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To cite this article: F Wei et al 2018 IOP Conf. Ser.: Earth Environ. Sci. 186 012063

View the article online for updates and enhancements.
The effect of dispersant on the properties
PSN-PMS-PNN-PZT piezoelectric ceramics

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Abstract. Pb(Sb1/2Nb1/2)0.01(Mn1/3Sb2/3)0.01(Ni1/3Nb2/3)0.5(Zr0.3Ti0.7)0.48O3 piezoelectric ceramics were prepared by traditional solid-state sintering method. Firstly, the dispersant of PSN-PMS-PNN-PZT piezoelectric ceramics was determined and the effect of dispersants doping on the phase structure, microstructure morphology and electrical properties of ceramics was studied. The results show that all samples are single perovskite phase. When both balls are added to the dispersant, ceramics exhibit the optimum properties: d33=907 pC/N, εr=6889, kₚ=65.62%, tanδ=1.53%. Performance of the sample has been greatly improved compared with that without dispersant doping.

1. Introduction
Nowadays, the rapid development of society cannot be separated from progress of high and new technology. As a functional material, the special performance of piezoelectric ceramics is that it can convert between mechanical energy and electrical energy. It is widely used in electronic communications, agriculture, household electrical appliances, aerospace and other fields [1-3]. In order to meet various needs, it is required to have better piezoelectric and dielectric properties. For example, high piezoelectric constant (d33), high electromechanical coupling coefficient (kₚ) and low dielectric loss (tanδ). Hu S [4] pointed out that adding ammonium citrate dispersant can effectively improve the piezoelectric properties of PNN-PZT piezoelectric ceramics and performance of the sample is more stable. Jiao F [5] prepared acrylic acid as the dispersants of ZnO. The result shows that the stability and electrical properties of ZnO system are improved. Although the raw materials have been fully mixed in the process of ceramic preparation, the mass and specific gravity of the raw materials are different, which leads to inhomogeneity of precipitation and agglomeration of different degrees. Adding dispersant can optimize the rheological properties of the slurry, improve the strength of the ceramic after molding and then affect the performance of the sample [6]. Du J [7] added ammonium citrate (TAC) and ammonium methacrylate (PMAA-NH₄) dispersant in the PMN-PZT piezoelectric ceramics. The result shows that the two dispersants can reduce the particle agglomeration in the ceramic slurry. Ji F [8] mentioned that adding dispersants can effectively prevent the accumulation of particles and improve electrical properties. Dispersant was not added in the piezoelectric ceramic powder, which the interaction force is van Edward's force. After the dispersant is added to the slurry, the adsorption of the dispersant increases the effective radius of the particles, which results in steric hindrance in the slurry. This dispersion mechanism is used in ceramic particles [9-11].
2. Experiment procedure

In this experiment, the basic formulation is \( \text{Pb(Sb}_{1/2}\text{Nb}_{1/2})_{0.01}(\text{Mn}_{1/3}\text{Sb}_{2/3})_{0.01}(\text{Ni}_{1/3}\text{Nb}_{2/3})_{0.5-}
\text{(Zr}_{0.3}\text{Ti}_{0.7})_{0.48}\text{O}_{3} \). It was prepared by traditional solid-state sintering method. The raw materials are analytical-grade metal oxides and carbonate powders: \( \text{Pb}_{3}\text{O}_{4}, \text{MnO}_{2}, \text{Sb}_{2}\text{O}_{3}, \text{Ni}_{2}\text{O}_{3}, \text{Nb}_{2}\text{O}_{5}, \text{ZrO}_{2} \) and \( \text{TiO}_{2} \). According to the chemical measurement of the formula, the ceramic samples were weighed. The quality of \( \text{Pb}_{3}\text{O}_{4} \) overdose 1 wt.% to compensate for \( \text{Pb} \) volatilization in sintering process.

2.1 Screening experiment of dispersant

In this experiment, a dispersant with excellent dispersion effect was selected for PSN-PMS-PNN-PZT ceramics. Polyethylene glycol, acrylic acid, ammonium poly acrylate and ammonium citrate solution of 2 wt.% were prepared. Ceramic slurry was mixed with a suitable amount of dispersant solution in the test tube. Mixed slurry was observed the simulated sedimentation at 0, 10, 20, 30, and 40 minutes of centrifugation and then select the best dispersant.

2.2 Preparation of ceramics

With ammonium polyacrylate as dispersing agent, dispersant solution with concentration of 1, 2, 3 and 4 wt.% was prepared. Nine ball milling tanks were numbered 1-9 respectively. Before the first ball milling only, the prepared dispersant solution was added to No. 1-4. Then the mixtures were homogenized by ball-milling in alcohol for 10 h. The resulting powders were dried and then sintered at 920°C for 4 h. During the second ball milling only, the dispersant solution was added to No. 5-8 separately. Then the calcined powders were subsequently ball-milling in the same nylon jar. After drying, the powders were pressed into tablets with 6 wt.% paraffin under 8 MPa with the size of Ø12 mm×1.2 mm. Finally samples were sintered at 1280°C for 2 hours. The ceramic plated are coated with silver electrodes in both sides and measured after poling in silicone oil at 50°C under a DC electric field of 2 kV/mm for 30 min. The optimum dispersants concentration of the first and second ball milling only was obtained respectively.

A ball milling tank is marked as No.10. Dispersant solution of 3 wt.% was added in the first ball milling only and dispersant solution of 2 wt.% was added in the second ball milling only. Then the experiment repeat above procedure.

2.3 Sample characterization

The sample composition was analyzed by the pert-PRO X-ray diffractometer (XRD). The microstructure of ceramic samples was observed by scanning electron microscopy (SEM). The piezoelectric constant \( \text{d}_{33} \) of ceramic samples was measured by ZJ-6A quasistatic \( \text{d}_{33} \). Dielectric loss (tan\( \delta \)) and capacitance (\( \text{e}_{p} \)) values were measured by the TH2826 capacitance tester, and the relative dielectric constant was calculated. The electromechanical coupling coefficient (\( \text{k}_{p} \)) is calculated by HP4294A impedance analyzer.

3 Results and discussion

3.1 Analysis of dispersant screening experiment

Figure 1(a) is the initial state of the ceramic powder after adding four dispersants. They were fully shaken by ultrasonic (from left to right: polyethylene glycol, acrylic acid, ammonium polyacrylate, ammonium citrate). Figure 1(b) is settlement diagram of the mixed slurry after centrifugation for 40 min by a centrifuge.
From Figure 1 (b), it can be seen that the ceramic slurry in suspension appeared different degrees of sedimentation after centrifugation. After centrifugation for 40 min, the concentration of ceramic slurry with polyethylene glycol and ammonium citrate is the most obvious. The ceramic slurry with acrylic acid and ammonium polyacrylate appeared obvious sedimentation. However, the precipitation rate of ammonium polyacrylate was slower than that of acrylic acid. Because acrylic acid does not produce ions, the ceramic slurry is suspended in a space-stable mechanism. Ammonium polyacrylate can produce ammonium ions and cause the surface charge of ceramic particles to change, resulting in electrostatic steric hindrance. At the same time, because of the adsorption effect, the effective radius of the particles is increased to generate steric hindrance [12]. Thereby, the effect of ammonium polyacrylate in reducing sedimentation is better than that of acrylic acid. Finally, the ammonium polyacrylate dispersant was selected in this experiment.

3.2 Analysis of dispersant concentration

Figure 2 presents a comparison of the ceramic sample d33 in two scenarios: the dispersant solution is added at the first ball milling only, and the dispersant solution is added at the second ball milling only.

It can be seen from figure 2 that the value of d33 increase firstly and then decrease when the first ball milling and the second ball milling separately add dispersant. And the maximum value was reached at 3 wt.% and 2 wt.%, respectively. This is due to the high concentration of ceramic slurry during ball milling, which has a negative effect on the dispersion effect of ceramic slurry [13]. Therefore, the concentration of the dispersant was 3 wt.% for the first ball milling only and 2 wt.% for the second ball milling only.

3.3 Phase structure of ceramics

Figure 3 shows the piezo-ceramic XRD patterns with dispersant in the first ball milling only (A), in the second ball milling only (B), in twice ball milling (C) and without dispersant in twice ball milling (D). All the samples show single stable perovskite (ABO3) structure with no impurity phase. After
adding the dispersant, the diffraction peak of ceramic sample gradually became sharper and the
diffraction peak intensity is higher, indicating that crystallinity of perovskite phase added with the
dispersant is improved. The best degree of crystallinity is the addition of dispersant to both ball milling.

![XRD diagram of adding dispersants at different stages.](image)

3.4 Microstructure of ceramics
Figure 4 shows the SEM images of adding dispersants at different stages. It can be seen that adding
dispersant samples show excellent compactness. The first or second ball milling only added dispersant
shows trans-granular fracture. But when the dispersant is added to both, inter-granular fracture occurs. The
 ceramic grains are plump. The grain boundaries are tightly bonded and the angularity is clear. In figure
4 (d), the density and grain growth of ceramics is poor. There are a few pores in the structure. Ball
milling without adding dispersant leads to agglomeration [14]. It can be seen that the addition of
dispersant allows the ceramic slurry to be more uniformly dispersed in the solvent, effectively avoid
agglomeration between the ceramic particles. The uniform grain size improves the overall electrical
performance of the sample.

![Microstructure of the samples.](image)

3.5 Electrical properties of ceramics
Figure 5 shows the electrical performance of sample A, B, C and D. It can be seen from figure 5(a),
the piezoelectric constant (d_{33}) and the electromechanical coupling coefficient (k_P) show the maximum
value when the dispersants are added in both ball milling. The best grain development, dense grains
and uniform grain size are showed from the SEM image at this time. On the other hand, the addition of
dispersant during ball milling disperses large particles in the ceramic powder into smaller particles.
The result shows that the ceramic slurry is kept in a stable suspension state and piezoelectric properties
of the sample being improved [15]. As can be seen from the figure 5(b), dielectric loss (\tan\delta) are
significantly reduced after adding dispersant. So when both ball milling are added dispersant, ceramic
samples present the best performance values: d_{33} = 907 pC/N, \varepsilon_r = 6889, k_p = 65.62\%, \tan\delta = 1.53\%.
4. Conclusion
In conclusion, ammonium polyacrylate has obvious dispersive effect on PSN-PMS-PNN-PZT piezoelectric ceramic. All samples have single-stable ABO$_3$ perovskite structure. When both ball milling was added dispersant, it shows inter-granular fracture. The ceramic grains are plump and the grain boundaries are tightly bonded. After adding dispersants, the piezoelectric properties of the ceramic samples are improved and the ceramic sample shows the best properties value when both ball milling are added dispersants: $d_{33}=907$ pC/N, $\varepsilon_r=6889$, $k_p=65.62\%$, $\tan\delta=1.53\%$.

Acknowledgments
The authors acknowledge the support of the National Natural Science Foundation of China (NSFC) (project number: 51762009).

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