Effect of solid content variations on PZT slip for tape casting

Gang Jian[1,*], Qingxian Hu[1], Sheng Lu[1], Dongxiang Zhou[2], Qiuyun Fu[2]

[1]*School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China*

[2]*MOE Engineering Research Center for Information Functional Ceramics, Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China*

Received 22 October 2012; received in revised form 2 December 2012; accepted 21 December 2012

Abstract

Lead zirconate titanate (PZT) particles with pure tetragonal structure were synthesized by solid-state reaction method and used for preparation of slurries with different solid contents (34–80 wt.%). Then, PZT thick films were fabricated by the nonaqueous tape casting method. It was shown that the slurry prepared from ball-milled particles exhibited better rheology properties than slurry from particles which were not ball-milled. Measurement of sedimentation volumes and zeta potentials indicated particle aggregation, resulting in weak stability of the slurries with high solid contents. The microstructure, piezoelectric and ferroelectric properties of PZT sintered films were investigated in terms of solid contents. Ceramic films prepared from the slurry with solid contents of 73 wt.% had the optimal structure and properties. After poling at 200 °C with an applied field of 1.2 kV/cm, a d_{33} of 294 pC/N was achieved; typical ferroelectric properties were also observed with a P_s of 38 μC/cm^2.

Keywords*: lead zirconate titanates, tape casting, piezoelectric properties, structural characterization*

I. Introduction

Lead zirconate titanate (PZT) is a ferroelectric ceramic material used in many advanced applications such as sensors, actuators, ultrasonic motors, and piezoelectric transformers [1–4]. PZT thick films have been fabricated by sol-gel [5], sputtering [6], electrophoretic deposition [7] and hydrothermal method [8]. The microstructure and processing for each are quite different.

Tape casting is a low cost and useful process for preparing ceramic sheets which are utilized to fabricate multilayer components, like, e.g., capacitors, inductors, high integrated circuits and actuators [9–12]. Tape casting is applicable for the preparation of ferroelectric thick films with controlled thickness from 10 μm to 1 mm. Tape cast PZT layers are the basic building blocks for production of multilayer actuators, transducers and sensors [13,14]. Slurry preparation is a critical step to obtain uniform, dense and high quality ferroelectric tapes and ceramics. To form proper slurry for tape casting, low particle aggregation, low viscosity with good shear thinning behaviour, and high solid loading is required [15]. Traditionally, the study of the PZT slurry has been focused on slurry stability [16] and rheology [17,18] properties, while neglecting the impact of solid content variations such as particle size and solid loading in the tape casting process.

The purpose of this study is to develop a basic understanding of the effects of the solid content variations on the microstructure and properties of the PZT films. The PZT thick films were fabricated by tape casting from organic slurries. The influence of different particle sizes and solid contents in a wide range was investigated. The PZT tape characteristics before and after sintering were investigated, including surface morphology, relative density and sample sizes. Additionally, piezoelectric and ferroelectric properties of the ceramic films were evaluated.

II. Experimental

The PZT ($Pb_{1.05}(Zr_{0.52}Ti_{0.48})O_3$) (5 at.% of Pb was used to compensate the PbO evaporation) powders were prepared by solid-state reaction from the appropriate proportion of three individual oxides (PbO, 99.9%; ZrO_2, 99.95%; TiO_2, 99.9%). Then the mixture was ball-

* Corresponding author: tel: +86 511 84407569
fax: +86 511 84407381, e-mail: *jiangang456@126.com*

milled in deionized water using a planetary ball milling machine (QM-3SP04, CN) at 300 rpm for 3 h. The powders were then calcined at 800 °C for 2 h. The calcined products were again ball-milled for 2 h. The powders were characterized by X-ray diffraction (XRD, X'Pert PRO), field emission gun scanning electron microscopy (FEG-SEM, Sirion 200, PRO) and particle size analyzer (Zetasizer 3000 HAS, Malvern Instruments Ltd., UK).

Two differently processed PZT powders (without and with ball-milling) were used for preparation of the PZT slurries with different solid contents, from 34 to 80 wt.% (approximately corresponding to 6–32 vol.%). Mixture of ethanol and methylbenzene (AR in purity, 5 : 3 in volume) was chosen as the solvent. The dispersant, defoamer and binder were commercially supplied by Zhaoqing Lingguang Electronic Chemical Material Technology Co., Ltd, China. Powders, solvent, dispersant and defoamer were mixed and used as the starting materials, and then they were ball-milled for 2 h. After that, the binder was added and the mixtures were ball-milled again for 3 h. The compositions of the prepared PZT slurries are given in Table 1. As can be seen, it was necessary to gradually decrease amount of solvent, increase dispersant content and decrease amount of binder in order to prepare stable slurries with increasing solid content (from R1 to R6). The obtained PZT slurries were characterized by the measurement of sediment volume and zeta potential. The sediment volume was measured by settling 10 mL of the original slurries in cylinders for at least 3 weeks and calculated as a volume of sediment per its mass. Zeta potentials were measured using diluted slurries (diluted by the corresponding solvents to a concentration of 10 mg/L) by a zeta potential tester (Zetasizer 3000 HAS, Malvern Instruments Ltd., UK). Rheology properties were examined by a rotary viscometer (NDJ-1, Mydream Electronic Ltd., China) with variable shear rates in the range of 5–100 r/min.

The PZT tapes were shaped, dried, laminated (×10 layers), cold isostatic pressed (30 MPa at 58 °C for 20 min) and cut in small pieces. Finally, the resin was removed by heating at 280 °C for 4 h and flexible tapes with size of ~3 mm × ~2 mm × ~380 μm were obtained. The tapes were sintered at 1200 °C for 2 h with a heating rate of 5 °C/min to form ceramic thick films. The micro-morphology of the sintered films was characterized by SEM. The poling process of the PZT R5 sample (~2 mm × ~1.4 mm surface, ~260 μm thick) was conducted in silicone oil, whereas the different poling temperatures (140–200 °C) and poling fields (0.2–1.6 kV/mm) were investigated. The piezoelectric coefficient was measured by a quasistatic d_{33} tester (ZJ-2A, Institute of Acoustics, Chinese Academy of Science, China). Ferroelectric properties were examined by a ferroelectric materials parameters tester (Multiferroics, Radiant Co. Ltd., USA).

III. Results and discussion

Figure 1 shows the XRD pattern of the PZT powder after calcination at 800 °C for 2 h and followed by ball-milling for 2 h. All diffraction pattern peaks match well with the normal characteristic diffraction of PZT (JCPDs No. 33-0784). It is clear that the sample is single phased and can be indexed in a tetragonal structure. The SEM morphology of the PZT powders prepared by solid-state reaction method is presented in Fig. 2. Powders undergone ball-milling have more uniform shapes and smaller sizes than those prepared without ball-milling. Particle size was also determined by a laser particle size analyser (not shown here), which indicates an average size of ~800 nm for the ball-milled particles and ~1.1 μm for the non-ball-milled particles.

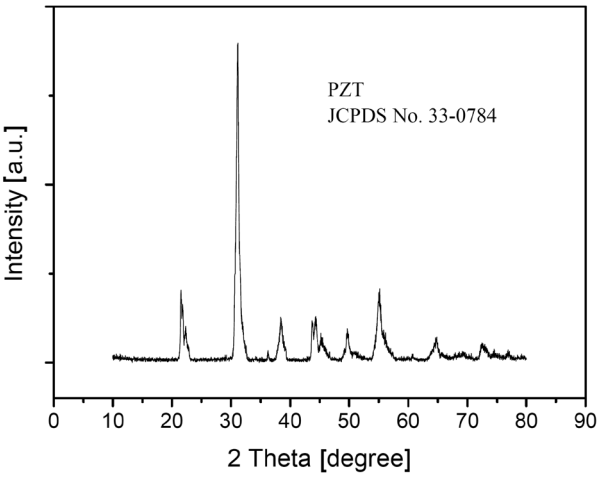

Figure 1. XRD pattern of PZT powder prepared by solid-state reaction method

Table 1. PZT slurry formulations with different solid contents used for the tape casting

	R1 [wt.%]	R2 [wt.%]	R3 [wt.%]	R4 [wt.%]	R5 [wt.%]	R6 [wt.%]
PZT powders	34	40	56.6	61.5	73	80
Solvents	36.5	32.7	26.5	24	17.3	12
Dispersant	0.13	0.13	0.16	0.20	0.22	0.26
Defoamer	0.17	0.16	0.14	0.15	0.15	0.14
Binder	27.2	27.01	16.6	14.15	9.33	7.6
Total	100	100	100	100	100	100

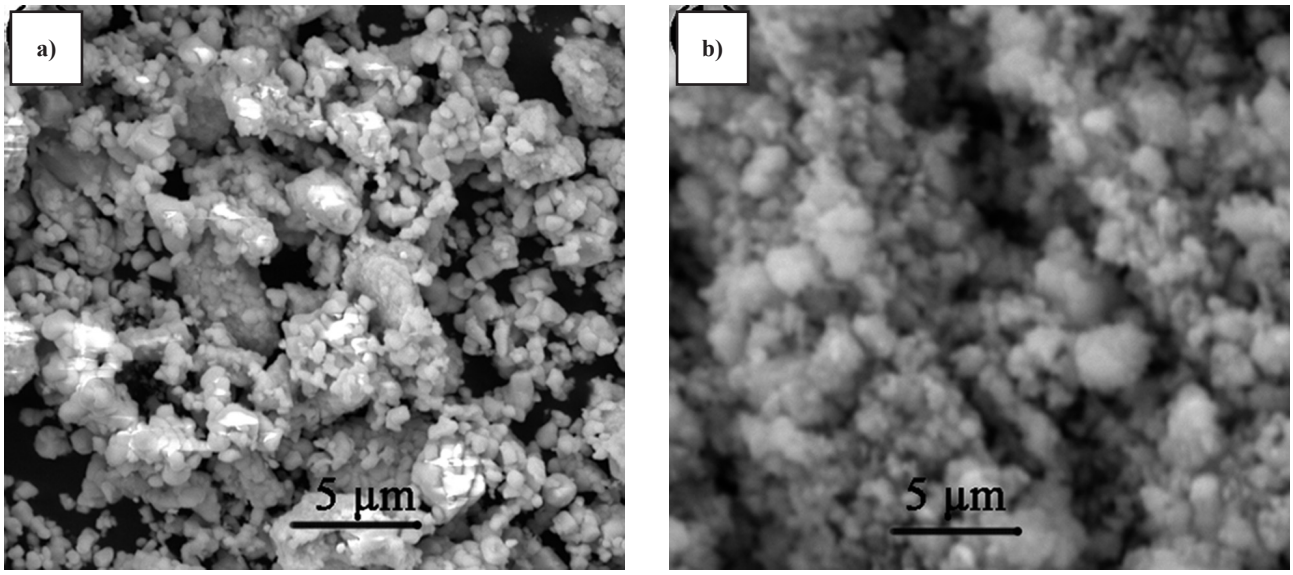

Figure 2. SEM micrograph of the prepared PZT powders: a) without ball-milling and b) ball-milled for 2 h

Figure 3 shows the slurry viscosity (shear rate of 8 s^{-1}) at different solid contents for the ball-milled and non-ball-milled PZT particles. For both curves, viscosity is low and steady at low solid contents while it increases rapidly when solid contents are high. As solid contents increased to some degree, particles in slurry were not fully dispersed and more aggregates were generated which hampered the shearing effect and increased the viscosity. When the solid content was further increased, the whole solid-liquid two phase system may have been turned into a large aggregate with some strength, and the viscosity increased irreversibly. The slurry obtained from the ball-milled PZT particles has better rheology properties than that from the non-ball-milled particles. The reason may be attributed to the bimodal particle size distribution and existence of particle clusters in the non-ball-milled particle samples. At a fixed solid content of 73 wt.% (the sample R5) the ball-milled PZT slurry has viscosity of ~460 mPa s, while it is somewhat higher (~510 mPa s) for the non-ball-milled slurry. Thus, the ball-milled slurry was used in the study to further investigate the influence of PZT solid content on the tape casting process.

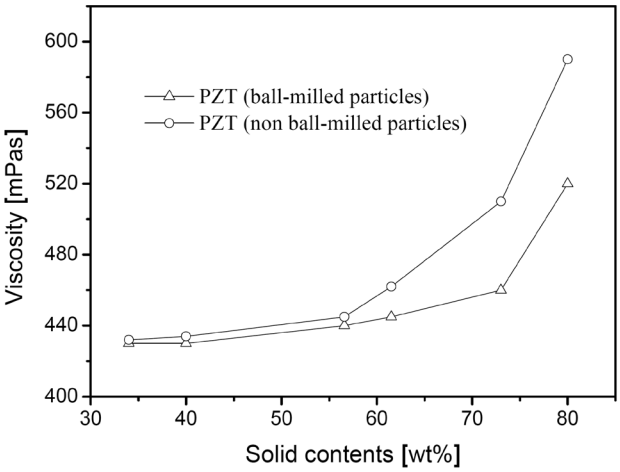

Figure 3. Influence of different solid contents and particle sizes on the viscosity of PZT slurries

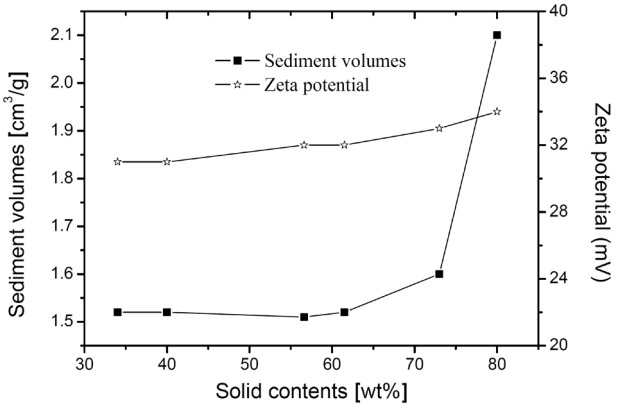

Figure 4. Sediment volumes and zeta potential of PZT slurries with different solid contents

Figure 4 shows the stability analysis of PZT slurries with different solid contents. The zeta potential was measured using diluted slurry (10 mg/L), which showed that similar zeta potential values (around 32 mV) were observed for different slurries (R1–R6). It indicates that the diluted slurries exhibit almost the same stabilities. On the other hand, the sediment volumes measured using the original slurry showed the different results. Sediment volume is small for slurry with solid contents of 34–61.5 wt.% (R1–R4) and it increases a little at solid content of 73 wt.% (R5), while it increases rapidly at solid content of 80 wt.% (R6). The smaller sediment volume indicates better stability and weaker aggregation [19]. Therefore it can be concluded that with the increased solid content highly agglomerated and less stable slurries are obtained. Thus, the slurry R6 has the worst stability and this might be attributed to the fact that particles are not fully infiltrated in the high solid loading slurry.

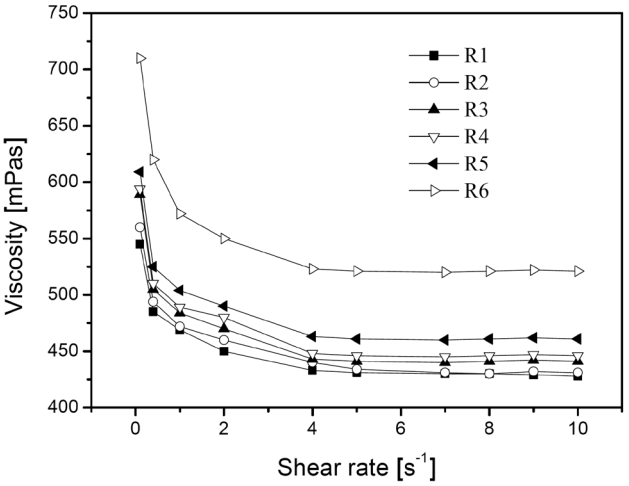

Figure 5. Viscosity of PZT slurries vs. shear rate for different solid contents

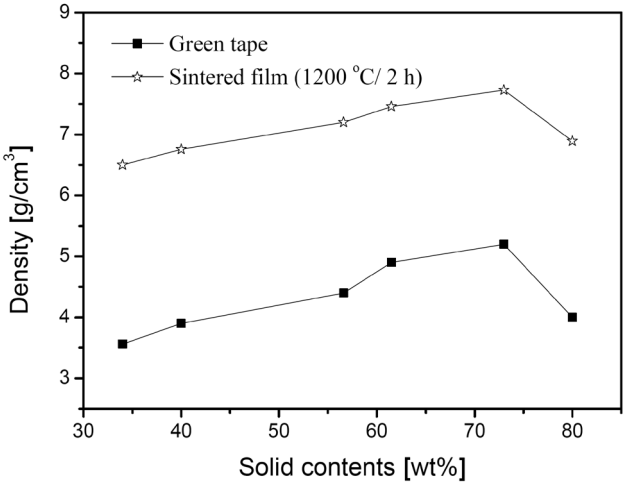

Figure 6. Density of PZT green tape and sintered ceramics (1200 °C/2 h) prepared from slurry with different solid contents

Figure 5 shows shear rate dependent slurry viscosity for all investigated samples (R1–R6). It can be seen that viscosity is large at low shear rate, and comparatively low and steady viscosity is obtained when shear rate is high. The phenomenon is in accordance with the non-Newtonian flow behaviour [20]. The highest viscosity is observed for the R6 sample at any measuring shear rate. Furthermore, the non-Newtonian behaviour indicated that the shaping of the PZT tapes should be conducted at a comparatively high tape velocity which was adopted as 8 cm/s in this study.

To investigate the solid content effect on the structure of the green tapes and sintered films, the density of green tapes (resin removed) and ceramic films (1200 °C /2 h) derived from the different slurries (R1–R6) was measured. Figure 6 shows that the green tapes density at first increases with increasing solid loadings in the range of 34–73 wt.%, the peak is obtained at 73 wt.%, and then turns to decrease rapidly at higher solid content (80 wt.%). This indicates that high solid content is essential for the formation of high quality tapes, while too high solid loading deteriorates the tape structure. Higher density of the PZT sintered ceramic films (1200 °C/2 h) was obtained for the samples prepared from denser green tapes. The sample film R5 has the highest density of 7.728 g/cm^3, i.e. the relative density of 96.6 %TD (considering the theoretical density of 8.01 g/cm^3 for PZT [21]). The volume shrinkage and density changes data of the R5 samples during the whole tape casting process are presented in Table 2.

Figure 7 shows the representative SEM images of the PZT green tapes (after removal of resin) and sintered films (1200 °C/2 h) derived from the slurries R4, R5 and R6. In Figs. 7a,d large pores are observed in the R4 tapes and ceramic films, which are attributed to the high organic contents. Figures 7b,e show tape and sintered film prepared from the slurry R5, confirming smooth and dense structure. At the same time, existence of aggregations and pores in the R6 tapes and sintered films prepared from the slurry with solid content of 80 wt.% are clearly seen in Figs. 7c,f and can be attributed to the bad slurry properties.

The piezoelectric coefficients, d_{33}, of the PZT film R5 sintered at different temperatures, are given in Fig. 8a. The optimal piezoelectric properties with d_{33} of 294 pC/N were obtained for the PZT ceramic films sintered at 1200 °C corresponding to the sample with higher density. Figure 8b shows the poling field effect on the d_{33} values. The d_{33} values are low for poling fields below 10 kV/cm, while they are relatively high above that point. After poling with an electric field of 12 kV/cm, a d_{33} of 294 pC/N was determined. Randomly oriented ceramics had to undergo 180° and non-180° domain switching to exhibit piezoelectricity. A high static electric field was needed during the process which is normally larger than the coercive field of the materials. Figure 8c gives the poling temperature effect on the d_{33} values. The results showed that d_{33} increased slowly as poling temperatures increased. Suitable poling field and temperature should be used for effectively forcing domains and domain walls' movement and orientation in the polarization process. In this study,

Table 2. Thickness and density of PZT sample R5 during the tape casting process

Process	Wet tape	Dried tape	Laminated (×8)	CIP treated	Resin removed	Sintered (1200°C /2 h)
Thickness [μm]	100	42	330	326	320	260
Density [g/cm^3]	3.24	5.6	5.65	5.7	5.2	7.728

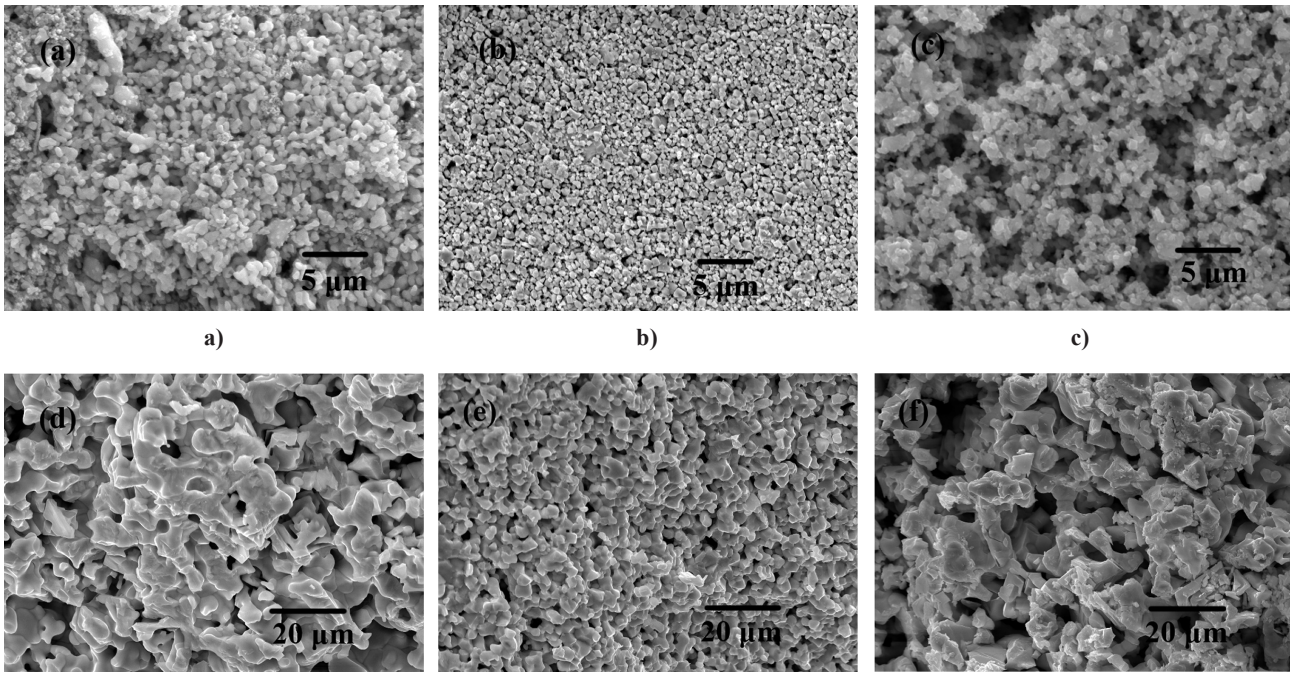

Figure 7. SEM micrographs of the PZT green tapes (a–c) and sintered films (d–f) prepared from slurries with different solid contents: R4 (a) and (d); R5 (b) and (e); R6 (c) and (f)

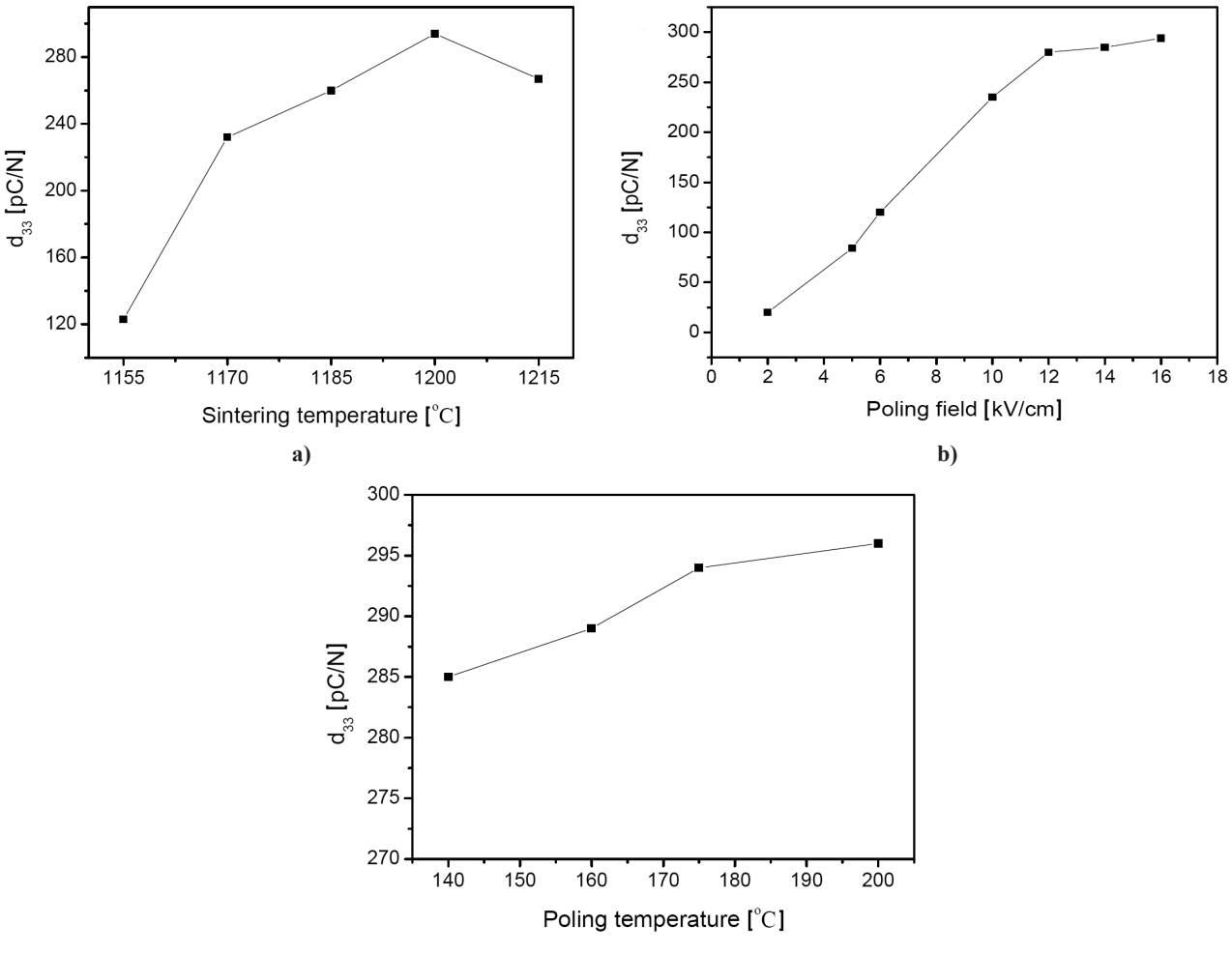

Figure 8. Piezoelectric coefficient d_{33} of R5 PZT film as function of: a) sintering temperature, b) poling field and c) poling temperature

Table 3. Saturation polarization P_s and piezoelectric coefficient d_{33} of PZT ceramic films derived from slurries with different solid contents

Ceramic sample	P_s [μC/cm^2]	d_{33} [pC/N]
R1	26	103
R2	28	123
R3	34	232
R4	36	260
R5	38	294
R6	36	234

poling field of 12 kV/cm and poling temperature of 200 °C was used. The room temperature electric hysteresis loop of the PZT ceramic films sintered at 1200 °C for 2 h is presented in Fig. 9. Typical ferroelectric properties were obtained, with saturation polarization P_s, remnant polarization P_r and coercive field E_c of 38 μC/cm^2, 31 μC/cm^2 and 9.8 kV/cm, respectively. Furthermore, the detailed d_{33} and P_s values of PZT sintered films prepared from the slurries R1–R5 are shown in Table 3. The optimal properties were observed in the film R5 sintered at 1200 °C for 2 h.

IV. Conclusions

PZT ferroelectric particles with pure tetragonal structure were prepared by solid-state reaction method. The slurry prepared using the ball-milled particles showed better rheology properties than that using the non-ball-milled particles. Different solid contents slurry was investigated, 73 wt.% slurry had the highest solid contents and preserved good stability and rheology properties at the same time. A high tape velocity of 8 cm/s was adopted in accordance with the flow behaviour study. PZT sintered films (1200 °C/2 h) prepared from 73 wt% solid content slurry have dense structure (relative density of 96.6 %TD) and exhibited piezoelectric (1.2 kV/cm, 200 °C polarized; d_{33} of 294 pC/N) and ferroelectric (P_s of 38 μC/cm^2) properties. The 80 wt.% solid content deteriorated the slurry and ceramic film properties having high viscosity and weak stability.

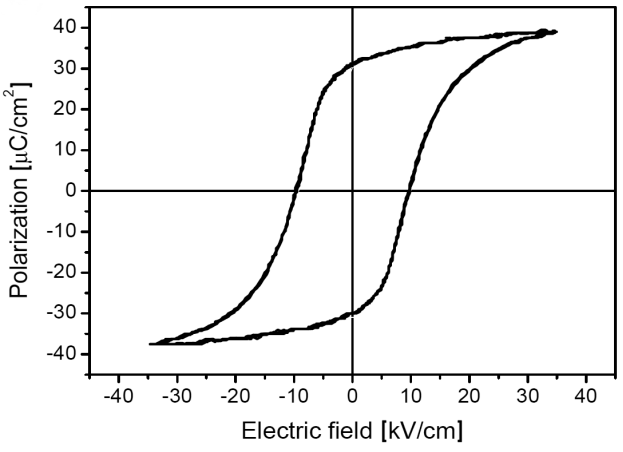

Figure 9. Room temperature electric hysteresis loop of the sintered R5 PZT ceramic film (1200 °C/2 h)

Acknowledgements: This work was supported by the National Natural Science Foundation of China (Grant no. 60871017/f010612) and Provincial Nature Science Foundation of Hubei in China (Grant no.2009CDB372).

References

1. T. Tuchiya, T. Itoh, G. Sasaki, T. Suga, "Preparation and properties of piezoelectric lead zirconate titanate thin films for microsensor and microactuators by sol-gel processing", *J. Ceram. Soc. Jpn.*, **104** (1996) 159–163.
2. Y.H. Chen, J. Ma, T. Li, "Electrophoretic deposition and characterization of a piezoelectric FGM monomorph actuator", *Ceram. Int.*, **30** (2004) 1807–1809.
3. H. Kuepper, T. Leuerer, U. Scnakenberg, W. Mokwa, M. Hoffmann, T. Schneller, U. Boettger, R. Waser, "PZT thin film for piezoelectric microactuator applications", *Sensor. Actuat.*, **97** (2002) 680–684.
4. Y.C. Hsu, C.C. Wu, C.C. Lee, G.Z. Cao, I.Y. Shen, "Demonstration and characterization of PZT thin film sensor and actuators for meso- and micro-structures", *Sensor. Actuat. A Phys.*, **116** (2004) 369–377.
5. P. Jegatheesan, N.V. Giridharan, "Enhanced electrical properties of PZT thick films prepared by sol-gel technique through step-by-step crystallization process", *J. Mater. Sci.: Mater. Electr.*, **23** (2012) 1103–1107.
6. R.N. Castellano, L.G. Feinstein, "Ion-beam deposition of thin films of ferroelectric lead zirconate titanate (PZT)", *J. Appl. Phys.*, **50** (1979) 4406–4411.
7. A. Wu, P.M. Vilarinho, A.I. Kingon, "Electrophoretic deposition of lead zirconate titanate films on metal foils for embedded components", *J. Am. Ceram. Soc.*, **89** (2006) 575–581.
8. T. Hasegawa, M. Ishikawa, M.K. Kurosawa, S. Takeuchi, "Evaluation of small ultrasonic probe using lead zirconate titanate poly-crystal film deposited by hydrothermal method", *Electr. Commun. Jpn.*, **95** (2012) 1–8.
9. A. Heunisch, A. Dellert, A. Roosen, "Effect of powder, binder and process parameters on anisotropic shrinkage in tape cast ceramic products", *J. Eur. Ceram. Soc.*, **30** (2010) 3397–3406.
10. J. Gurauskis, C. Baudin, A.J.S. Herencia, "Tape casting of Y-TZP with low binder content", *Ceram. Int.*, **33** (2007) 1099–1103.

11. X. Cao, L. Yang, H. Pan, Z. Yang, "Fabrication, temperature stability and characteristics of $Pb(Zr_xTi_y)O_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$ piezoelectric ceramics bimorph", *Ceram. Int.*, **38** (2012) 3377–3382.
12. S.S. Kim, J.K. Chung, I.S. Kim, J.S. Song, C.J. Kim, W.J. Kim, "Dielectric properties of ferroelectric $(Ba_{0.6}Sr_{0.4})TiO_3$ thick films prepared by tape-casting", *J. Electroceram.*, **17** (2006) 451–454.
13. C. Galassi, E. Roncari, C. Capiani, P. Pinasco, "PZT-based suspensions for tape casting", *J. Eur. Ceram. Soc.*, **17** (1997) 367–371.
14. A. Navarro, R.W. Whatmore, J.R. Alcock, "Preparation of functionally graded PZT ceramics using tape casting", *J. Electroceram.*, **13** (2004) 413–415.
15. M.N. Muralidharan, E.K. Sunny, K.R. Dayas, A. Seema, K.R. Resmi, "Optimization of process parameters for the production of Ni-Mn-Co-Fe based NTC chip thermistors through tape casting route", *J. Alloy Compd.*, **509** (2011) 9363–9371.
16. J.-K. Song, W.-S. Um, H.-S. Lee, M.-S. Kang, K.-W. Chung, J.-H. Park, "Effect of polymer molecular weight variations on PZT slip for tape casting", *J. Eur. Ceram. Soc.*, **20** [6] (2000) 685–688.
17. A. Navarro, J.R. Alcock, R.W. Whatnore, "Aqueous colloidal processing and green sheet properties of lead zironate titanate (PZT) ceramics made by tape casting", *J. Eur. Ceram. Soc.*, **24** (2004) 1073–1076.
18. S.B. Reddy, P.P. Singh, N. Raghu, V. Kumar, "Effect of type of solvent and dispersant on nano PZT powder dispersion for tape casting slurry", *J. Mater. Sci.*, **37** (2002) 929–934.
19. M.C. Bennett, "Zeta potential and sedimentation behavior in flocculated cane sugar juice", *Nature*, **182** (1958) 1439–1440.
20. A. Wonisch, P. Polfer, T. Kraft, "A comprehensive simulation scheme for tape casting: From flow behavior to anisotropy development", *J. Am. Ceram. Soc.*, **94** (2011) 2053–2060.
21. S. Dougdaw, T. Uchikoshi, Y. Noguchi, C. Eamchotchawalit, Y. Sakka, "Electrophoretic deposition of lead zirconate titanate (PZT) powder from ethanol suspension prepared with phosphare ester", *Sci. Technol. Adv. Mater.*, **6** (2005) 927–932.