PZT ceramics are widely used in ultrasonic transducers and other electromechanical devices because of their high piezoelectric coefficients. Commercially available PZT ceramics were modified with either acceptor dopants, which create oxygen (anion) vacancies, or donor dopants, which create metal (cation) vacancies. The high piezoelectric behavior of both soft and hard PZT ceramics [4]. Nonlinear dielectric properties of Pb(Zn1/3Nb2/3)O3–xPbTiO3 single crystal was also reported, both second and third order responses were detected in the crystal [5]. On the other hand, Ken Yamada et al. studied the vibration nonlinearity of the piezoelectric materials. For the vibration of a homogenous plate, the odd harmonic was evident, while the piezoelectric constants were not homogenous after heat treatment, which induced the second harmonic [6]. In this work, we report the time dependence of the nonlinear behavior of PZT ceramics after poling. Note: the higher harmonics of a piezoelectric resonator come from the resonator geometry and boundary condition constraints, which considered the material to be linear. The higher harmonics in our study refer to the harmonics generated in a nonlinear material when a wave is propagating. The amplitude of the nonlinearity increases as the propagation distance increases. There is no resonance involved in the harmonic generation technique.

Hard PZTs, such as PZT-4 and PZT-8 used in this study, are commercially available from Piezo Kinetics, Inc., [7] as PKI-406 and PKI-802, respectively, while PZT-5 is commercially available from TRS Technologies Inc. [8]. The experimental setup is depicted in Fig. 1. A tone burst signal from an arbitrary generator (Wavetek) is fed into a power amplifier (LogiMetrix). Then the output was
Table 1
Variations of ratios of second and third harmonic amplitude over the fundamental amplitude at different time after poling in PZT-4.

<table>
<thead>
<tr>
<th></th>
<th>Before poling</th>
<th>One hour after poling</th>
<th>One day after poling</th>
<th>Two days after poling</th>
<th>Three days after poling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_2/p_1$</td>
<td>$p_3/p_1$</td>
<td>$p_2/p_1$</td>
<td>$p_3/p_1$</td>
<td>$p_2/p_1$</td>
</tr>
<tr>
<td>PZT-4</td>
<td>0.268</td>
<td>0.171</td>
<td>0.074</td>
<td>0.080</td>
<td>0.121</td>
</tr>
<tr>
<td>PZT-8</td>
<td>0.212</td>
<td>0.175</td>
<td>0.085</td>
<td>0.093</td>
<td>0.129</td>
</tr>
<tr>
<td>PZT-5A</td>
<td>0.201</td>
<td>0.076</td>
<td>0.065</td>
<td>0.070</td>
<td>0.136</td>
</tr>
</tbody>
</table>

The phenomenon is more obvious in soft PZT (see Table 1), because domain switching is much easier in soft PZTs than in hard PZTs.

In summary, the nonlinearity of hard and soft PZT ceramics was studied before and after poling. Our results showed that the nonlinear phenomena are classical type before poling, with
the amplitude of the second harmonic larger than that of the third harmonic. On the other hand, after poling, the nonlinear phenomena became the non-classical type with the amplitude of the third harmonic larger than that of the second harmonic. Such phenomena are more obvious in soft PZTs than in hard PZTs. Microcracks induced by domain switching are thought to be responsible for such interesting nonlinear phenomena. The nonlinearities also change with time initially, but become stable two days after poling.

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