

Available online at www.sciencedirect.com





Journal of the European Ceramic Society 28 (2008) 2597-2604

www.elsevier.com/locate/jeurceramsoc

Effect of organic additives on the zeta potential of PLZST and rheological properties of PLZST slurries

Yu-Ping Zeng^{a,b,*}, Andre Zimmermann^b, Fritz Aldinger^b, Dongliang Jiang^a

^a Shanghai Institute of Ceramics, Chinese Academy of Sciences, Ding-Xing Road 1295, Shanghai 200050, PR China ^b Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, Heisenbergstr. 3, D-70569 Stuttgart, Germany

> Received 15 December 2007; received in revised form 19 March 2008; accepted 28 March 2008 Available online 19 May 2008

Abstract

In order to investigate the effect of organic additives on the zeta potential of PLZST ($Pb_{0.97}La_{0.02}Zr_{0.66}Sn_{0.25}Ti_{0.09}$), the zeta potential of PLZST powder with addition of dispersant, binder, plasticizer were performed. The experimental results indicated that the zeta potentials of PLZST without any organic addition were tightly related to the titration sequence and their IEPs (isoelectric point) were also not constant. The zeta potentials of PLZST with organic additives were strongly dependent on the structure, polarity and weight of the added organic additives. The dispersant did not greatly reduce the zeta potential of PLZST due to its good polarity and ionization. Compared to the IEP of PLZST without dispersant addition, the IEP of PLZST with dispersant addition switched from 8.7 to 3.5. The zeta potential of PLZST mixed with dispersant, binder and plasticizer addition was dominated by the dispersant. pH variation has great effect on the viscosity of PLZST slurries without organic addition; however, pH variation did not show an obvious influence on the viscosity of PLZST slurries with organic additives.

Keywords: Slurry; Zeta potential; Isoelectric point; Viscosity; Sedimentation; Organic additives; PLZST

1. Introduction

(Pb,La)(Zr,Ti)O₃ and other lead zirconate titanate (PZT) type materials are widely used in actuators, ultrasonic transducers, and sensors because of their excellent piezoelectric properties. Recently, the thick film ceramic preparation processes, such as, screen printing, tape casting have been used to prepare PZT and related materials.^{1–5} Tape casting is a convenient and useful method for the large-scale preparation of ceramic substrates, capacitors, and multilayered structural composites for various applications, such as: Al₂O₃,^{6,7} AlN^{8,9} substrates, BaTiO₃ capacitors,^{10,11} solid electrolytes,^{12–14} solid oxide fuel cells,^{15–20} or PZT and PZST ceramic sheets.^{21–25} In the past, the traditional tape casting focused on organic solvent systems due to their low latent heat of evaporation and low surface tension. Recently, more effort has been concerned to the development of aqueous tape casting process because of safety, environmen-

Tel.: +86 21 52415203; fax: +86 21 52413903.

tal, and cost considerations.²⁶ Regardless of non-aqueous and aqueous slurries, a well-dispersed and stable slurry is a very important guarantee for preparation high quality ceramic parts via slurry processing.

According to the DLVO theory, which was developed by Verwey and Overbeek,²⁷ the stability of aqueous slurries can be controlled by adjusting the surface charge of suspended ceramic particles, resulting in the mutual repulsion or attraction of ceramic particles. Therefore, the dispersibility of a ceramic slurry can be adjusted via the pH value and ionic strength of slurry. However, it is hardly possible to provide sufficient electrostatic repulsion energy in non-aqueous system so that a well-dispersed slurry can be received. In order to improve the dispersibility of ceramic particles, especially for non-aqueous ceramic slurries, a charged polymer with high molecular weight, a so-called polyelectrolyte, which can provide the "electrosteric" stabilization for both aqueous and non-aqueous ceramic slurries, is widely used in slurry processing. Polyelectrolyte dispersants have been widely offered to disperse Al₂O₃, ZrO₂, PZT and other ceramic slurries.^{28–31} Apart from the polyelectrolyte, many other organic additives, such as plasticizer, binder, defoamer, etc. are often used to modify the properties of slurries.

^{*} Corresponding author at: Shanghai Institute of Ceramics, Chinese Academy of Sciences, Ding-Xing Road 1295, Shanghai 200050, PR China.

E-mail address: yuping-zeng@mail.sic.ac.cn (Y.-P. Zeng).

^{0955-2219/\$ -} see front matter © 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.jeurceramsoc.2008.03.043

Several works focusing on the effect of the dispersant on the zeta potential have been reported.^{32–35} However, the PLZST ceramic slurry for tape casting contains several kinds and a large amount of organic additives, which would have great effects on the dispersibility and stability of the PLZST ceramic slurries for tape casting. Compared to other ceramic powder, PLZST powder is easy to leach ions during slurry preparation. The leaching ions are also have great effect on the zeta potential of PLZST particles and the stability of slurry. Therefore, the effects of dispersant, binder, plasticizer on the zeta potential of PLZST powder and their rheological properties should be investigated to get the well-dispersed and stable PLZST slurries so that the high density and uniform sintered PLZST tape can be received. In this work, we will investigate the effect of dispersant, binder, plasticizer and their mixture on the zeta potential of PLZST slurries and their rheological properties.

2. Experimental procedure

2.1. PLZST powder preparation

PLZST (lanthanum-doped lead zirconate stannate titanate) powder is not commercially available; the powder preparation was performed in our laboratory. The composition of Pb_{0.97}La_{0.02}Zr_{0.66}Sn_{0.25}Ti_{0.09} was selected in the experiment. First, appropriate amounts of reagent grade raw oxides, lead oxide (PbO), zirconia (ZrO₂), tin oxide (SnO₂) and titanium dioxide (TiO₂) were weighted. 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 0.51 μ m and 11.62 m²/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. Polyethyleneglycol (PEG) was selected as plasticizer, and polyvinyl alcohol (PVA), was selected as binder. Fig. 1 shows the molecular structure of the organic additives.

2.2. Zeta potential measurement

The zeta potential was determined with a Zetasizer 3000HS (Malven Instruments Ltd., Malven, Worcestershire, UK) by measuring the electrophoretic mobility of the particles using 0.001 M KCl as the electrolyte. After adding the organic additives, 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 3000HS.

2.3. Sedimentation experiments

The sedimentation experiments were conducted by adjusting the pH value and dispersant concentration, respectively. PLZST



Fig. 1. The molecular structure of organic additives (1) binder (2) plasticizer (3) dispersant.

powder was first shake milled for 6 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 5 min to break up soft agglomerates. Each cell was then capped to minimize solvent loss during the experiment. The slurries were finally allowed to settle, and the sedimentation height was recorded.

2.4. Rheological properties

The rheological properties of the PLZST slurries were studied using the rheometer RheoStress 1 (ThermoHaake, Karlsruhe, Germany). The apparent viscosity was measured as a function of shear rate.

3. Results and discussion

3.1. Variation of the ionic concentration and pH value of PLZST during ball milling

Fig. 2 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 when the leaching and re-adsorption of ions reaches a balance with increasing ball milling time. With 1 wt.% dispersant, the pH of



Fig. 2. Relation between the pH value of slurry and ball milling time.

the slurry decreases to 7.1 since the dispersant is a weak acidic organic compound, and the pH further decreases and reaches a balance with ball milling time. The results indicated that the pH variation of the slurry was influenced by the leaching of metal ions from the powder surface. Normally, the ceramic powders have amphoteric surfaces which can develop a negative or a positive surface charge during long time ball milling in water, resulting in the variation of the pH and the ionic strength of slurry. The free metal ions in the slurry can also hydrolyze to form hydrated cations or hydrated anions with the variation of the pH of the slurry. The variation of pH induced precipitation or dissolution of metal ions from the powder surface. For different compounds, their solubility product constants are different; therefore, the ionic concentration is totally different and is also strongly dependant on the pH of the slurry. Fig. 3 is the pH dependence of the metal ionic concentrations in the 5 vol.% aqueous PZST slurry after 24 h mixing at room temperature.³⁶ It is clear that the ionic concentration of Ti⁴⁺, Zr⁴⁺, and Sn⁴⁺ is relatively small and it is not sensitive to the variation of the pH. However, the ionic concentration of La³⁺ and Pb²⁺ is much higher than that of other ions, and it depends also on pH. In fact, the surface composition of PLZST powder is very complex due



Fig. 4. The zeta potential of the raw materials.

to PbO evaporation and condensation during powder calcination, the surface of PLZST powder is PbO enriched, which is condensed from PbO atmosphere during cooling down, PbO can also react with CO_2 in the air and form PbCO₃ on the particle surface. Therefore, the ion leaching from the powder surface is a very complex process.

3.2. Zeta potential of powder without any organic additives

Fig. 4 shows the zeta potential of the raw materials $(SnO_2,$ TiO₂, PbO, and ZrO₂ and La₂O₃). Their isoelectric points (IEP) and zeta potentials are different due to the different powder surface properties. A complete zeta potential curve of SnO₂, TiO₂, and ZrO₂ can be easily measured from pH 2 to 11. However, the zeta potential curves of PbO and La2O3 are somewhat different from others. In acid solution PbO exhibits a strong solubility. The adjustment of pH does not seriously affect the Pb²⁺ concentration, resulting in an almost constant potential of PbO in the acidity area. As an alkaline oxide, La₂O₃ easily dissolves in acidic solvent. This is because the zeta potential of La₂O₃ cannot be measured at pH < 6.5. Fig. 5 shows the zeta potential of PLZST with different titration sequences. The results exhibited that the IEPs and zeta potentials are somewhat different. The zeta potential of PLZST was measured by different approaches (1) just mixing the powder with distilled water, followed by titration



Fig. 3. pH dependence of the metal ionic concentrations in 5 vol.% aqueous PLZST slurry after 24 h shaked milling.



Fig. 5. The zeta potential of PLZST powder.

of the slurry whose pH is about 7 to the aimed pH 2 or pH 11, respectively. Finally, the two lines were combined into the whole one. (2) Acid or alkali hydroxide was firstly added to adjust the pH of the slurry to 2 or 11, then the slurry was titrated to pH 11 or 2. The results showed that not only the zeta potential but also the IEPs are different. The reason is that the addition of alkali hydroxide or acid changed the ionic concentration of the slurry and the surface properties of the PLZST particles, resulting in different zeta potential and IEP.

The line A was directly titrated from pH 2 to 11. The abnormal behaviour of the zeta potential observed at pH 2.3-3.4 and 9.8-10.5 can be mainly attributed to the variation of ionic concentration and surface properties of the PLZST particles. The PLZST slurry was firstly adjusted to pH 2, resulting in a large amount of ions leaching from powder surface due to HCl addition, therefore, the metal ionic concentration of the slurry was very high. With pH increase, a high amount of metal ion was deposited on the particle surface as a hydrate, a carbonate, or basic carbonate, etc., which covered the particle surface of the PLZST powder. Therefore, the zeta potential of PLZST was mainly dominated by the properties of the covered compounds. However, the precipitation of metal ions is a very complex process, which is related to a lot of factors, such as pH, specific area of particle, solubility product constant, carbon dioxide partial pressure, temperature, etc. Here, we just discuss Pb²⁺. As shown in Fig. 3, the concentration of Pb²⁺ sharply decreases with an increase of pH. The complex formation between Pb²⁺ and OH^- can form a lot of ions, such as $Pb(OH)_3^-$, $Pb_4(OH)_4^{4+}$, Pb₂OH₃³⁺, Pb₃(OH)₄²⁺ PbOH⁺, Pb₆(OH)₆⁶⁺, and Pb₆(OH)₈⁴⁺ together with dissolved Pb(OH)₂ in solution before precipitation starts.³⁷ Pb(OH)₂ (K_{sp} 1.42 × 10⁻²⁰)³⁸ will precipitate on the particle surface with pH increase. Since PLZST slurry used for the measurement is uncovered in air atmosphere, and CO₂ has high solubility at basic solution, another possibility is that Pb²⁺ transforms into PbCO₃ (K_{sp} 1.46 × 10⁻¹³)³⁸, or precipitates as a basic carbonate of lead 2PbCO₃·Pb(OH)₂. Therefore, the surface properties of PLZST particles are very complex and always change with pH variation. At pH 9.8-10.5, the zeta potential of PLZST decreases with pH increase. The result is quite similar to that of the pure La_2O_3 whose zeta potential is low at the high pH area in Fig. 4. The result suggested that PLZST particle surfaces were covered by La(OH)₃ ($K_{\rm sp}$ 1 × 10⁻²⁰)³⁷ or Lanthanum related carbonate such that the zeta potential is low.

If the PLZST slurry was firstly adjusted to pH 11 and then titrated to pH 2 like line C in Fig. 5, the variation of ionic concentration variation was just reverse, i.e. the concentration of metal ions should be low at high pH area, and it will be generally increased with decrease pH due to PLZST powder dissolution and leaching metal ions from particle surface. The ionic strength was also generally increasing with decreasing pH since the metal ions were always leached from the particle surface. Thus, the PLZST particle surfaces were always fresh so that the abnormal behaviours like line A could not be observed. Line B shows the result for the zeta potential of the PLZST slurry without initial pH adjustment. Since the pH of the PLZST slurry whose pH was about 7.6 was not previously adjusted, there were no too much Pb^{2+} and La^{3+} ions dissolved from the PLZST powder surface,



Fig. 6. Zeta potential of PLZST with dispersant addition.

this means that the ionic concentration and particle surface properties were not highly modified. The zeta potential of PLZST is highly related to the ionic concentration, surface chemical properties of the particles as well as the pH of the slurry. Therefore, the titration sequence can greatly influence the zeta potential and the IEPs.

3.3. Zeta potential of PLZST with dispersant addition

Fig. 6 shows the zeta potential of the PLZST slurry with dispersant addition. It is obvious that the zeta potential and IEPs are completely changed after dispersant addition. Firstly, the IEPs switch to about 2.5, and increase with rising dispersant concentration, while the absolute value of the zeta potential of PLZST decrease slightly. The variation is related to the dispersant dissolution and absorption on the particle surface which changes the surface properties. For ceramic slurry processing, a dispersant is always used to disperse the powder so that a high solid content ceramic slurry can be obtained. In order to be absorbed on the particle surface, the dispersant should have a good solubility. Normally, the solubility of the dispersant is mainly determined by the pH of the solution. It was reported³⁵ that precipitation of P(MAA-b-PEO) was observed at pH<3, while the polyelectrolyte can completely dissolve if the pH is above 3. The degree of ionization of the dispersant is also tightly related to the pH. The polyelectrolyte P(MAA-b-PEO) consists of two parts according to the molecular structure, namely, MAA groups and PEO groups. Since the PMAA block behaves as a weak polyelectrolyte with a pK_a of the acid groups of about 4.8, the PMAA block starts to be negatively charged at pH > 4.8and is completely dissociated at pH>8.5 in salt-free solution. MAA is completely protonated at <pH 3.4. Therefore, the zeta potential of PLZST with dispersant is mainly determined by the properties of the dispersant. Due to the electrostatic forces the dispersant can easily be absorbed on the particle surface and change the surface properties of the particle. Ion leaching from the particle surface and ion precipitation on the particle surface will be difficult due to the present of the dispersant. Therefore, the solubility, adsorption and the degree of ionization of the dispersant are the most important factors.

Apart from the adsorption and the degree of ionization of the dispersant, the conformation of the adlayer can affect the dis-



Fig. 7. Zeta potential of PLZST as a function of binder concentration.

persibility. At high pH, the adsorbed dispersant is highly charged with a more stretched conformation, resulting in a increase of the steric length and a strong repulsion of PLZST particles. If the pH value is lower, the dispersant chains relax into a highly coiled conformation with a low electrosteric repulsion. According to the literature,³⁵ a zeta potential of 25 mV is a prerequisite to minimize coagulation by means of electrostatic repulsion. However, a slurry with a polyelectrolyte dispersant, which provides an extra steric stabilization, can be stabilized at lower zeta potential.

3.4. Zeta potential of PLZST with binder, and plasticizer addition

Fig. 7 shows the zeta potential of PLZST as a function of binder concentration. It is obvious that the binder (PVA) is harmful to achieve the high zeta potential. As mentioned above, the molecular weight, molecular structure, solubility, as well as the degree of ionization are main factors which affect the zeta potential of the PLZST slurry with organic additives. PVA used as a binder in the experiment is a polymer with a large molecular and weak polarity, although PVA dissolves in water without problem. The adsorbed PVA molecules on the particle surface screen the electrostatic action among the particles; therefore, the zeta potential of the PLZST slurry with binder addition is strongly decreasing and also not sensitive to the pH variation. Fig. 8 shows the zeta potential of PLZST as a function of plasticizer concentration. Compared to PVA, PEG has a lower molecular



Fig. 8. Zeta potential of PLZST as a function of plasticizer concentration.



Fig. 9. Mixture of organic additives effect on the zeta potential of PLZST.

weight and high polarity. Therefore, PEG cannot completely screen the electrostatic action such that the zeta potential of PLZST with plasticizer addition is not seriously decreasing, and the zeta potential is also sensitive to the pH variation. Fig. 9 shows the effect of a mixture of organic additives on the zeta potential of PLZST. The zeta potential of the PLZST with a mixture of organic additives is quite similar to the zeta potential of PLZST with dispersant addition. When PLZST powder is mixed with organic additives, the organic additives will be adsorbed on the particle surface. However the highly polar dispersant molecules have priority for the absorption on the polar particle surface, resulting in the variation tendency of the measured zeta potential of PLZST with the mixed organic additives is quite similar to the zeta potential of PLZST with the addition of pure dispersant; however, the binder and plasticizer screening make the zeta potential of PLZST with mixture organic addition decrease.

3.5. Sedimentation test

The dispersibility of PLZST powder with dispersant addition was characterized by sedimentation experiments. A welldispersed slurry settles slowly with time, leading to high sedimentation height and density. On the other hand, a poorly dispersed slurry will rapidly settle and the sedimentation density will be low. Since PLZST is a high density powder, it is very difficult to get a well-dispersed slurry through adjusting the pH of slurry. The density of PLZST is leading to fast sedimentation due to gravitational forces. Fig. 10 shows the effect of the dispersant concentration on the sedimentation height of the slurries. The results show that the concentration of dispersant have significantly influence the sedimentation height and P(MAAb-PEO) is a very efficient polyelectrolyte for the dispersion of water-based PLZST slurries. When the concentration reaches 0.32 wt.%, further addition of dispersant has no beneficial effect on the dispersion of the PLZST slurry.

3.6. Rheological properties of PLZST slurries

The rheological properties were investigated by measuring the viscosity of PLZST slurries under different conditions. Vis-



Fig. 10. Relation between the sediment height and the concentration of dispersant.

cosity versus shear rate for 60 wt.% PLZST slurries without any organic addition at different pH is shown Fig. 11. The results indicated that the pH adjustment could greatly influence of the viscosity of the PLZST slurry. However, the variation of viscosity for the slurries is not in agreement with the measured zeta potential. The maximum viscosity is found at pH 4.4 and the minimum viscosity at pH 8.6. In fact, a lot of factors can affect the zeta potential; as shown in Fig. 8, the order of titration can influence the zeta potential and IEPs. Paik and Hackley reported³⁹ that particle surface charge is influenced by solids loaded in aqueous slurries of BaTiO₃, resulting in the shift of the IEPs and differences of the zeta potential. In the experiment, the solid content of the slurries used in the viscosity measurement is much higher than that of the zeta potential measurement, and a lot of acid or base was also added to adjust the pH of the slurry during zeta potential measurement. Thus, the surface properties of the PLZST particles and the ionic strength should be different. This leads to the deviation between the measured viscosity and the zeta potential according to Fig. 5.

Viscosity versus shear rate for 60 wt.% PLZST slurries with dispersant addition at different pH is shown Fig. 12. It is obvious that the addition of dispersant is significantly influenced on the viscosity. 0.5 wt.% dispersant addition drastically decreases the



Fig. 11. Viscosity versus shear rate for 60 wt.% PLZST slurries without any organic addition at different pH.



Fig. 12. Viscosity versus shear rate for 60 wt.% PLZST slurries with dispersant addition at different pH.

viscosity of 60 wt.% slurry, and the viscosity further decreases with increasing amount of dispersant. An analogous decrease in viscosity occurs for all slurries. However, when the dispersant addition reaches 1.4 wt.%, the slurry viscosity exhibiting no obvious variation, and all slurries show the shear thinning behaviour. Fig. 13 shows viscosity versus shear rate for 60 wt.% PLZST slurries with 1.4 wt.% dispersant addition at different pH. As indicated in Fig. 13, 1.4 wt.% dispersant addition for 60 wt.% PLZST slurry can reach the minimum viscosity. The results indicated that the pH variation could also modify the viscosity of PLZST slurries with dispersant addition. It can, thus, be assumed that the electrostatic repulsion is still an important factor to be considered in the slurry preparation. As mentioned above, the pH variation of slurries can influence the zeta potential via modifying the solubility of the dispersant, the degree of ionization of the dispersant as well as the conformation of the dispersant. However, the variation of the viscosity with the addition of dispersant is not in agreement with the zeta potential measurements in Fig. 6. The measured results in Fig. 6 showed that the zeta potential of PLZST with dispersant is decreasing with rising pH. However, the minimum viscosity of the PLZST slurry is observed at pH 8.5, and the viscosity is increasing when pH is above 8.5. Compared with the solids loading used in zeta potential measurement, the solids loadings used in the viscosity



Fig. 13. Viscosity versus shear rate for 60 wt.% PLZST slurries with 1.4 wt.% dispersant addition.



Fig. 14. Viscosity versus shear rate for PLZST slurries used for tape casting at different pH.

measurement is much higher. Therefore, the pH adjustment will lead too drastic variation of the ionic concentration. In the mean time, chemical reactions and the precipitation of metal ion can also change the zeta potential of PLZST powder.

Fig. 14 shows the viscosity versus shear rate for PLZST slurries used for tape casting at different pH. The formulation of PLZST used for tape casting is also shown in this figure. In order to form PLZST tapes with proper mechanical properties, binder and plasticizer were added to the slurry. The measured viscosity of slurries with different pH is almost the same, and a strong viscosity variation cannot be observed. A possible explanation is that the high concentration of binder and plasticizer screen the electrostatic repulsion, especially for binder. As indicated in Fig. 7, the zeta potential of PLZST particles with binder addition becomes very small and is also not sensitive to the variation of pH. Compared to the slurry used for zeta potential measurement, much more binder and plasticizer were added to the slurry for tape casting, therefore, the electrostatic screening is very strong and, the pH adjustment cannot greatly change the zeta potential, resulting in small changes of the measured viscosity.

4. Conclusions

The effects of the organic additives used for tape casting slurry preparation on the zeta potential of PLZST were investigated. As a polyelectrolyte, poly(methacrylic acid)-b-(ethylene oxide) is a high efficient dispersant for dispersing PLZST powder. Besides the steric stabilization, poly(methacrylic acid)b-(ethylene oxide) can also contribute electrostatic repulsive energy since the dispersant has a high solubility and a high degree of ionization. Compared to the zeta potential of PLZST without dispersant addition, the measured data showed that the zeta potential of PLZST with dispersant addition is not seriously decreasing. Since binder PVA, and plasticizer PEG are weakly polar organic additives, the electrostatic repulsive interaction among particles was screened, resulting in the decrease of the zeta potential of PLZST. The organic additives affect not only the zeta potential but also the IEPs (isoelectric point). With dispersant addition, the IEP of PLZST switched to about 2.3. Binder PVA, and plasticizer PEG can also modify the IEPs. Therefore, the IEP of PLZST can also be influenced by the titration sequence since the ionic concentration and the surface properties of the PLZST particles are tightly related to the starting pH of the slurry. Both sedimentation test and viscosity measurement showed that the dispersant is very efficient for the dispersion of PLZST powder. The pH and dispersant concentration can greatly affect the viscosity of PLZST slurries. However, pH variation cannot seriously influence the viscosity of the slurry used for tape casting.

References

- 1. Thiele, E. S. and Setter, N., Lead zirconate titanate particle dispersion in thick-film ink formulations. *J. Am. Ceram. Soc.*, 2000, **83**, 1407–1412.
- Nieto, E., Fernandez, J. F., Moure, C. and Duran, P., Multilayer piezoelectric devices based on PZT. J. Mater. Sci.: Mater. Electron., 1996, 7, 55–60.
- Fernandez, J. F., Nieto, E., Moure, C., Duran, P. and Newnham, R. E., Processing of porous and dense PZT thick films on Al₂O₃ substrates. *J. Mater. Sci.*, 1995, **30**, 5399–5404.
- Mikeska, K. R. and Cannon, W. R., Non-aqueous dispersion properties of pure barium titanate for tape casting. *Colloids Surf.*, 1988, 29, 305–321.
- Smay, J. E. and Lewis, J. A., Structural and property evolution of aqueousbased lead zirconate titanate tape-cast layers. *J. Am. Ceram. Soc.*, 2001, 84, 2495–2500.
- Mistler, R. E. and Shanefield, D. J., Tape casting: the basic process for meeting the needs of the electronic industry. *Am. Ceram. Soc. Bull.*, 1990, 69, 1022–1026.
- Shanefield, D. J. and Mistler, R. E., Fine-grained alumina substrates: II. Properties. Am. Ceram. Soc. Bull., 1974, 53, 564–568.
- Jarrige, J., Lecompte, J. P., Mullot, J. and Müller, G., Effect of oxygen on the thermal conductivity of aluminium nitride ceramics. *J. Eur. Ceram. Soc.*, 1997, **17**, 1891–1895.
- Chartier, T., Streicher, E. and Boch, P., Preparation and characterization of tape cast aluminum nitride substrates. J. Eur. Ceram. Soc., 1992, 9, 231–242.
- Hyatt, P., Making thin flat ceramic: a review. *Am. Ceram. Soc. Bull.*, 1986, 65, 637–638.
- Morris, JR, Cannon, WR. Rheology and component interactions in tape casting slurries. Mater. Res. Soc. Symp. Proc. Vol. 60, Defect Properties and Processing of High-Technology Nonmetallic Materials. In Chen, Y, Kingery, WD, Stokes, RJ., eds. Pennsylvania, 1986, pp. 135–142.
- Fukui, T., Ohara, S., Murata, K., Yoshida, H., Miura, K. and Inagaki, T., Performance of intermediate temperature solid oxide fuel cells with La(Sr)Ga(Mg)O₃ electrolyte film. *J. Power Sources*, 2002, **106**, 142–145.
- Sahibzada, M., Benson, S. J., Rudkin, R. A. and Kilner, J. A., Pdpromoted La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ cathodes. *Solid State Ionics*, 1998, 113–115, 285–290.
- Zhu, B., Rundgren, K. and Mellander, B.-E., Ceramic membranes–potential uses for solid state protonic conductors. *Solid State Ionics*, 1997, 97, 385–439.
- Schäfer, W., Koch, A., Herold-Schmidt, U. and Stolten, D., Materials, interfaces and production techniques for planar solid oxide fuel cells. *Solid State Ionics*, 1996, 86–88, 1235–1239.
- Fukui, T., Ohara, S., Okawa, H., Hotta, T. and Naito, M., Properties of NiO cathode coated with lithiated Co and Ni solid solution oxide for MCFCs. *J. Power Sources*, 2000, 86, 340–346.
- Zhitomirsky and Petric, A., Cathodic electrodeposition of polymer films and organoceramic films. *Mater. Sci. Eng. B*, 2000, 78, 125–130.
- Van herle, J., Ihringer, R., Vasquez Cavieres, R., Constantin, L. and Bucheli, O., Anode supported solid oxide fuel cells with screen-printed cathodes. *J. Eur. Ceram. Soc.*, 2001, **21**, 1855–1859.
- Lu, C., Worrell, W. L., Wang, C., Park, S., Kim, H., Vohs, J. M. and Gorte, R. J., Development of solid oxide fuel cells for the direct oxidation of hydrocarbon fuels. *Solid State Ionics*, 2002, **152–153**, 393–397.
- Maffei, N. and de Silveira, G., Interfacial layers in tape cast anode-supported doped lanthanum gallate SOFC elements. *Solid State Ionics*, 2003, 159, 209–216.

- Galassi, C., Roncari, E., Capiani, C. and Pinasco, P., PZT-based suspensions for tape casting. J. Eur. Ceram. Soc., 1997, 17, 367–371.
- Schwarzer, S. and Roosen, A., Tape casting of piezo ceramic/polymer composites. J. Eur. Ceram. Soc., 2000, 19, 1007–1010.
- Song, J. K., Um, W. S., Lee, H. S., Kang, M. S., Chung, K. W. and Park, J. H., Effect of polymer molecular weight variations on PZT slip for tape casting. *J. Eur. Ceram. Soc.*, 2000, **20**, 685–688.
- Feng, H., Ferguson, L. G. and Dogan, F., Processing of buffer sheets for sintering of PLZT tapes. J. Mater. Sci. Proc. Tech., 2001, 111, 47– 52.
- Feng, J. H. and Dogan, F., Aqueous processing and mechanical properties of PLZT green tapes. *Mater. Sci. Eng. A*, 2000, 283, 56–64.
- Hotza, D. and Greil, P., Aqueous tape casting of ceramic powders. *Mater. Sci. Eng. A*, 1995, **202**, 206–217.
- Verwey, E. G. W. and Overbeek, J. T. G., *The Theory of the Stability of Lyophobic Colloids*. Elsevier, Amsterdam, The Netherlands, 1948.
- Guo, C., Zhang, Y., Uchida, N. and Uematsu, K., Adsorption effects on the rheological properties of aqueous alumina suspensions with polyelectrolyte. *J. Am. Ceram. Soc.*, 1998, 81, 549–556.
- Liu, Y. and Gao, L., Effect of 2-phosphonobutane-1,2,4-tricarboxylic acid adsorption on the stability and rheological properties of aqueous nanosized 3-mol%-yttria-stabilized tetragonal-zirconia polycrystal suspensions. J. Am. Ceram. Soc., 2003, 86, 1106–1113.
- Boaro, M., Vohs, J. M. and Gorte, R. J., Synthesis of highly porous yttriastabilized zirconia by tape-casting methods. *J. Am. Ceram. Soc.*, 2003, 86, 395–400.

- Palmqvist, L. M. and Lange, F. F., Dispersion and consolidation of alumina using a bis-hydrophilic diblock copolymer. J. Am. Ceram. Soc., 2000, 83, 1585–1591.
- Lewis, J. A., Matsuyama, H., Kirby, G., Morissette, S. and Young, J. F., Polyelectrolyte effects on the rheological properties of concentrated cement suspensions. J. Am. Ceram. Soc., 2000, 83, 1905–1913.
- Andersson, K. M. and Bergström, L., Effect of the cobalt ion and polyethyleneimine adsorption on the surface forces between tungsten oxide and cobalt oxide in aqueous media. J. Am. Ceram. Soc., 2002, 85, 2404–2408.
- Palmqvist, L. M., Lange, F. F., Sigmund, W. and Sindel, J., Dispersion and consolidation of alumina using a bis-hydrophilic diblock copolymer. *J. Am. Ceram. Soc.*, 2000, 83, 1585–1591.
- Orth, J., Meyer, W. H., Bellmann, C. and Wegner, G., Stabilization of aqueous a-al₂o₃ suspensions with block copolymers. *Acta Polym.*, 1997, 48, 490–501.
- 36. Rosinus, A. Kolloidchemische Grundlagen f
 ür das Foliengie
 ßen w
 ässriger PZT-und PZST-Suspensionen. Ph.D. thesis. Institut f
 ür Nichtmetallische Anorganische Materialien Universit
 ät Stuttgart Max-Planck-Institut f
 ür Metallforschung Abteilung Aldinger, Stuttgart, 2001.
- Bailar, J. C. and Emeleus, H. J., Comprehensive Inorganic Chemistry, Vol 1. Pergamon Press Reprint Ltd., 1973.
- Lide, D. R., Handbook of chemistry and physics, Vol 74. CRC Press, Inc., 1993.
- Paik, U. and Hackley, V. A., Influence of solids concentration on the isoelectric point of aqueous barium titanate. *J. Am. Ceram. Soc.*, 2000, 83(10), 2381–2384.