MRS Advances © 2018 Materials Research Society
DOI: 10.1557/adv.2018.235

Polarization switching in ferroelectric thin film induced by a single-period terahertz pulse

Elena Mishina[1,*]; Kirill Grishunin[1]; Vladislav Bilyk[1]; Natalia Sherstyuk[1]; Alexander Sigov[1]; Vladimir Mukhortov[2]; Andrey Ovchinnikov[3]; Alexey Kimel[1,4]

[1]*Moscow Technological University (MIREA), Vernadsky Ave. 78, 119454, Moscow, Russia.*

[2]*Southern Scientific Center of Russian Academy of Sciences, Chehova st. 41, Rostov-on-Don, 344006, Russia.*

[3]*Joint Institute for High Temperatures of Russian Academy of Sciences (JIHT) Izhorskaya st. 13 Bd.2, 125412, Moscow, Russia.*

[4]*Radboud University Nijmegen, Institute for Molecules and Materials, 6525 AJ, Nijmegen, The Netherlands*

ABSTRACT

We report here an experimental study of ultrafast response of the dielectric polarization in $(Ba_{0.8}Sr_{0.2})TiO_3$ thin films to a strong electric field of a nearly single-cycle THz pulse. The phenomenon of Second Harmonic Generation (SHG) is used as a probe of the polarization in the terahertz pump-optical probe experiment. SHG loops for THz pulses of different amplitudes were obtained. The SHG response is modelled assuming that the ferroelectric material is split into 180-degree domains. It is shown that intuitive model based on forced harmonic oscillator does not fully describe to the observed ultrafast ferroelectric response

INTRODUCTION

The ability to switch dielectric polarization in ferroelectrics is responsible for their unique functionalities allowing them to serve as key components in memories, actuators, other electronic and electro-optic devices. The speed of switching determines the maximum operational frequency of such devices. Fundamentally, the polarization reversal cannot be done faster than the period of optical phonon which is about $\tau_0 \approx 10^{-13}$ s [1]. The fastest experimentally observed switching of the dielectric polarization was completed in 220 ps with the help of photoconductive switch [2].

Recently sub-cycle THz pulses were proposed to control the order parameter in ferroics. Similarly, it was proposed to control the magnetic order parameter and trigger spin-reorientation [3] using the electric component of a nearly single cycle THz pulse. In ferroelectrics, the possibility of a dynamical switching of the dielectric polarization by a strong THz pulse was also discussed previously [4]. Since the action of electric

component of light on charges is the strongest perturbation in light-matter interaction, order parameter switching in ferroelectrics by strong THz pulses remains to be a promising direction of research.

Since the phenomenon of optical second harmonic generation (SHG) is sensitive to both spatial inversion (SI) and time reversal (TI) symmetry breaking, it provides a powerful experimental technique for investigation of ferroic materials (see for review [5,6]). The SHG is able to provide information on surface structural phase transition in $SrTiO_3$ [7,8]. Phonon relaxation excited by optical pulse was studied by the SHG in [9]. Very recently SHG was used to probe of transient processes in crystal lattice under intense THz excitation [10,11] and the possibility of an ultrafast reversal of the dielectric polarization under strong THz pulse was suggested [12]

In this paper, we present experimental results revealing ultrafast dynamic response of the polarization in ferroelectrics to the electric field of a nearly single-cycle THz pulse.

STUDIED MATERIAL AND EXPERIMENTAL PROCEDURE

We studied ferroelectric 400-nm thick film of barium strontium titanate $(Ba_{0.8}Sr_{0.2})TiO_3$ (BST). The film was fabricated by RF-sputtering of stoichiometric polycrystalline target on MgO substrate. The details of the sample preparation are described in Ref. [13]. Pure MgO substrate was measured in our experiments as well in order to isolate the signal from film. In-plane aluminum electrodes with a gap of 20 μm were deposited on BST to compare ultrafast and conventional quasi-static response.

We have used single-cycle THz pulses to excite ferroelectric polarization in the samples. Schematic of the experiment is shown in Fig. 1(a). The details of the THz generation process and characteristics of the terahertz pulse are described elsewhere [14]. The peak electric field of the THz pulse was up to 1 MV/cm and the duration was about 1 ps. The result of the excitation was probed by a Cr:Forsterite laser with an amplified and chirped pulse with the central wavelength of 1240 nm. The pulse width was 100 fs and the repetition rate was 100 Hz. THz wave was focused by parabolic mirrors into a spot of about 800 μm in diameter. The optical probe was focused by a lens into the spot of 200 μm in diameter. The pump and probe beams were at normal incidence. The time delay τ_d between the THz-pump and the optical-probe pulses was changed by a delay line. Zero time delayed was assumed to the delay corresponding to maximum in the time-domain SHG signal.

Upon non-linear interaction of the THz pulse with the ferroelectric medium, second harmonic light was generated with the central wavelength of 620 nm. Details of the SHG detection could be found in [4]. All experiments were performed in a dry atmosphere and at room temperature.

The pump beam was characterized by terahertz time-domain spectroscopy (THz-TDS) similar to those described in Ref. [3]. This technique allowed us to measure the electric field of the transmitted THz radiation as a function of time. The infrared light is used to detect the electromagnetic transient via electro-optic sampling in a 1-mm-thick [110] ZnTe crystal. The THz pulse profile is shown by dashed line in Fig. 1(b).

RESULTS

Fig. 1 (c) shows time dependence of the SHG intensity in BST film under an intense THz pulse excitation.

Two different shapes of the nonlinear optical curves were observed. The first type we define as "quadratic". Qualitatively, it looks like the square of THz pulse (curve 4 in Fig. 1(c)). It appears when SHG signal from unperturbed sample is very low or zero. The second type we define as "linear". The shape of the SHG response in this case is similar to the shape of the THz pulse (curves in Fig. 1(b) and (c)). It appears in cases when SHG signals from unperturbed sample are relatively high in comparison with those from excited sample. In these cases an interference of several sources of the nonlinear signal (dependent and independent on THz field) occurs. The contribution of different signals to the SHG intensity and their interference are described in details in Ref [4]. Curves 2 and 3 in Fig. 1(c) represent an intermediate case between "linear" and "quadratic" types of the dependencies. The SHG intensity time dependences from the MgO substrate is of "quadratic" type. The SHG intensity of the MgO is at least 400 times lower than the SHG signal from BST and could originate from nonlinear optical effects at the sample surface.

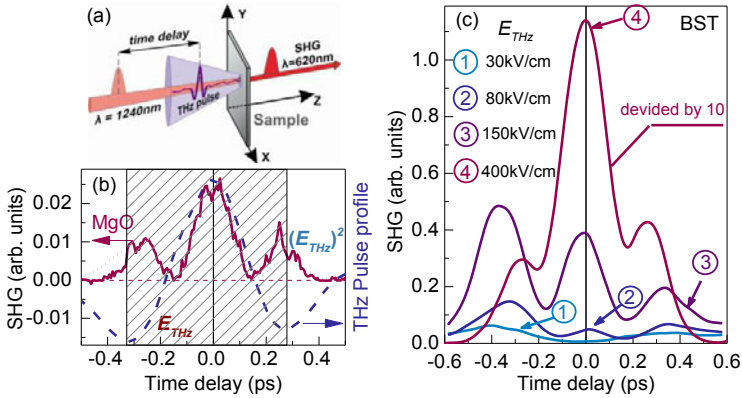

Fig.1. (a)-schematic of the experiment; (b) THz electric field profile E_{THz} (dashed line), its square $(E_{THz})^2$ (dotted line) and time-domain SHG intensity for MgO at 400 kV/cm; patterned area – the "major" part of the pulse; (c) - time-domain SHG intensity for BST at different amplitudes of THz field.

For further understanding of the dynamics of ferroelectricity in the BST film, we plot the results in the form of SHG loop, analogously to "static" nonlinear characterization of ferroelectric materials. Figs. 2(c) shows evolution of the SHG hysteresis loop for the BST film upon an increase of the amplitude of the THz field. The results can be compared with the "static" SHG loop in the same sample (inset in Fig. 2a).

For the lowest field, $I^{2\omega}(E_{THz})$ is almost linear. With the THz amplitude field increase, the $I^{2\omega}(E_{THz})$ dependence turns to be quadratic. For THz field higher than 150 kV/cm, the SHG loops possess the same structure: for the major part of the THz pulse, the loops look very similar to the static one. Additionally, a low-intensity "tail" appears for negative residual of the THz pulse.

For the highest amplitude of the THz field curve looks more as a loop with two possible values of the signal at zero field. Initial and final values of SHG response at zero field are always lower than for its zero values in the middle of the pulse.

The static $I^{2\omega}(E_0)$ dependence is quadratic and symmetric. For $|E_0| \le 20$ kV/cm hysteresis loop exists with the coercive field $E_0 = 10$ kV/cm. Thus, a quadratic dependence and hysteresis behavior are observed in static regime at much lower fields

than for the case of THz excitation. The THz loops, however, qualitatively agree with the conventional hysteresis for BST measured at low frequencies, when a frequency increase results in narrowing of the loop [15].

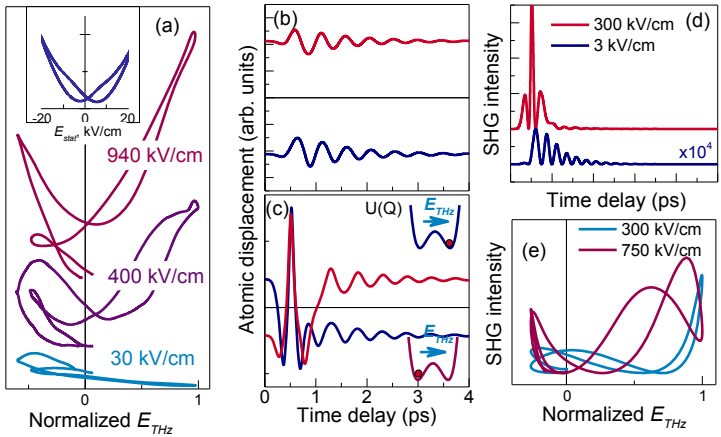

Fig.2. (a) experimental SHG hysteresis loops obtained from graphs in Fig. 1(c), the loops are shifted vertically for clarity; inset – experimental SHG hysteresis loop for static field; (b)- and (c) – calculated transients for atomic displacement for 3 and 300 kV/cm, insets in (c) – schematic view of two-minima potential well with positions of ion regarding to electric field direction; (d)- correspondent SHG intensity; (e)- calculated SHG hysteresis loop for 300 and 750 kV/cm.

DISCUSSION

Presently, several attempts to describe ion movement in ferroelectrics using nonlinear Duffing oscillator have been done [16–18]. There are two problems for this approach. The first one is that the Duffing equation gives unstable solutions: a subtle change of parameters in the equation may results in a drastic change of solutions. Although there are methods to increase the range of stability in different systems, for ferroelectrics so far even formulation of possible physical approaches does not exist. The second problem is more physical and fundamental. In fact, an intense THz excitation can also change the potential. How and how fast the changes occur is not clear. The lack of knowledge seriously hampers our intuitive understanding of the ultrafast response of the ferroelectric polarization in terms of a forced oscillator.

Nevertheless, in the following we would like to show the results of calculations of SHG hysteresis loops using the Duffing equation:

$$\frac{\partial^2 Q(t)}{\partial t^2} + \Gamma \frac{\partial Q(t)}{\partial t} + \frac{dU(Q)}{dQ} = \mathrm{E}_{\mathrm{THz}}.$$

The input parameters in the calculations are the potential energy $U(Q) = aQ^2 + bQ^4$, where Q is ion coordinate ($a/b = 40$ as in [19,20]), $a < 0$), decay constant $\Gamma = 1/\tau_{dec}$, $\tau_{dec1} = 1.5$ ps. External force is $F = E_{THz}/e$, where THz electric field

is approximated as $E_{THz}(t) = A\exp(-4(t-t_0)^2/\tau^2)\mathrm{sinc}(2\pi t + \varphi)$, τ - width of the THz pulse, φ - initial phase.

Note that without any electric filed the net polarization of the ferroelectric is suppressed by splitting the sample into 180-degrees domains (domain size [21] is much smaller than the probe beam diameter). It means that SHG signal is also expected to be zero. The domains are mutually compensated which means that half of the domains (we call them positive domains) are oriented oppositely to the rest of the (negative) domains. Although presently the domain wall velocity is considered to be as fast as 4.4 km/s [22], we will avoid the notion "domains" due to its complexity and will consider unit cells. Then we can introduce positive and negative unit cells, in which ions occupy right or left minimum of the potential well U, respectively (inset in Fig. 2(c)). These two types of the cells will be described by different initial conditions for the Duffing equation. As a result, we have two solutions $Q^+(t)$ and $Q^-(t)$. SHG field $E^{2\omega}(t)$ is proportional to the dielectric polarization $P(t)$ [23,24] that is

$$E^{2\omega}(t) \propto P(t) = \sum_V e\left(Q^+(t) + Q^-(t)\right),$$

where e is the electron charge, and summation holds over the probe illuminated volume V. The measured SHG intensity is electric field squared: $I^{2\omega} = \left(E^{2\omega}(t)\right)^2$. Thus together with THz field transient we have parametrically determined hysteresis loop for SHG intensity.

Two possible scenarios may occur. For low amplitude of THz field no switching can be observed (fig. 2 (b)), ions in both positive and negative wells oscillate around their equilibrium positions. SHG transient for this case (fig. 2 (d)) corresponds to a damped oscillator and differs much from the observed experimental dependences (fig. 1 (c)).

For high THz field a switching takes place. Each ion performs several high amplitude oscillations and finally get trapped by second minimum (see fig, 2 (c)). For this case, the calculated SHG transient coincides qualitatively with the observed experimental ones. Appropriate hysteresis loops are shown in Fig. 2(e). Similar to the experimental loops, the initial tails for negative residual of the THz pulse as well as strong hysteresis can be observed. Contrary to the experiment, minimal values of SHG signal within the loop equal zero. This happens due to the intersection of the zero line of the ion coordinate during switching from negative to positive minimum of the well (see Fig.2(c)) and summation of the signals of oppositely switched ions. Nonzero values of the SHG intensity in the minima of the transients can be achieved if incoherence of nonlinear response (dephasing) of all ions involved occurs disturbing the constructive interference of contributions from all ions.

CONCLUSION

We studied experimentally the processes of ultrafast polarization switching in barium-strontium-titanate thin film by strong electric field of single-cycle THz pulse. Second harmonic generation was used as the measure of polarization and SHG loops within the applied THz pulse were obtained. The observed results are explained as the polarization switching under the action of ultrafast electric field. However, the ultrafast switching is less efficient and the hysteresis loops obtained at THz frequencies are flatter than in the static regime. The observed phenomena may be useful for realization of ultrafast optoelectronic devices and THz modulators, in particular.

ACKNOWLEDGMENTS

The work is supported by Russian Science Foundation (Grant No16-12-10520). The work of V.B. and N.S. (theoretical analysis) is supported by Ministry of Education and Science of the Russian Federation State task for the University (3.1923.2017/4.6)

REFERENCES

1. A. K. Tagantsev, I. Stolichnov, N. Setter, J. S. Cross, and M. Tsukada, Phys. Rev. B **66**, 214109 (2002).
2. J. Li, B. Nagaraj, H. Liang, W. Cao, C. H. Lee, and R. Ramesh, Appl. Phys. Lett. **84**, 1174 (2004).
3. S. Baierl, M. Hohenleutner, T. Kampfrath, A. K. Zvezdin, A. V. Kimel, R. Huber, and R. V. Mikhaylovskiy, Nat. Photonics **10**, 715 (2016).
4. K. A. Grishunin, N. A. Ilyin, N. E. Sherstyuk, E. D. Mishina, A. Kimel, V. M. Mukhortov, A. V. Ovchinnikov, O. V. Chefonov, and M. B. Agranat, Sci. Rep. **7**, 687 (2017).
5. E. D. Mishina, N. E. Sherstyuk, D. R. Barskiy, A. S. Sigov, Y. I. Golovko, V. M. Mukhorotov, M. De Santo, and T. Rasing, J. Appl. Phys. **93**, 6216 (2003).
6. M. Fiebig, V. V. Pavlov, and R. V. Pisarev, J. Opt. Soc. Am. B **22**, 96 (2005).
7. E. D. Mishina, T. V. Misuryaev, N. E. Sherstyuk, V. V. Lemanov, A. I. Morozov, A. S. Sigov, and T. Rasing, Phys. Rev. Lett. **85**, 3664 (2000).
8. E. D. Mishina, A. I. Morozov, A. S. Sigov, N. E. Sherstyuk, O. A. Aktsipetrov, V. V Lemanov, and T. Rasing, J. Exp. Theor. Phys. **94**, 552 (2002).
9. Y. M. Sheu, S. A. Trugman, L. Yan, Q. X. Jia, A. J. Taylor, and R. P. Prasankumar, Nat. Commun. **5**, 5832 (2014).
10. T. Miyamoto, H. Yada, H. Yamakawa, and H. Okamoto, Nat. Commun. **4**, 2586 (2013).
11. H. Yamakawa, T. Miyamoto, T. Morimoto, H. Yada, Y. Kinoshita, M. Sotome, N. Kida, K. Yamamoto, K. Iwano, Y. Matsumoto, S. Watanabe, Y. Shimoi, M. Suda, H. M. Yamamoto, H. Mori, and H. Okamoto, Sci. Rep. **6**, 20571 (2016).
12. R. Mankowsky, A. Von Hoegen, M. Först, and A. Cavalleri, Phys. Rev. Lett. **118**, (2017).
13. A. S. Sigov, E. D. Mishina, and V. M. Mukhortov, Phys. Solid State **52**, 762 (2010).
14. C. Vicario, M. Jazbinsek, A. V Ovchinnikov, O. V Chefonov, S. I. Ashitkov, M. B. Agranat, and C. P. Hauri, Opt. Express **23**, 4573 (2015).
15. V. B. Shirokov, S. V. Biryukov, V. M. Mukhortov, and Y. I. Yuzyuk, Tech. Phys. **56**, 1175 (2011).
16. E. V Kazantseva and A. I. Maimistov, Quantum Electron. **30**, 623 (2000).
17. E. V. Kazantseva, A. I. Maimistov, and J.-G. Caputo, Phys. Rev. E **71**, 56622 (2005).
18. S. Grübel, J. A. Johnson, P. Beaud, C. Dornes, A. Ferrer, V. Haborets, L. Huber, T. Huber, A. Kohutych, T. Kubacka, M. Kubli, S. O. Mariager, J. Rittmann, J. I. Saari, Y. Vysochanskii, G. Ingold, and S. L. Johnson, arXiv 1 (2016).
19. V. B. Shirokov, Y. I. Yuzyuk, V. V. Kalinchuk, and V. V. Lemanov, Phys. Solid State **55**, 773 (2013).
20. V. B. Shirokov, R. A. Shakhovoy, A. G. Razumnaya, and Y. I. Yuzyuk, J. Appl. Phys. **118**, 24101 (2015).
21. E. D. Mishina, N. E. Sherstyuk, D. R. Barskiy, A. S. Sigov, Y. I. Golovko, V. M. Mukhorotov, M. De Santo, and T. Rasing, J. Appl. Phys. **93**, 6216 (2003).
22. A. Q. Jiang, H. J. Lee, C. S. Hwang, and J. F. Scott, Adv. Funct. Mater. **22**, 192 (2012).
23. G. Dolino, J. Lajzerowicz, and M. Vallade, Phys. Rev. B **2**, 2194 (1970).
24. E. Mishina, N. Sherstyuk, Y. Golovko, V. Muhortov, and A. Sigov, Integr. Ferroelectr. **92**, 65 (2007).