EFFECTS OF NITROGEN DOPING ON PHOTOVOLTAIC PROPERTY OF LEAD LANTHANUM ZIRCONATE TITANATE FERROELECTRIC CERAMICS

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Abstract

For decades, the phenomenon effects of ferroelectric ceramics have been known and called the photostrictive effect. The photostrictive effect is the superposition of photovoltaic and piezoelectric effects and this study concentrated on the method to improve the photovoltaic effect and optical absorption edge of lead lanthanum zirconatetitanate [$(Pb_{0.97}La_{0.03})$ $(Zr_{0.52}Ti_{0.48})_{1-0.03/4}O_3$ or PLZT, (3/52/48)] by nitrogen doping. The ceramics which were doped were prepared by replacing the content of the TiO_2 precursor with TiN and mixed by ball milling in an ethanol medium. The bulk pellets of the doped PLZT ceramics exhibited a photocurrent (I_{ph}) and photovoltage (E_{ph}) higher than that of the undoped PLZT. These differences are due to the characteristics of the nitrogen ion substituted at the O-site in the lattice of the PLZT unit cell. The UV/VIS spectroscopy data indicated that the range of the optical absorption edge of doped PLZT ceramics was wider than that of the undoped PLZT. This material has also the advantage of the improved conversion process of light energy to electrical energy.

Keywords: Photovoltaic effect, PLZT, ferroelectric, nitrogen doped

Introduction

The photostrictive phenomenon of ferroelectric ceramics is of interest to be used for energy converting applications. Especially, its photovoltaic property has been intensively researched for transforming light into electricity (Ichiki *et al*., 2004; Huang 2010; Ji *et al*., 2010; Yang *et al*., 2010; Zhou 2012). These materials can generate a high photovoltage, about 1000 V/cm, which is higher than 10^3 times that of asilicon based

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p-n junction solar cell. Lead lanthanum zirconatetitanate (PLZT 3/52/48) is interesting and widely used for an energy transducer because of its wide-ranging properties and applications (Ichiki *et al.*, 2005; Qin *et al.*, 2008). However, its photovoltaic effect only responds under UV light (approximately 365 nm). There are 3 methods to improve the photovoltaic properties of PLZT: 1. Decreasing thickness, 2. Preferential crystalline orientation, and 3. Ion doping in the lattace (Nonaka *et al.*, 1995; Ichiki *et al.*, 2004; Ichiki *et al.*, 2005; Ichiki *et al.*, 2005; Yao *et al.*, 2005; Qin *et al.*, 2007; Qin *et al.*, 2008; Qin *et al.*, 2009). Various cationdopings are interesting to decrease the energy band gap of PLZT to make it close to the energy of the visible light region but they are still in the UV region (Nonaka *et al.*, 1995; Nonaka *et al.*, 1996; Yao *et al.*, 2005; Lallart 2011). Asahi *et al.* reported the photocatalysis improvement of titanium dioxide to respond to visible light by nitrogen doping because it could shift the absorption edge to a lower energy (Asahi *et al.*, 2001). Moreover there is much evidence to prove that nitrogen doping is the cause of the lower energy band gap of materials (Chen and Burda 2004; Livraghi *et al.*, 2006; Wu *et al.*, 2008; Trenczek-Zajac *et al.*, 2009; Xing *et al.*, 2009; Zhou *et al.*, 2011). Nitrogen doping would be useful to improve the photovoltaic effect of PLZT. In this study, nitrogen ion was used to dope into PLZT ceramics by replacing the TiO_2 precursor with TiN. Improvements in the absorption edge and photovoltaic effect of PLZT samples were also achieved as explained in this research.

Materials and Methods

Sample Preparation

Lead lanthanum zirconatetitanate ferroelectric ceramic (PLZT (3/52/48) or $Pb_{0.97}La_{0.03}Zr_{0.52}Ti_{0.48}O_3$) samples were prepared by a conventional ball milling technique. This composition is corroborated by the highest photovoltaic power of PLZT reported in 1999 (Poosanaas and Uchino, 1999). The laboratory grade oxide precursors were used as reactants such as PbO (> 99.0%, Sigma-Aldrich Corp., St. Louis, MO, USA), La_2O_3 (99.98%, Fluka Analytical, Buchs, Germany), ZrO_2 (3% HfO_2, Fluka), and TiO_2 (> 99%, Fluka). The excess lead oxide as 2 mol% was used to compensate for lead loss to achieve high density ceramics. Substitution of 0-100 at% of TiN for the TiO_2 precursor was used in this research. The calculated ratios of the oxide mix and TiN were ball milled in a polypropylene bottle with zirconia balls and 80 ml of absolute ethanol medium for 20 h. The mixtures were dried at 60°C with a rotary evaporator and screened though a 100 mesh sieve.

After calcining at 950°C in a closed alumina crucible for 10 h, the powder mixtures were ball milled and screened through a 100 mesh sieve again. One gram of calcined powder was pressed into a 13mm diameter pellet at 50 MPa. Three grams of $PbZrO_3$ powder was pressed into a 13 mm diameter and put in the center of an alumina crucibleto provide the PbO atmosphere during sintering. The pellet samples were laid on an undoped PLZT powder layer to preventmelting and cracking. The pellet samples were sintered in a closed crucible at1, 250°C for 2 h. The sample preparation is shown by the flow chart in Figure 1.

Characterizations

The bulk density of the PLZT samples was measured by the Archimedes' principle. The theoretical density of the samples was calculated from the molecule weight of the mixture divided by the lattice volume of each composition. X-ray diffractometer (D8-Advance, Bruker Corp., Billerica, MA, USA) with Cu-Kα radiation was used for monitoring the sample phases. Diffraction data were collected over the 2θ range from 10 to 80° with a step size of 0.02°. Lattice parameters were determined by high resolution 2θ data from 40 to 50° with a step size of 0.001°. The silicon powder was added by 20 wt% of PLZT powder to refference 2θ at 47.305°. Lattice parameters were calculated from 2θ of the (002) and (200) peaks.

Sintered samples were cut to be 3×5×1 mm^3 and polished to 1 μm of diamond paste on both 3×5 mm^2 surfaces. High purity silver paint emulsion was painted on 2 opposite 5×1 mm^2 surfaces for the electrode. Before the electromechanical measurements, the samples were pooled by 2 kV/mm of applied voltage in a silicone oil bath at 120°C for 15 min.

The dielectric constant (k) and dissipation factor (D) were determined 24 h after poling by a 4192A LF impedance analyzer (Hewlett-Packard Co., Palo Alto, CA, USA). The resonance/anti-resonance method according to the Institute of Radio Engineers standard was used to measure the k and D at various frequencies such as 10 kHz, 100 kHz, and 1 MHz. The piezoelectric strain coefficient (d_{33}) of each sample was measured with a YE2730A d_{33} meter (APC International, Ltd., Mackeyville, PA, USA).

The photovoltaic measurement was operated by an illuminated perpendicular UV light to the 3×5 mm^2 polished surface. High intensity UV light was emitted from a short arc mercury lamp (Ushio Optical Modulex H500, Ushio Inc., Tokyo, Japan). An optical filter (Oriel No. 59060, Newport Corp., Irvine, CA, USA) was used to obtain a monochomatic light with the maximum around 365 nm wavelengths. This wavelength has been reported to provide the maximum photovoltaic properties (Poosanaas and Uchino, 1999). The UV light intensity used in this study was 2.10 mW/cm^2 (Wasanapiarnpong, 2002). A picoammeter with a voltage source (487 Picoammeter/Voltage Source, Keithley Instruments Inc., Cleveland, OH, USA) was used to measure the photocurrent while samples were illuminated with the UV light, and the plot of the measured current and applied voltage (from -100 V to + 100 V step size 10V). The photovoltage (E_{ph}) was

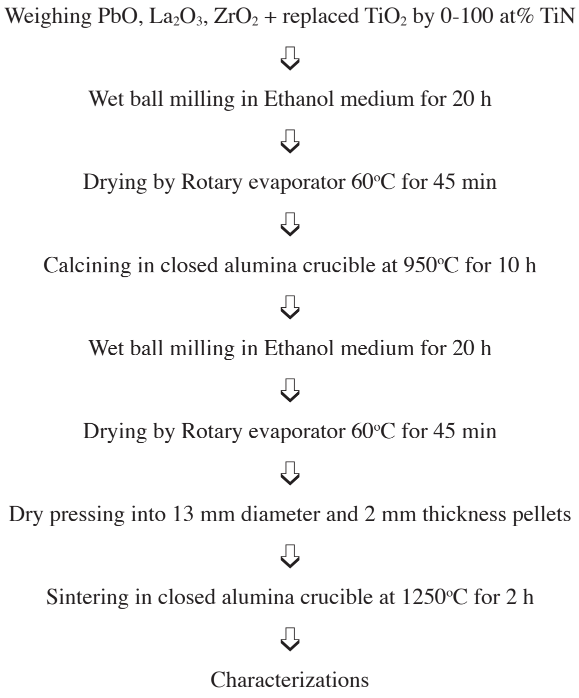


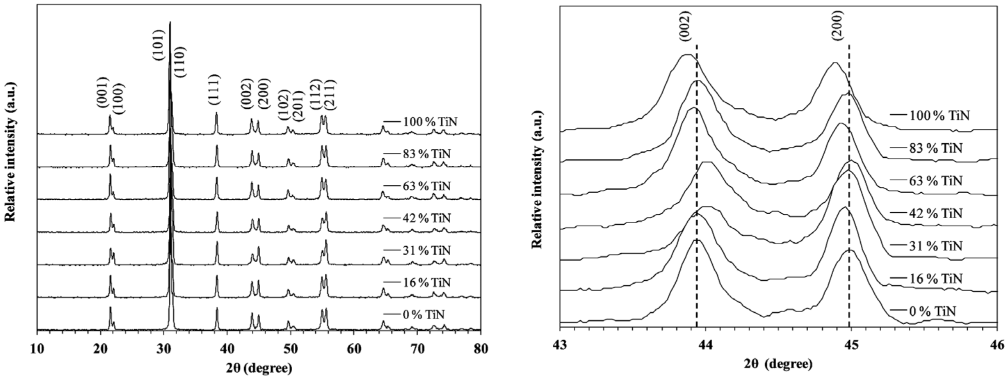
Figure 1. Flow chart diagram of samples preparation by the conventional ball milling technique

indicated by the intercept of the applied voltage axis. The photocurrent (I_{ph}) was indicated by the intercept of the current axis.

Results and Discussion

XRD patterns of the sintered samples are shown in Figure 2(a). All the compositions consist of only PLZT (3/52/48) single phase. The changing lattice parameters are observed shifting to lower than 2θ at the (002) and (200) peaks while the increase of the TiN content, is shown in Figure 2(b). This means that the lattice parameters increase with the increasing substitution of TiN on the TiO_2 content, as shown in Figure 3. The lattice parameters (a and c axis) are calculated by the XRD method from 2θ of the (002) and (200) of the PLZT (3/52/48) peaks (Joint Committee on Powder Diffraction Standards No. 33-0784).

The bulk density of all samples is around 7.7 g/cm^3 which is close to another report (Wasanapiarnpong, 2002). Theoretical densities are calculated by the molecular weight of each composition per lattice volume, which is calculated from the XRD. The theoretical density is about 8.0 g/cm^3. The bulk density of each sample reached 96% of the theoretical density. The tetragonality of



(a) (b)

Figure 2. (a) XRD patterns of sintered PLZT samples and (b) Expanded 2θ of the (002) and (200) peaks as increasing the TiN content

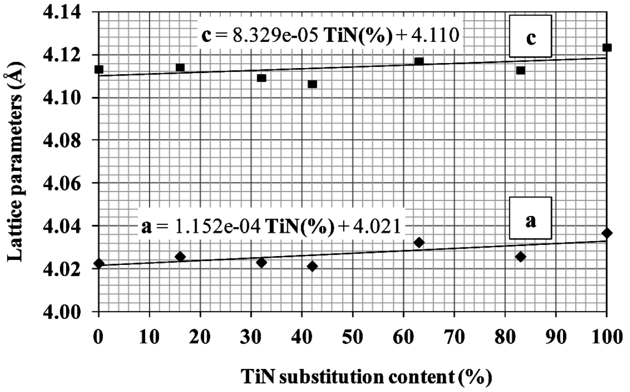


Figure 3. Lattice parameter for a and c axis of PLZT corresponding to content of TiN replacement

the sample decreased with the increasing TiN content, as shown in Table 1.

The room temperature dielectric constant (k) and dissipation factor (D) of the samples were measured at 10 kHz, 100 kHz, and 1 MHz of the electrical frequency. The k of every sample reached over 1000. The D increases while the electrical frequency increases, as shown in Table 2. The piezoelectric strain coefficient of every specimen reached over 330 pC/N, as shown in Table2.

The photovoltage (E_{ph}) and photocurrent (I_{ph}) are determined to explain the photovoltaic effect of the PLZT samples. The voltage source is applied from the 487 Picoammeter/Voltage Source (Keithley) and measured the current is measured from a plot of the I-V curve in the range from -100 to + 100 V. The hotovoltage and photocurrent are obtained from the intercept of the voltage axis and current axis, respectively (Poosanaas and Uchino, 1999; Wasanapiarnpong, 2002). The photovoltage of the undoped PLZT in this study is established at 433 V/cm which is close to other previous reports (Poosanaas and Uchino, 1999; Wasanapiarnpong, 2002). The trend of the photovoltage dramatically inceases while the content of TiN replacing the TiO_2 increases, as shown in Figure 4(a). The photovoltage increases from 400 to 800

Table 1. **Bulk density, theoretical density, relative density, and tetragonalityof PLZTsamples**

TiN content (%)	Bulk density (g/cm^3)	Theoretical density (g/cm^3)	Relative density (%)	Tetragonality (c/a ratio)
0	7.7218	8.0743	95.63	1.0225
16	7.7303	8.0564	95.95	1.0220
31	7.7703	8.0731	96.25	1.0214
42	7.7618	8.0831	96.02	1.0212
63	7.7449	8.0132	96.65	1.0210
83	7.7035	8.0428	95.78	1.0216
100	7.7215	7.9741	96.83	1.0215

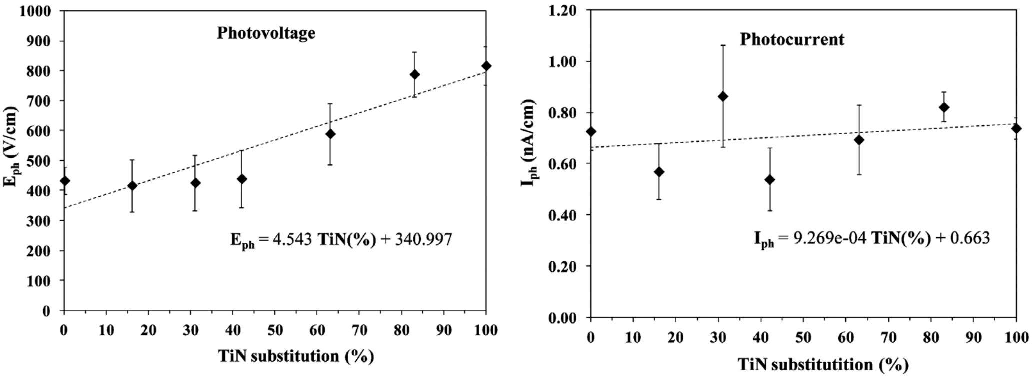
Table 2. **Dielectric constant (k) and dissipation factor (D) at 10 kHz, 100kHz, and 1 MHz and piezoelectric constant (d_{33}) of PLZT ceramic samples**

TiN content (%)	10 kHz		100 kHz		1 MHz		d_{33} (10^{-12}C/N)
	k	D	k	D	k	D	
0	1444	0.0202	1515	0.0217	1196	0.1335	338
16	1499	0.0182	1557	0.0729	1115	0.2144	338
31	1156	0.0163	1179	0.0190	1103	0.0770	322
42	1446	0.0210	1512	0.0603	1004	0.3219	348
63	1454	0.0189	1512	0.0231	1099	0.4095	324
83	1483	0.0198	1539	0.0240	1151	0.0702	337
100	1464	0.0188	1527	0.0214	1153	0.0498	339

V/cm when TiN substituted for the TiO_2 precursor increases from 0 to 100 wt%. The photocurrent of every sample is in the range of 0.7-0.8 nA/cm. The trend of the photocurrent slightly increases while the content of the TiN increases as shown in Figure 4(b).

The photovoltaic power (P_{ph}) is calculated by the multiple of the photocurrent and photovoltage ($P_{ph} = I_{ph} \times E_{ph}$), so the photovoltaic power increases from 300 to 600 nW/cm^2. The photovoltaic conductance (G_{ph}) is calculated from the photocurrent divided by the photovoltage ($G_{ph} = I_{ph} / E_{ph}$). The photovoltaic conductancedecreases from 1.68×10^{-12} to 0.90×10^{-12} ohm^{-1} while the TiN content increases from 0-100 wt%, as shown in Table 3.

The efficiency of the photovoltaic effect is explained from the percentage of the output energy per input energy. In this work, the output energy is decribed by the photovoltaic power of each sample and the input energy is decribed by the light intensity (2.1 mW/cm^2). The efficiency of the photovoltaic effect increased from 0.015 to 0.030% along with the increasing content of TiN replacing the TiO_2 by 0-100 wt%, as shown in Table 3. This means that the replacing of TiN for the TiO_2 precursor content can improve the photovoltaic effect of PLZT ceramics.



(a) (b)

Figure 4. (a) Photovoltage and (b) Photocurrent as a function of replacing content of TiN

Table 3. Photocurrent (I_{ph}), Photovoltage (E_{ph}), Potovoltaic power (P_{ph}), Photovoltaic conductance (G_{ph}), and Energy conversion efficiency of PLZT ceramic samples

TiN content (%)	I_{ph} (nA/cm)	E_{ph} (V/cm)	P_{ph} (nW/cm^2)	G_{ph} (x10^{-12} ohm^{-1})	Efficiency (%)
0	0.7270	432.96	314.76	1.68	0.015
16	0.5694	416.54	237.17	1.37	0.011
31	0.8641	425.87	368.01	2.03	0.018
42	0.5387	439.28	236.64	1.23	0.011
63	0.6942	589.40	409.15	1.18	0.019
83	0.8216	788.20	647.55	1.04	0.031
100	0.7385	816.71	603.10	0.90	0.029

Conclusions

The substitution of TiN for the TiO_2 precursor and sintering in a closed crucible causes a single phase of PLZT (3/52/48). Moreover, this method expands the lattice parameters while causing no effect on the bulk density and relative density of the samples. On the other hand, it has been found that the preparation method improves the photocurrent and photovoltage of PLZT ceramics and provides high efficiency of the photovoltaic effect of PLZT.

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