ELSEVIER

Ceramics International 32 (2006) 583–586

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of electrolysis of water on the properties of soft lead zirconate titanate piezoelectric ceramics

X.P. Jiang [a,b,*], W.P. Chen [b], Z. Peng [b], M. Zeng [a], H.L.W. Chan [b], C.L. Choy [b], Q.R. Yin [c]

[a] *Department of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen, 333001 Jiangxi, China*
[b] *Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, China*
[c] *The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, 1295 Dixi Road, Shanghai 200050, China*

Received 9 December 2004; received in revised form 26 February 2005; accepted 7 April 2005
Available online 20 June 2005

Abstract

Water-induced degradation in soft lead zirconate titanate (PZT) piezoelectric ceramics has been studied using electrochemical hydrogen charging, in which the silver electrodes of the piezoelectric ceramics is made a cathode in a 0.01 M NaOH solution to evolve hydrogen by electrolysis of water. It is found that with increasing hydrogen charging time, the impedance at the resonance frequency Z_r increases, and the difference between the resonance and anti-resonance frequency ($f_a - f_r$) decreases. The dielectric permittivity and piezoelectric coefficient d_{33} decreases while the dielectric loss increases. *I–V* measurement shows that the resistivity decreases after hydrogen charging. These degradation behaviors in the soft piezoelectric ceramics can be explained as hydrogen incorporating into the lattice and forming hydroxy (OH^-) bonds in the perovskite structure, which restrains the Ti ions from switching. The soft piezoelectric ceramics is partially depolarized after hydrogen charging which is quite different from that of hard lead zirconate titanate piezoelectric ceramics.

PACS: 77.84.Dy; 77.22.Ej; 82.80.Fk

Keywords: Lead zirconate titanate; Degradation; Electrolysis; Hydrogen

1. Introduction

Lead zirconate titanate (PZT) based-ceramics have been widely used because of their superior piezoelectric properties. Doped with a small amount of different ions, their properties can be changed greatly and adapted to different applications. The soft PZT, doped by higher valence ions such as La^{3+} in A-site or Nb^{5+} in the B-site of its perovskite structure, has larger piezoelectric coefficients, larger electromechanical coupling factors, higher bulk resistivity, and can be used in actuator, hydrophone, vibrators, high-power loudspeakers, etc. One of the major problem for soft PZT devices, as well as for hard PZT (doping with lower valence ions such as K^+ in the A-site or Mn^{2+} in the B-site of the perovskite structure) devices, is the stability and reliability of their operating characteristics. Sometimes serious degradation occurs for piezoelectric ceramic devices, especially for those used under high electric field, humidity and mechanical stress. Study on reliability is very important and some investigations have been carried out in perovskite-structure bulk materials (such as $BaTiO_3$ [1]) and PZT thin films [2–4]. Humidity or water, especially in the existence of electricity, can lead to seriously degradation. It is generally believed that the role of water facilitates the electromigration of silver along the grain boundaries of piezoelectric ceramics [5,6]. In other words, water reacts with the metallic component of the piezoelectric devices. Some recent studies [7–9], however, show that, in the presence of electricity, water has a profound influence on hard lead zirconate titanate ceramics and zinc oxide (ZnO)-based varistors, and a reduction reaction mechanism was proposed.

* Corresponding author. Tel.: +86 798 8491446; fax: +86 798 8491446.
E-mail address: jiangxp@hotmail.com (X.P. Jiang).

0272-8842/$30.00
doi:10.1016/j.ceramint.2005.04.014

For hard PZT ceramics, water in the presence of electricity cause the increase in dielectric loss and decrease in mechanical quality factor [7], but the piezoelectric constant d_{33} and the frequency difference between resonance frequency f_r and anti-resonance frequency f_a remains unchanged. It is well-known that the properties of soft PZT is totally different from that of the hard PZT, the degradation behavior may also be totally different. The objective of this study is to explore the effects of electrolysis of water on the degradation behavior of soft PZT. The results show that soft piezoelectric ceramics are influenced by electrolysis of water in a quite different way from the hard PZT piezoelectric ceramics. And it is of great importance to prevent water-induced degradation in soft piezoelectric ceramics.

2. Experimental processing

The soft PZT disk samples, with size of 1 mm × ∅ 13 mm, were sintered at 1260 °C using PZT 552 powders supplied by Piezo-Kinetics in USA. Samples coated by silver electrodes on the two major surfaces were poled in silicone oil at 120 °C for 20 min. Characteristics were measured after aging for 120 h as the initial data. Two kinds of different treatments were performed on the samples for comparison. In the first treatment, samples were immersed in a 0.01 M NaOH solution for some long periods of time and then taken out. They were washed by deionized water, then dried and measured. In the second treatment, some samples were placed in a 0.01 M NaOH solution and dc voltages were applied between the silver electrode of the disks and a steel anode in the solution. Electrolysis of water occurred due to the applied dc voltages and hydrogen was evolved on the silver electrodes of the samples while oxygen was evolved on the anode. So this treatment is referred to as "hydrogen charging" hereafter. The solution was kept agitated by a magnetic agitator and the temperature was kept constant at 25 °C. The dc voltages were removed after some designated periods of time and the samples were taken out. They were washed, then dried and measured. Impedance/phase versus frequency spectra of the soft PZT samples were measured using an Agilent 4294A impedance analyzer. A ZJ-3D piezoelectric d_{33} meter (manufactured by Beijing Institute of Acoustics, China) was used to measure the piezoelectric coefficient d_{33} of the disk samples. *I–V* characteristics of the samples were recorded by a Keithley 6517A electrometer. Micro-structural analyses were carried out by a scanning electron microscope (SEM STEROSCAN 440).

3. Results and discussions

The SEM microstructure analysis shows that the soft PZT samples have dense microstructure, which is important to prevent the permeation of water into the disks. In the first treatment, the samples were immersed in the NaOH solution for 10 days and no noticeable change in their properties was observed. These facts suggest that, in the absence of an electric field, the dilute NaOH solution does not influence the properties of soft PZT samples.

In the second treatment, serious degradation occurred after the samples were treated by hydrogen charging for a few hours. The influence of hydrogen charging on the spectra of impedance/phase versus frequency for the planar vibration mode is shown in Fig. 1. Fig. 1(a) is the spectra of the initial sample. The peak of minimum impedance corresponds to the resonance of the planar vibration mode, and the corresponding resonance frequency and impedance are marked by f_r and Z_r, respectively. The peak of maximum impedance corresponds to the anti-resonance of the planar vibration mode, the corresponding anti-resonance frequency and impedance are indicated by f_a and Z_a, respectively. The soft PZT sample was placed in a 0.01 M NaOH solution and subjected to a dc voltage of 3 V between its silver electrode and the anode in the solution. Under this voltage the cathode current density was around 0.2 mA/cm^2. This treatment was

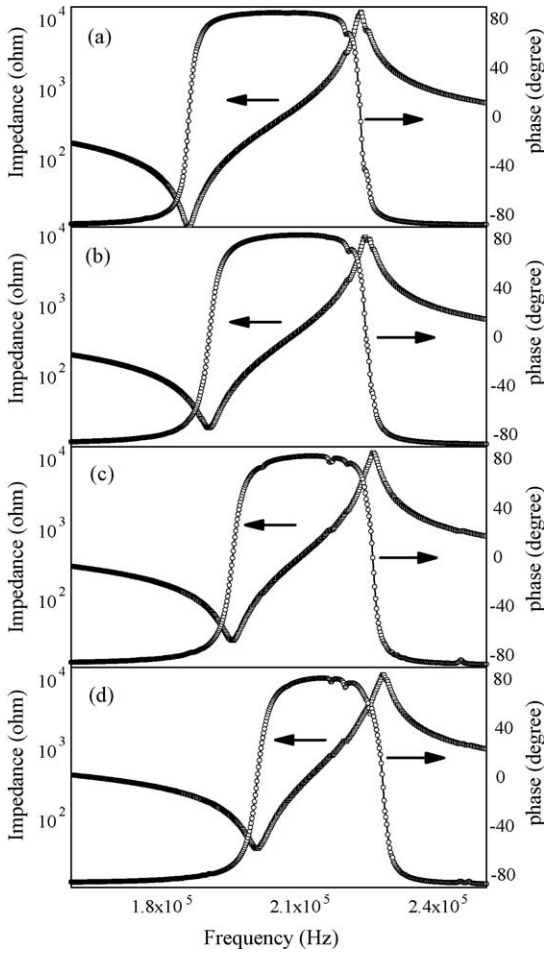

Fig. 1. Spectra of impedance/phase vs. frequency for the planar vibration mode: (a) initial sample; (b) hydrogen charged for 30 min; (c) hydrogen charged for 60 min; (d) hydrogen charged for 120 min.

interrupted several times and the sample was taken out for measurement. Fig. 1(b)–(d) shows the impedance/phase spectra of the planar vibration mode for the sample treated with hydrogen charging for 30 min, 60 min and 120 min, respectively. It is obvious that the resonance impedance Z_r increases with the increase in hydrogen charging time, but the anti-resonance impedance Z_a remains unchanged. Both the resonance frequency f_r and anti-resonance frequency f_a are shifted to higher frequency after the hydrogen charging, with f_r being shifted to higher frequency much faster than that of f_a. So the difference between f_r and f_a decreases by the hydrogen charging. It implies that the planar coupling factor k_p decreases with the increase in hydrogen charging time, i.e. less electrical energy can be converted to mechanical energy after hydrogen charging. This is quite different from the result obtained in hard PZT. For hard PZT, with the increase in the hydrogen charging time, f_r and f_a increases simultaneously while the difference between f_r and f_a almost remain unchanged [7].

Fig. 2 shows the influence of hydrogen charging on the dielectric permittivity and dielectric loss at 1 kHz. With the increase in hydrogen charging time, the dielectric permittivity decreases while the dielectric loss increases. According the formula $\varepsilon = 1 + \chi$, where χ is dielectric susceptibility, the decrease in dielectric permittivity indicates that the macroscopic polarization P of the soft PZT sample decreases as the hydrogen charging time increases. The increase of in dielectric loss is due to the reduction reaction of hydrogen atom and the diffusion of hydrogen ions into the ceramics, which will be discussed in following section.

Fig. 3 shows the influence of hydrogen charging time on the piezoelectric coefficient d_{33}. With increase in the hydrogen charging time, the piezoelectric coefficient d_{33} decreases, It means that the soft PZT sample partially depolarizes as the hydrogen charging time increases. For hard PZT, however, the hydrogen changing treatment has no noticeable influence on piezoelectric coefficient d_{33} [7].

The degradation of PZT thin film when it is annealed in an atmosphere containing hydrogen has been reported and a hydrogen incorporation mechanism has been proposed to explain the degradation in the ferroelectric properties [2].

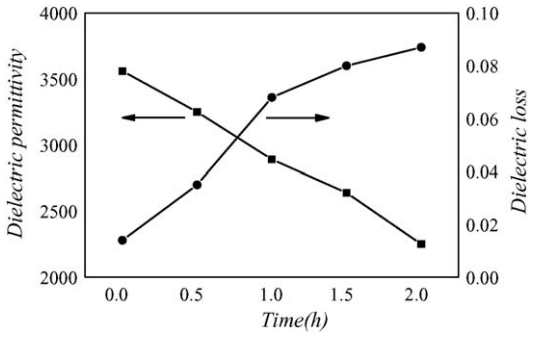

Fig. 2. The influence of hydrogen charging time on the dielectric permittivity and dielectric loss at 1 kHz.

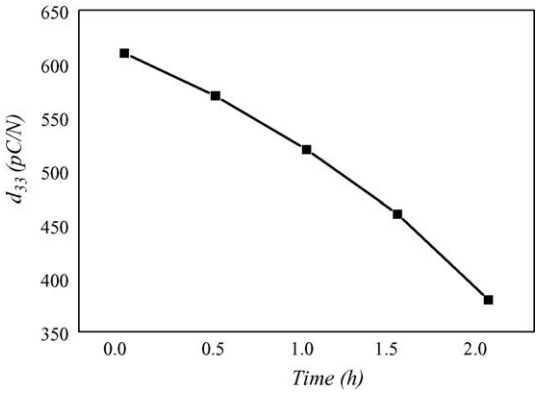

Fig. 3. The influence of hydrogen charging time on the piezoelectric coefficient d_{33}.

According to this hydrogen incorporation mechanism, the hydrogen ion is bonded with one of the apical oxygen ions of the tetragonal structure, forming a polar hydroxy ion. The hydroxy ion in the tetragonal structure suppresses the spontaneous polarization of the PZT film and prevents the Ti ion from switching. In this study, the degradation behavior of soft PZT in the electrolysis water can also be explained using similar hydrogen incorporation mechanism.

The evolution of hydrogen on the silver electrode of the soft PZT sample can be written as:

$$H_2O + e^- \rightarrow OH^- + H_{ads} \quad (1)$$

$$H_{ads} + H_{ads} \rightarrow H_2 \quad (2)$$

where H_{ads} represents an adsorbed hydrogen atom. Hydrogen atoms are very reactive and exist only as intermediate products [10]. Some of them may react with other materials encountered in their paths, although most of them combine with one another to form hydrogen molecules. In this study, the incorporation of hydrogen into the soft piezoelectric ceramics can be written as:

$$H_{ads} \rightarrow H_i + e^- \quad (3)$$

where H_i represents an interstitial proton. After this reduction reaction, the hydrogen ion diffuses into the ceramics,

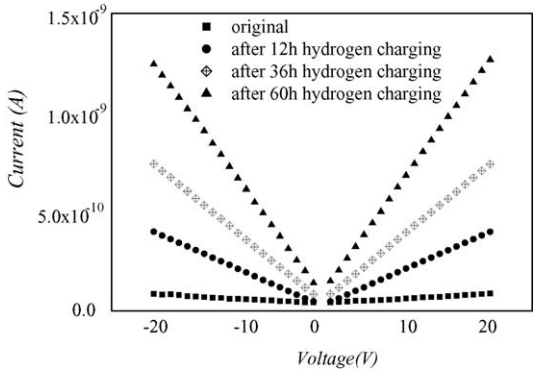

Fig. 4. The *I–V* characteristic of soft PZT samples after hydrogen charging for 0 h, 12 h, 36 h and 60 h.

forming hydroxy bonds with one of the apical oxygen ions along the polarization axis in the octahedra. The hydroxy bond prevents the switching of the Ti or Zr ions and suppresses the polarization. The free electrons in the ceramics reduce the resistivity and the dielectric loss increases correspondingly. The *I–V* characteristic of the soft PZT piezoelectric ceramics shows, as shown in Fig. 4, that the leakage current *I* increases with the increase in the hydrogen charging time, and the dc resistivity decreases correspondingly.

Direct observation of deuterium incorporated into (Ba,Sr)TiO_3 thin film annealed in D_2/N_2-containing furnace has been detected by secondary ion mass spectrometry [11]. It is reasonable to suppose that hydrogen diffuse into the perovskite structure and cause the degradation. Hydrogen is very harmful to the ferroelectricity for both bulk materials and thin films. In the forming gas annealing of PZT thin films, the hydrogen reduction reaction occurs at elevated temperature [2,12,13]. However, in our experiment, the reduction reaction occurs at ambient temperature. The cause of the reduction may be due to atomic hydrogen rather than molecular hydrogen and the electricity plays a vital role in the degradation [7].

In summary, serious degradation occurs in soft PZT ceramics induced by hydrogen in water in the presence of electricity. The degradation behavior induced by hydrogen in water is different from that of hard PZT. With the increase in the hydrogen charging time, the frequency difference of f_r and f_a decreases. Also, the dielectric permittivity and d_{33} decrease while the dielectric loss increases. The degradation behavior of the soft PZT samples can be explained by hydrogen atom reduction reaction and hydroxy ion bonds formed in the perovskite structure.

Acknowledgement

This work is supported by the natural science foundation of Jiangxi province (No.: 0450023), the Centre for Smart Materials and the Postdoctoral Research Fellowship Scheme of The Hong Kong Polytechnic University.

References

[1] R. Waser, J. Am. Ceram. Soc. 71 (1988) 58.
[2] S. Aggarwal, S.R. Perusse, C.W. Tipton, R. Ramesh, H.D. Drew, T. Venkatesan, D.B. Romero, V.B. Podobedov, A. Weber, Appl. Phys. Lett. 73 (1998) 1973.
[3] Y. Shimamoto, K. Kushida-Abdelghafar, H. Miki, Y. Fujisaki, Appl. Phys. Lett. 70 (1997) 3096.
[4] J.-H. Ahn, P.C. Mclntyre, L.W. Mirkarimi, S.R. Gilbert, J. Amano, M. Schulberg, Appl. Phys. Lett. 77 (2000) 1378.
[5] G.H. Haertling, J. Am. Ceram. Soc. 82 (1999) 797.
[6] M.D. Hill, G.S. White, C.S. Hwang, J. Am. Ceram. Soc. 79 (1996) 1915.
[7] W.P. Chen, H.L.W. Chan, F.C.H. Yiu, F.C.H. Yiu, K.M.W. Ng, P.C.K. Liu, Appl. Phys. Lett. 80 (2002) 3587.
[8] W.P. Chen, H.L.W. Chan, J. Am. Ceram. Soc. 85 (2002) 1625.
[9] W.P. Chen, J.Q. Qi, Y. Wang, X.P. Jiang, H.L.W. Chen, J. Appl. Phys. 95 (2004) 5920.
[10] C.J. Raub, Plat. Surf. Finish. 80 (1993) 30.
[11] J.H. Ahn, P.C. Mclntyre, L.W. Mirkarimi, S.R. Gilbert, J. Amano, M. Schulberg, Appl. Phys. Lett. 77 (2000) 1378.
[12] S. Seo, J.G. Yoon, T.K. Song, B.S. Kang, T.W. Noh, Y.K. Lee, C.J. Kim, Y.S. Park, Appl. Phys. Lett. 84 (2002) 697.
[13] S. Aggarwal, S.R. Perusse, B. Nagaraj, R. Ramesh, Appl. Phys. Lett. 74 (1999) 3023.