% water solution) was selected as binder and ethylene glycol (EG) as plasticizer. The amount of the PCA-NH_4, PVA, EG used here is expressed as a dry weight of the

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powder basis (dwb). NHO_3 and NH_4OH were utilized to modify the pH value.

Processing

The LNT suspensions were prepared by mixing powders, distilled water and dispersant under constant stirring. Suspensions were ball-milled for 24 h with ZrO_2 balls. Before tape casting, PVA and EG were added to the suspensions, followed by ball milling at a very low speed for 15 minutes.

LNT slurries were prepared at 40, 45, 50 and 55 wt% to characterize the effect of solids content on the rheological properties. Tape casting was done with a moving single doctor blade on a glass substrate. The casting speed was constant at 2 cm/s and the gap between the blade and the carrier substrate adjusted at 200-300 μm. After tape casting, the tapes were left to dry at room temperature for 2 h, and then dried at 80 °C for another 15 minutes. Then the tapes were peeled off from the carrier.

Characterization

The zeta potential of the LNT suspensions with and without PCA-NH_4 were determined by a Zeta-Probe Analyzer (Colloidal Dynamics Corp., USA) at various pH levels. The rheological properties of the slurries were investigated using a controlled stress rheometer (Haake VT550, Germany) at 25 °C. The shear dependent behavior of the system examined under steady shear conditions was evaluated by ascending and descending the shear rate. The relative density of the green tape was asured by mercury porosimetry (AutoPore IV 9510, Micrometric Corp., USA). The microstructure of the green tape was observed using a scanning electron microscope (SEM, Hitachi S-570, Japan).

Results and Discussion

Zeta potential

Zeta potential studies were performed to identify the optimum pH value and dispersant content for stable suspensions with and without the addition of PCA-NH_4. As shown in Fig. 1, LNT powder has an isoelectric point (IEP) at pH 3.7. A dramatic shift of IEP occurs when the PCA-NH_4 dispersant was added to the suspension. At the same time,

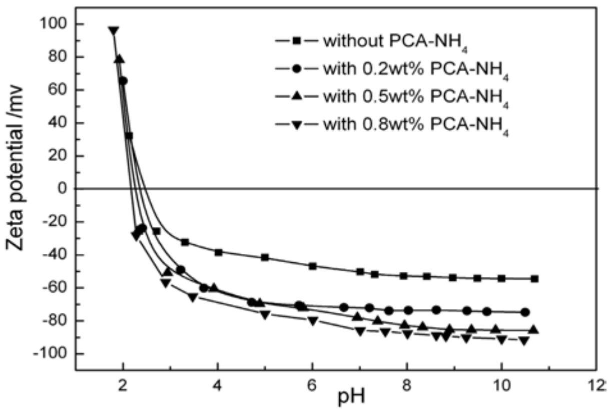

Fig. 1. Effect of dispersant as a function of pH value.

the IEP was displaced towards more acidic values. The differences between pure LNT and doped dispersants occur in the range of pH 2-11, in which the zeta potential becomes more sensitive to changes of pH values. For the suspension containing 0.8 wt% PCA-NH_4, a relatively high zeta potential (absolute value) of 95 mv is reached in the pH range 9-10. So it can be postulated that the stability of the LNT suspension can increase over the basic pH range 9-10 in the presence of PCA-NH_4.

Moreover, the amount of dispersant greatly affected the interaction between LNT particles in aqueous suspensions. PCA-NH_4 is an electrosteric type dispersant with electrostatic and steric stabilization mechanisms. The steric stabilization mechanism of the dispersant results in an increase in the distance and repulsive interaction between particles because organic molecules were adsorbed onto the surface of the particles. Distinct changes in surface charge of PCA-NH_4-dispersed-LNT suspensions 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 type of dispersant can dissociate in an aqueous solution with a pH value higher than 3 [16, 17]. With such an enhanced negative surface charge, the suspension can be stabilized more easily and sustained for a fairly long time. Thus, the optimum conditions for the stable dispersed slurries are a dispersant coverage of 0.8 wt% at a pH value of 9-10 (Fig. 1).

Effects of PVA and EG contents on rheological properties of the slurries

Based on the results presented above, the dispersant concentration was fixed at 0.8 wt%, while the concentration of solids was kept at 50 wt%. Fig. 2 shows the effect of the amounts of PVA added on the rheological properties of the slurries. The amounts of binder added varied in the range of 4.0-6.0 wt%.

An increasing trend of viscosity is observed with an increase in the amounts of PVA added. All the viscosity curves presented a shear thinning branch within the shear rate range. A shear thinning behavior is desired for the tape casting process. This enables structural decomposition when the suspension passes under the blade and it is leveled out, and the structural regeneration after passing the blade, avoiding particle segregation and unwanted post-casting flows.

In order to increase the flexibility and consequently easy handling of the green tapes, an EG plasticizer was tested. Fig. 3 shows the rheological properties of the slurries containing 50 wt% solids content with a fixed amount of PVA (5 wt%) and different amounts of EG. The shear thinning behavior of the suspensions was kept. Increasing the amounts of EG added enhances the fluidity of the slurries, an opposite effect in comparison with the binder. This is according to the low viscosity of the plasticizer and to its specific role in the tape casting process, improving the viscous character of the green tapes in detriment to the elastic properties.

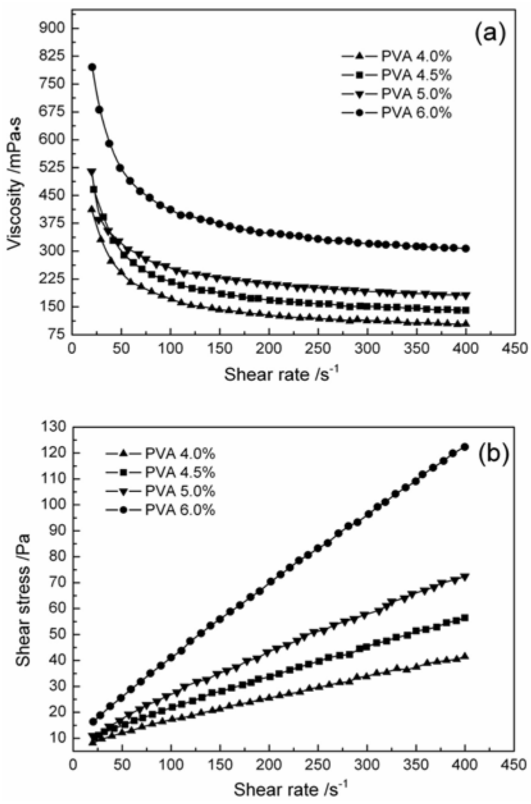

Fig. 2. Rheological properties of the LNT slurries with different PVA contents: (a) shear rate vs. viscosity curves; (b) shear rate vs. shear stress curves.

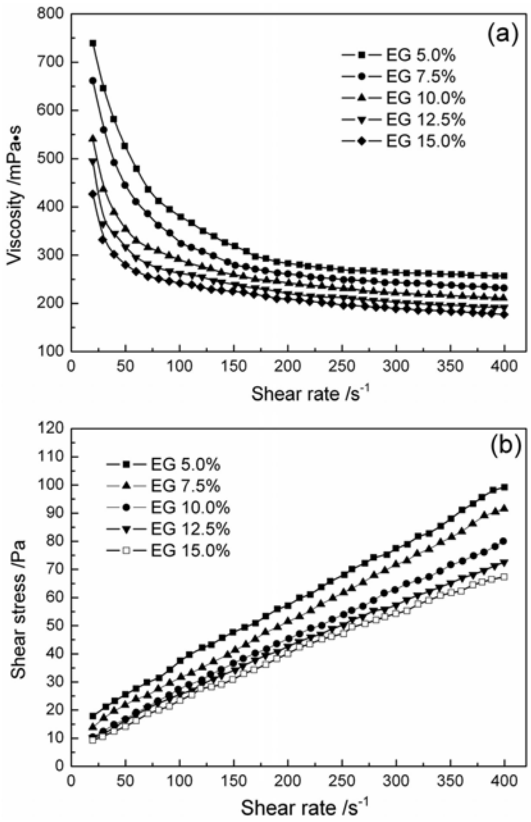

Fig. 3. Rheological properties of the slurries with different EG contents: (a) shear rate vs. viscosity curves; (b) shear rate vs. shear stress curves.

An increase in the PVA content resulted in a more viscous fluids phase which increased the slip viscosity. By contrast, a larger amount of EG produced a slight decrease in the viscosity of the fluid part and consequently in the slip viscosity. Based on these observations, combinations of 5 wt% of PVA with 10 wt% of EG was selected for the next experiments.

Properties of aqueous tape casting LNT slurries

According to the zeta potential measurements, the 0.8 wt% dispersant of PCA-NH_4 was used for stabilization of a slurry containing 40, 45, 50, 55 wt% LNT powder with an adjusted pH of 9-10. The rheological properties of the tape casting slurries with various solids contents are shown in Fig. 4. It can be seen that the curve for 40 wt% loading exhibited close to Newtonian behavior, although a slight shear-thinning behavior was observed. The characteristics are typical of a stable colloidal slurry. When the solids content were increased to 45 wt%, 50 wt% and 55 wt%, the slurries showed an obvious shear-thinning behavior. And with the increase of the solids content, the viscosity increased.

The shear thinning behavior is usually associated with the slurry structure. Under near rest conditions the interfacial forces dominate the particulates system and at low shear rates, liquid might be immobilized in void spaces within flocks and the flock network. As the shear rate increases, the flocks and flock network breaks down and the entrapped

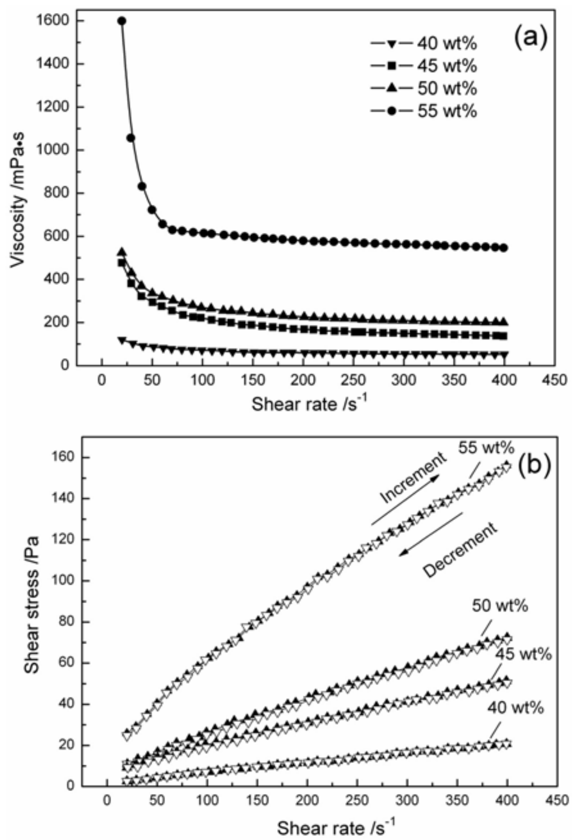

Fig. 4. Rheological properties of slurries with different solid loadings: (a) shear rate vs. viscosity curves; (b) shear rate vs. shear stress curves.

liquid is released and a more ordered structure in the flow direction is formed offering less resistance to flow [18, 19].

Maximizing the solids content is essential to obtain non-cracked tapes with high thickness. The maximum viscosity corresponds to 55 wt% solid content, this formula being too viscous to be used for tape casting. Contrarily, the slurry with 40 wt% solid loading showed the lowest viscosity, but was also unsuitable for tape casting. Cracks mostly originate from the slow drying of the tapes when higher volumes of water are present in a slurry leading to high drying shrinkage values of the tapes.

Accordingly, from experimental results, it was concluded that the optimum composition of a slurry included, LNT powder 50 wt%, PCA-NH_4 0.8 wt%, PVA 5 wt%, EG 10 wt%, and deionized water 34.3 wt%.

Characteristics of the green tape

The qualities of the green tape, such as surface quality, homogeneity and cracks greatly affect the properties of a LNT ceramic. Fig. 5 shows an example of the LNT green tapes produced. The as-dried tapes were flexible, defect-free and had smooth surfaces. These tapes exhibit excellent strength and flexibility. They can be rolled without any mechanical damage, and can be easily cut and stacked together. The tapes prepared from 50 wt% solid content were dried without any cracks or warping. The relative density of the tape prepared from 50 wt% solid loading was approximately 46.7%. This suggests that highly close-packed structures were reached.

The microstructure of the green sheets of LNT is shown in Fig. 6. Both sides (top and bottom surface) of the tapes display very smooth surfaces. No obvious differences are observed between the top and bottom surfaces. The homogeneity of the particle packing is ascribed to the fact that the LNT suspensions are well dispersed.

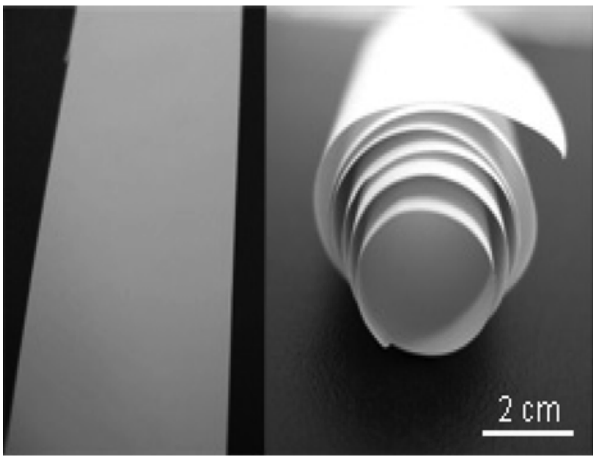

Fig. 5. LNT green tapes prepared from 50 wt% solid loading.

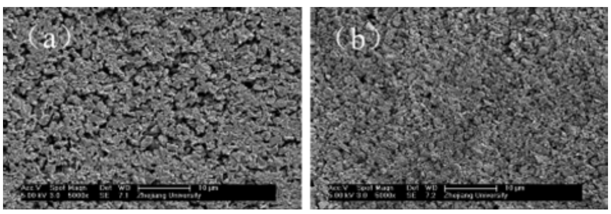

Fig. 6. SEM micrographs for dried tapes: (a) top surface; (b) bottom surface.

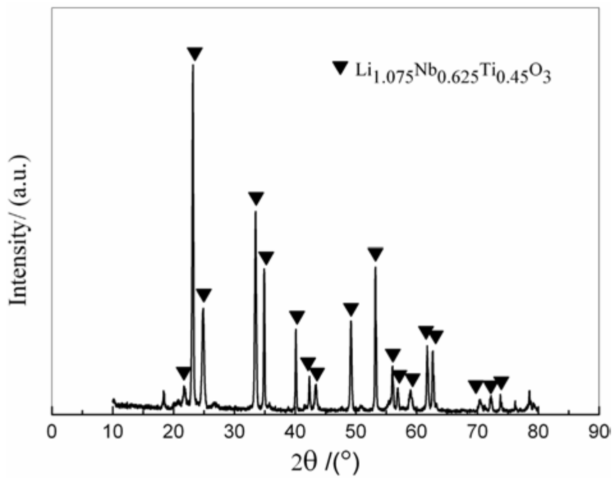

Fig. 7. XRD pattern for aqueous LNT green tape.

In order to confirm that there was no reaction between the LNT particles and the deionzed water in this slurry, XRD measurements of the tape after de-binding was carried out and the results showed that all the peaks belonged to the $Li_{1.075}Nb_{0.625}Ti_{0.45}O_3$ phase confirming no phase change (Fig. 7).

Conclusions

In this study, using PCA-NH_4 as dispersant, PVA as binder, EG as plasticizer, and deionized water as solvent, flexible and smooth LNT tapes have been successfully prepared by a tape casting process. The zeta potential measurements revealed that the IEP for LNT powders in the absence of a dispersant was 3.7. In the presence of different dispersants in the range of 0.2-0.8 wt% of PCA-NH_4, the IEP moved to more acidic values. The value of the zeta potential is up to its maximum near pH 9-10. For aqueous LNT slurries, the PVA, EG contents and solid content affect the rheology of the slurries. Slurries containing 0.8 wt% PCA-NH_4, 5 wt% PVA, 10 wt% EG, and 50 wt% LNT powder exhibit shear thinning behavior, indicating that the slurry is homogenous and well stabilized. Both sides of the green tapes revealed smooth surfaces, no cracks were detected. No other crystalline phase was detected by XRD in LNT green tape. SEM micrographs exhibited that the cast tapes have a very uniform microstructure. The results show that aqueous tape casting can be used to produce high quality dense LNT tapes.

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References

1. Q. Zeng, W. Li, J.L. Shi, J.K. Guo, M.W. Zuo and W.J. Wu, J. Am. Ceram. Soc. 89[5] (2006) 1733-1735.
2. Q.L. Zhang, H. Yang, X.Y. Liu and D.L. Lu, J. Chin. Ceram. Soc. 33[7] (2005) 793-798.
3. A. Borisevich and P.K. Davies, J. Eur. Ceram. Soc. 21[10-11] (2001) 1719-1722.
4. Q. Zeng, W. Li, J.L. Shi, X.L. Dong and J.K. Guo, J. Am. Ceram. Soc. 91[2] (2008) 644-647.
5. D.H. Kang, K.C. Nam, H.J. Cha; J. Eur. Ceram. Soc. 26[10-11] (2006) 2117-2121.
6. K. Schindler and A. Roosen, J. Eur. Ceram. Soc. 29[5] (2009) 899-904.
7. D.H. Yoon and B.I. Lee, J. Eur. Ceram. Soc. 24[5] (2004) 753-761.
8. S.B. Savignat, M. Chiron and C. Barthet, J. Eur. Ceram. Soc. 27[2-3] (2007) 673-678.
9. M.P. Albano, L.B. Garrido, Ceram. Int. 31[1] (2005) 57-66.
10. I. Toshihiro, H. Yuji and W. Koji, J. Am. Ceram. Soc. 90[11] (2007) 3720-3724.
11. D.H. Yoon and B.I. Lee, J. Eur. Ceram. Soc. 24[5] (2004) 739-752.
12. B. Bitterlich and J.G. Heinrich, J. Eur. Ceram. Soc. 22[13] (2002) 2427-2434.
13. X.J. Luo, B.L. Zhang, W.L. Li and H.R. Zhuang, Ceram. Int. 30[8] (2004) 2099-2103.
14. T. Tian, D.L. Jiang, J.X. Zhang and Q.L. Lin, J. Eur. Ceram. Soc. 27[7] (2007) 2671-2677
15. S.C. Li, Q.L. Zhang and H. Yang, J. Mater. Sci. Technol. 25[2] (2009) 269-272.
16. B.P. Singh, R. Menchavez, M. Fuji and M. Takahashi, J. Colloid Interface Sci. 291[1] (2005) 181-186.
17. L.H. Luo, A.I.Y. Tok and F.Y.C. Boey, Mater. Sci. Eng. A 429[2] (2006) 266-271.
18. Y.L. Song, X.L. Liu, J.Q. Zhang, X.Y. Zou and J.F. Chen, Powder Technol. 155[1] (2005) 26-32.
19. S.M. Olhero and J.M.F. Ferreira, J. Mater. Process. Technol. 169[2] (2005) 206-213.