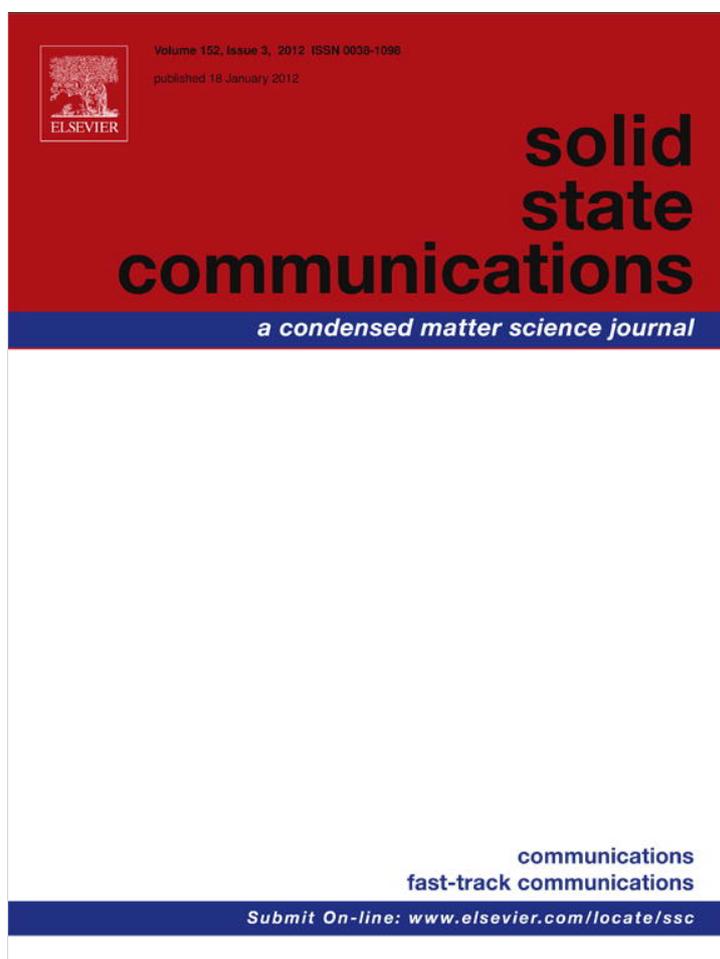


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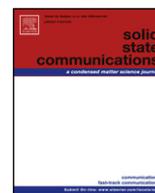
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Poling induced higher order nonlinearity changes in lead zirconate titanate ceramic

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ABSTRACT

High order nonlinear behaviors in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) ceramics were studied using the harmonic generation technique, both before and after poling. It was found that the amplitude of the third harmonic is smaller than that of the second harmonic before poling, but the situation is reversed after poling with a substantial increase of the third harmonic amplitude. Noticeable time dependence of nonlinearities were observed in poled ceramics, which gradually decreased and saturated after about two days. These facts confirmed the generation of microcracks during poling.

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$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) piezoelectric ceramic and its derivatives 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. They are categorized as hard PZT (such as PZT-4 and PZT-8, generally modified by acceptor dopant $\text{Mn}^{2+,3+}$ and $\text{Fe}^{2+,3+}$, respectively) and soft PZT (like PZT-5A, generally modified by donor dopant Nb^{5+}). Soft PZTs (PZT-5) have a higher piezoelectric constant, but larger loss due to internal friction caused by domain wall motions, while in hard PZTs, domain wall motion is pinned by the impurities, thereby lowering the losses in the material, but at the expense of a reduced piezoelectric coefficient. A hard PZT is usually used for high power applications while a soft PZT is used for sensors or low power transmitter applications.

In high power applications, nonlinear effects cannot be neglected [1]. The nonlinear electric and electromechanical responses of PZT ceramics under external AC electric field have been measured under different driving levels [2]. Nonlinear dielectric responses of soft and hard PZTs were experimentally studied below the coercive field level, and the influence of defect disordering to the nonlinear dielectric response and hysteresis

were discussed. Dielectric nonlinearity is related to defect disorder, which leads to dominant odd harmonics [3]. Numerical results were obtained based on nonlinear constitutive relations and the results showed satisfactory agreement with the observed inelastic behavior of both soft and hard PZT ceramics [4]. Nonlinear dielectric properties of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ 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

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Table 1
Variations of ratios of second and third harmonic amplitude over the fundamental amplitude at different time after poling in PZT-4.

	Before poling		One hour after poling		One day after poling		Two days after poling		Three days after poling	
	p_2/p_1	p_3/p_1	p_2/p_1	p_3/p_1	p_2/p_1	p_3/p_1	p_2/p_1	p_3/p_1	p_2/p_1	p_3/p_1
PZT-4	0.268	0.171	0.074	0.107	0.080	0.121	0.082	0.123	0.084	0.125
PZT-8	0.212	0.175	0.085	0.121	0.093	0.129	0.095	0.133	0.092	0.134
PZT-5A	0.201	0.076	0.065	0.126	0.070	0.136	0.073	0.139	0.072	0.141

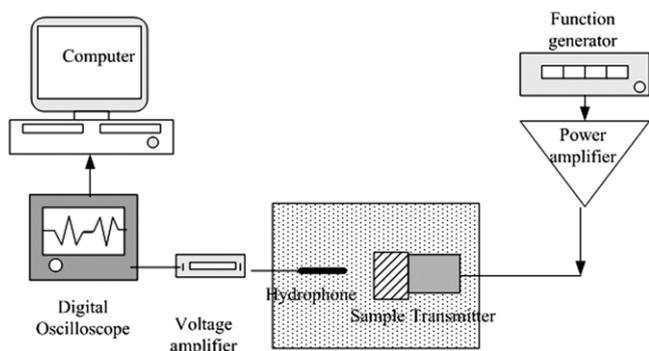


Fig. 1. The experimental setup.

attributed to the nonlinearity of the ceramic samples. Harmonic responses of waves propagating in PZT ceramics change with time as summarized in Table 1. The amplitude of the third harmonic is smaller than that of second harmonic before poling, but the amplitude of the third harmonic was found to be higher than that of the second harmonic after poling. The nonlinearity of poled PZT becomes more and more stable with the increase of time and saturates to constant two days after poling.

Before poling, ceramic materials are generally regarded as isotropic, the amplitude of second harmonic is greater than that of the third harmonic, which are characteristics of nonlinearity in common solids [9]. It is known that the elastic energy can be expanded in the powers of the elastic strain. For common solids, the linear term dominates, while higher order contributions become smaller as the power of the strain goes higher. If there are microcracks in the solids, the nonlinear behavior will change because microcracks may influence more on higher order nonlinearity than lower order nonlinearity, we call this non-classical nonlinearity. After poling, the ferroelectric material shows strong anisotropy because of the nonzero polarization. Due to domain switching during the poling process, mechanical damages may occur, so that material nonlinearity becomes non-classical and there is an obvious hysteretic relation between the stress and the strain. Due to the occurrence of non-classical nonlinearity, there is a greater increase of the third harmonic than that of the second harmonic, which caused a higher amplitude of the third harmonic than that of the second harmonic. This picture is in good agreement with the results in Ref. [3]. 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

applied onto a transmitting transducer (with center frequency of 1.22 MHz). After the signal traveled through the sample, it was detected by a hydrophone (PVDF, frequency 1–10 MHz, aperture 1 mm) and sent to a digital oscilloscope, then downloaded to a personal computer. The dimensions of the PZT-4, PZT-8, PZT-5A samples are $3.02 \times 2.01 \times 1.74$, $2.94 \times 2.14 \times 1.83$, $3.22 \times 2.26 \times 1.97$ cm³, respectively. The samples were immersed in silicon oil and poled at a temperature of 140 °C for 20 min under a 4 kV/mm field. The wave propagation direction is the same as the poling direction. The waveform and its corresponding spectrum received by the hydrophone in water are given in Fig. 2 for the case without ceramic sample. In this case, the second and third harmonics from the transducer are negligibly small. The waveform and corresponding spectrum of PZT-4 before poling is shown in Fig. 3, while the waveform and corresponding spectrum of PZT-4 one hour after poling is given in Fig. 4. The second and third harmonics can be observed clearly for both cases, which are

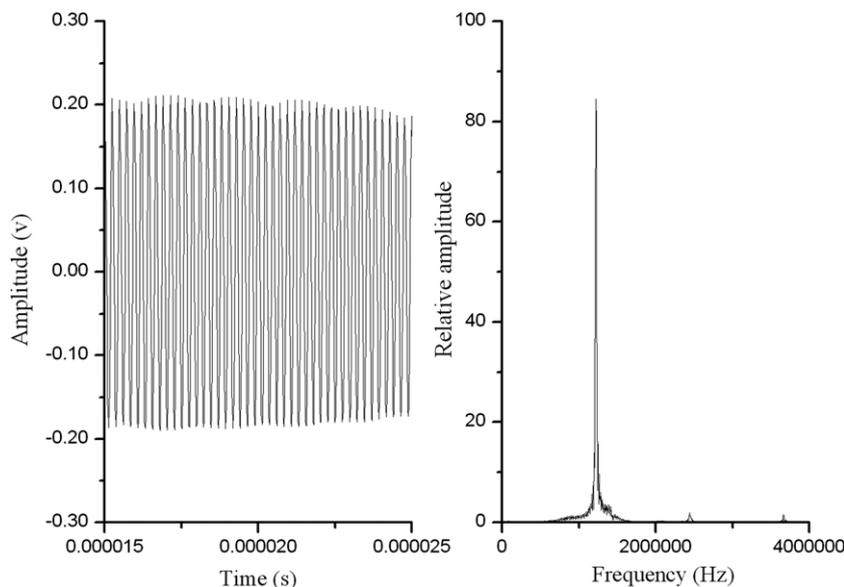


Fig. 2. The waveform and its corresponding spectrum received by a hydrophone in water without sample.

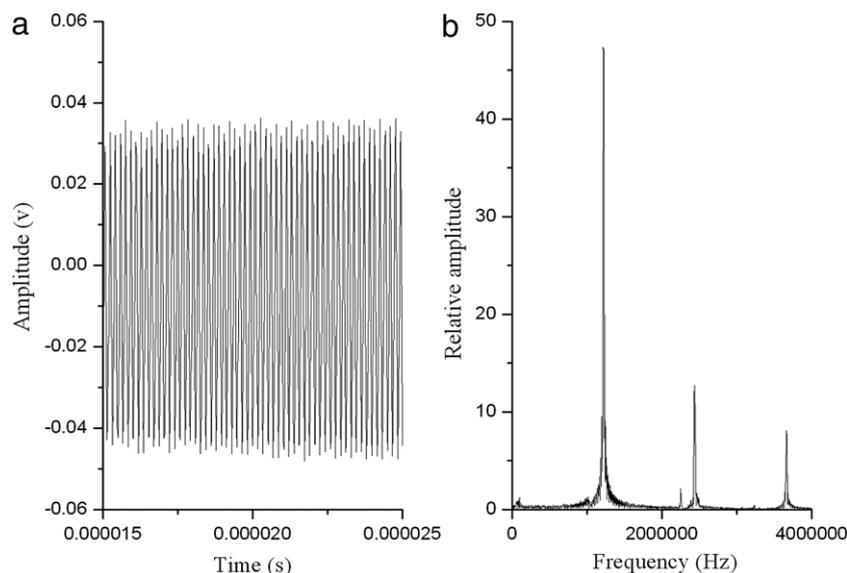


Fig. 3. The waveform (a) and its corresponding spectrum (b) of PZT-4 before poling.

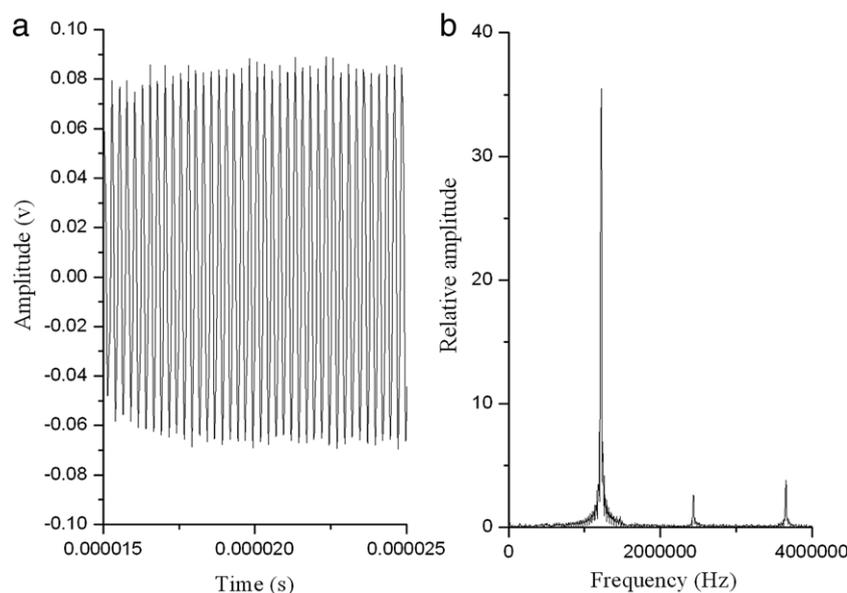


Fig. 4. The waveform (a) and its corresponding spectrum (b) of PZT-4 one hour after poling.

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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