ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Photoelectric Effects in Single Domain $BiFeO_3$ Crystals

Reda Moubah, Olivier Rousseau, Dorothée Colson, Alla Artemenko, Mario Maglione, and Michel Viret*

Energy harvesting from sunlight is essential in order to save fossil fuels, which are found in limited amount in the earth's crust. Photovoltaic devices converting light into electrical energy are presently made of semiconducting materials, but ferroelectrics are also natural candidates because of their internal built-in electric field. Although they are clearly uncompetitive for mainstream applications, the possibility to output high photovoltages is making these materials reconsidered for targeted applications. However, their intrinsic properties regarding electronic transport and the origin of their internal field are poorly known. Here, it is demonstrated that under intense illumination and electric field, oxygen vacancies can be controllably generated in $BiFeO_3$ to dramatically increase the conductance of $BiFeO_3$ single crystals to a controllable value spanning 6 orders of magnitude while at the same time triggering light sensitivity in the form of photoconductivity, diode, and photovoltaic effects. Properties of the bulk and the Schottky interfaces with gold contacts are disentangled and it is shown that bulk effects are time dependent. The photocurrent has a direction that can be set by an applied field without changing the ferroelectric polarization direction. The self-doping procedure is found to be essential in both the generation of electron hole pairs and the establishment of the internal field that separates them.

1. Introduction

Ferroelectrics (FE) have been the object of some interest regarding their possible application as photovoltaic materials. However, it turns out that their carriers recombination rate is high and most of them have too large bandgaps to harvest photons in the visible spectrum. Although it seems hard to imagine that these materials could ever rival classical semiconductors in mainstream usage, they could however be appealing for some specific applications owing to their multifunctionalities. For instance, ferroelectrics have also piezoelectric properties. Even more interesting are multiferroics which also possess magnetic order. These have attracted much attention in recent years due to their potential as magnetic memory-storage cells based on the magnetoelectric effect.[1] $BiFeO_3$ (BFO) is a most promising candidate as it combines, at room-temperature, coupled FE and magnetic orders, as well as a rather low direct band gap of about 3 eV,[2] a property of interest for photo-electric effects.[3] However, although this field of research started over 30 years ago, it appears that the actual mechanism leading to charge separation in ferroelectrics is unclear and a deeper understanding of it is essential.[4–7] This will only come from the study of the simplest possible system, i.e., a single FE domain BFO crystal, which is the object of the present report.

2. Results and Discussion

We report here on photovoltaic and photoconductance properties of single domain high quality BFO crystals contacted with gold electrodes. The schematic of the device used in this study is shown in **Figure 1**. It was first measured in the virgin state where its total resistance is around 100 GOhm, and does not change at voltages up to 40 V, for which the electrical polarization does not reverse. The photocurrent is also found to be negligible (below 1 pA) whereas a 10% photoconductance effect is measured in a

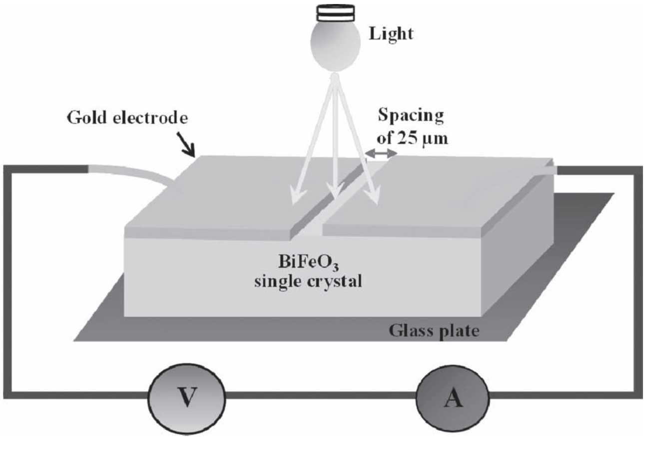

Figure 1. Schematic illustration of the sample geometry used for the electrical measurements of BFO single crystals.

Dr. R. Moubah, Dr. O. Rousseau, Dr. D. Colson,
Dr. M. Viret
Service de Physique de l'Etat Condensé
CEA Saclay, DSM/IRAMIS/SPEC, URA CNRS 2464
Gif-sur-Yvette, 91191 France
E-mail: Reda.Moubah@cea.fr

Dr. A. Artemenko, Dr. M. Maglione
ICMCB, Univ Bordeaux, CNRS 33600 Pessac, France

DOI: 10.1002/adfm.201201150

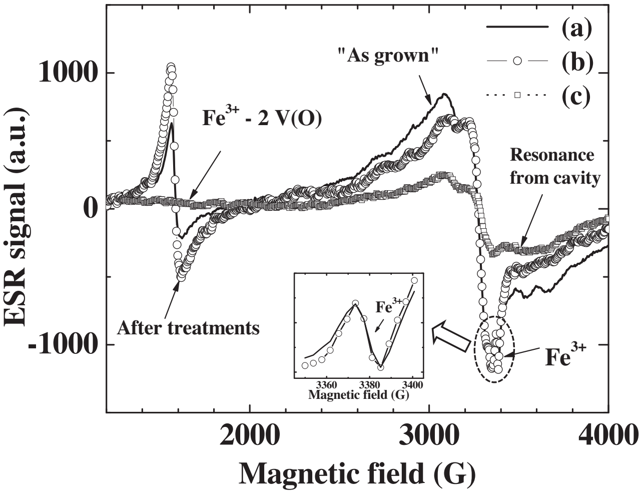

Figure 2. Electron spin resonance measurements on a BFO crystal a) in its virgin state and b) after subsequent exposure to intense light and electric field. Resonances are due to Fe ions in different local environments, marked as Fe^{3+} and Fe^{3+} - 2 V(O). The broad resonance, centered at 3350 G, is attributed by Lin et al.[18] to the cycloidal spin structure, i.e., "normal" Fe^{3+} sites in the BFO lattice. After treatment, the Fe^{3+} - 2 V(O) line is significantly enhanced indicating that new oxygen vacancies were created. c) Resonance from the empty cavity.

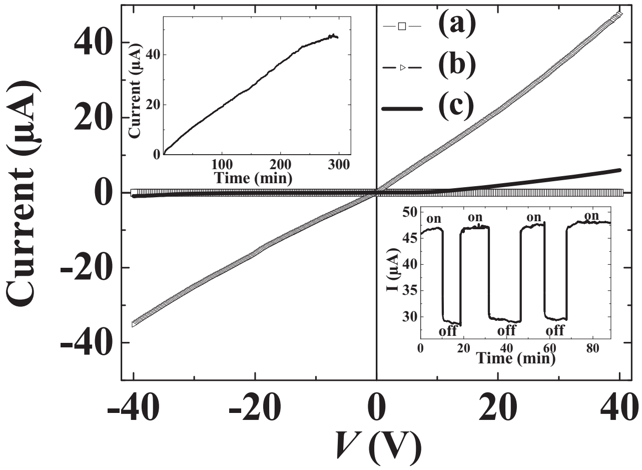

Figure 3. Current as function of applied electric field in a Au/BFO/Au device where BFO is a ferroelectric monodomain BFO single crystal: a) in the dark, before the first exposure; b) under white light of 50 W cm^{-2}, after illumination for 6 h in a voltage of 40 V; and c) in the dark, 7 days after switching off the light. The top left inset is the time evolution of the current during the treatment with light under a 40 V applied voltage. The photoconducting effect of the device is shown in the bottom right inset as light is turned on and off in time while photoinduced currents are monitored at an applied voltage of 40 V.

50 W cm^{-2} white light when the applied voltage is 40 V. These rather disappointing effects in highly resistive bulk BFO are, in fact, not a complete surprise considering that recombination rates are known to be very fast in ferroelectrics and their bandgap around 3 eV is quite high to rely on conversion of mainly visible photons into electron-hole pairs. One way around this intrinsic limitation could be to dope the crystals and create states in the gap. One can think of using natural impurities like oxygen or Bi vacancies for this, but these are possibly not that numerous in our crystals, for which we spent time minimizing leakage currents.[8] In order to circumvent this problem, we have determined an easy procedure to generate active oxygen vacancies with a controllable density. This can be done remembering that light can remove electrons from the valence band, mainly composed of oxygen 2p states, to populate the conduction band (mainly Fe 3d states) as well as defect states. It is therefore possible that locally, some oxygen ions are rendered off-stoechiometric. When light is turned off, electrons relax back and the original state is recovered. However, it is known that oxygen vacancies can easily migrate in these compounds over millimeter distances under the action of an electric field.[6,9] The required fields are usually rather large and accompanied by polarization reversal.[6] However, we find that under intense light illumination, electric fields below the coercivity can move oxygen ions. Therefore, this procedure allows to permanently generate oxygen vacancies, as confirmed in **Figure 2** by electron spin resonance measurements on a sample in its virgin state and after subsequent exposure to intense light and electric field. The most significant change in the spectrum is a redistribution of spectral weight enhancing the Fe^{3+} - 2 V(O) line indicating that new oxygen vacancies were created and moved to increase significantly and permanently (at least at the scale of weeks) the concentration of defects with two oxygen vacancies.

This has a dramatic effect on the electrical transport properties as shown in the I(V) characteristics of **Figure 3**. The as grown monodomain BFO single crystal has a dark current of about 10^{-11} A in a voltage of 40 V, corresponding to a resistivity of the order of 10^{11} Ohm cm. As shown in the top left inset of Figure 3, during activation with intense light and electric field the current increases dramatically by about six orders of magnitude. This effect is much larger than that observed in thin films or bad insulator crystals,[5,6,10] which may be due to both the BFO crystalline quality and the high light intensity used here. Importantly, the percentage change of the conductivity can vary significantly from sample to sample, which we attribute to the uncontrolled variation of the as grown defect density. We recall that the applied electric field has a value smaller than the FE coercivity, thus leaving the crystal in its original single domain state. Interestingly, while the virgin I(V) curves vary linearly with voltage, the ones obtained after treatment are highly non-linear and asymmetrical (Figure 3). This diode effect in ferroelectrics has been known for a long time and is attributed to the presence of an internal electric field stemming from the existence of the spontaneous polarization.[11] It was recently observed in BFO and simply explained considering the direction of the FE polarization: at positive bias, the FE polarization vector is parallel to the electric field direction inducing a maximum current.[5] At negative bias, these vectors are antiparallel and the current is minimum. However, this explanation cannot account for our measurements for several reasons. First, in the virgin state, our single domain crystals show symmetrical I(V) characteristics despite their large saturated polarization. The I(V) asymmetry is instead systematically induced after activation with electric field and light, in a direction that always follows that of the applied electric field, independently of the polarization

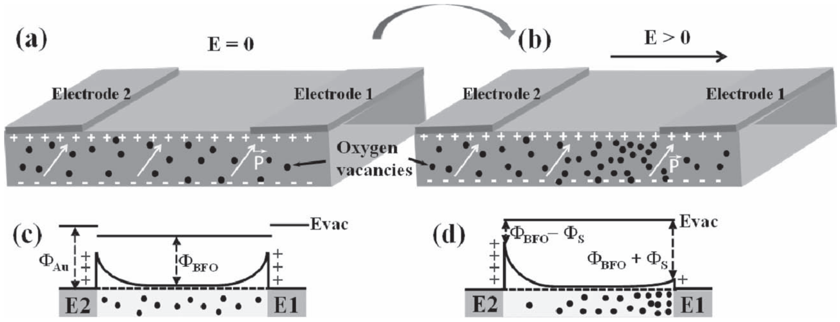

Figure 4. Schematic representations of the mechanism leading to the creation of the diodelike structure: a) in the virgin state, the distribution of oxygen vacancies (black dots) is homogenous and b) under illumination with an applied electric field, positively charged oxygen vacancies are created and electromigrate, following the field direction, towards the E1 interface. This generates a concentration gradient responsible for the diodelike behavior in the circuit. The electric field necessary to create the diodelike structure being smaller than the FE coercivity, the polarization direction is left unchanged. Energy band diagrams at the contact between gold and BFO are also represented c) in the virgin state where the system is symmetrical and d) after electromigration of oxygen vacancies (inducing an asymmetry of the barriers heights). Φ_{Au} and Φ_{BFO} are the work functions of the gold electrodes and BFO, respectively. Φ_{BFO} = 3.3 eV is smaller than that of the gold (5.1 eV). Φ_S is the barrier height of the created Schottky diode (its value is estimated around 0.4 eV).

direction. Because our procedure preserves the $BiFeO_3$ polarization state, we conclude that the direction of polarization is not the central parameter defining the diode-like characteristic. We argue that this behavior is linked to the effect of electromigration of positively charged oxygen vacancies towards the negative electrode. This is likely to create a doping gradient as well as a local doping at the interface.[6,9] This breaks the intrinsic device symmetry and produces diode-like I(V) curves as schematically represented in **Figure 4**. Our asymmetries are obtained for rather high voltages indicating that the dominant effect in our samples is likely to be the oxygen vacancy gradient in the gap between the electrodes and not the unbalance of the Schottky barriers as in Ref.[6] After the light and electric field procedure, the sample presents a large photoconductivity as seen in the bottom right inset of Figure 3 where illumination is simply turned on and off while measuring the current. Under illumination the current reaches 47 μA and just after turning off the light it decreases sharply to 28 μA, thus producing a 60% effect. This can be understood qualitatively as under illumination, electrons are excited into the conduction band and can be captured by traps created by structural defects such as oxygen vacancies. These trap levels are progressively filled with photogenerated holes accounting for the slow current increase in the top left inset of Figure 3. It is interesting to note that the variation of the photocurrent as function of integrated light varies less than linearly. Similar observations were reported in $BaTiO_3$ and explained by the accumulation of holes optically excited from the donors in shallow acceptors. As these acceptors get filled the fraction of busy donors varies, and the lifetime of free carriers changes, inducing a nonlinearity.[12] Therefore, during the light and voltage treatment, the doping increases as well as the number of photogenerated carriers excited into the conduction band and further trapped in the defects states. Once the light is turned off, charge carriers are thermally released from the traps and partly populate the conduction band, which makes the conductance relax with time (on the order of several weeks in some samples) to a finite value. This behavior, called persistent photoconductivity, has already been observed in some ferroelectrics,[13,14] and evidences the presence of trapping impurities.

The photovoltaic effect in our crystals can be clearly seen in the I(V) curves of **Figure 5** (see zoom in inset). After the intense light and (positive) voltage treatment, a photocurrent of about –0.6 nA is observed under illumination (it was zero in the virgin state). Interestingly, when the same treatment is carried out subsequently in a reversed electric field, the zero voltage photocurrent is also reversed as can be seen in the inset of Figure 5. Therefore, the sign of the photocurrent is always opposite to the voltage direction of the last treatment, independently from both directions of polarization and diode effect (which are both left unchanged). This is in contrast to previous conclusions for the same system[5,6] and the idea that the photovoltaic effect is due to the ferroelectric polarization.[4] It is to be noted that photovoltages were also reported in configurations parallel and perpendicular to the FE polarization vector.[4,7,15,16] Therefore, the direction of the internal field driving the photovoltaic effects in ferroelectrics is complex, but the importance of previously applied electric fields in our case can be understood: under light, photoinduced electron-hole pairs are separated under the action of the internal field composed of the applied and depolarizing fields. These charges accumulate near surfaces and interfaces (probably inducing space charge fields as observed in $Pb_{1-x}La_xZr_{0.58}Ti_{0.42}O_3$ (PLZT)

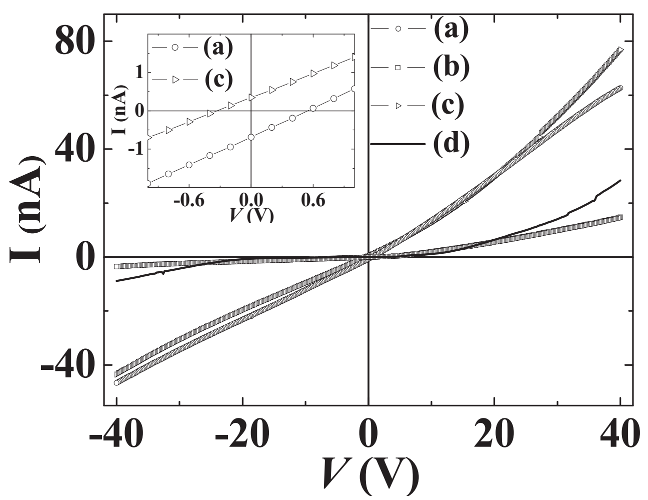

Figure 5. Room temperature *I–V* curves of the Au/BFO/Au device after application of an external electric field under high power light for 4 h either a,b) parallel and or c,d) antiparallel to the diode direction. Measurements (a,c) are under light and (b,d) in the dark. The inset shows a zoom of the (a) and (c) I(V) curves around zero field, evidencing the switching of the photocurrent direction while preserving the direction of the diode effect.

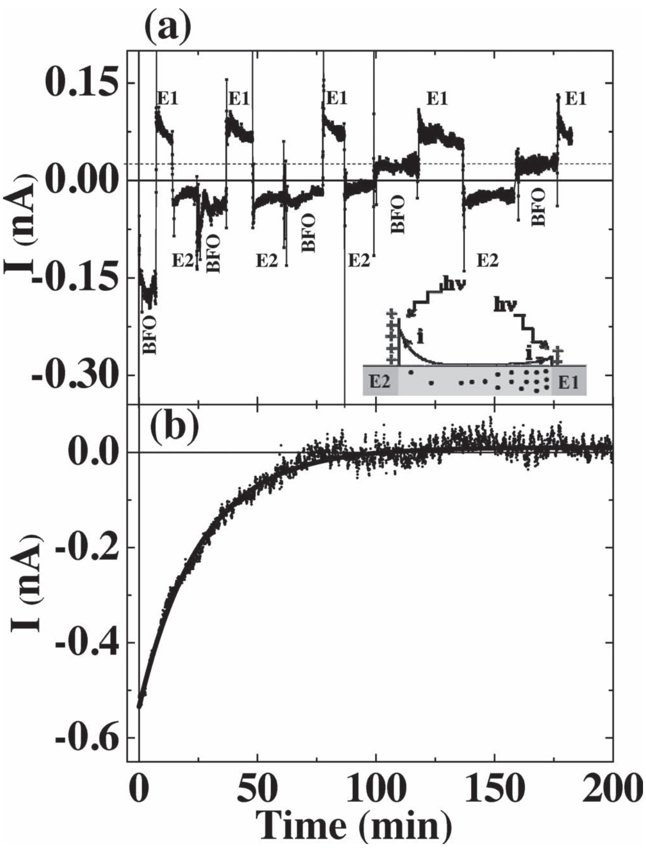

Figure 6. a) Variation of the photocurrent as function of time as the light spot is moved over different regions on the sample including the pure BFO crystal, electrode E1, and electrode E2. The measurement was carried out in zero applied electric field after a 4 h exposure to high power white light in the presence of a voltage of 40 V. The signal for the pure $BiFeO_3$ is contaminated by a small contribution from the gold electrodes, which is subtracted in the measurement (b). Time zero corresponds to the end of the treatment in an electric field of 40 V under high power light. This zero bias field measurement is fitted by exponential decay (solid black line) with a typical time constant of 1600 s. The inset in (a) is a schematic representation of the mechanism leading to the photocurrent sign change associated to the Schottky interfaces: illumination on either electrode injects carriers into the gold, thus inducing a current of different sign.

ceramics)[17] to screen the internal field and can be further trapped at defects like oxygen vacancies responsible for energy levels in the gap. Once the applied field is removed, the trapped carriers produce a significant internal field with a component opposite to the previous voltage, responsible for the photovoltaic properties. The carriers then slowly rearrange and at long timescales, the screening is large and the photovoltage decreases accordingly. In order to disentangle the different photovoltaic effects present in our crystals, the variation of the photocurrent during sequential illumination of electrodes and pure BFO is presented in **Figure 6**a. This measurement was carried out by scanning the light spot over the different areas of the sample, while monitoring the photocurrent. It allows to distinguish the two sources of photovoltaic effects related i) to the bare BFO and ii) to the Au/BFO Schottky junctions at the interfaces with the (semi-transparent) electrodes. Starting with light in between the electrodes, i.e., directly on the bare BFO crystal, a photocurrent of –0.2 nA is obtained, opposite to the diode effect (corresponding to Figure 5a). Subsequent scans evidence a slow decrease with a time constant of 1600 s in this sample (Figure 6b). When light impinges on the electrodes, the Schottky barrier E1 gives a photocurrent of +0.08 nA while E2 gives –0.02 nA. This sign difference can be understood considering the head to head geometry of the interfaces in the Au/BFO/Au circuit. The work function of the gold electrode (5.1 eV) being larger than that of the BFO (3.3 eV), the induced local electric field tends to attract electrons out of the BFO into the Au (see Figure 4). As a consequence, the electrodes produce opposite local photocurrents. Moreover, the potential barriers are rather different on either side because of the migrated oxygen vacancies towards electrode E1 after the light and electric field treatment. Thus, the larger carrier density of electrode E1 also induces a stronger photocurrent. In contrast, when illuminating the whole sample in its virgin state, the contributions of both electrodes cancel out as they have roughly the same magnitude with opposite signs. As no effect is found in this state, the pure BFO is therefore not photoactive until its treatment. An internal field is likely to be slowly established in the direction of the applied external voltage by the trapping of photo-generated carriers at defect sites and surfaces. The slow decrease of the photocurrent associated to BFO (Figure 6b) can be fitted by an exponential decay with a long relaxation time $\tau \approx$ 1600 s, which we attribute to a slow carrier release which progressively screens the internal field and thus the photovoltaic effect. In contrast, the electric field generated at the Schottky barriers by band bending is stable with time.

3. Conclusion

In summary, we have demonstrated the central role of the internal field and carrier density played in the photo-electric properties of ferroelectric monodomain $BiFeO_3$ single crystals. The key parameter for maximizing photovoltaic effects is the establishment of a strong internal field, in an appropriate direction, which we show here, is not solely defined by the ferroelectric polarization. Internal fields could be maximized with some material processing, for instance at interfaces between two differently polarized media (this includes domain walls where promising photovoltaic effects[3] have been measured) or perhaps in hybrid structures comprising ferroelectrics and normal semiconductors. We would like to point out here that other compounds like electrets, in which internal fields can be established by an external procedure, could also be interesting candidates for photovoltaic applications.

4. Experimental Section

The BFO single crystals were grown by a spontaneous crystallization in air from a Bi_2O_3–Fe_2O_3 flux, as detailed in ref. [8] With this procedure, millimeter sized platelets were obtained with the short dimension along the (001) direction (in pseudocubic lattice description). About 90% of the as grown samples were monodomain with the polarization along the (111) direction. Two 15 nm thick gold electrodes were deposited by electron beam evaporation through a shadow mask directly onto the flat side of the single crystals. The electrodes were spaced by 25 μm (Figure 1) with lateral dimensions of around 200 μm and compose the plus and minus in an electrical circuit consisting of a voltage source and a picoAmpmeter. In this symmetrical geometry, two Schottky junctions were established at the gold interfaces with equivalent polarization induced surface charges. The electrical circuit could be schematically modeled by two head to tail similar Schottky junctions across crystalline BFO. An ordinary Philips white light bulb (12 V, 100 W) was used for illumination whose light power density was changed by focusing it on the sample using an optical microscope. The maximum density, obtained for the ×100 magnification, was estimated to be about 50 W cm^{-2}.

Acknowledgements

This research project was supported by the French RTRA contract 'MULTIFERRO'. For ESR investigations financial support from a Marie Curie International Incoming Fellowship within the 7th European Community Framework Programme (EPREXINA, GA 255662) is gratefully acknowledged.

Received: April 25, 2012
Published online: July 23, 2012

---

[1] R. Ramesh, N. A. Spaldin, *Nat. Mater.* **2007**, *6*, 21.
[2] R. Moubah, G. Schmerber, O. Rousseau, D. Colson, M. Viret, *Appl. Phys. Express* **2012**, *5*, 03580.
[3] S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C.-H. Yang, M. D. Rossell, P. Yu, Y.-H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, R. Ramesh, *Nat. Nanotechnol.* **2010**, *5*, 143.
[4] W. Ji, K. Yao, Y. C. Liang, *Adv. Mater.* **2010**, *22*, 1763.
[5] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, S.-W. Cheong, *Science* **2009**, *324*, 63.
[6] H. T. Yi, T. Choi, S. G. Choi, Y. S. Oh, S.-W. Cheong, *Adv. Mater.* **2011**, *23*, 3403.
[7] W. Ji, K. Yao, Y. C. Liang, *Phys. Rev. B* **2011**, *84*, 094115.
[8] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, S. Fusil, *Phys. Rev. B* **2007**, *76*, 024116.
[9] C.-H. Yang, J. Seidel, S. Y. Kim, P. B. Rossen, P. Yu, M. Gajek, Y. H. Chu, L. W. Martin, M. B. Holcomb, Q. He, P. Maksymovych, N. Balke, S. V. Kalinin, A. P. Baddorf, S. R. Basu, M. L. Scullin, R. Ramesh, *Nat. Mater.* **2009**, *8*, 485.
[10] S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, X. Xu, J. L. Musfeldt, *Appl. Phys. Lett.* **2008**, *92*, 091905.
[11] V. Fridkin, *Photoferroelectrics*, Springer, New York **1979**.
[12] D. Mahgerefteh, J. Feinberg, *Phys. Rev. Lett.* **1990**, *64*, 2195.
[13] P. Tayebati, D. Mahgerefteh, *J. Opt. Soc. Am. B* **1990**, *8*, 1053.
[14] A. Rose, *Concept of photoconductivity and Allied problems*, Wiley, New York/London **1963**.
[15] F. S. Chen, *J. Appl. Phys.* **1969**, *40*, 3389.
[16] A. Anikiev, L. G. Reznik, B. S. Umarov, J. F. Scott, *Ferroelectr. Lett. Sect.* **1985**, *3*, 89.
[17] C. E. Land, *Ferroelectrics* **1980**, *27*, 143.
[18] J. W. Lin, Y. H. Tang, C. S. Lue, J. G. Lin, *Appl. Phys. Lett.* **2010**, *96*, 232507.