Photostriction in Lead Lanthanum Zirconate Titanate Ceramics
Enhanced by the Additive Effect

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1. Introduction

Photostriction materials convert light directly to physical movement.1)3) The mechanism of photostriction is explained by superposition of the photovoltaic effect and piezoelectricity. When homogeneous noncentrosymmetric materials such as ferroelectric single crystals and polarized ferroelectric ceramics are uniformly illuminated, a high voltage is generated which considerably exceeds band gap energies is generated without external fields.5) In certain ferroelectrics with a photovoltaic effect many factors such as material composition, microstructures, material preparation method, and impurity doping have been investigated.2)3)

We have reported the effects of heat treatments3)6) and of doping of various impurity elements,9) as well as their combined effects,10) on the photovoltaic properties of PLZT ceramics. Both photovoltaic current and photovoltage are found to be markedly improved by the heat treatment in nitrogen. Concerning the doping effects, we found a clear relationship between the photovoltaic response and the kind of doped ions such as donor, acceptor, easily variable valency, and remainders. In order to introduce doping effects, sample preparation considering charge compensation for electroneutrality is found to be critical. The photovoltaic response is increased by doping with donor ions such as Ta and W.11) It is also clarified that additivity holds for the effect of nitrogen treatment and that of donor doping. We investigated the photovoltaic response for the samples doped with various amounts of Ta, before and after the nitrogen treatment.10) Before the nitrogen treatment, both the photovoltaic current and photovoltage exhibited maxima for around 1.5 mol% of doped Ta. Similar changes in photovoltaic behavior with various doping amounts of Ta were also observed in the nitrogen-treated sample. However, the values of photovoltaic current and

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photostriction were, on the whole, notably increased in comparison with those of the doped samples pretreated in nitrogen. We concluded from this result that the nitrogen treatment and the doping with Ta contribute to the photovoltaic effect through different mechanisms, which were discussed in detail in a previous paper. 10)

The present paper describes the improvement of photostriction in PLZT ceramics caused by the additive effect of the nitrogen treatment and the doping with Ta. Piezoelectric parameters and photostrictive responses were measured in various samples and the obtained results were evaluated with those of the photovoltaic measurements10) previously reported.

2. Experimental procedure

2.1 Sample preparation

Samples of (Pb0.97,La0.03)(Zr0.52, Ti0.45)1-0.03/4O3 (PLZT (3/52/48)) ceramics doped with various amounts of Ta were prepared by the conventional solid-state reaction process. The basic composition of PLZT (3/52/48) has been reported to show the highest photostrictive efficiency. 6) The detailed preparation technique was described in an earlier paper.12) To ensure electroneutrality on doping, the basic composition was modified to compensate for an increase in positive charge due to Ta by creating Pb vacancies according to the amount of doped Ta. The amounts of Ta were expressed in terms of molar concentrations of Ta relative to the total amounts of Zr and Ti whose initial molar ratio of 52/48 was fixed for all samples. One face of the samples was optically polished as an illumination plane. These samples were cut into 3×3×8 mm3 bars. To investigate the effect of heat treatment in nitrogen, they were placed in a magnesia crucible and then heat-treated in nitrogen at 900°C for 1 h. Before the heat treatment in nitrogen, the samples were also examined for comparison. Silver electrodes were fired onto the 3×3 mm2 faces for the piezoelectric measurements and onto the 3×8 mm2 faces for the photostrictive measurements at 480°C. Samples were poled in silicon oil at 150°C by applying a dc field of 2 kV/mm for 30 min.

2.2 Measurements

An ultrahigh-pressure mercury lamp (500 W) was used as the light source. Using optical glass filters, light with wavelength ranging from 300 to 400 nm with a maximum strength around 365 nm was obtained and illuminated on the optically polished 3×8 mm2 face of the sample. Piezoelectric parameters were measured with a vector impedance analyzer (HP-4392A). The photostriction was recorded using a strain gauge attached to the bottom plane opposite to the illuminating surface.

3. Results and discussion

3.1 Piezoelectric properties

Figure 1 shows the variation in piezoelectric parameters with heat treatment in nitrogen for the samples doped with various amounts of Ta. In the samples pretreated in nitrogen, the values of k33, d33 and dielectric constant were increased by doping with Ta and showed maxima for around 1.5 mol% of doped Ta. This increase in the piezoelectric parameters is well-known as the softening effect of donor doping.13) Very similar results were obtained from the nitrogen-treated samples. Before and after the nitrogen-treatment, these piezoelectric parameters were found to change negligibly, in contrast to the notable change in the photovoltaic properties mentioned above. Prisedsky14) studied the effect of oxygen nonstoichiometry on piezoelectric properties of a PZT material and reported that the lowering of oxygen partial pressure during heat treatment of nondoped sample produces an effect similar to that of doping with donor ions, but such treatment does not give as large an effect as that of impurity doping.

3.2 Photostrictive response

The photostriction can be expressed by

\[ x(t) = d_{33} E \left(1 - \exp\left(-\frac{t}{RC}\right)\right) \]

where \( x(t) \) is the photostriction, \( E \) the saturated photovoltaic field, \( R \) the resistance under illumination, and \( C \) the capacitance.1),3),4) An increase in the photovoltaic current decreases the values of \( R \) and contributes to the overall response. It is also reported that the values of \( C \) are little affected by illumination and depend mostly on the dielectric constant.4) Then, we also estimated the values of \( C \) from the dielectric constant shown in Fig. 1.

When the sample is optically irradiated, photostriction occurs progressively following RC as the time constant, in order to achieve the maximum strain of \( d_{33} E \).

Figure 2 shows the variation in the time constant, RC with heat treatment in nitrogen for the samples doped with various amounts of Ta. The values of \( R \) were calculated from the ratio of the photovoltage and the photovoltaic current previously reported.10) Before the nitrogen-treatment,
the samples showed minimum of $RC$ around 1 mol% of doped Ta. Above 3 mol% of doped Ta, $RC$ again decreased slightly due to the lower densities of the samples. After the nitrogen-treatment, the values of $RC$ further decreased and showed a minimum value similarly around 1 mol% of doped Ta. The value of $RC$ was thus found to be lowered due to such a combined effect resulting in an improved photostrictive response. By comparing the value of $RC$ in the sample doped with 1 mol% Ta before the nitrogen-treatment with that in the nondoped sample after the nitrogen-treatment, the latter was noted to be fairly low. It was thus found that the degree of contribution toward lowering the value of $RC$ by the nitrogen-treatment was somewhat larger than that by the doping with Ta.

Figure 3 shows the photostrictive response for the various samples. In this figure, photostriction curves calculated from Eq. (1) were involved. The parameters used for the calculation are summarized in Table 1, wherein the actually measured and the calculated strains were also given. Before the nitrogen-treatment, the sample doped with Ta revealed an increased photostrictive response compared with the nondoped sample. We also confirmed that the photostrictive response can be further enhanced by the combined effect of the doping with Ta and the nitrogen-treatment. Thereby, the maximum strain became 60% larger than that in the nondoped sample. It should be also noted that by the combined effect, a striction rate roughly 4 times higher than that in the nondoped sample can be obtained at strains of up to $0.6 \times 10^{-4}$. This result is supposed to be useful for the application of PLZT ceramics in photophonic devices because they require quick response rather than large strains.

The strains actually observed in the initial part are found to agree well with those calculated from Eq. (1) in each sample, but later the measured strains gradually became somewhat larger than the calculated values. This result suggests that the values of $d_{33}E$ for the measured strain curves are larger than those calculated with the parameters given in Table 1: to clearly explain the reasons for this difference a further experiment is needed. Considering the strain ratios among the samples, however, the ratios ($r_3$) estimated from the measured strain data ($x_{\text{meas}}$) are in close accordance with those ($r_3$) estimated from the calculated strain data ($x_{\text{cal}}$) for each sample as shown in Table 1; the ratios are expressed in terms of relative strain values when $x_{\text{meas}}$ and $x_{\text{cal}}$ in the nondoped sample (pretreated in nitrogen) are the units. This result indicates that the increase in the photostrictive response actually measured implies the real improvement, which is expected from the effects of the nitrogen-treatment and of the doping of Ta, as well as from their combined effect.
4. Summary

We have investigated the photostriction response in the PLZT ceramics doped with various amounts of Ta and subsequently heat-treated in nitrogen. Both photovoltaic and piezoelectric properties were improved by doping with Ta. On the other hand, nitrogen-treatment heightened the photovoltaic response, but scarcely affected the piezoelectric parameters. By the combined effect of doping with Ta and nitrogen-treatment, the photostriction response was confirmed to be markedly enhanced.

References