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OPTIMISATION OF BARIUM TITANATE SLIP FOR TAPE CASTING

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ABSTRACT

Tape casting is the feasible method for preparing ceramic tapes with different electrical and magnetic properties for multi layer ceramic devices. The preparation of stable, well-dispersed slip is a critical step in tape casting technology. As the miniaturization stresses the use of nano size powders and less and less thickness of tape to increase the effective surface area in the same volume of material with improved properties, the optimization of suitable parameters to achieve the defect free tape with specified properties is a difficult task. Dispersion of barium titanate nano powder of average particle size ~ 30nm in different solvent systems of tape casting (toluene-ethanol, methyl ethyl ketone-ethanol, xylene-ethanol) along with Triton x-100, phosphate ester as dispersants has been studied using sedimentation experiments. The optimal concentration of dispersant was determined from the minimum in slip viscosity. Poly vinyl butyral was used as a binder. The influence of different parameters such as type of solvent system, dispersant and concentration of dispersant on $BaTiO_3$ slip dispersion, viscosity and the properties of green tape were studied.

Key words: Tape Casting, Barium Titanate, Dispersion, Rheology, Viscosity

1. INTRODUCTION

The electroceramics are proving most promising for use in miniature devices for industrial and commercial applications, because of their unique properties, namely high piezoelectric and electro-mechanical coupling on poling, very high dielectric permittivity in Relaxor system and high pyroelectric as well as electro-optic coefficients[1]. The dielectric, piezoelectric and pyroelectric properties of barium titanate (BT), lead zirconium titanate (PZT) and modified PZT with rare earth metal oxides have been studied extensively. These high permittivity ceramics have proved to be excellent materials in monolithic multilayer capacitors (MLCs), resonators and delay lines in communication applications, in noiseless printing heads for bubble jet printers, ultrasonic imaging, accelerometers, hydrophones and high resolution tomography. Reduction in dimension of all passive components without compromising on performance and improved reliability is the trend in electronics technology[2]. One of the means of achieving this goal, especially in electronic ceramics, is to go in for multiple layer ceramics. Compared to bulk electroceramics, multiple layer ceramics offer several advantages in terms of performance reliability, cost and space savings. The first and most critical step involved in the fabrication of multiple layer devices is tape casting[3].

Tape casting of ferroelectric materials that are used in commercial applications are $BaTiO_3$, $Pb(Zr,Ti)O_3$, $BiTiO_3$, $PbNb_2O_6$, $PbTiO_3$, $LiNbO_3$ and $LiTiO_3$. Among these $BaTiO_3$ is primarily used in the capacitor industry because of its optimum dielectric constant, dielectric strength, Curie temperature and mechanical properties. The basic essential requirements for $BaTiO_3$ multiple layer capacitors application are phase pure fine powders and a defect free green ceramic tape[4]. Though tape casting process for these materials is well established for above materials with larger powder sizes and for larger tape thickness, the processes are not well established for the nano-size powders and micron thick tapes. As the miniaturization stresses the use of nano size powders and less and less thickness of tape to increase the effective surface area in the same volume of material with improved properties. A concentrated dispersion of tape casting slurry is necessary for uniform and high density dielectrics. The state of particle dispersion has very sensitive role to play in the rheological properties of the slurry[5]. Powder dispersion is not only dependent on the dispersant but also on the type of solvent used[6]. It is well established that a slurry composed of two or three solvents has greater adoptability and solubility for the different additives used for the slurry preparation, than a slurry composed of single solvent. Further more adsorption of dispersant molecules can be optimized by using a binary or ternary solvent system[7]. The dispersability of particles in the liquid has been well studied using sedimentation height and sediment density. The good dispersion is evaluated by slower rate of settling of the particles and higher final sediment density. The state of particle dispersion has a very sensitive role in rheological properties of the slip[8]
Realizing the importance of dispersion of nano $BaTiO_3$ powders for tape casting, the influence of different parameters such as the type of solvent system (binary solvent mixtures namely, toluene-ethanol, methyl ethyl ketone-ethanol and xylene-ethanol on the dispersability of $BaTiO_3$ powders with different types of dispersants namely, triton x-100 and phosphate ester, concentrations of dispersant and solid loading on $BaTiO_3$ slip viscosity and the properties of green tape were studied. Poly vinyl butyral was used as binder as well as dispersant. Dibutyl phthalate and polyethylene glycol as plasticizer. This study also involves the rheological behaviour of slurry.

2. EXPERIMENTAL PROCEDURE

2.1 Powder synthesis and characterization techniques

Barium titanate powders are synthesized by wet chemical method (polymeric precursor method). The titanium solution was prepared by dissolving titanium tetraisopropoxide (Aldrich 97%) to a solution of citric acid (SRL, 99.5%) and ethylene glycol (SRL, 98%), mixed in a molar ratio of 1:4. The required quantity (Ba: Ti=1:1) of $BaCO_3$ (Qualigens, 99%) was dissolved in this solution. This solution was heated at 90°C with a constant stirring until it became clear transparent yellow solution. This solution was heated at 200°C for 5 hrs in an oven to promote polymerization and remove solvents. With continued heating at this temperature the solution became more viscous with a change in color from pale yellow to brown, but without any visible formation of precipitation or turbidity and finally solidified into dark brown, glassy resin. Charring the resin at 400°C for 2 hrs in an electric furnace resulted in a black solid mass, which was lightly ground into a powder, using Agate Mortar and pestle. This powder after heat treating at 900 °C in air for 5 hrs, in Al_2O_3 boat gives barium titanate powder.

2.2. Dispersability studies with different solvent mixtures

The dispersability of Barium titanate nanocrystalline powder particle in three selected Binary systems, viz., azeotrophic mixtures of Toluene-Ethanol, Methyl ethyl Ketone -Ethanol and zeotrophic mixture of Xylene-Ethanol was studied by conducting sedimentation tests on 3.3 vol % suspensions of powders. Suspensions were prepared by maintaining constant volume of solvent mixtures in three cases. Glass measuring cylinder of 10 ml volume with stopper is used to avoid evaporation of solvents from the suspension. The cylinder is well shaken and ultra sonicated for 5 min to break up the soft agglomerates of ultrafine barium titanate. Sediment height was recorded at definite intervals from the interface between the dense sediment and supernatant solvent. The sediment density was calculated by H/H_o (the ratio of instantaneous sediment height to initial height). The variation of sediment density as a function of time was found.

2.3 Dispersability studies with different solvent mixtures with different dispersants

$BaTiO_3$ powders suspensions with three solvent mixtures of same volume (3.3 vol%) are prepared. Two selected dispersants (0.5%) were added to each suspension separately and 30 min was allowed for the dispersant to adsorb on the particle surface. Then the sedimentation height was recorded at regular intervals of time. The variation of value of H/H_o as a function of time was found.

2.4 Fabrication of green tapes using different solvent systems

Ceramic slurries were made from barium titanate with mean particle diameter of 30 nm (grains are spherical) and organic components; three selected Binary solvent systems, viz., azeotrophic mixtures of Toluene-Ethanol, Methyl ethyl Ketone-Ethanol and zeotrophic mixture of Xylene-Ethanol, Triton X and phosphate ester as dispersants, Polyvinylbutyral (PVB) as binder and the plasticizers polyethylene glycol (PEG) and dibutyl phthalate (DEHP). Each run of the suspensions was prepared in three steps. In the first one the powder is immersed in the solvent and the dispersant is mixed in. When a homogeneous mixture is obtained and particles are appropriately repelled, the plasticizers and binder are added as the second step. The order of addition of the components is critical; the dispersing agent must be added before the other organic compounds to prevent competitive adsorption onto the particle surface. In the first phase $BaTiO_3$ powder, solvent and dispersant were homogenized in a plastic mill for 12 h, after that in the second phase, binder and plasticizer were added and homogenized for another 12 h. The order of addition of each component influences dispersion of particles in the slip and, thereby, slip viscosity. In the third phase the slip was aged for 12 h without milling.

The optimal concentration of dispersant was determined from the minimum slip viscosity. Viscosity measurements were performed using Brookfield viscometer, HBTDV-11CP) at shear rates up to 750 s^{-1}.

Preliminary experiments on the slip viscosity and adherence of green tape to a casting carrier film were conducted to determine the minimum and maximum concentrations of PVB, DEHP and PEG. The criterion for the minimum and maximum concentrations was a slip viscosity at about 1 Pa s, which from our experience is an adequate viscosity for tape casting with a suspension prepared from a $BaTiO_3$ powder of 30 nm spherical particles. The second criterion was the easy release of the green tape from the carrier substrate

3. RESULTS AND DISCUSSIONS

3.1 Dispersability studies with different solvent mixtures

The sedimentation height as a function of time in 3.3 vol% barium titanate suspensions of three selected solvent systems without dispersant is shown in Fig 1. For better dispersability the suspension should have longer settling time and higher sediment density represented by lower H/H_o value. MEK-ethanol almost remains constant and gives lower sediment density. Xylene-ethanol and Toluene-ethanol shows gradual decrease in initial settling time but Toluene-Ethanol leaves lower sediment density whereas Xylene-ethanol shows higher sediment density.

3.2 Dispersability with different dispersants

Figs 2-4 shows the dispersability of 3.3 vol% $BaTiO_3$ powder suspensions in three selected solvent systems (Toluene-Ethanol, Methyl ethyl Ketone-Ethanol and Xylene-Ethanol) with two dispersants Phosphate ester and Triton X. From which it has been inferred that phosphate ester with xylene-ethanol combination shows better dispersion characteristics than other systems. As suggested by Parish[8], the intensity of the interactions between organic functional groups and $BaTiO_3$ were expressed by Alcohol > Ester > Ketone > Hydrocarbon. If the $BaTiO_3$ surface is regarded as alkaline, the adsorption of electron accepting liquids onto the surface may be regarded as an acid base reaction. Like wise if the $BaTiO_3$ surface is regarded as acidic, electron donating liquids may adsorb on the surface with a similar type of acid base reaction. Alcohols may behave both as Lewis base or a Lewis acid depending upon their position and their associated / dissociated form. Alcohol have an oxygen with an attached hydrogen which are Lewis base and acid atoms, respectively, only slightly hindered by the hydrophobic section of the molecule. Therefore alcohols are good hydrogen bonding molecules. Carbonyl groups have double bonded oxygen, resulting in the oxygen's lone pairs being more accessible for bonding. Hydrocarbon has no functional groups yet the Pi bonded electrons in an aromatic ring are available for donation as a Lewis acid [8]. Thus ethanol has greater interaction also it has strong hydrogen bonding capacity hence it has strong preference to $BaTiO_3$ surface. In Methyl ethyl ketone-ethanol system, since Methyl ethyl ketone is weakly polar, the solvents Methyl ethyl ketone, ethanol and dispersant competes for the oxide surface. In the other two systems, toluene and xylene are non polar hence only ethanol and dispersant competes for the oxide surface i.e., the adsorption effect of the dispersant are given preference[9].

In all the solvent systems, phosphate ester shows better dispersability than Triton X. There are two main mechanism of dispersion as electrostatic repulsion and steric hinderance[4]. Triton x-100 has large molecular size and longer chain hence seems to have steric hinderance. Phosphate ester undergoes electrostatic repulsion mechanism. The free photons liberated during dissociation of the phosphate ester are subsequently adsorbed onto the $BaTiO_3$ surface making it positively charged. The anionic end of the amphipathic phosphate ester is attracted to the positively charged oxide surface by the coulombic forces. The non polar hydrocarbon tail extends into the non polar organic medium[10].

3.3 Optimization of Concentration of Dispersants

Figs 5-7 shows the variation of slip viscosity with percentage of dispersants in three different solvent systems. The concentration of $BaTiO_3$ powder in the homogenized slip was kept constant for all the systems as 62 wt%. The minimum slip viscosity for three selected Binary solvent systems, viz., azeotrophic mixtures of Toluene-Ethanol, Methyl ethyl Ketone-Ethanol and zeotrophic mixture of Xylene-Ethanol with Triton X was found to be 0.5 wt%, 1.5 wt% and 0.8 wt % respectively. The concentration of dispersants varies for different solvent system.

3.4 Viscosity of the slurry

The rheological behaviour of the tape casting slurry is shown in Fig 8. Its given by change of viscosity with the shear rate. As shear rate increases, the viscosity decreases, indicating the shear thinning behaviour of the slurry, which is desirable to have the dimensional accuracy. As close dimensional tolerance has to be maintained for all electronic devices.

3.5 Comparative study of green tapes

The green tape made using Xylene-ethanol solvent system with Phosphate ester dispersant gives better tapes than other systems which supports the initial dispersion studies. Adhesion is characterized by visual inspection marking poor when its impossible to release the tape and very good when its easily removed[11]. The tape green density was measured on three samples from the same tape with volume and weight measurements and the mean value of the three measurements was calculated[12]. The viscosities of all the suspensions were measured immediately after suspension preparation.

4. CONCLUSION

Of all the dispersion studies conducted Phosphate ester was found to be the best dispersant and among the three solvent systems, Xylene-ethanol is better than other systems. The slip prepared for tape fabrication showed shear thinning behaviour. Visual inspection of adherence, tape green density and solid content of the green tapes supported the dispersion studies.

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TABLE

Table 1 Comparison of green tapes with phosphate ester in different solvent system

Parameters	Toluene-ethanol system (32:68)	Xylene-ethanol system (65:35)	Methyl ethyl ketone-ethanol system (60:40)
Green Density (g/cc)	3.29	3.45	3.27
Solid Loading	61	62.5	61.5
Adherence	Good	Very good	Good
Strength	Good	Very good	Poor
Flexibility	Low	Very good	good
Viscosity	0.1051	0.0658	0.1325

FIGURES

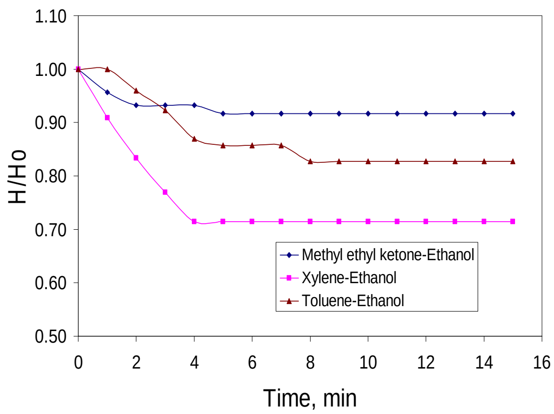

Fig.1 Dispersability of $BaTiO_3$ powder in different solvent systems.

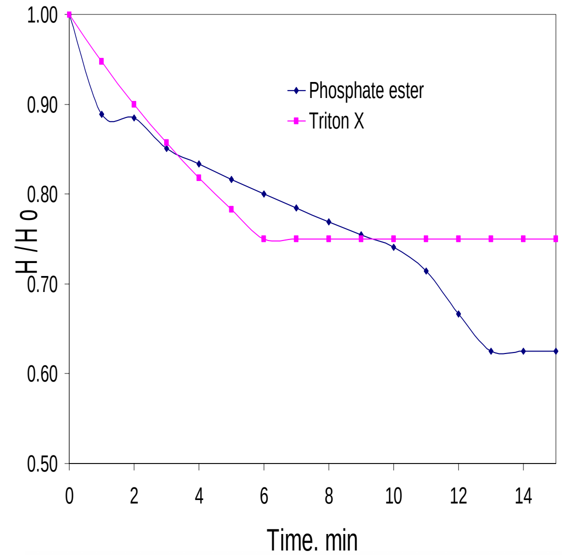

Fig 2 Dispersability of $BaTiO_3$ powder in Methyl ethyl Ketone-Ethanol System with different types of dispersants

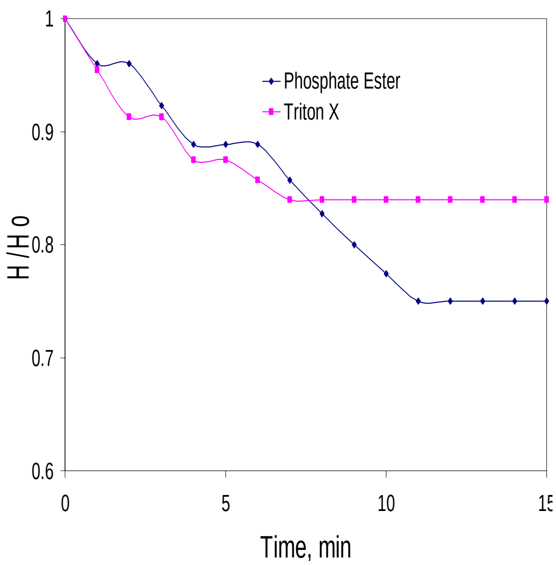

Fig 3 Dispersability of $BaTiO_3$ powder in Toluene-Ethanol System with different types of dispersants

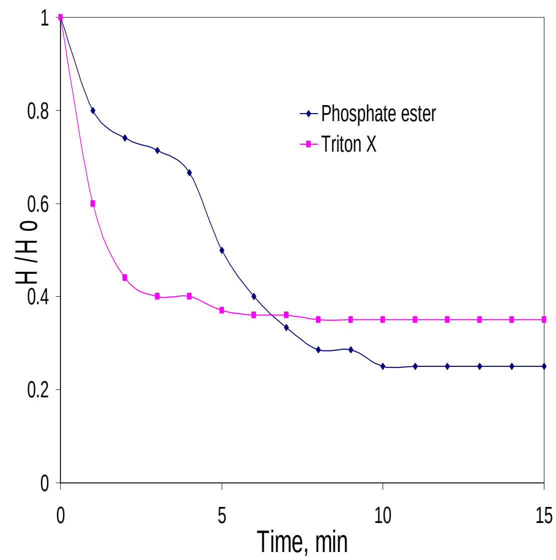

Fig 4 Dispersability of $BaTiO_3$ powder in Xylene-Ethanol System with different types of dispersants

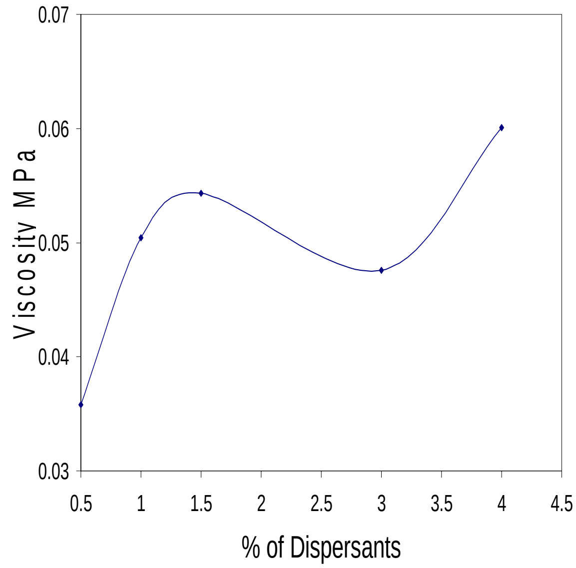

Fig. 5 Viscosity of Toluene-Ethanol Slurry System

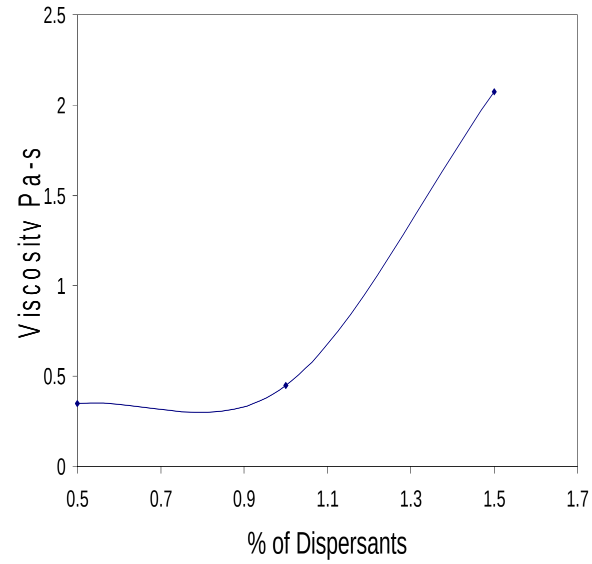

Fig. 6 Viscosity of Xylene-Ethanol Slurry System

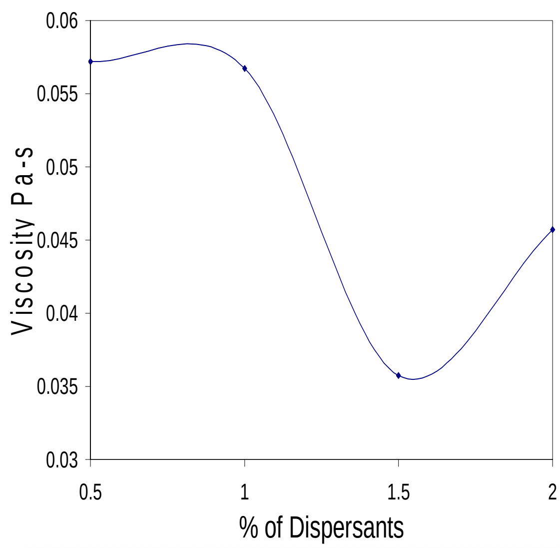

Fig 7 Viscosity of Methyl ethyl Ketone-Ethanol Slurry System

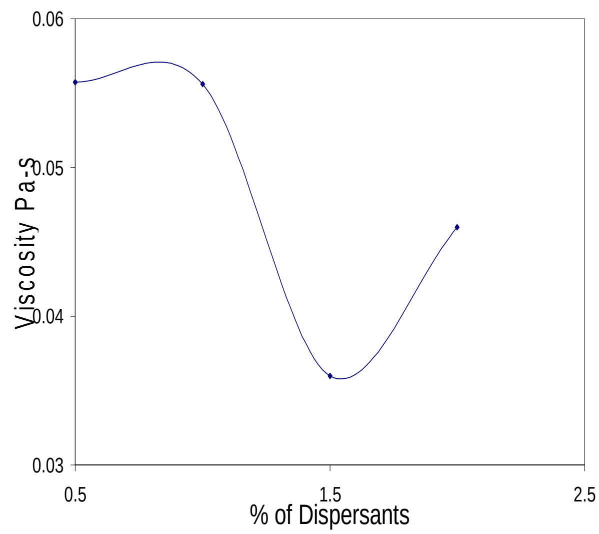

Fig 8. Viscosity vs Shear rate for $BaTiO_3$ slurry for different solvent systems