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Tape casting of PLZST tapes via aqueous slurries

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Abstract

A well-dispersed aqueous slurry for tape casting of PLZST ($Pb_{0.97}La_{0.02}Zr_{0.66}Sn_{0.23}Ti_{0.11}$) was prepared. Properties of PLZST slurries with and without polyelectrolyte dispersant were characterized by zeta potential, sedimentation etc. The experimental results show that the pH value of the slurries is changing with ball-milling time, and that the polyelectrolyte dispersant has a significant effect on the isoelectric point of PLZST. TGA analysis indicates that the organic additives in the green tapes can be completely removed by heat treatment at 600 °C. The density of PLZST ceramics is tightly related to the plasticizer and the sintering temperature. However, the results demonstrated that it is possible to prepare a dense PLZST thick film through aqueous slurry tape casting.

Keywords: Density; PLZST; Slurry; Tape casting

1. Introduction

Tape casting is a convenient and highly useful method for the large-scale preparation of ceramic substrates, capacitors, and multilayered structural composites for various applications. Tape casting has been used to produce many materials such as Al_2O_3[1–3] and AlN[4] substrates, $BaTiO_3$ capacitors,[5,6] solid electrolytes,[7] solid oxide fuel cells,[8,9] lead zirconium titanate ceramic sheets and is well established in industrial practice since a long time.[10,11] Tape casting also has been utilized recently to design laminated structural ceramics with improved mechanical properties.[12–14] In the past, the traditional tape casting focussed on systems based on organic solvents system due to the their low latent heat of evaporation and low surface tension. Recently, with the development of aqueous slurry additives, such as highly effective dispersants, binders etc., it became possible to achieve a high solid loading and proper dispersion with aqueous ceramic slurries. Therefore, more effort has been addressed to the development of aqueous tape casting processing because of safety, environmental, and cost considerations.[15] As well, a large effort has been undertaken to understand the stabilizing mechanisms and properties of ceramic powder suspensions,[16–24] This knowledge allows to prepare high quality slurries for tape casting.

The preparation of slurries for tape casting is closely coupled with the effectiveness of the selected dispersant, the properties of ceramic powders, organic additives, etc. Each of them can affect the properties of ceramic tapes such as thickness, surface quality, microstructure, and porosity. The current work focuses on the preparation of well-dispersed PLZST ceramic slurries for tape casting. The relationship between organic additives and the zeta potential as well as the sedimentation behavior of PLZST slurries was investigated. Furthermore, the relation between the density of the PLZST ceramics and the sintering temperature was investigated.

2. Experimental

2.1. PLZST powder preparation

Since PLZST (Lanthanum-doped Lead Zirconate Titanate Stannate) powder is not commercially available, the powder preparation was performed in our laboratory. Fig. 1 displays the ternary phase diagram for the $La_{0.02}$ doped PZST system at room temperature. A composition (C_5) near the antiferroelectric/ferroelectric morphotropic phase boundary was chosen for this study. PLZST C_5 powder was prepared by a mixed-oxide process. First, appropriate amounts of reagent

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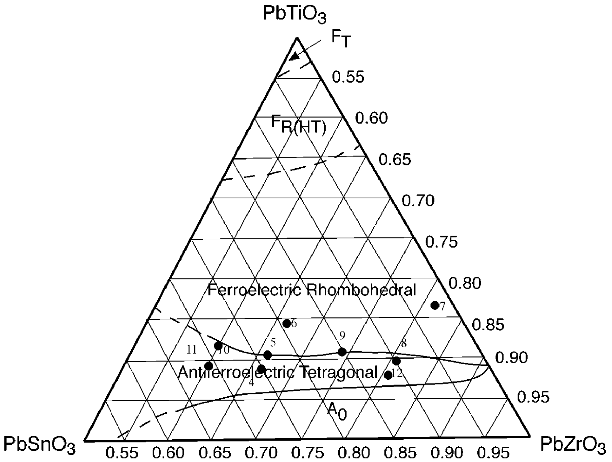

Fig. 1. The ternary phase diagram for the $La_{0.02}$ doped PZST system.

grade raw oxides were weighted, namely lanthanum oxide (La_2O_3), lead oxide (PbO), zirconia (ZrO_2), tin oxide (SnO_2) and titanium dioxide (TiO_2) with a chemical purity >99%. The powder was attrition milled for 3 h using zirconia as a milling medium at 1000 PMR and subsequently calcined at 740 °C for 2 h after evaporation of the solvent. The calcined PLZST powder was again attrition milled under the same conditions to improve the particle size distribution. The average particle size and the specific surface area were measured to be 0.52 μm and 11.62 m^2/g, respectively, using the Mastersizer 2000 (Malven Instruments Ltd., Malven, Worcestershire, UK). In this study, a water soluble diblock copolymer polyelectrolyte, poly[(methacrylic acid)-b-(ethylene oxide)], [P(MAA-b-PEO)] was chosen as a dispersant to prepare PLZST slurries. Glycerin and polyethyleneglycol (PEG) were selected as plasticizers. In order to achieve a more uniform slurry, the binder, polvinylalcohol (PVA), was pre-dissolved in water by heating up to 80 °C for 10 h and stirring to assure complete dissolution.

2.2. Zeta potential measurement

The zeta potential was determined with a Zetasizer 300HS (Malven Instruments Ltd., Malven, Worcestershire, UK) by measuring the electrophoretic mobility of the particles using 0.001M KCl as the electrolyte. PLZST powder was dispersed in an ultrasonic bath for 5 min to break up soft agglomerates before the measurement. The pH value of the slurry can be automatically adjusted through addition of 0.25 M KOH and 0.25 M HCl by the Zetasizer 300HS.

2.3. Sedimentation experiments

The sedimentation experiments were conducted by adjusting the pH value and dispersant concentration, respectively. PLZST powder was first shake-milled for 4 h in double-distilled water. The slurries were then stored in a closed glass tube after adjusting the pH and dispersant concentration and placed in a water bath for ultrasonication for 5 min to break up soft agglomerates. The slurries were finally allowed to settle and the sedimentation height was recorded.

2.4. Slurry preparation and tape casting

Slurry preparation can be divided into two steps: PLZST powder, dispersant, and water were first shake-milled in a plastic jar with zirconia media for 24 h, the slurry was then shake-milled for another 24 h after adding binder and plasticizer. The slurries were de-aired in vacuum to remove entrapped air bubbles and cast on a glass substrate. The cast tapes were naturally dried at 25 °C. A typical composition of the slurries is listed in Table 1.

2.5. Tape characterization

The burn-out characteristics of organic additives in the tape was conducted by TGA. Microstructure and phase analysis were carried out by SEM and XRD, and the density of the cast tape was measured by Helium pycnometry.

3. Results and discussion

3.1. Zeta potential measurement

Fig. 2 shows the zeta potential of the raw materials (SnO_2,TiO_2, PbO, and ZrO_2). Their isoelectric points (IEP) and zeta potentials are different due to the powder surface properties. Fig.3 provides the zeta potential of PLZST with and without dispersant addition. It is clear that PLZST powder has three isoelectric points, which are located at 3.9, 6.5 and 7.7, respectively. The first one (3.9) is within the range of those of SnO_2 TiO_2 and ZrO_2. The zeta potential of PLZST slurry with 0.15 wt.% dispersant addition strongly differs from the slurry without dispersant addition. Especially, there is only one IEP at pH = 3.1, being in the same range. The

Table 1
Formulation of the water-based C_5 slurry used for the production of PLZST tapes

Additives	Function	(wt.%)
PLZST (C_5)	Powder	55.2
P(MAA-b-EO)	Dispersant	1.50
PVA	Binder	6.98
PEG	Plasticizer	5.29
Water	Solvent	30.81
Agitan 280	Defoamer	0.22

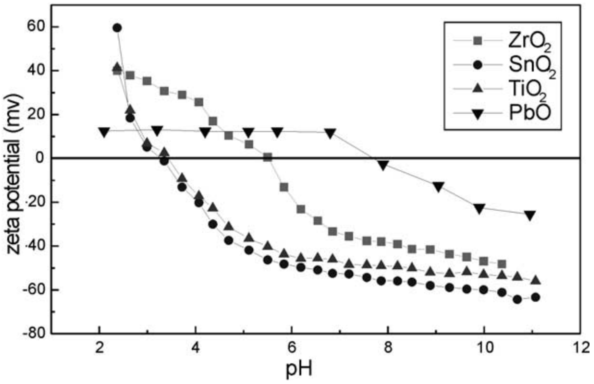

Fig. 2. The zeta potential of the raw materials.

two higher IEP values are due to the modification of the surface of PLZST in aqueous solutions.

Experiments on the leaching of powders showed that the lead ion concentration in the solvent exceeds the concentration of the other metallic ions by far.[25] Furthermore, the lead ion concentration depends strongly on pH.[25] At low pH, the powder surface has been found to be more or less free of lead and, thus, dominated by zirconium, tin and titanium. If the pH is increased, excess lead ions are adsorbed on the powder surface. The modified surface with high lead concentration is associated with the isoelectric point at pH = 7.7, which is very near to the IEP of pure PbO powder. The behavior was also obversed for barium titanate.[26]

Since the chemical composition of the surface depends on pH, the zeta potential needs to rise from negative to positive values between the first and the third IEP. This explains the appearance of the third IEP at pH = 6.5. The addition of dispersant will influence the zeta potential of PLZST particles (Fig. 3). Polyelectrolyte-type dispersant will adsorb on the particle surface, which means that the structure of the original double layer will be changed completely.

With polyelectrolytes, the insolubility in aqueous solution is strongly dependent on the pH. It was reported[27] that P(MAA-b-PEO) precipitates at pH < 3, while it completely dissolves if the pH is above 3. The degree of ionization of the dispersant is also tightly related to the pH. Since the PMAA block behaves to the polymer as a weak polyelectrolyte with a pK_a of the acid groups of about 4.8, it is completely protonated at < pH 3.4. It starts to be negatively charged at pH > 4.8 and is completely dissociated at pH > 8.5 in salt-free solution.[28]

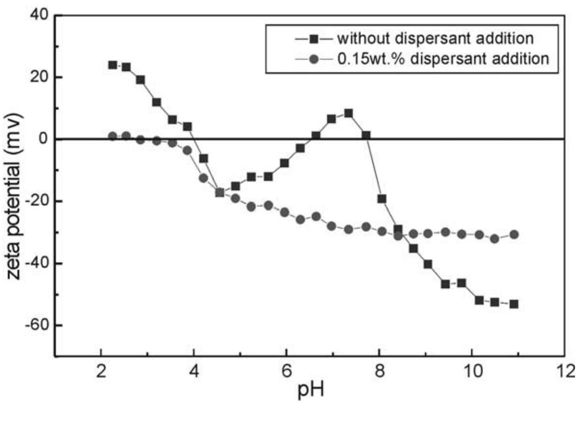

Fig. 3. Zeta potential of PLZST with and without dispersant addition.

Apart from the adsorption and the degree of ionization of the dispersant, the conformation of the adlayer can affect the dispersibility. At high pH, the adsorbed dispersant is highly charged with a more stretched conformation, resulting in an increase in the steric length and a strong repulsion of PLZST particles. At low pH value, the dispersant chains relax into a highly coiled conformation with a low electrosteric repulsion. According to the literature, a zeta potential of 25 mV is a prerequisite to minimize coagulation by means of electrostatic repulsion.[27] However, a slurry with a polyelectrolyte dispersant, which provides an extra steric stabilization, can be stabilized at lower zeta potential.

Fig. 4 shows the influence of the ball milling time on the pH of the slurry. The pH of the slurry without the addition of dispersant increases and reaches a nearly constant level with the leaching and re-adsorption of ions, reaching a balance with increasing ball milling time.

3.2. Sedimentation test

The dispersibility of PLZST powder with and without dispersant addition was characterized by sedimentation experiments. A well-dispersed slurry settles slowly with time, leading to high sedimentation height and high density. On the other hand, a poorly dispersed slurry will rapidly settle and the sedimentation density will be low. Fig. 5 indicates the effect of pH on the sedimentation height of slurries without dispersant. The results show that PLZST powder is hardly dispersed at low pH, since the density of PLZST is leading to fast sedimentation. At pH 1.5–4.5, the slurries settle almost

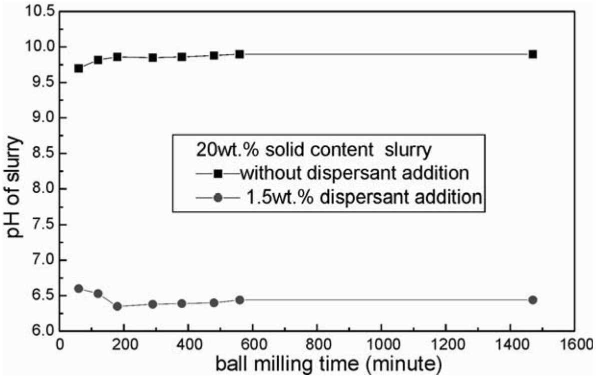

Fig. 4. The relation between the pH of the slurry and the ball milling time.

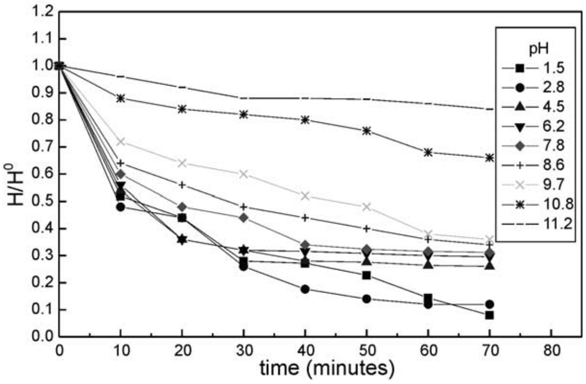

Fig. 5. The effect of pH on the sedimentation height of slurries without dispersant addition.

totally within 40 min, such that it is impossible to get well-dispersed PLZST slurries through adjusting the pH only.

Fig. 6 shows the effect of the dispersant concentration on the sedimentation height of the slurries. The results show that P(MAA-b-PEO) is a very efficient agent for the dispersion of water based PLZST slurry. When the concentration is as high as 1.25 wt.%, the sedimentation height has a tendency to decrease with rising concentration of the dispersant. This means that further addition of dispersant in excess of 1.25 wt.% deteriorates the quality of the slurry.

3.3. TGA analysis

During removal of the organic additives, the organic additives in the tape decompose or degrade, releasing a large amount of gas. When the heating rate is too rapid, the green tapes may easily form cracks or bubbles. Therefore, the binder removal process was monitored by TGA. Fig. 7 shows the TGA curves of two green tapes in air atmosphere containing two different kinds of plasticizers.

Apparently, the binder removal behavior of both different kinds of tapes was quite similar. It differs only because of differences in the content of organic additives. Since the tapes were dried naturally, there was a small amount of remnant water in the tapes which caused the weight loss from room temperature to 120 °C. The weight loss at ~125 °C in the present study resulted from the decomposition of organic additives such as PEG and PVA. When the temperature exceeds 600 °C, no further weight change was observed since all organic additives were burnt out. The weight loss above 870 °C was caused by the evaporation of PbO. Following these results, in this study, the binder was removed at a rate of 1 °C/min in air atmosphere up to a maximum temperature of 600 °C, and that temperature was maintained for 2 h to ensure that all of the organic additives were completely removed.

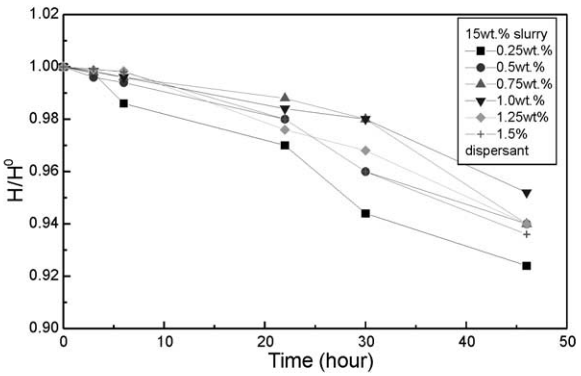

Fig. 6. Relation between the concentration of dispersant and the sedimentation height of slurries.

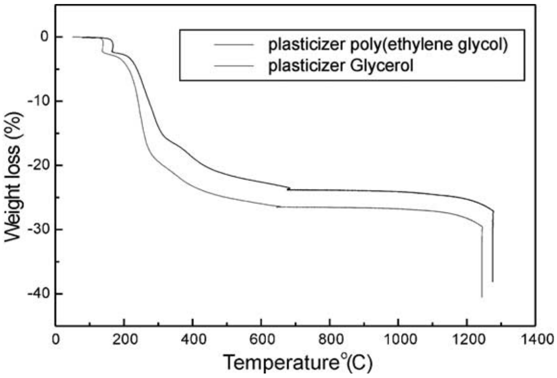

Fig. 7. TGA curves of the green tapes in air atmosphere.

3.4. Density and microstructure

Fig. 8 shows an example of PLZST green tape produced. The tape exhibits excellent flexibility. It can be rolled without any mechanical damage. After binder removal in air, the green tapes were moved to a tube furnace and sintered in oxygen atmosphere. Table 2 shows the densities of C_5 ceramics obtained with differ-

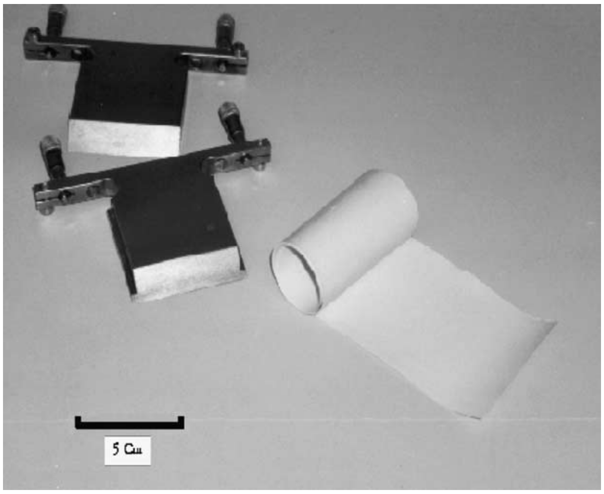

Fig. 8. Tape-cast PLZST green tape.

Table 2
Density of C_5 with different plasticizer (g/cm^3)

Temperature (°C)	PEG	Glycerol
1200	8.034	7.793
1250	8.0850	7.836
1300	8.1428	8.055

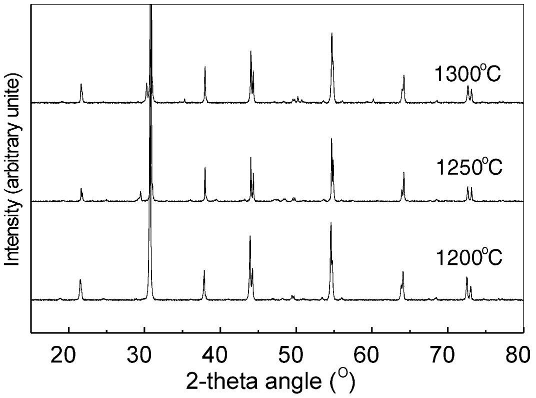

Fig. 9. XRD diffraction patterns of PLZST sintered at different temperature.

ent sintering temperatures. The density increases with the sintering temperature. The tapes with PEG poly(ethylene glycol) reach a somewhat higher density. A potential explanation for this effect is the ability of glycerin to absorb water, resulting in a lower density of the green tapes and by that of the sintered samples. Fig. 9 shows XRD diffraction patterns of PLZST sintered at different temperatures. The results indicate that the binary oxides have completely reacted to PLZST. Fig. 10 provides SEM micrographs of PLZST sintered at 1250 °C. Both surface of the sintered tapes and fracture surface show that the tapes have a very uniform microstructure.

4. Conclusions

Tape casting was successfully used to produce PLZST tapes through water-based slurries. Zeta potential measurements show that PLZST has three isoelectric points (IEP) due to the complex powder composition. However, PLZST with dispersant addition has only one IEP point. Sedimentation experiments show that pure adjustment of pH is insufficient to get a stable PLZST slurry, since PLZST powder has a high density, such that the powder rapidly settles down within several hours. The dispersant P(MAA-b-PEO) shows a high efficiency for the dispersion of PLZST via electrosteric repulsion. TGA analysis shows that the organic additives can be completely removed at about 600 °C, and the cast PLZST tape can be sintered to nearly full density. SEM micrographs exhibited that the cast tape has a very uniform microstructure. The results show that water-based tape casting can be used to produce high quality dens PLZST tapes.

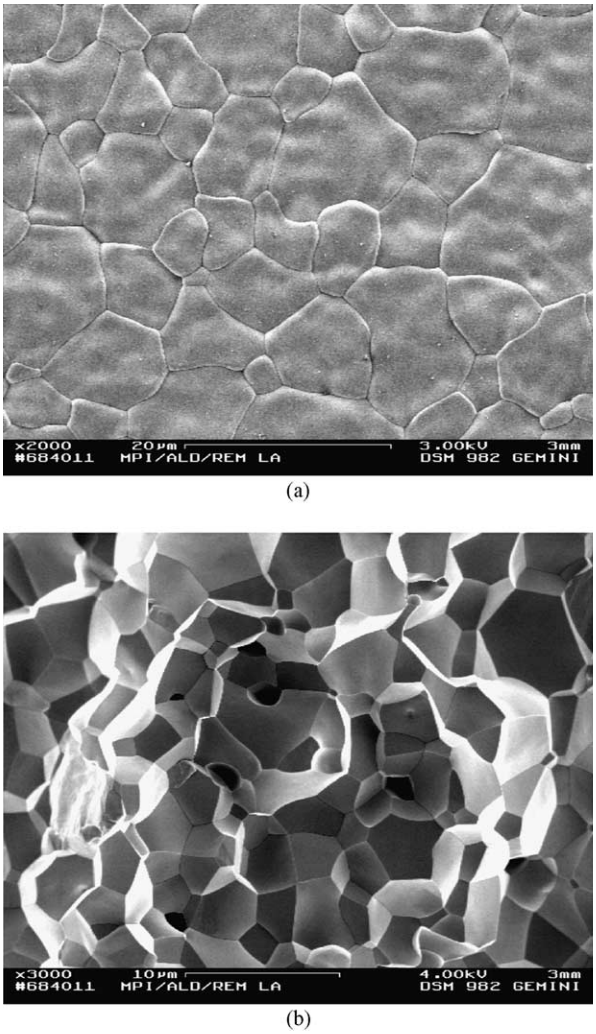

Fig. 10. SEM micrographs of PLZST sintered at 1250 °C (a) surface of the as-sintered tape (b) fracture surface.

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