Fabrication and Characteristics of Small Sized PZT Powders by using a Propyl Alcohol based Sol-Gel Method

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ABSTRACT

The PZT(lead, zirconium, titanium) based ceramics which, are reported to be ferroelectric materials have their important applications in the areas of surface acoustic waves (SAW), filters, infrared detectors, actuators, ferroelectric random acess memory, speakers, electronic switches etc. Moreover, these PZT materials possess the large electromechanical coupling factor, large spontaneous polarization, low dielectric loss and low internal stress etc. Hence, keeping in view the unique properties of PZT piezoelectric ceramics we also tried to synthesize indigenously the small sized PZT ceramic powder in the laboratory by using the modified sol-gel approach.

In this paper, propyl alcohol based sol-gel method was used for preparation of PZT piezoelectric ceramic. The powder obtained by this sol-gel process was calcined and sintering to reach a pyrochlore-free crystal phase. The characterization of synthesized material was carried out by the XRD analysis and the surface morphology was determined by high resolution scanning electron microscopy.

Key Words : PZT, Sol-Gel

Ⅰ. Introduction

Due to their distinctive energy conversion function, lead zirconate titnate (PZT) based ceramics are used for sensors, transducers, and capacitors[1],[2] the magnitudes of piezoelectric voltages, movements, or forces are small and often require amplification piezoelectric materials have been adapted to an impressive range of applications[3] also PZT possesses a large electro-mechanical coupling factor, large spontaneous polarization, low dielectric loss and low internal stress. The piezoelectric effect and inverse piezoel-ectric effect is used in sensing and actuation applications, such as in sensor generators, actuators transducers and in generating sonic and ultrasonic signal. In most applications for piezoelectric materials there is continual demand for improved performance, greater movement, higher temperature limits, longer lifetime etc.

Several methods were presented for the preparation of the PZT powders viz., hydrothermal solutions, solid state reaction, spin-coating co-precipitation and sol-gel etc[4]-[6]. Among these we adopted the Sol-gel method to prepare PZT powders because of its possibility to composed nanoscale powders for implementations in nano structure devices. A propyl alcohal based sol-gel method was used to prepare the nanoscale PZT powders[7],[8]. The present investigation deals the detailed method of the preparation of the small sized PZT powders as applying by various firing condition and then to determine its resistivity towards the temperature in terms of the change in resonance and anti resonance frequency at various temperatures.

Ⅱ. Preparation of PZT

PZT precursor solution of the composition $Pb1Zr._{53}Ti._{47}$ was prepared from the $Pb(CH_3CO_2)_2.3H_2O$(lead acetate trihyd rate), $Zr(C_3H_7O)_4$

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(zirconium tetra propoxide) 70% wt solution in1-proponal and $Ti[(CH_3)2CHO]_4$ (Titanium(IV) isopropoxide)97%[8] also shown in flow diagram(*cf* figure 1). Lead acetate was dissolved into the propyl alchol by the ratio 15:1. Dehydare the solution at 110℃and then reflux it under stirring for 2 hrs at the same temperature i.e., 110℃. Cooled down the solution mixture to 90℃and then to add $Zr(C_3H_7O)_4$ and glacial acetic acid to check the pH as to be kept constant as about ~5. Again stirred the solution and refluxed at 110℃ for ca 1h. Further, in this lead zircounium solution, added $Ti[(CH_3)2CHO]_4$ solution again checked the pH of the solution and controlled it by addition of glacial acetic acid. Stirred and reflux the solution mixture for ca 2 hrs at 110℃a clear yellow PZT solution was obtained which was returned to gel form while cooled down at room temperature. Further, the gel was evaporated at 120℃to obtained yellowish white PZTpowders. The powder was grind by mortar and calcined at 900℃for various time intervals i.e., from 1 hrs to 4 hrs in the alumina crucible. The calcined powders were further subjected for the preparation of disk as by using the die-pressing machine. These disks were encapsulated in alumina crucible to avoid any loss of lead in sintering process as was then sintered at1000℃, 1050℃, 1100℃, 115 0℃, 1200℃.

Now we can obtain the PZT Ceramic. The crystal phase was determined by the X-ray diffraction method by using the Rigakeu (D-max-2200) X-ray diffraction meter (XRD). These are scanned from 10℃ to 40℃at a scanning speed of 0.01/min. Moreover, the surface morphology was analyzed by using high-resolu-tionscanning electron microscope (SEM). Ag polished the PZT ceramics cleaned and coating. The silver electrode can enable to get a better ohamic contact to allow better electric properties measurements. The modified Sawyer Tower circuit[9] was used to ascertain the ferroelectric property(a hysteresis loop) of PZT ceramic. HEWLETTPACKARD 4284A was used for determining the dielectric constant and dielectric

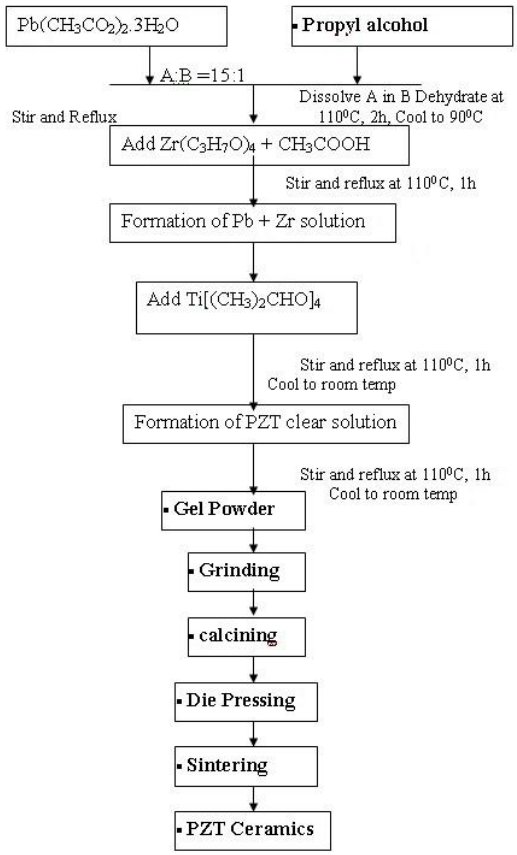

Fig. 1. Flow diagram for the preparation of PZT

losses. The grain size of the PZT sample was estimated by the SEM analysis and it was found to be in the range of 500 to 600nm.

Ⅲ. Result and discussion

The X-ray diffraction analysis obtained for calcined powders at 900℃ for 1h, 2h, 3h, 4h are shown in figure 2. The figures clearly demonstrate that the amount of pyrochlore phase was gradually decreased with increasing the calcining period as after 4h of calcining no pyrochlore phase was existed, only the perovskite phase occurred. Also it was noted that when the calcining time was 2h or more, the (100), (200) and (211) planes were splited into two peaks. Hence, it can be concluded that the tetragonal phase and rhombohedral phase coexisted during longer calcining period. Thus, suitable calcining

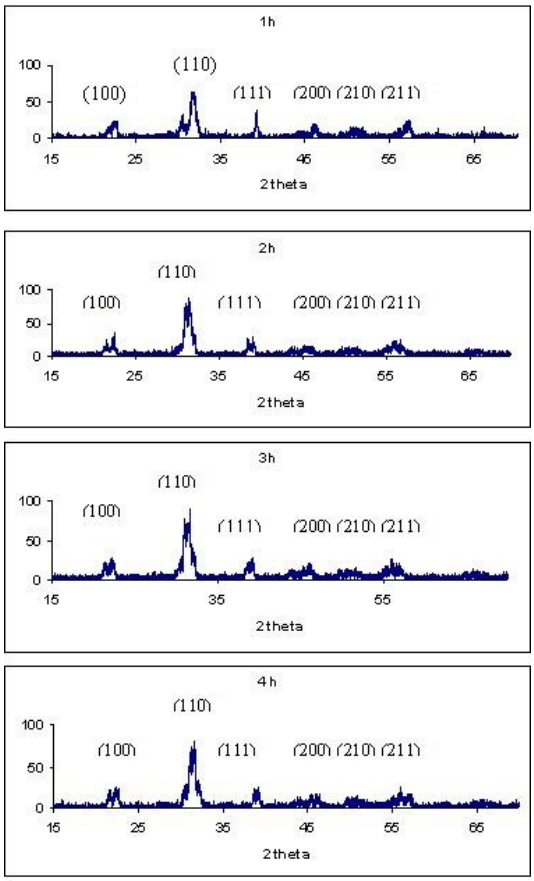

Fig. 2. X-ray diffraction patterns for PZT powders calcined at 900℃ as a function of calcining time

time is an important factor to make PZT powders. Calcined powders at 900℃ for 4h were ground and subjected for disk preparation. Disks were prepared as ca12mm in diameter and 0.5mm in thickness.

These disks were further sintered at 1000 ℃, 1050℃, 1100℃, 1150℃, and 1200℃ for 2h and the morphology of PZT ceramics were obtained by the SEM taking its SEM images. The SEM images for these PZT ceramics sintered at various temperatures were returned in figure 3. It was to be noted that reasonably a good homogeneous grain distribution was obtained for the PZT ceramics when sintered at 1100℃ and posses minimum average grain size.

However, at lower sintering temperature i.e., 1000℃ average grain sizes are big as may be due to the reaction was incomplete. Moreover, at

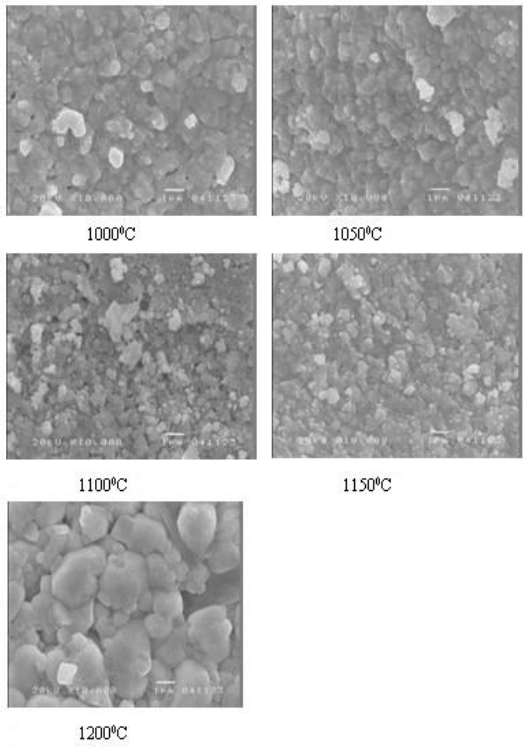

Fig. 3 SEM morphology of PZT ceramic calcined at 9000C for 4h and sintered at 1000℃, 1050℃, 1100℃, 1150℃, 1200℃ for 2h

higher sintering temperature i.e., at 1200℃ the grain size was larger as due to the loss of Pb, deviated from the perovskitetype lattice and precipitated along the grain boundary. Hence, the particle size was increased. Further, the grain size was estimated at 1100℃ and it was found to in the range of 400 to 500nm.

These PZT sintered disks were used for the evaluation of dielectric constant and dielectric loss and the values obtained were returned in table 1.

Table 1. Dielectric constant and dielectric loss of the PZT ceramics calcined at 900℃ then sintered at various temperature under 1, 10, 10^2KH

Sintering	f=1KHz		f=10KHz		f= 10^2 KHz	
temp ℃	ε_r	D × 10^{-3}	ε_r	D × 10^{-3}	ε_r	D × 10^{-3}
1000	723	101	701	80	669.2	10
1050	797	18	768	25	736	28
1100	880	15	851	26	829	34
1150	827	28	801	30	781	21
1200	792	105	762	71	738	49

It was noted that the dielectric constant er were decreased with increasing the frequency. Moreover, when it was sintered at 1100 ℃, 2h showed maximum dielectric constant i.e., 880 and showed minimum dielectric loss. Hence, this PZT material is likely to be a promising candidate for its possible applications in RF MEMS and microwave communication systems to meet the requirements for both high isolations and small device size, because the device size and the quality factor are inverse proportional to the $\sqrt{e}$ r and the dielectric loss respectively[10].

The above studies enabled that the PZT powder calcined at 900℃ for 4h, and sintered at 1100℃ for 2h were chosen for further assessment of electrical properties as due to the reasons, maximum dielectric constant, smaller particle size, homogeneous grain distribution, disappearance of pyrochlore. The ferroelectricity showed the hysteresis loop which was obtained by the modified shower tower circuit[9]. Poling voltage used were 3kVmm^{-1}, applied for 20min at 120℃[10]. The polarization and electric field are 4.27uC/cm2 and 15.6kV/cm per division respectively.

The impedance of PZT as a function of frequency was obtained and showed in figure 4. It is to be noted that when the PZT was exposed to an A.C. electric field, the impedance of PZT changes cyclically, at the cycling frequency of the field as the frequency of cycling is increased. Then the temperature dependence of resonance frequency, anti resonance frequency and impedance was measured.

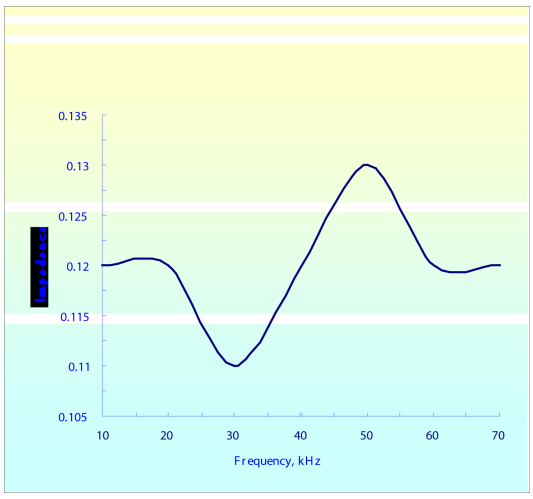

Fig. 4. Impedance as a function of frequency

Fig 5 shows that at the beginning at room temperature resistance is low and produce a large current after that increasing the temperature the resistance increases drastically hence the current will be reduce. Therefore, a smart self-regulating heating circuit is found. Smart structures are an integration of sensors, actuators, and control system[11].

Fig 6 shows that the temperature dependence resonance frequency and anti resonance frequency. The change in slope indicates the phase change. Consequently, for a mixture of rhombohedral and tetragonal phase a TCF will be low (near to zero) this shows the great piezoelectric properties.

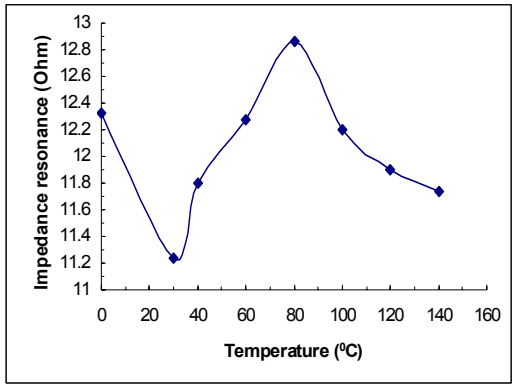

Fig. 5. Impedance resonance as a function of temperature

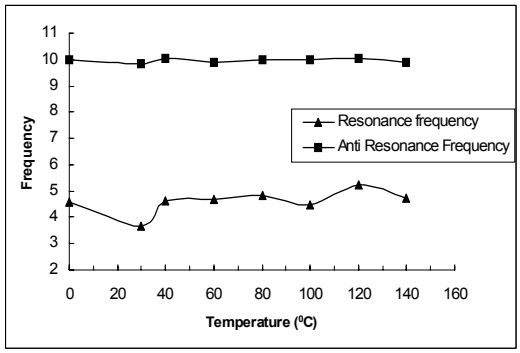

Fig. 6. Resonance frequency and anti resonance frequency as a function of temperature

Ⅳ. Conclusions

PZT nano powders and ceramics were prepared using a sol-gel method and it has been shown that the sol-gel method is a simple and effective way to prepare PZT powders and ceramics. The sol-gel method is mainly affected by the firing conditions and must use the excess of Pb to recover the loss of Pb during the sintering process. XRD data obtained at various calcining time at 900℃showed that the pyrochlore phase was completely disappeared at the calcining time 4h. Dielectric constant, dielectric loss , resonance frequency and temperature dependence Impedance were measured. We found that the PZT samples have good piezoelectric property and will have the potential for application such as various piezoelectric transducers and sensors.

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