Atomic force microscopy of domains and volume holograms in $Sr_{0.61}Ba_{0.39}Nb_2O_6:Ce^{3+}$

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Ferroelectric domains have been investigated by atomic force microscopy (AFM) within *c* planes of $Sr_{0.61}Ba_{0.39}Nb_2O_6:Ce^{3+}$ at room temperature. The structures are observed during polarization switching in noncontact and contact mode. They are due to piezoelectric and electrostrictive indentations, respectively. Volume holographic recording has been visualized on *a* planes by AFM via surface corrugation. It is due to light-induced charge-density waves along the polar *c* axis and nondiagonal piezoelectric coupling.

I. INTRODUCTION

Studies on domain structures in ferroelectric crystals by atomic force microscopy have aroused great interest in recent years since the pioneering work of Saurenbach and Terris.[1] So far several procedures, including electric force microscopy (EFM),[2–4] lateral force microscopy (LFM),[2,5] the piezoelectric response,[6,7] and topographic modes,[5,8–10] have been developed to visualize and even to control domains in ferroelectrics. The topographic mode has mainly been used to examine surface undulations due to 90° *a* and *c* domains of perovskites.[8–10]

Recently, nanoscale visualization of 180° domains in GASH crystals has been reported.[11,12] Prolate spheroids are found on the surface when a dc voltage is applied between the tip and sample during scanning. The authors[11,12] attributed the surface deformations to piezoelectric compression and stretching of domains with opposite signs. On the other hand, Lüthi and Meyer[13] and Takata[14] suggested that the observed prolate spheroids result from electrochemical interactions between the sample and tip, which may lead to hillocks and holes on the surface. That means that the observed topographic protrusion may be unrelated to domain configurations. It is still a challenging task to detect 180° domains by the topographic mode, although in principle piezoelectric effect should always play a role in the topography provided that depolarizing fields exist. In addition, it is also desirable to observe the dynamic evolution of domain structures under an external electric field. Bearing this in mind, we designed an experiment to study the domain structures in *c* plates of Ce^{3+} doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61:Ce) crystals by detecting the surface deformation using an atomic force microscope (AFM).

Owing to their high photorefractivity at room temperature, SBN crystals have become most important candidates for holographic recording.[15] In the last few years interesting scanning probe techniques have been developed to visualize volume holographic recording by virtue of surface modifications. In particular, light-induced space charge carriers have been detected on the surface of photorefractive crystals like $BaTiO_3$ and $Bi_{12}SiO_{20}$ (BST) via electric force microscopy (EFM).[16] In this paper we present the possibility of detecting a volume hologram in a photorefractive material via piezoelectric coupling between the spatially modulated internal electric field and its lateral dimensions. SBN proves to be a good candidate for this effect because of its extremely high piezoelectric response.

II. EXPERIMENT

SBN61:Ce undergoes a paraelectric (4/mmm)-ferroelectric (4mm) phase transition when cooled to below the Curie temperature T_C. The crystals used in this work were doped with 0.8 wt % Ce yielding $T_C = 315$ K. At room temperature, they contain needlelike 180° domains, whose diameters are in the order of micrometers.[17] In order to distinguish positive and negative domains, where the spontaneous polarization P points up from and into the crystal, respectively, silver paste was deposited on both top and bottom surfaces of the *c* plates with area $10 \times 10\,mm^2$ and thickness $d = 1.2$ mm. In the top electrode a small square area of about $0.4 \times 0.4\,mm^2$ was left open in the center such that topographic changes in this region can be observed directly with a commercial AFM (TopoMetrix Explorer). A dc voltage was applied between top and bottom electrodes in order to reverse domains. Since the sample's high susceptibility[18] tends to concentrate the stray field to the vicinity of the electrode's rim, the areas inspected by the AFM tip must be chosen to lie very close to the adjacent to it. It should be noted that transverse field components, which emerge by symmetry, do not play any role in the observed domain reversal, since only *z*-directed domains are expected in the uniaxial ferroelectric SBN61:Ce.

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the crystal topography scanned in the noncontact mode at different external volt-

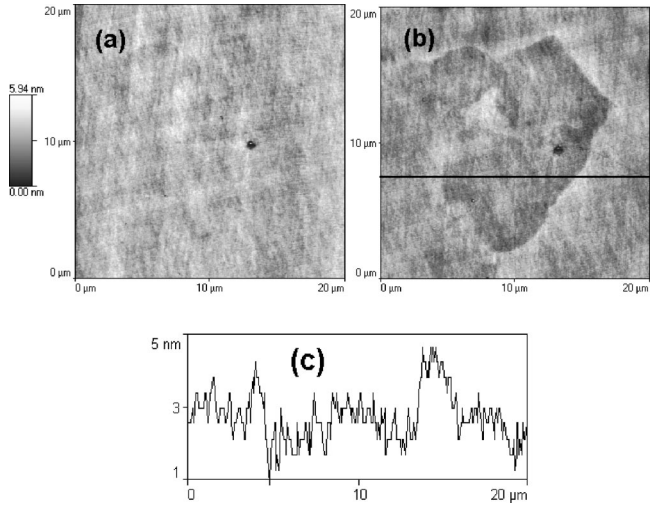

FIG. 1. SBN61:Ce surface probed by AFM in noncontact mode under normal external electric fields $E=0$ (a) and 200 V/mm (b) and (c), respectively.

ages. Before applying electric fields, the surface is flat [Fig. 1(a)]. An area with a small pit close to the center was chosen for sake of safe recognition. After applying an electric voltage $U=200\,\mathrm{V}$, a shallow indentation was found [Fig. 1(b)]. The height difference between this indented region and the surroundings is about 2 nm. Its area shrinks and becomes shallower at increasing field. At approximately $U=400\,\mathrm{V}$ the surface is flat again. The above voltages needed for polarization reversal are compatible with the coercive field measured for SBN61:Ce with $x=0.8\,\mathrm{wt.\%}$, $E_c \approx 200\,\mathrm{kV/m}$.[15] Obviously, the stray fields experienced close to the electrode rim are still in the order $E_z=U/d$ as in the flat condenser region.

Very probably the indentation at 200 V is due to piezoelectric effects. Presumably, in the indented region the switching lags behind that of the surroundings, e.g., due to a local agglomeration of pinning centers. As pointed out previously[18] such pinning centers are probably due to the charge disorder inherent to SBN and its doped descendants. They give rise to quenched random fields, whose fluctuations are at the origin of local enhancements of the coercivity. Hence the spontaneous polarization in this region is antiparallel to the external field, while that in the surrounding material is parallel to it. Under the external field, this region contracts vertically while the surroundings elongate by the reverse piezoelectric effect. A domain length of about 60 μm is estimated from the indentation of 2 nm by using the piezoelectric constant of SBN61,[15] $d_{33}=200\,\mathrm{pm/V}$. During the measurement, we also found that there is a height difference between regions with different distances from the electrodes during the switching process. Obviously the domains near to the electrodes are switched first.

It is interesting to note that there are also surface indentations before applying an external electric field [Fig. 2(a)]. They are only observed in the contact mode. After applying a constant external voltage of 200 V, the indented area gradually shrinks at increasing time. This is shown in Figs. 2(b)–(d), which were observed at 2, 5, and 15 min, respectively, after applying the electric field. At an electric voltage of 300 V, the area gets flat [Fig. 2(e)].

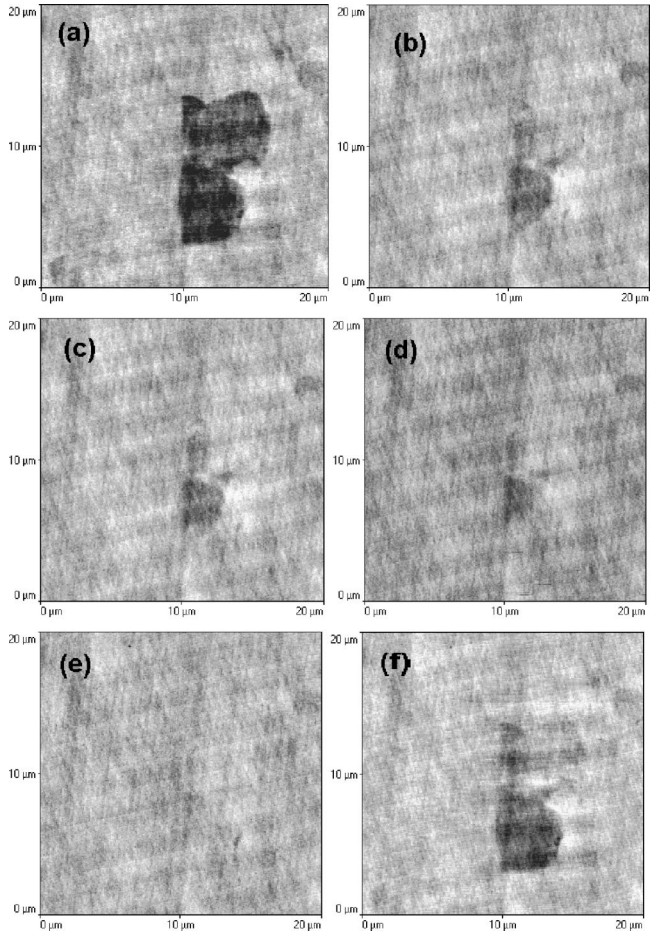

FIG. 2. SBN61:Ce surface probed by AFM in contact mode under normal electric fields $E=0$ (a), 200 [after 2(b), 10(c), and 15 min (d)], 300 (e), and, again, 0 V/mm (f), respectively.

The results might be understood by assuming permanent charges loaded on the Si_3N_4 tip during scanning. Before applying the electric field, the surface charges on the indented region have a sign opposite to that on the tip, which results in an additional attractive force between the tip and the surface. Under an electric field, the domain in this region begins to switch and the surface charges gradually decrease. When the domain is completely switched, the surface charges in this region have the same signs as those in the surrounding areas and the observed topography becomes flat again. When the external field is switched off, the region nearly regains its original appearance [Fig. 2(f)]. Obviously the domain relaxes back into its original state. The result agrees with the experience[15] that room-temperature poling is not efficient for the SBN crystals. Only by field cooling from temperatures far above T_C the crystal can be poled satisfactorily.

Finally, we present yet another way to produce surface corrugations on the crystal surface of SBN:Ce, which have nothing to do with locally inverted ferroelectric domains, but with piezoelectric response to internal electric fields. These are due to space charges, which accompany the registration of a volume hologram due to the well-known photorefractive effect of SBN:Ce.[15] Figure 3(a) shows two geometries for holographic recording as realized at room temperature with two HeNe laser beams with a power of 10 mW. By using two beams of *p* polarized light either entering the crystal

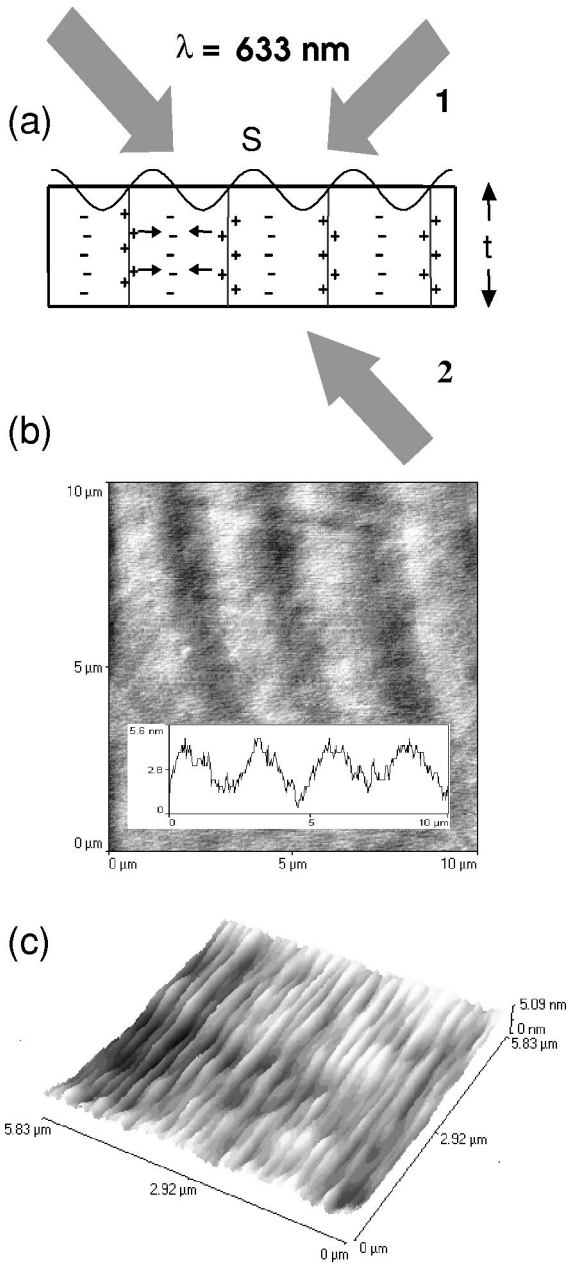

FIG. 3. Recording geometries 1 and 2 (a) showing the light beams, the crystal cross section (thickness t) with space charges, electric-field vectors and surface corrugation S, and AFM surface topographies due to volume holograms in SBN61:Ce recorded in geometry 1 (b) and 2 (c), respectively. The inset in (b) shows a cross section referring to 7-μm vertical height position.

from one surface under small angles of incidence (transverse recording, 1) or hitting one another under retroreflecting conditions (longitudinal recording, 2) one obtains periodic intensity distributions with a large field component parallel to the polar c axis. The intensity grating, where $k\|c$ for the transverse geometry (as sketched), then gives rise to photoionization of Ce^{3+} centers and field-induced migration of free carriers.

Similar volume holograms were recorded recently in photorefractive BST and $BaTiO_3$ by Soergel, Krieger, and Vlad,[16] who probed the photoinduced carriers by an EFM on the surface of the sample. Here we propose an alternative method to discover the internal space charges. Since they build up an internal electric field, which has the same periodicity as the volume hologram, one can expect a corrugation wave, $S=d_{31}E$, by virtue of nondiagonal piezoelectric coupling. This is, indeed, established and evidenced by AFM [Figs. 3(b) and (c)]. In our recording geometries 1 and 2, periods of $\Lambda\approx 2.5$ and 0.25 μm, respectively, are obtained. Owing to bleaching by carrier diffusion it is observed that the height contrast of the gratings fades away after several days of storage in the dark. Two days after recording we observe indentation wells of $\Delta z\approx 3$ nm for the transverse geometry [Fig. 3(b), inset]. When inserting the sample thickness $t=1$ mm and the coefficient $d_{31}=70$ pm/V,[15] one may calculate the internal field strength, $E\approx 40$ kV/m. This value is smaller than that of the coercive field [$E_c\approx 200$ kV/m for SBN61 with 0.4 wt % of Ce (Ref. 15)] and hence does not suffice to reverse the ferroelectric polarization of the sample. Here we notice that all holographic experiments were done on poled samples, whose single-domain character is far from being destroyed by the internal space charge field. In the case of the longitudinal geometry 2 [Fig. 3(c)] a smaller indentation of $\Delta z\approx 1.6$ nm is observed, since the condition $k\|c$ is not perfectly met in this case.

IV. CONCLUSION

Despite the instability of surface charges released during the polarization reversal of the axial ferroelectric SBN61:Ce it proves possible to visualize its polar domains by virtue of surface corrugations using an AFM in the topographic mode. This observation became possible for the first time by investigating the switching process *in situ*. SBN61:Ce proved to be particularly suited for this experiment, since it contains very powerful pinning centers, which temporarily stabilize certain parts of the sample while switching the rest of the sample with an external electric field. Here the relaxor properties of SBN61:Ce play a stabilizing role.[18]

On the other hand, we also succeeded in observing stable, viz. pinned domains, although their depolarizing fields should be completely screened in equilibrium by surface charges. In this case a static charge on the contacting AFM tip is believed to interact with the screening charges such as to indent the domain with respect to its differently charged environment. It should be noticed that this mode of observation differs from the EFM one, which is usually operated in the noncontact mode.

The first observation of volume holograms via topographic surface corrugation is, again, a fortunate case owing to the high piezoelectric response of SBN61:Ce. It will be interesting to test this method on other photorefractive materials like BST and $BaTiO_3$.

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