Ferroelectric Switching in $Bi_4Ti_3O_{12}$ Nanorods

Mehrnoosh Azodi, Catalin Harnagea, Vincenzo Buscaglia, Maria Theresa Buscaglia, Paolo Nanni, Federico Rosei, and Alain Pignolet

Abstract—We report the piezoelectric and ferroelectric properties of individual one-dimensional objects made of $Bi_4Ti_3O_{12}$ (BiT). The nanorods and nanowires investigated in this study were fabricated by a two-step process: 1) preparation of reactive templates using hydrothermal-like synthesis and colloidal chemistry and 2) transformation of the reactive templates in $Bi_4Ti_3O_{12}$ by solid-state reaction, overcoming the morphological instability problem of 1-D templates. Using piezoresponse force microscopy (PFM) with both out-of-plane and in-plane detection capability, we show that both types of objects exhibit strong piezoelectric activity and good switching ferroelectric behavior. Analysis of the PFM hysteresis loops obtained revealed that the coercive voltage of the in-plane PFM signal can be either equal to or different from that of the out-of-plane response. We associate these situations with two types of polarization switching mechanisms: direct 180° switching, and via rotation of polarization, resulting from the independent switching of the components along the *a*- and *c*-crystallographic axes. In a few instances, we observe a negative piezoelectric coefficient, which we explain by the specific shape of the piezoelectric surface of $Bi_4Ti_3O_{12}$.

I. INTRODUCTION

ONE-DIMENSIONAL ferroelectric nanostructures such as nanowires (NWs) and nanotubes (NTs) have recently received much attention because 1) they are candidate components for the fabrication of next generation fully three-dimensional FeRAM structures with very high bit density and 2) detailed *ab initio* calculations have predicted a new kind of ferroelectric order in nanorods and nanodisks, opening a new avenue for the use of ferroelectric nanostructures in data storage [1].

The piezoelectric properties of nanowires, nanorods, and nanofibers of a variety of different materials have been reported by several authors. Piezoelectricity of an individual 1-D nanobject (ZnO nanobelts) was first demonstrated by Zhang *et al.* [2] Since then, several other materials, including GaN [3], Sb_2S_3 [4], and even more complex systems, such as nanotube heterostructures [5] or 1-D biomaterials

[6]–[8] have been investigated at the nanoscale and proven to be piezoelectric. Regarding ferroelectric materials, Wang *et al.* studied the electromechanical properties of individual integrated potassium niobate ($KNbO_3$) nanostructures by piezoresponse force microscopy (PFM) and reported displacements in the range of 3 to 13 pm under a V_{ac} of 2 V, with a maximum nominal piezoelectric coefficient of 7.9 pm/V [9]. Piezoelectric properties of crystalline orthorhombic sodium niobate ($NaNbO_3$) nanowires with diameters around 100 nm and up to several hundred micrometers long have also been reported [10], as it has been for $PbTiO_3$ [11] and $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) nanowires [12] or nanotubes [13], [14]. Generally, to prove the ferroelectric nature of a nanowire or of any nano-object, one must show that polarization can be switched by an external electric field, and the only method available to do that is PFM, in which this is achieved by simply applying sufficiently high bias pulses. Alternatively, the technique termed switching spectroscopy can be used [15], i.e., recording the PFM signal as a function of a slowly varying (0.01 to 1 Hz) voltage bias applied. Because the PFM signal is related to the spontaneous polarization, this curve resembles the polarization hysteresis curve. Direct ferroelectric polarization switching of a single-crystal $BaTiO_3$ nanowire along its length axis under axial dc bias has been reported by Wang *et al.*, evidenced with the lateral mode of PFM [16]. They estimated a polarization shell thickness of ~10 nm for a $BaTiO_3$ nanowire having a diameter of ~120 nm. Finally, Yu *et al.* studied the converse piezoelectric effect of $BaTiO_3$ single-crystalline nanowires synthesized by a solid-state reaction with diameters ranging from 50 to 200 nm, and lengths up to tens of micrometers [17].

Bismuth titanate ($Bi_4Ti_3O_{12}$ or BiT) is a ferroelectric material which has a layered perovskite-like structure; it belongs to the Aurivillius family with a general formula (Bi_2O_2) $[A_{m-1}(B)_mO_{3m+1}]$. At room temperature, the symmetry of BiT is monoclinic, but it can be considered an orthorhombic structure with $a = 0.5448$, $b = 0.411$ and $c = 3.283$ nm [18]. The spontaneous polarization P_s of single-crystalline BiT has been shown to be greater than 30 $\mu C/cm^2$ and it lies in the monoclinic *a-c* plane in a direction tilted by less than 5° from the *a* axis [19], [20]. These results also indicated that two types of switching, 90° and 180°, are possible for the major component of P_s in the *a*–*b* plane.

BiT has a high Curie temperature (675°C) and shows very little ferroelectric fatigue [18]–[21] when subjected to extensive voltage cycling, which makes it a very good candidate for high-temperature piezoelectric devices. Moreover, as a ferroelectric material, it has a broad field of ap-

plications ranging from capacitors to non-volatile memory devices, including various types of sensors.

Although extensive studies on BiT [21]–[24] films synthesized by various techniques have been reported in the literature, there is no report on the electromechanical properties of BiT nanowires or nanorods. The fabrication of 1-D BiT nanostructures has been recently achieved by Buscaglia *et al.* [25]. Here, we investigate the piezoelectric properties and ferroelectric switching behavior of individual BiT nanorods using both in-plane and out-of-plane PFM.

II. Experiment

A. Synthesis of BiT Nanowires

As described in detail in [25], the general approach used for sample preparation is a two-step process: Reactive templates were first prepared using hydrothermal-like synthesis and colloidal chemistry, and $Bi_4Ti_3O_{12}$ nanorods were subsequently obtained by solid-state reaction of the reactive templates at 600°C to 700°C. Two different kinds of reactive templates with a core–shell structure were produced by colloidal chemistry methods. The first type of reactive templates were $Bi_6O_5(OH)_3(NO_3)_5 \cdot (H_2O)_3$ precursor rods coated with a shell of nanocrystalline TiO_2 anatase, whereas the second type consists of single-crystal nanowires of layered hydrogen titanate (LHT) of probable composition $H_2Ti_2O_5 \cdot 3H_2O$ decorated with bismuth oxycarbonate Bi_2CO_5 crystals. The precursor nanorods and nanowires were placed in alumina boats and calcined in air inside a box furnace. Thermal treatments were performed for 4 h at 400°C to 700°C on both templates and resulted in two types of BiT nanorods a few micrometers in length and 0.5 to 1.5 μm in width with thicknesses of the order of tens of nanometers. The first type consists of single-crystalline nanorods of BiT, with a relatively large size distribution and somewhat irregular shape that tend to agglomerate [Fig. 1(a)], whereas the second type are polycrystalline nanorods with a narrower size distribution [Fig. 1(b)].

To perform the piezoelectric measurements, both kinds of nanorods were dispersed in absolute ethanol and a drop of the suspension was deposited on gold-coated alumina substrates. The substrates were then annealed at 500°C for 2 h to improve adhesion of nanorods to the substrate.

B. Piezoresponse Force Microscopy

Piezoresponse force microscopy (PFM) is an efficient technique for studying ferroelectric domains and polar regions. Based on the converse piezoelectric effect, a small ac voltage applied between the conductive tip of an atomic force microscope (AFM) in contact mode and the bottom electrode of a ferroelectric sample induces mechanical oscillations of the sample that are transmitted to the AFM cantilever and are then measured using a lock-in detection scheme [26], [27].

We used an atomic force microscope (DI-Enviroscope, now Bruker AXS, Santa Barbara, CA) equipped with conductive cantilevers and tips [28]. We first employed medium-stiff cantilevers (Pt/Ir-coated, $k = 1$ to 5 N/m; NSC36, Mikromasch, Tallinn, Estonia), then soft cantilevers, (Cr/Au-coated, CSC 38, Mikromasch) to reduce the contact force applied during the measurements. Attempts to perform measurements in contact mode (for PFM imaging), even at low contact force, resulted in the BiT nanorod being displaced by the AFM tip. Therefore, in a typical experiment, we first located the 1-dimensional object by imaging large areas in noncontact mode, then subsequently switched to contact mode after stopping the AFM tip above the desired place to measure the piezoelectric signals and hysteresis loops.

To this end, an ac signal (typically 0.5 V_{rms}, and frequency ~30 kHz) was applied between the AFM tip (in contact with the specific nanorod) and the conductive substrate. Using two lock-in amplifiers, both out-of-plane (OP) and in-plane (IP) components of the piezoelectric deformations were measured simultaneously. For hysteresis measurements, a dc source (2400, Keithley Instruments Inc., Cleveland, OH) in series with the ac driving voltage has been used to cycle the bias voltage.

III. Results and Discussion

The piezoelectric measurements were performed on several nanorods of different sizes. Few of them were subject to electric breakdown during the measurements, which could be seen as a sudden increase in the current measured simultaneously with PFM signals that became zero. All of the nanowires that did not break down exhibit a strong piezoresponse which, upon the application of a series of suitable dc bias, demonstrates hysteretic behavior. The presence of hysteresis proves the existence of a switchable polarization and, thus, the ferroelectric nature of the nanorods. In a few instances, the shape of the piezoelectric hysteresis loop resembled that of $(110)_{orth}$-oriented BiT crystallites embedded in a (001)-oriented matrix, reported previously [24], [29].

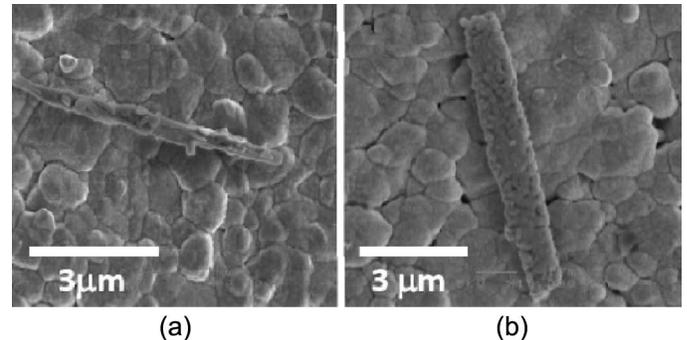Fig. 1. Scanning electron micrograph images of (a) a $Bi_4Ti_3O_{12}$ (BiT) single-crystalline nanorod, (b) a BiT polycrystalline nanorod.

This shape, showing a decrease of the effective piezoelectric coefficient d_{zz} at high electric fields, implies an anomalous switching behavior, and was explained by the highly non-homogeneous electric field at the tip apex, combined with the increased number (eight) of possible polarization states in the highly anisotropic BiT. In these 1-D objects, however, we observed and studied another interesting phenomenon: the coercive fields of the IP and OP hysteresis loops, measured simultaneously, are very often different, as shown in Figs. 2(b) and 2(c), where we show the switching behavior of a nanorod, probed at two different locations. The piezoelectric hysteresis loops of Figs. 2(b) and 2(c) show a relatively low OP-PFM response, suggesting that the polarization is oriented close to the rod's longitudinal axis, and we shall consider this in our analysis.

Simultaneous measurement of OP and IP hysteresis loops has been previously reported by Roelofs *et al.* [30] for assessing the type of switching occurring in individual grains of a $PbTiO_3$ polycrystalline film. The tetragonal symmetry of this material allows only six domain variants in the crystal, and only 180° or 90° switching can occur [31]. Based on the pairs of OP and IP hysteresis loops recorded from different grains, the authors concluded that 90° switching does not take place. Similarly, Kalinin *et al.* assessed the degree of inclination of the polar axis in $SrBi_2Ta_2O_9$ grains and correlated this with the coercive fields observed in the corresponding hysteresis loops. Modeling the hysteresis loop shape proved to be a

challenging task, because the local tip–sample geometry is generally unknown. The models they proposed converged toward a Landau–Ginsburg–Devonshire thermodynamic approach [32]–[34], which typically requires the elastic Green function for the specific geometry to be known. For our particular case, because BiT has a monoclinic symmetry and the orientation of the crystalline axes is arbitrary, we would need to consider the general theory with both dielectric and piezoelectric anisotropies (that also switch when the polarization switches). In the following, however, because our purpose is not to model the hysteresis loop shape, but only to compare the effective coercive fields for IP and OP PFM signals measured simultaneously, we are using a simple approach considering only the piezoelectric anisotropy in a uniform field.

A. Polarization Switching Mechanism

The effective coercive field was calculated from the coercive voltage of the hysteresis loop, divided by the height of the nanorod at the probing location. We summarized our measurements performed on several nanorods in Table I. It should be mentioned here that although the width and length of the nanowire are affected by the tip shape, the height measured is not. We estimate that the width of the nanorods (measured at half height), is 100 to 200 nm thinner than the width measured on the image. Most of the crystallites were measured at two locations to check the uniformity of the ferroelectric properties. In few in-
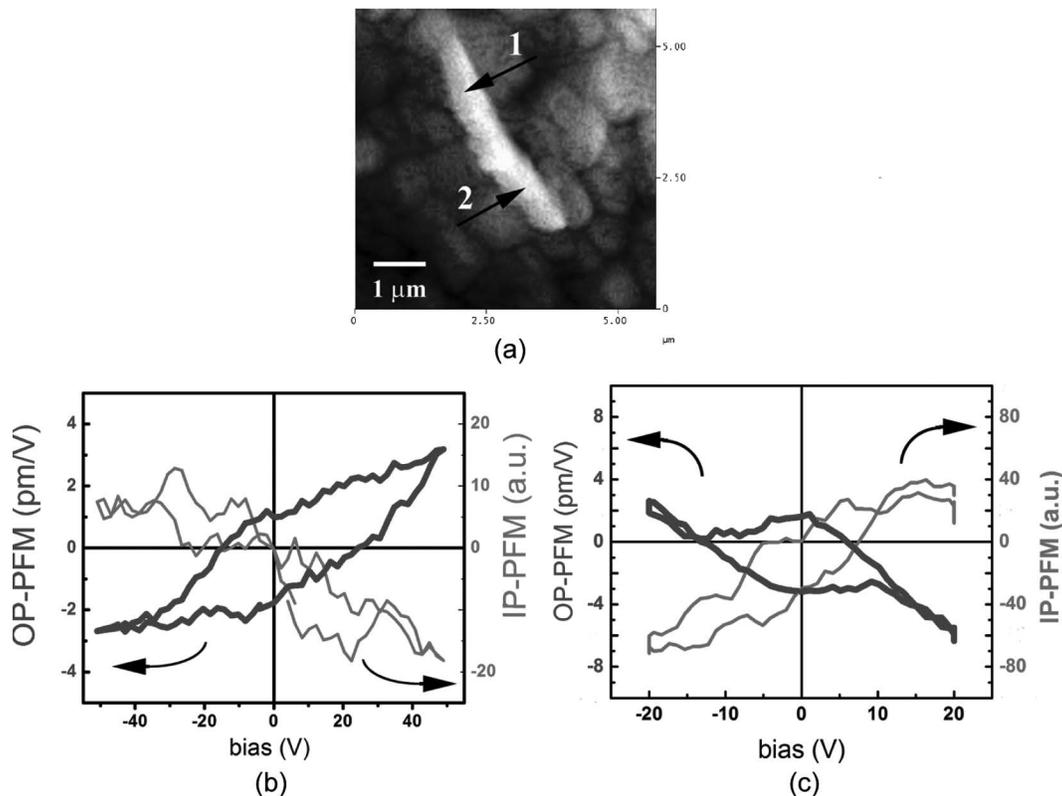

Fig. 2. (a) Atomic force microscopy image of a single-crystalline nanorod and the in-plane and out-of-plane piezoresponse hysteresis loops at locations (b) 1 and (c) 2.

TABLE I. SUMMARY OF THE SWITCHING EXPERIMENTS PERFORMED ON SIX $Bi_4Ti_3O_{12}$ (BiT) NANO OBJECTS.

BiT nanorod ID	Dimensions (μm) (L × W × H)	Coercive field (kV/cm)				Switching mechanism	
		1		2		1	2
		IP	OP	IP	OP		
BiT SC1	4 × 0.72 × 0.56	450	420	100	200	180°	rot
BiT SC2	4.92 × 0.94 × 0.37	250	250	—	250	180°	180°
BiT SC3	3.4 × 0.7 × 0.42	250	350	—	—	rot	—
BiT PC1	8.4 × 2.9 × 0.53	200	250	200	50	180°	rot
BiT PC2	6.85 × 1.9 × 0.65	150	250	100	100	rot	180°
BiT PC3	2.65 × 0.88 × 1.3	0	250	—	—	—	—

stances (such as those labeled BiT SC3 and BiT PC3) this was not possible and only one set of measurements is shown, indicating that the measurement was performed in the middle of the nanorod.

First, we looked at the possible role of the shape anisotropy on the coercive field. The dimensions of the studied nanorods vary within a relatively large range; however, no specific relation between the aspect ratio and ferroelectric properties has been observed.

Next, we analyzed in more detail the values of the effective coercive fields, noting that they vary from one nanorod to another, that they depend on the probing location within the same object, and, more importantly, that they are not always the same for the IP and OP loops measured simultaneously at the same location.

This variation of the absolute values of coercive field could be due to several effects, such as the electric field distribution, which is non-homogenous at the tip apex, and may be even more complex for the geometry of the AFM tip in contact with a 1-D object. These effects could account for variations between measurements done at different locations, but not for differences between loops measured simultaneously. The large differences observed, up to about 75%, together with the fact that these loops are obtained simultaneously, suggests that this is due to the nature of the ferroelectric object and not to other factors.

According to previous studies by Cummins and Cross on single-crystal BiT, the polarization components along the a and c crystallographic axes can switch independently in bismuth titanate, with the c-axis polarization component that switches more easily than the a-axis component [8]. Hence, we interpret our data as follows:

1) 180° switching. This is the case when the coercive fields of both IP and OP hysteresis loops are similar; thus, both components of polarization switch simultaneously, as shown in Fig. 3(a). This type of switching was identified in the following measurements (see Table I): BiT SC1 (1), BiT SC2 (1 and 2), BiT PC1 (1), and BiT PC2 (2), considering that a difference of 50 kV/cm or less is within the experimental errors.

2) Switching via sequential rotations of the total polarization, resulting from the independent switching of the polarization components along the a- and c-

crystallographic axes. Considering that $P_a = 50$ μC/cm², and $P_c = 4$ μC/cm², we illustrate in Fig. 3(b) the schematic switching of polarizations in two steps, first by 9.2°, occurring when P_c switches by 180° (step marked as t_2), then by 171.8° with the occurrence of the 180° switching of the P_a component of polarization (step marked as t_3). Switching in the opposite direction occurs similarly, as shown by the stages t_4 and t_5. We identified this type of switching mechanism for the hysteresis loops labeled as BiT SC1 (2), BiT SC3, BiT PC1 (2), and BiT PC2 (1). The switching for the case of BiT PC3 cannot be uniquely resolved because, due to its orientation being almost parallel to the cantilever axis, a significant component of polarization may be along the cantilever, and is thus not detectable.

B. Negative Piezoelectric Coefficient Along Certain Crystallographic Directions

As previously mentioned, PFM measurements were carried out at different locations to assess the uniformity of the piezo/ferroelectric properties along BiT 1-D structures.

Fig. 2 presents the PFM investigation of a single-crystalline nanorod having dimensions 4 μm × 715 nm × 560 nm (L × W × H). The piezoelectric hysteresis loops of Fig. 2(b) and 2(c) show a relatively low piezoelectric out-of-plane response suggesting that the polarization is oriented close to the rod's longitudinal axis. Comparing the loops measured at different locations in Fig. 2, we observe a significant change in the slope (at saturation) of the OP-hysteresis; the loop in Fig. 2(b) is a normal loop superimposed with a linear contribution with a negative slope. The linear contribution to the PFM signal depends on both the electrostatic interaction between cantilever and substrate and the local dielectric permittivity. This indicates that, because the electrostatic interaction is not expected to change significantly over such a small distance, there is significant change in local permittivity, possibly resulting from either the different crystallographic orientations or to stresses in the structure. Because the sign of the slopes of the IP-loops also changes with location, we conclude that, because the IP signal is not influenced by the electrostatic interaction, the 1-D single-crystalline object is split twins.
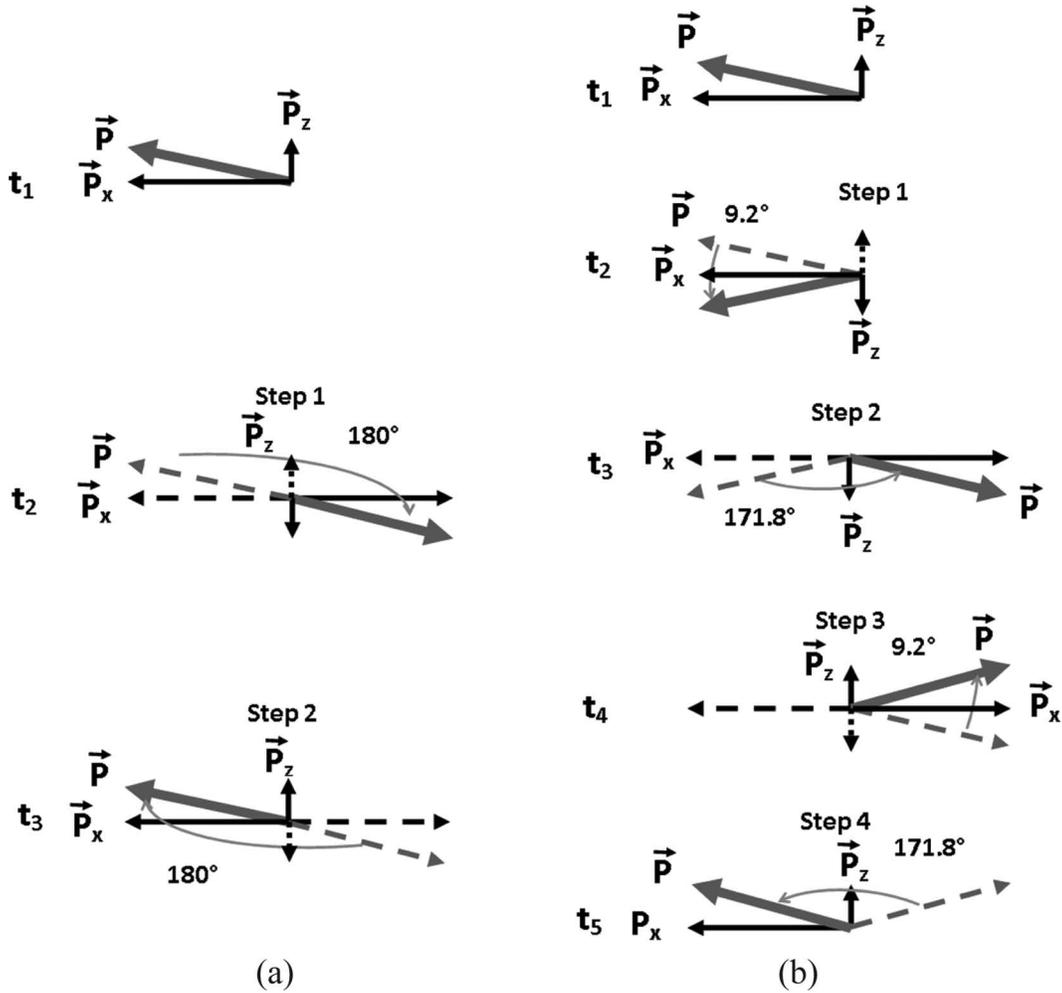
Fig. 3. Switching polarization behavior of $Bi_4Ti_3O_{12}$ (BiT) nanorods as deduced from hysteresis loops. (a) 180° switching (b) switching via independent reversal of the 2 components of polarization resulting in an apparent rotation of the total polarization in steps of 9.2° and 171.8°.

The same experiment was performed on polycrystalline nanorods, and a representative result is shown in Fig. 4. Again the object, with dimensions of $6.8 \times 1.9 \times 0.65$ µm $(L \times W \times H)$ exhibits a distinct PFM response that is switched upon cycling the dc bias.

Besides demonstrating clearly ferroelectric switching of polarization, comparing the hysteresis loops measured at different locations, we observed a strong variation of the loop shape and characteristics (saturation, coercive field, imprint), confirming the polycrystalline nature of the structure. The most striking result, however, is the change in the sign of the piezoelectric coefficient: although the loop in Fig. 4(b) is positive (i.e., positive signal, excluding any linear contribution, at saturation for positive bias applied to the conductive substrate) the loop in Fig. 4(c) is negative (negative saturation signal, excluding any linear contribution, for a positive bias applied). It is important to specify that, because this is a small signal measurement, there were no changes in the experimental configuration between the two measurements that would affect the reversal of the PFM signal: the reference phase of the lock-in was the same; the dc bias was always applied to the bottom electrode (substrate) and the ac voltage to tip.

Another parameter that could have affected the polarity of the measured hysteresis loop is the stress applied by the tip; that, in principle, could have changed as a result of tip erosion during scanning or because of the application of the bias voltage, even though the force applied was kept constant (around 60 nN). To ascertain whether this could have been the cause for the negative piezoelectric coefficient measured, we decided to perform the same measurement at a much reduced force of 4 nN (using a cantilever ten times softer, with a spring constant of 0.1 N/m); the result is shown in Fig. 5. The BiT polycrystalline object, with dimensions of $8.4 \times 2.9 \times 0.53$ µm $(L \times W \times H)$, comparable to that shown in Fig. 4, again exhibits a high variation of the loop parameters, consistent with the polycrystalline nature of the object.

We therefore believe that the contact force applied did not influence the shape of the hysteresis loops (and thus does not affect their sign).

To explain the presence of a negative longitudinal piezoelectric coefficient in BiT, we have to look at the crystalline orientation dependence of the piezoelectric coefficient [20], [35]. Fig. 6(a) shows the cross-section of the piezoelectric surface in the $(a{-}c)$ plane of the crystal lat-
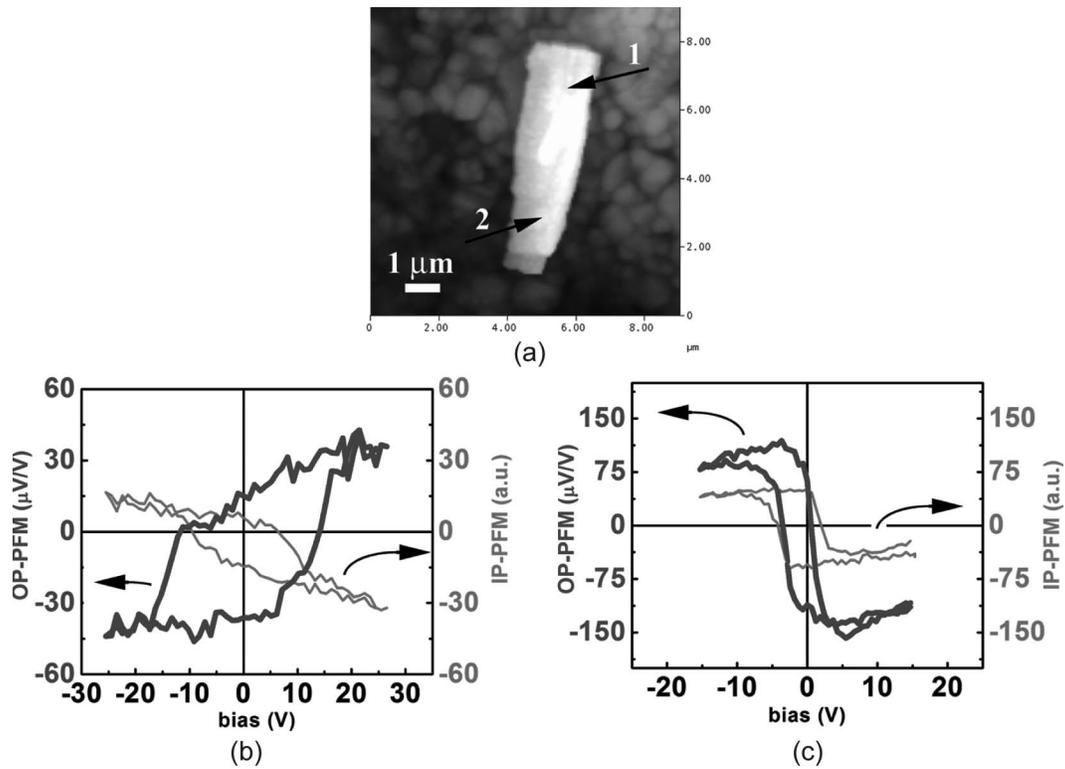
Fig. 4. Piezoresponse force microscopy (PFM) experiment on a polycrystalline $Bi_4Ti_3O_{12}$ (BiT) nanorod. (a) Topography and local PFM at locations (b) 1 and (c) 2.
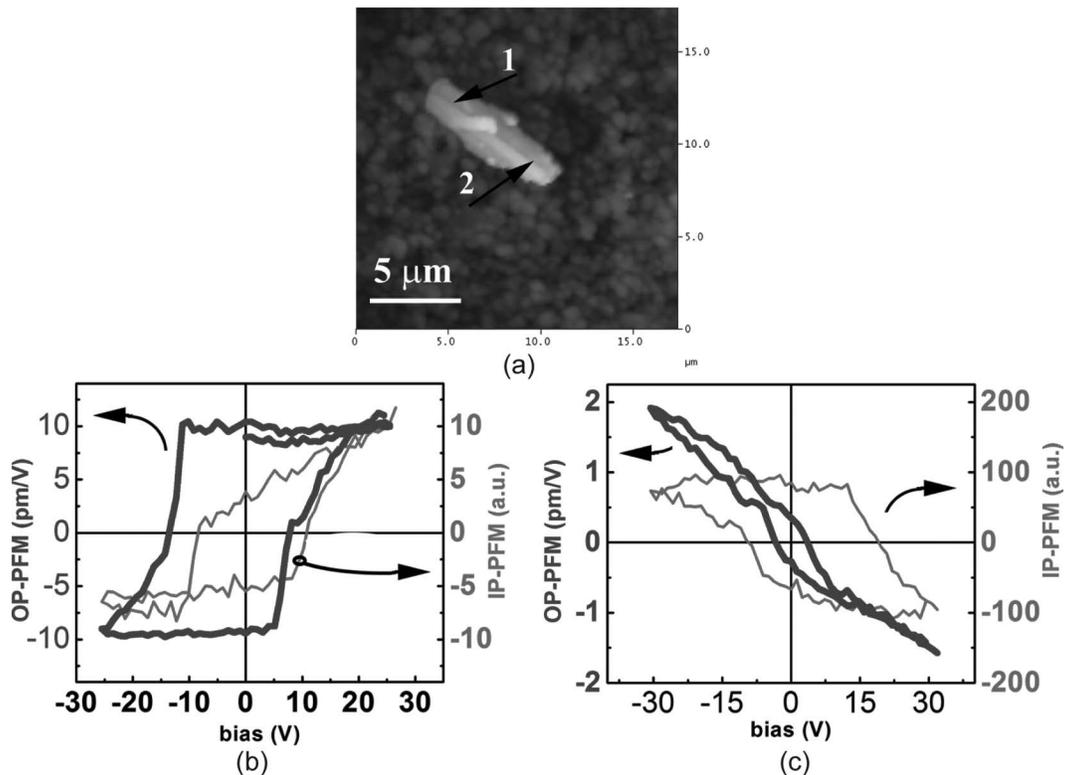

Fig. 5. Piezoresponse force microscopy (PFM) measurement at low contact force of a polycrystalline $Bi_4Ti_3O_{12}$ (BiT) nanorod distinct from that of Fig. 4. (a) Topography measured in non-contact mode and PFM hysteresis loops measured at locations (b) 1 and (c) 2.
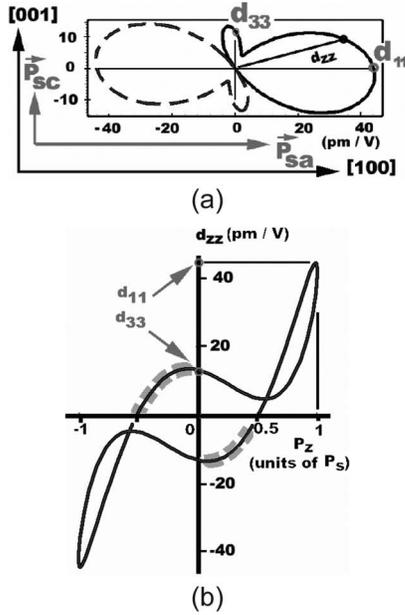
Fig. 6. (a) Dependence of the longitudinal piezoelectric coefficient d_{zz} of $Bi_4Ti_3O_{12}$ (BiT) as a function of the orientation of the measurement direction z. (b) dependence of d_{zz} on P_z (the component of polarization along the measurement direction z).

tice (where a and c are the two directions of the unit cell having a nonzero component of the spontaneous polarization).

This curve should be interpreted as follows: The vector from the origin to a point of the curve represents the magnitude of d_{zz} along that direction. The d_{zz} is considered positive when the measurement direction and the total polarization form an angle smaller than 90° (solid line), and negative otherwise (dashed line). The curve is composed of two contiguous parts (solid or dashed), each obtained for one sign of both P_s components (P_{sa} and P_{sc}) of polarization (positive, the solid part, or negative, the dashed section). The change in sign of both polarization components corresponds to a switching of the total polarization by 180°. We observed that for positive P_{sa} and P_{sc}, the curve is mostly in the quadrants 1 and 4 but it also extends into quadrant 2 of the plot (more specifically, where the angle between the direction of P_s and the observation direction exceeds 90°), which is equivalent to a change in sign of the piezoelectric coefficient. To see this more clearly, in Fig. 6(b) we represented the piezoelectric coefficient d_{zz} as a function of the projection of the spontaneous polarization P_s on the measurement direction z, the angle between the direction c and the observation direction being the free parameter. The curve clearly shows that for specific orientations, the d_{zz} coefficient takes negative values (part of the curve lies in the quadrants 2 and 4), thus confirming that the behavior we observed is indeed possible. For the coefficients we used in our calculations [21], [36], we find that d_{zz} is negative for angles between the c-axis and the direction of observation z in the range of approximately 143° to 174°.

IV. CONCLUSION

The piezoelectric and ferroelectric properties of individual one-dimensional $Bi_4Ti_3O_{12}$ nanorods, either single-crystalline or polycrystalline, have been investigated by piezoresponse force microscopy. A detailed analysis of the out-of-plane and in-plane piezoresponse showed that the BiT nanorods exhibit prominent piezoelectric activity and their polarization lies mostly along the nanorod axis. We found two types of ferroelectric switching behaviors and associated them with either direct 180° switching or sequential switching of a-and c-components of polarization, resulting in a switching via rotation of the total polarization vector. Furthermore, we observed unusual piezoresponse hysteresis loops that we associated with a negative piezoelectric coefficient. The negative piezoelectric coefficient is explained by the specific shape of the piezoelectric surface of the strongly anisotropic crystal structure of $Bi_4Ti_3O_{12}$.

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Merhnoosh Azodi completed the B.Eng. degree in chemical engineering at the Sharif University of Technology, Iran, in 2007 and received her master's degree in chemical engineering from Amirkabir University of Technology, Iran, in 2010. She has been a Ph.D. student at INRS-EMT (Institut National de la Recherche Scientifique, Centre Énergie Matériaux Télécommunications) since 2011. Her research interests include fabrication and properties of nano- and biomaterials and their biotechnological applications. Her research at INRS currently focuses on the piezoelectric properties of nano-fibers, i.e., collagen fibrils, and their potential applications as piezoelectric biosensors.

Catalin Harnagea (M'04) obtained his M.Sc. degree in physics from the Al. I. Cuza University of Iasi, Romania, in 1996 and his Ph.D. degree in 2001 from the Martin Luther University of Halle, Germany. Between 1997 and 2003, he worked at the Max-Planck-Institut fuer Mikrostrukturphysik, Halle, studying the properties of ferroelectric thin films and nanostructures by means of voltage-modulated force microscopy. He continued his research at the National Institute for Scientific Research (INRS-EMT), in Varennes, QC, Canada. His research interests include scanning probe microscopy applied to the study of functional properties of nanostructures of semiconductors, simple/complex oxides, and biomaterials. Dr. Harnagea has coauthored more than 75 peer-reviewed publications, with a significant impact on the understanding of the nanoscale electromechanical measurements on ferroelectric films and the ferroelectric behavior of nanostructures.

Vincenzo Buscaglia is senior researcher and head of the Electroceramics laboratory at the National Research Council, Institute of Energetics and Interphases (CNR-IENI), Genoa, Italy. He obtained a diploma in industrial chemistry from the University of Genoa. Since 1990, he has been working at CNR-IENI on powder synthesis and functional ceramic oxides in the framework of national, bilateral, European, and industrial projects. His main research interests are the solid-state and chemical synthesis of ferroelectric nanostructures and microstructure–property correlations in ceramic oxides. He is currently an associate editor of the *Journal of the European Ceramic Society*.

Maria Teresa Buscaglia earned her diploma in industrial chemistry and her Ph.D. degree in chemistry for engineering from the University of Genoa in 1994 and 1999, respectively. Since 2002, she has been a Researcher at the Institute for Energetics and Interphases (IENI) of the National Research Council.

Her research activity is focused basically on the synthesis of perovskite-like oxides by means of inorganic chemical routes, characterization of powders and ceramic materials, and ceramic processing. In particular, she has developed innovative processes and new strategies for designing advanced materials with complex architectures

(core-shell particles, hollow spheres, nanowires, and materials with controlled dopant distribution) through the use of colloidal chemistry methods.

Dr. Maria Teresa Buscaglia is co-author of 68 original papers in ISI journals and she holds two patents.

Paolo Nanni was a Professor of chemistry at the University of Genoa, Italy, Engineering Faculty until November 1, 2011. He obtained his degree in chemistry and Libera Docenza (equivalent to a Ph.D. degree) in spectroscopy. He performed his postdoctoral activity in oxide sintering at the National Physical Laboratory, Teddington, UK, and UMIST, Manchester, UK. His scientific interests are in the fields of nanoscience and nanotechnology, synthesis, and sintering of nanoparticles of oxides with perovskite-like structure. He was Project Coordinator of the Italian Space Agency project on sintered components and coatings of aluminium titanate for space applications; Team Coordinator of Strategic Projects on Innovative Materials of the Italian Ministry of Education and of the Italian Research Council. He was member of the International Advisory Board of several EcerS Congress on Electroceramics. He has been Italian Government delegate for COST 525, 539, and MP0904 Action. He is referee of many leading journals and of scientific projects of the Ministry of Science and Environmental Protection of the Republic of Serbia and Referee of Italian National Projects of the Italian Ministry of Education, University, and Research. He is an author of about 160 papers.

Federico Rosei has held the Canada Research Chair in Nanostructured Organic and Inorganic Materials since 2003. He is Professor and Director of Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec, Varennes, QC, Canada. He received M.Sc. and Ph.D. degrees from the University of Rome "La Sapienza" in 1996 and 2001, respectively.

Dr. Rosei's research interests focus on the properties of nanostructured materials, and on how to control their size, shape, composition, stability, and positioning when grown on suitable substrates. He has extensive experience in fabricating, processing, and characterizing inorganic, organic, and biocompatible nanomaterials. He has published more than 125 articles in prestigious international journals (including *Science*, *Proceedings of the National Academy of Sciences*, *Advanced Materials*, *Angewandte Chemie* Int. Ed., *Journal of the American Chemical Society*, *Nanoletters*, *Small*, *Physical Review Letters*, *Applied Physics Letters*, *Physical Review B*, etc.), has been invited to speak at more than 130 international conferences, and has given more than 130 seminars and colloquia in 37 countries on all inhabited continents. His publications have been cited more than 2700 times and his H index is 28. He is a Member of the Sigma Xi Society, Fellow of the Institute of Nanotechnology, Fellow of the Institute of Physics, Fellow of the Institute of Materials, Metallurgy, and Mining, Fellow of the Institution of Engineering and Technology, and Fellow of the Royal Society of Chemistry. He has received several awards, including the FQRNT Strategic Professorship (2002–2007), the Tan Chin Tuan visiting Fellowship (NTU 2008), the Senior Gledden Visiting Fellowship (UWA 2009), Professor at Large at UWA (2010–2012), a Marie Curie Postdoctoral Fellowship from the European Union (2001), a Canada Research Chair since 2003 (renewed in 2008 for a second five-year term), a Friedrich Wilhelm Bessel Award from the Alexander von Humboldt Foundation, and the Rutherford Medal in Chemistry from the Royal Society of Canada.

Alain Pignolet (IEEE member) earned his bachelor's degree in engineering physics and his Ph.D. degree in physics from the École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, in February 1986 and April 1992, respectively. He joined the IBM Research Division (Thomas Watson Research Center, Yorktown Heights, NY) as a postdoctoral researcher and began working on high-permittivity relaxor materials, then moved to the Materials Research Laboratory, Penn State University, University Park, PA, to continue his research, working mainly with pulsed laser deposition (PLD), reactive multitarget magnetrons, and ion-beam sputtering.

Returning to Europe in October 1994, Dr. Pignolet, with a Research Staff Position at Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany, set up a laboratory for deposition of ferroelectric thin films using large-area PLD. He also worked on the optimization and better understanding of piezoresponse force microscopy.

Back in North America, Dr. Pignolet has been an Associate Professor at the Centre Énergie Matériaux Télécommunications of the University of Quebec's Institut National de la Recherche Scientifique (INRS) near Montréal, Canada, since April 2002. His is the head of the Ferroic-Lab, working on piezoresponse force microscopy of biological materials such as collagen fibers, magneto-optic epitaxial films for integrated photonics, as well as the deposition, growth, and characterization of films and nanostructures of functional materials, such as piezoelectrics, ferroelectrics, and multiferroics. His group has reported the first growth and characterization of epitaxial thin films and nanostructures of $\text{Bi}_2\text{FeCrO}_6$, exhibiting a clear cation ordering and good multiferroic properties at room temperature, exceeding the properties predicted by *ab initio* calculation.

Dr. Pignolet is a member of several Québécois and Canadian strategic research networks, has published more than 100 publications in top international journals, and has been invited to many international conferences. His research has led to more than 1200 citations in the literature.