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Effect of Pb/(Zr + Ti) Molar Ratio on the Photovoltaic Properties of Lead Zirconate-titanate Ceramics

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Abstract

Lead zirconate-titanate ceramics having various Pb/(Zr + Ti) molar ratios ranging from 0·90 to 1·01 and a fixed Zr/Ti molar ratio of 50/50 have been sintered at 950–1250°C for 2 h to investigate the change in photovoltaic properties, as well as their grain size dependence on ultraviolet irradiation. The photovoltaic current increased abruptly when the molar ratio was less than 1·00, whereas the photovoltage gave scattered results and decreased between the molar ratio of 0·99 and 1·00, which was caused by grain growth. The maximum output power discernibly increased, confirming a net increase in photovoltaic efficiency. The grain size dependence of the photovoltage revealed an opposite tendency in two samples with different molar ratios of 0·992 and 1·00. From these results, it is proposed that creating Pb vacancies on the perovskite lattice is essential for the photovoltaic properties of the samples. © 1999 Elsevier Science Limited. All rights reserved

Keywords: photovoltaic properties, sintering, defects, PZT, functional applications.

1 Introduction

Uniform illumination of homogeneous non-centrosymmetric 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 carders 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.[8–12] Tanimura and Uchino[13] 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 Ta^{5+} and W^{6+}. 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.

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In this paper, we report the experimental results on the photovoltaic effect in lead zirconate-titanate (PZT) ceramics having various Pb/(Zr + Ti) non-stoichiometries. The objective of this work is to clarify the effect of Pb vacancies introduced onto the lattice structure. Photovoltaic current, photovoltage and photovoltaic power were measured in the samples. The formation of Pb vacancies was explained by the measurements of dark conductivity in the samples. Other than Pb vacancies, several factors such as grain size, composition shift, and precipitation of secondary phase were also presented to explain the photovoltaic measurement results.

2 Experimental

2.1 Sample preparation

Samples of PZT ceramics were prepared by the conventional solid-state reaction process. Powders of PbO (Rare Metallic Co., Ltd., 99·99% pure), ZrO_2 (Tosoh Co., TZ-0), and TiO_2 (Rare Metallic Co., Ltd., 99·99% pure) were used as raw materials. $Pb(Zr_{0\cdot5}, Ti_{0\cdot5})O_3$ 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. The raw materials were ball-milled for 48 h in a polyethylene pot containing zirconia balls and ethanol. Dried mixtures were prepressed into pellets and then calcined at 800°C for 10 h. The calcined pellets were ball-milled again for 48 h in a polyethylene pot containing zirconia balls and ethanol. They were then dried and sieved before die pressing at 30 MPa into 20 mm diameter, 5 mm thick pellets, followed by isostatic pressing at 200 MPa. The green pellets obtained were set in a magnesia crucible and sintered at 950–1250°C for 2 h. The sintered bodies used in the following experiments had relative densities higher than 95% of the theoretical value.

One face of the samples was optically polished as an illumination plane; these samples were cut into $3\times3\times8\,mm^3$ bars. Silver electrodes were fired onto the $3\times8\,mm^2$ faces for photovoltaic measurements. Samples were poled in silicone oil at 70°C by applying a dc field of $3\,kV\,mm^{-1}$ for 30 min.

2.2 Measurements

Crystalline phases formed were identified by a powder X-ray diffraction technique (XRD) using CuK_α radiation with Ni filter. 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 several drops of 48% HF in 100 ml of 5% HCl. Average grain sizes were estimated by calculating the equivalent circular sizes of about 200 grains on the SEM micrographs of each sample. Chemical compositions of the samples were measured by an X-ray fluorescence analysis (XRF) using LiF (200) crystal.

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 $3\times8\,mm^2$ face of the sample. The photo-induced current and voltage were, respectively, measured under short- and open-circuit conditions using an electrometer (Keithley 617). Dark conductivities were estimated by extrapolation of conductivities, which were calculated from ratios of the photovoltaic current and the photovoltage to various illumination intensifies, to the zero intensity.

3 Results and Discussion

3.1 Photovoltaic and dark conductivity measurements

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. The photovoltage decreased once between the molar ratios of 0·99 and 1·00, but increased thereafter to show a scattered distribution when the molar ratio was less than 0·99. 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 1·00.

Figure 2 shows the dark conductivities in PZT ceramics with various Pb/(Zr + Ti) molar ratios. When the molar ratio was decreased from 1·00 to 0·99, the conductivity increased abruptly to a value that is more than two orders of magnitude of that at the stoichiometric composition, 1·00. When the molar ratio was less than 0·99, the values of the conductivity remained almost unchanged. In general, PZT ceramics have p-type conductivity because of Pb vacancies. That are formed by PbO evaporation from PZT ceramics during the sintering process.[14] When the samples with various molar ratios were sintered at 1200°C for 2 h, the amounts of PbO losses were measured to be about 0·5 mol% by XRF. The concentration of Pb vacancies is somewhat higher than that of O vacancies because the oxygen deficiency can be compensated to a certain extent by supplying oxygen from the air. In the present

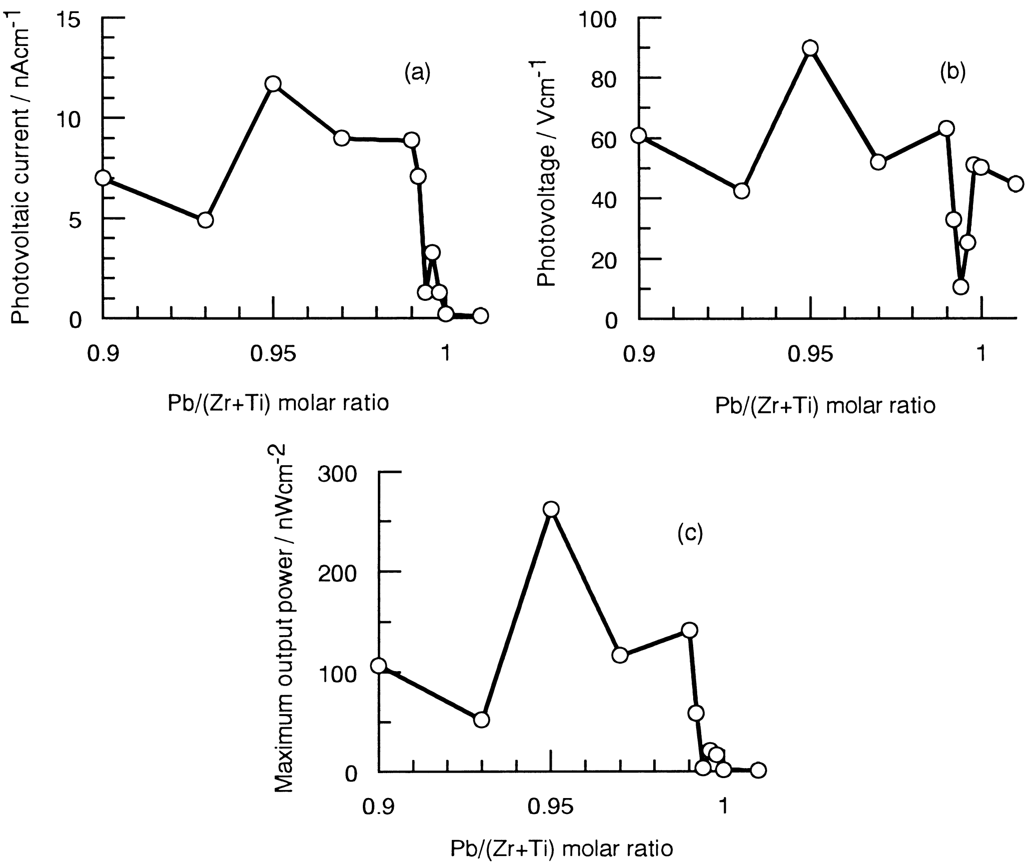

Fig. 1. Photovoltaic current (a), photovoltage (b), and maximum output power (c) as a function of molar ratio of Pb/(Zr + Ti) in PZT ceramics sintered at 1200°C for 2 h. (Illumination intensity: 40 mW cm^{-2}).

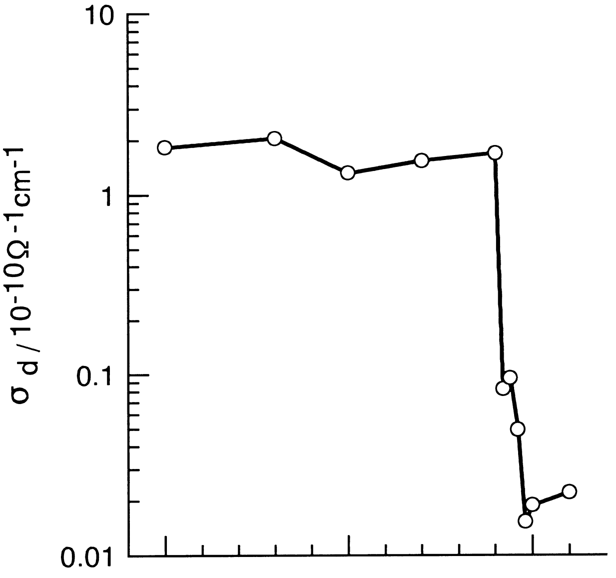

Fig. 2. Dark conductivity, σ_d, as a function of molar ratio of Pb/(Zr + Ti) in PZT ceramics sintered at 1200°C for 2 h.

study, it was found that decreasing the molar ratio of Pb/(Zr + Ti) tends to increase the concentration of Pb vacancies, which in turn leads to an increase in the dark conductivity in PZT ceramics. It has been reported that the perovskite lattice structure of Pb($Zr_{0.5}$, $Ti_{0.5}$)O_3 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 Fig. 2, the molar ratio of 0·99 corresponds to a concentration of Pb vacancies of 1 mol%. Below the molar ratio of 0·97, the lack of change in the dark conductivity can be attributed to the saturation of the concentration of Pb vacancies. These results indicate that Pb vacancies have been introduced into the PZT ceramics when the molar ratio of Pb/(Zr + Ti) is less than 1·00 and that the concentration of Pb vacancies increases with decreasing the molar ratio at least between 0·99 and 1·00.

3.2 X-ray analysis and SEM observation

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 ZrO_2 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.

Figure 3 shows the microstructures in PZT ceramics with various molar ratios of Pb/(Zr + Ti). The grains showed a tendency to decrease in size with decreasing molar ratio. The precipitation of small grains was observed at boundaries and also at interiors of the matrix grains in samples with molar ratios below 0·97. EDX analysis of the precipitates revealed that they contain zirconium, in agreement with the results of XRD analysis. Such a precipitation of ZrO_2 causes a composition change of the samples toward Ti-rich region. However, no secondary phase such as ZrO_2 precipitate were analyzed in the sample with molar ratio of between 0·99 and 1·00; which is supported by the previous investigation[15] mentioned above.

Figure 4 shows the variation of the average grain size with the molar ratio of Pb/(Zr + Ti) in PZT ceramics. The average grain size revealed a tendency to decrease with decreasing molar ratio from 1·01 to 0·90, but a less consistent result was obtained between molar ratios of 0·99 and 1·00. In this range, the grains become once large, reaching a maximum at the molar ratio of 0·994. It has been reported that an increase in grain size resulted in a decrease in photovoltage.[9,17] Focusing on the results obtained from samples with molar ratios between 0·99 and 1·00, the photovoltage in Fig. 1(b) was found to exhibit a completely opposite behavior to the average grain size in Fig. 4 with varying molar ratio. In this range, it can therefore be explained that the discontinuous decrease of the photovoltage is due to transit grain growth.

In this study, the grain size was shown to be an important factor that influences the photovoltaic effect in PZT ceramics. However, it still remains a question, whether the enhanced photovoltaic effect in Fig. 1 can be explained by only the effect of reduced grain size. Next, we discuss effect of reducing grain size on the photovoltaic effect. Samples with molar ratios of 0·996 and 0·998 possessed grains with size several microns larger than or almost equal to that of the sample with a stoichiometric composition of 1·00. As shown in Fig. 1(c), however, the maximum output power was obviously enhanced in the two samples with the nonstoichiometric compositions. This result indicates that the enhanced photovoltaic effect in PZT ceramics with nonstoichiometric composition is not evident and is not solely due to grain size.

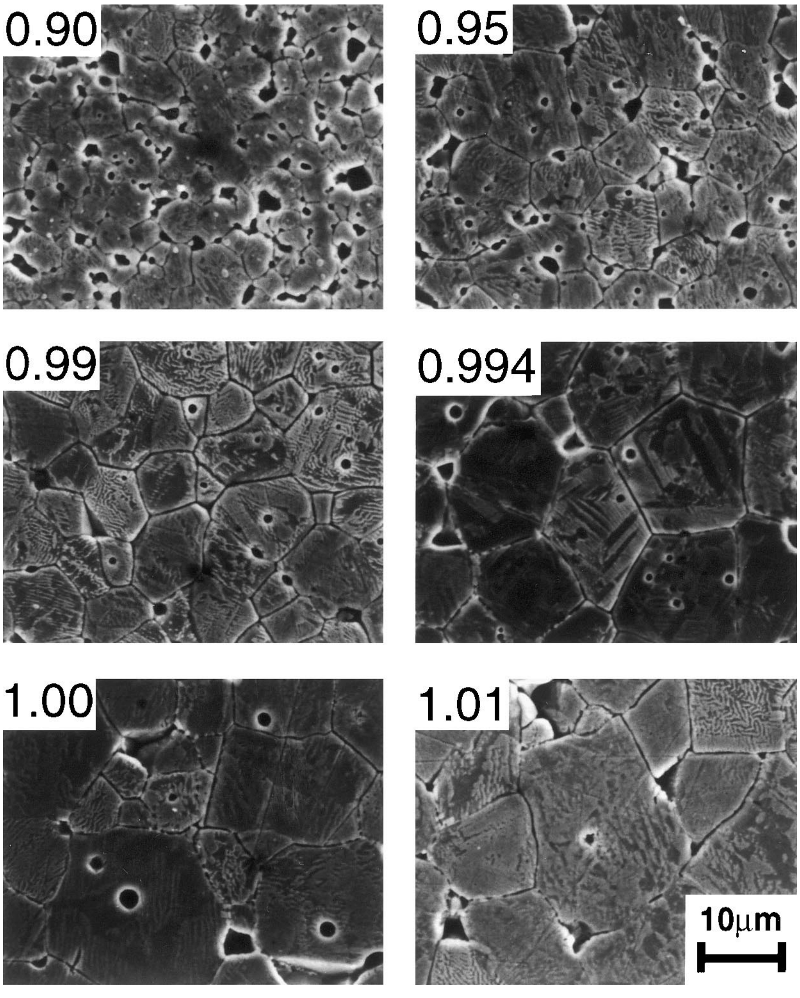

Fig. 3. Polished and chemically etched surfaces of PZT ceramics sintered at 1200°C for 2 h as observed by SEM, as a function of molar ratio of Pb/(Zr + Ti).

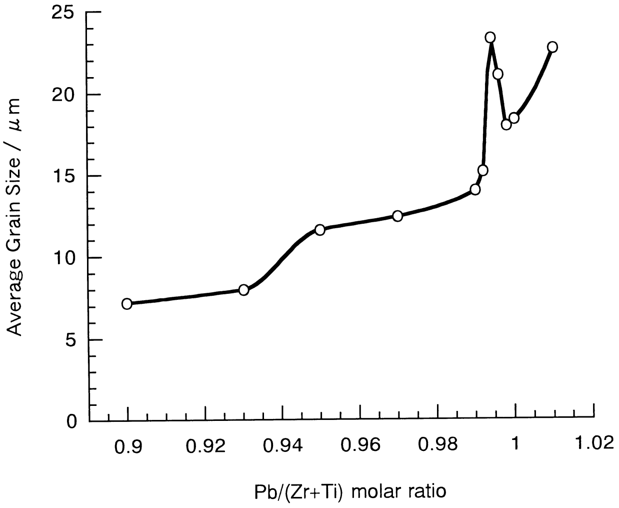

Fig. 4. Average grain size as a function of molar ratio of Pb/(Zr + Ti) in PZT ceramics sintered at 1200°C for 2 h.

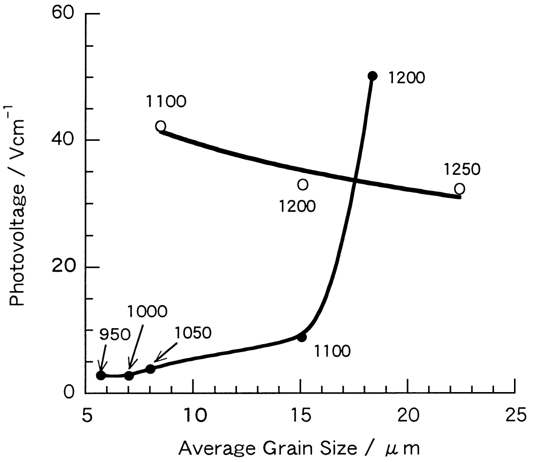

Fig. 5. Photovoltage as a function of average grain size in PZT ceramics sintered at various temperatures for 2 h. The open and closed circles, respectively, represent samples having Pb/(Zr + Ti) molar ratios of 0·992 and 1·00. Numbers in the figure denote the sintering temperatures for each samples.

3.3 Grain size dependence

Figure 5 shows the photovoltage variation with the average grain size in PZT ceramics with molar ratios of 0·992 and 1·00. The dependence of the photovoltage in the two samples on the average grain size revealed an opposite tendency. The photovoltage decreased with increasing average grain size in the sample with a molar ratio of 0·992. In contrast, in the sample with stoichiometric composition, the photovoltage increased exponentially with increasing average grain size. The photovoltage remained relatively low when the grain size was small. After the grain size became relatively large i.e. after the grains were sintered at temperatures above 1100°C, the photovoltage rapidly increased. The dependence of the photovoltage in the former sample agrees with that reported previously,[9,17] but for the latter sample another factor is required to understand the opposite tendency for the change of average grain size. This difference in tendency can be explained by the concentration of Pb vacancies formed in the samples. Previous investigations dealt with the grain size dependence of the photovoltaics in donor-doped PZT-based samples, and found that a certain concentration of Pb vacancies in the samples is necessary to maintain electroneutrality. In the present study, however, the sample with stoichiometric composition ideally has no Pb vacancies. In actuality, however, a small amount of Pb vacancies was created in the sample during sintering as mentioned above; the amounts of Pb vacancies were measured to be 0·3, 0·4 and 0·5 mol% for the samples sintered at 950, 1100 and 1200°C for 2 h, respectively. On the other hand, in the samples with a molar ratio of 0·992, the photovoltaic effect was considered to be influenced by grain size rather than by Pb vacancies due to PbO evaporation during sintering, because these samples had a high concentration of Pb vacancies due to Pb/(Zr + Ti) nonstoichiometry regardless of their sintering temperature. From these results and those in Figs 2 and 3, the formation of Pb vacancies is confirmed to be essential for the photovoltaic effect in the PZT ceramics.

Regarding the photovoltaic effect enhancement by donor doping, it is assumed that the existence of doped impurities has no significant meaning in itself, but probably plays a role in the formation of Pb vacancies. To answer this assumption, the photovoltaic properties have been investigated in PZT ceramics codoped with Na^+ and Ta^{5+}, the results of which will be shown in other reports.

4 Conclusions

The photovoltaic effect has been studied in PZT ceramics with various molar ratios of Pb/(Zr + Ti) ranging from 0·90 to 1·01. The results indicate that several factors, such as Pb vacancies, composition (Zr/Ti ratio), secondary phase (ZrO_2 precipitate and excess PbO), and grain size should be considered to elucidate understanding of the photovoltaic change. Among these factors, the formation of Pb vacancies is confirmed to be essential for inducing the photovoltaic effect in PZT ceramics.

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