

Photovoltaic Effect in PZT Ceramics Introduced with Pb Vacancies

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Lead zirconate-titanate ceramics introduced with Pb vacancies have been prepared by changing molar ratio of Pb/(Zr+Ti) from 0.90 to 1.01 and by multiple doping of Na and Ta in various combinations to investigate the change in photovoltaic properties with changes in the concentration of Pb vacancies, and also grain size, upon ultraviolet irradiation. Results confirmed that the photovoltaic current increased abruptly when the molar ratio was less than 1.00. At the same time, the photovoltage also showed an increasing tendency. Accordingly, the maximum output power markedly increased, confirming a net increase in photovoltaic efficiency. On the other hand, doped samples showed that the photovoltaic effect could be enhanced when the doping amount of Ta was greater than that of Na. From these results, it is proposed that creating Pb vacancies on the perovskite lattice is essential for the photovoltaic properties of the samples.

Key words: photovoltaic effect, lead zirconate-titanate ceramics, Pb vacancy, Pb/(Zr+Ti) molar ratio, multiple doping of Na and Ta

1. INTRODUCTION

Uniform illumination of homogeneous noncentrosymmetric crystals, as well as polarized ferroelectric polycrystallines, generates a steady-state electric current. Under an open-circuit condition, photovoltaic current can produce a high voltage that considerably exceeds band-gap energies without external fields.¹ Although the origin of this effect has yet to be clarified, it is understood in terms of the difference between the transfer probabilities of photoexcited charge carriers along the parallel and antiparallel polarization directions; the existence of impurities and the asymmetry of the crystal are shown to be important factors related to this effect. In certain ferroelectrics, photovoltage is of the kilovolt to megavolt order per centimeter. The production of such a high photovoltage is not only theoretically interesting, but is also of practical importance. Making use of this photovoltage, for example, new optical devices such as photodriven actuators, optically controlled modulators, and photo-acoustic components have been fabricated using ferroelectric ceramics.^{2,6}

Considering the practical applications of those devices, however, some problems remain, such as slow response speed resulting from relatively small photovoltaic current. It has been confirmed that the strain rate of actuators by illumination depends strongly on the photovoltaic current generated and that the maximum strain is dependent on the photovoltage.^{7,8} To realize such novel devices in practical applications, a clear indication of the material design should be presented. So far, the influence of several factors such as polarization, grain size, additive, electrode configuration, illuminating light, and heat treatment on the photovoltaic effect has been investigated.⁹⁻¹² Tanimura and Uchino¹³ previously examined the effects of impurity doping on the photovoltaic effect in lead lanthanum zirconate titanate ceramics. They found that both the photovoltaic current and the photovoltage were enhanced by doping donor ions such as Ta⁵⁺ and W⁶⁺. This effect has been explained by the asymmetric

photoexcitation from donor impurity levels induced by doped ions. It is widely recognized that such a doping of donor impurities causes the formation of Pb vacancies on the perovskite lattice to compensate for the extra positive charges present due to the dopants.¹⁴ However, the role of Pb vacancies formed in inducing the photovoltaic effect has not yet been taken into account.

In this paper, we report the experimental results on the photovoltaic effect in lead zirconate-titanate (PZT) ceramics introduced with Pb vacancies by changing molar ratio of Pb/(Zr+Ti) and by multiple doping of Na and Ta in various combinations. Such multiple doping affords control of the concentration of Pb vacancies in a certain range. Photovoltaic current and photovoltage were measured in the samples, as well as their grain size dependences.

2. EXPERIMENTAL

2.1 Sample preparation

Samples of PZT ceramics were prepared by the conventional solid-state reaction process. Powders of PbO, ZrO₂, TiO₂, Na₂CO₃, and Ta₂O₅ were used as raw materials. Pb(Zr_{0.5}, Ti_{0.5})O₃ was chosen as the basic composition, from which molar ratios of Pb/(Zr+Ti) in the samples were modified to range from 0.90 to 1.01 by adjusting the weights of the raw materials. The ratio of Zr/Ti was fixed at 50/50 in all the samples. Samples singly doped with 0-3 mol% of Ta and those multiply doped with 1 mol% of Na and 0-4 mol% of Ta were also prepared. Doped Na and doped Ta were assumed to substitute Pb and Zr/Ti, respectively, on the perovskite lattice structure, wherein the amount of original ions to be replaced was reduced in advance at the time of sample weighing. The raw materials were ball-milled for 48h, calcined at 800 °C for 2-10 h, and ball-milled again. The milled powders were then formed into 18-mm-diameter, 5-mm-thick pellets by isostatic pressing at 200 MPa. The green compacts obtained were set in a magnesia crucible and sintered at 1050-1300 °C for 2 h.

One face of the samples was optically polished as an illumination plane; these samples were cut into $3 \times 3 \times 8$ mm³ bars. Silver electrodes were fired onto the 3×8 mm² faces for photovoltaic measurements. Samples were poled in silicone oil at 70 °C by applying a dc field of 3 kV/mm for 30 min.

2.2 Measurements

Crystalline phases formed were identified by a powder X-ray diffraction technique (XRD) using Cu K_α radiation. Scanning electron microscopy (SEM) was used to examine the microstructures of the samples that were ground, polished and then chemically etched with 5 % HCl solution containing a little amount of HF. Average grain sizes were estimated by calculating the equivalent circular sizes of about 200 grains on the SEM micrographs of each sample.

An ultrahigh-pressure mercury lamp (500 W) was used as the light source. Using optical glass filters, light with wavelengths ranging from 300 to 400 nm with maximum intensity around 365 nm was obtained and illuminated on the optically polished 3×8 mm² face of the sample. The photoinduced current and voltage were, respectively, measured under short- and open-circuit conditions using an electrometer (Keithley 617).

3. RESULTS AND DISCUSSION

3.1 Effect of Pb/(Zr+Ti) Molar Ratio

Crystalline phases formed in the PZT ceramics with various molar ratios of Pb/(Zr+Ti) were analyzed by XRD. The primary phases were identified to be tetragonal PZT in all the samples, but a small amount of monoclinic ZrO₂ was detected as the secondary phase in the sample with a molar ratio of 0.90. In the sample with molar ratio of 1.01, spots colored in orange were observed, suggesting the precipitation of excess PbO. It has been reported that the perovskite lattice structure of Pb(Zr_{0.5}, Ti_{0.5})O₃ can hold a maximum concentration of Pb vacancies of 2.5 mol% at 1100 °C and that above this limit a secondary phase will be formed.¹⁵ In the present study, the molar ratio of 0.975 corresponds to the Pb vacancies of 2.5 mol%. Thus, the samples with molar ratios of 0.99 and 1 were at least considered to be single phases of tetragonal structure.

Figure 1 shows the photovoltaic properties of PZT ceramics having different Pb/(Zr+Ti) molar ratios. The photovoltaic current increased abruptly when the molar ratio was less than 1.00. At the same time, the photovoltage also showed an increasing tendency. Accordingly, the maximum output power increased abruptly when the molar ratio was less than 1.00. These results confirmed that a net enhancement of the photovoltaic effect can be obtained in PZT ceramics by decreasing the molar ratio of Pb/(Zr+Ti) to less than 1.

3.2 Effect of Multiple Doping

The crystalline phase formed was identified to be tetragonal PZT up to 4 mol% of doped Ta in cases of both single and multiple doping for the samples examined using XRD.

Figure 2 shows photovoltaic responses of the samples singly and multiply doped with various amounts of Ta. In the singly doped samples, the photovoltaic current

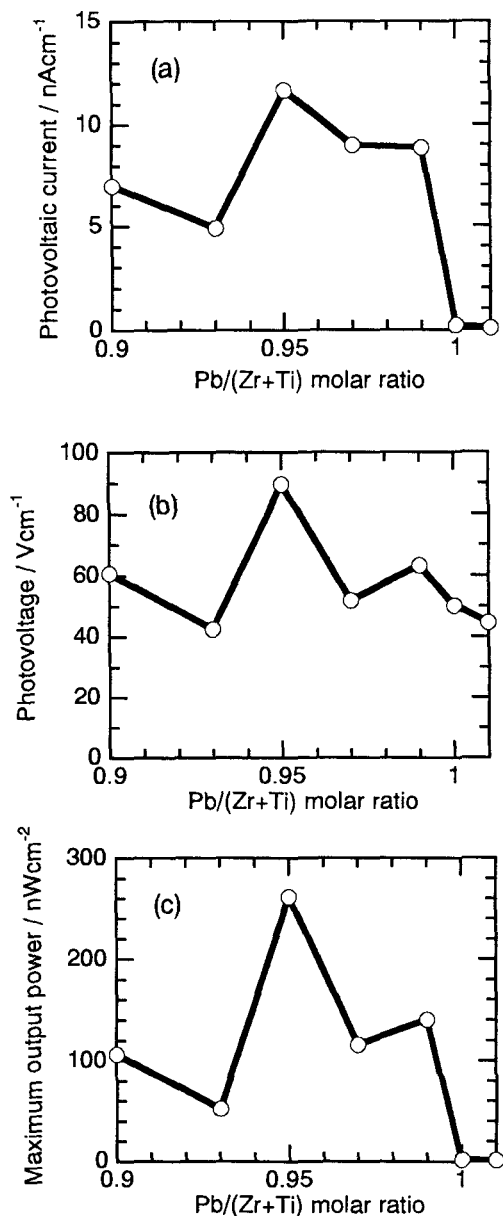


Fig. 1. Photovoltaic current (a), photovoltage (b), and maximum output power (c) as a function of molar ratio of Pb/(Zr+Ti) in PZT ceramics sintered at 1200 °C for 2h. (Illumination intensity: 40 mWcm⁻²)

markedly increased with increasing amount of doped Ta and revealed a maximum at around 1 mol% Ta. In contrast, in the multiply doped sample, the photovoltaic current remained at very low levels when the amount of doped Ta was less than 1 mol%. Beyond this limit, however, the photovoltaic current skyrocketed to a maximum at around 2 mol% of doped Ta. A similar difference, depending on whether samples were singly or multiply doped with various doping amounts of Ta, was also observed in photovoltage. These results indicate that the photovoltaic response can also be enhanced in the case of multiple doping when the amount of doped Ta is greater than that of doped Na (1 mol%). It has been confirmed that, for instance, for 1 mol% of doped Ta, which substitutes for Zr or Ti on the

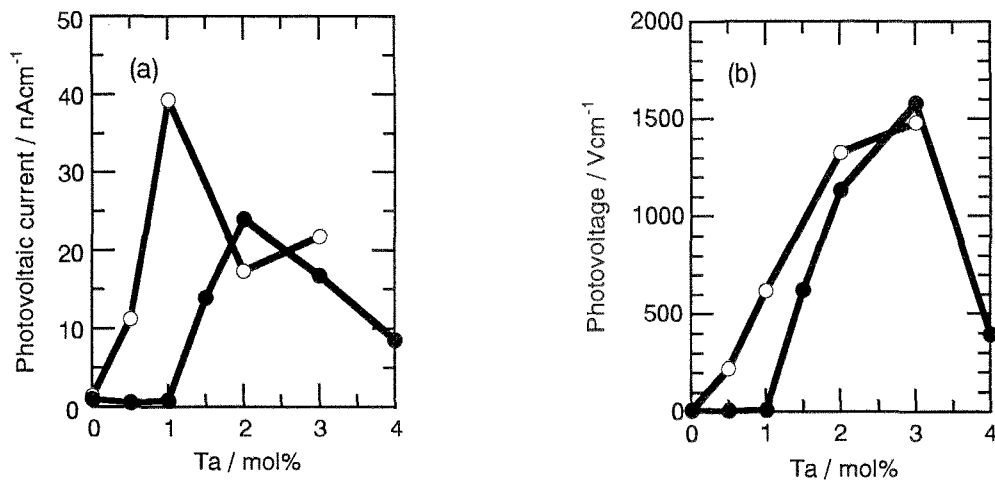


Fig. 2. Photovoltaic current (a) and photovoltage (b) as a function of amounts of doped Ta in the samples sintered at 1200 °C for 2h. The open and closed circles, respectively, denote the samples singly doped with Ta and those multiply doped with Na of 1 mol% and Ta. (Illumination Intensity: 40 mWcm⁻²)

perovskite lattice, 0.5 mol% of Pb vacancies occurs to maintain electroneutrality, as in the case of the singly doped samples.¹⁴ On the other hand, for 1 mol% of doped Na, which replaces Pb on the lattice, 0.5 mol% of oxygen vacancies is induced owing to the same reason as above. Accordingly, in the case of multiple doping, equimolar amounts of doped Ta and Na produce neither Pb nor oxygen vacancies. When the amount of doped Ta is greater than that of doped Na, certain amounts of Pb vacancies are thus created in the lattice, according to the relative amounts of doped Ta and Na.

From these considerations and the results in Fig. 1, the photovoltaic response is found to increase markedly with increasing concentration of Pb vacancies. This indicates that the formation of Pb vacancies, rather than the existence of doped Ta, has a fundamental significance in the photovoltaic effect in PZT ceramics.

3.3 Microstructure Observation

Figures 3 and 4, respectively, show the microstructures and average grain sizes of the samples singly and multiply doped with various amounts of Ta.

With increasing amount of doped Ta, the grain size in the singly doped samples decreased exponentially, whereas that in the multiply doped samples increased, becoming maximum at around 1 mol% Ta. At this point, the average grain size was very close to that for the nondoped sample (pure PZT).

Corresponding to these results, grain-growth inhibition upon doping of Al and Nb has been reported for PZT ceramics.¹⁶ Doped Al and Nb, respectively, induce oxygen vacancies and Pb vacancies on the lattice, similar to doped Na and Ta in the present study. In that report, grain size was reduced when either oxygen vacancies due to doped Al or Pb vacancies due to doped Nb were present, but doping of both Al and Nb did not effectively impede grain growth. In the present study, it is hence believed that the lattice vacancies of Pb and oxygen were formed in the doped samples according to the charge compensation mechanism explained above.

3.4 Grain Size Dependence

Figure 5 shows the variation of photovoltaic responses with average grain size in the sample singly

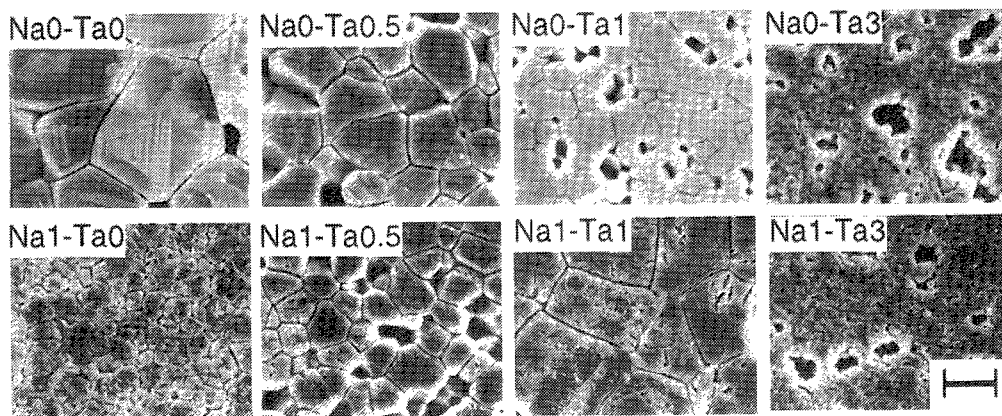


Fig. 3. SEM micrographs for various samples sintered at 1200 °C for 2h. Mol% of doped Na and Ta in various combinations are given in the figure. (Bar: 10 μm)

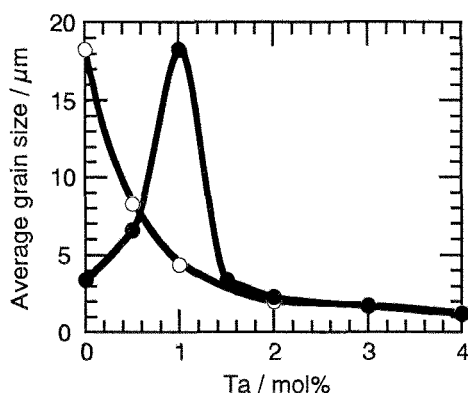


Fig. 4. Average grain size as a function of amount of doped Ta in the samples sintered at 1200 °C for 2h. Symbols are the same as those in Fig. 2.

doped with 1 mol% of Ta. In the region of relatively large grain size (>4 nm), both photovoltaic current and photovoltage increased gradually with decreasing average grain size. However, in the region of relatively small grain size (<4 nm), they each exhibited behavior opposite to that of the other. When the average grain size decreased further ($< 2-3$ nm), the photovoltaic current fell abruptly, whereas the photovoltage rose rapidly. Similar changes, which have also been observed in PLZT ceramics,^{9,17} are also expected in the other samples shown in Fig. 2. Accordingly, in the samples having average grain size larger than 4 nm in Fig. 2, which correspond to samples singly and multiply doped with less than about 1.5 mol% Ta as can be seen in Fig. 4, the photovoltaic responses observed were considered to be mildly influenced by the grain size change.

To discuss the results in Fig. 2 without considering such grain size effects, results obtained for two samples with adequate grain sizes were compared. The samples singly and multiply doped with 0.5 mol% of Ta are found to consist of grains with relatively large and uniform (6-8 nm) sizes, as shown in Fig. 4. However, as can be seen in Fig. 2, they each exhibited quite different photovoltaic responses to doping of Ta. In the multiply doped sample, no doping effect was observed on either the photovoltaic current or photovoltage owing to the lack of Pb vacancies.

These results led to the conclusion that the formation of Pb vacancies on the perovskite lattice, rather than the existence of doped Ta, has a fundamental significance on the photovoltaic properties in PZT ceramics.

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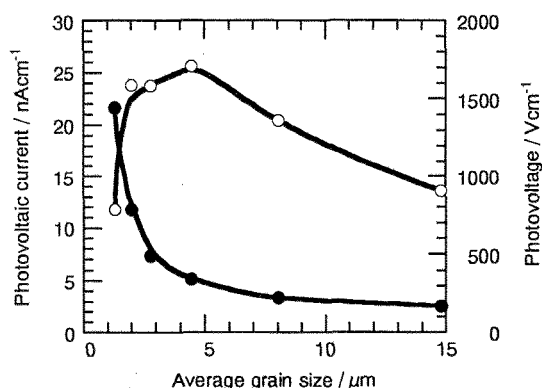


Fig. 5. Photovoltaic current (○) and photovoltage (●) as a function of average grain size in the samples singly doped with Ta of 1 mol%, followed by sintering at various temperatures ranging from 1050 to 1300 °C at 50 °C intervals for 2h. (Illumination Intensity: 40 mWcm⁻²)

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