Basic Energy Sciences

Domain Structures In Fatigue-Free $SrBi_2Nb_2O_9$

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Ceramic Epitaxial Films

SCIENTIFIC ACHIEVEMENT

We have succeeded in the first experimental observation of the domain structure in thin films of $SrBi_2Nb_2O_9$, a ferroelectric material that is fatigue-free, i.e. does not show a loss of switched polarization with increasing number of switching cycles. Observation of this domain structure furthers our understanding of the contributions of elastic strain, dipole-dipole interactions, and electrostatic field effects to the complex domain structures found in oxide ferroelectrics.

We have shown that crystallographic defects common in $SrBi_2Nb_2O_9$ films (out-of-phase boundaries, OPBs) are ferroelectrically inactive volumes of material, i.e. a film with a high density of OPBs would have a lower remanent polarization than a comparable film that was free of OPBs. OPBs in $SrBi_2Nb_2O_9$ have two main nucleation mechanisms, physical and chemical. Physical features that cause a *c*-direction misregistry of neighboring nuclei in a thin film, such as steps in the substrate surface, will nucleate OPBs. Chemically-nucleated OPBs form *after* the growth of a film, due to bismuth loss by desorption.

SIGNIFICANCE

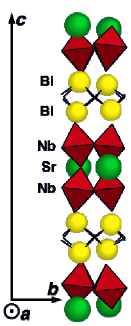
Little experimental or theoretical evidence exists for the relative importance of the various energetic contributions to ferroelectric domain morphology. The domain maps obtained in this investigation allow us to formulate a better understanding of these various components of the free energy balance used to describe domain structure.

OPBs in $SrBi_2Nb_2O_9$ (and many other complex oxides) had not been extensively studied. We have demonstrated their importance to film properties, and have begun to study the details of their nucleation and growth. This knowledge provides guidance for the synthesis of $SrBi_2Nb_2O_9$ and related compounds.

UNIQUE STRUCTURE OF $SrBi_2Nb_2O_9$

The orthorhombic ferroelectric phase $SrBi_2Nb_2O_9$ is structurally very similar to typical perovskite ferroelectrics having 90° domains, but is unique because its ferroelastic distortion is essentially zero, resulting in a ferroelectric domain structure that is independent of strain energy contributions. Additionally, because no spontaneous polarization exists along the *c* axis, the domain morphology along this azimuth is controlled by electrostatic field effects alone.

This material has a two-dimensional ferroelectric domain structure with the polarization parallel to the crystallographic *a*-axis.



Formula	Unit cell type	Lattice parameters (nm)	Polar axis	Ferroelectric domain morphology	Ferroelastic distortion (%)
$PbTiO_3$	tetragonal	$a = 0.3904$[a]	*c*	faceted walls	6.4
		$c = 0.4152$		high aspect ratio	
$BaTiO_3$	tetragonal	$a = 0.39945$[b]	*c*	faceted walls	1.0
		$c = 0.40335$		high aspect ratio	
$Bi_4Ti_3O_{12}$	monoclinic	$a = 0.54500$[c]	*a*[d]	faceted walls	0.82
		$b = 0.54059$		low aspect ratio[e]	
$SrBi_2Ta_2O_9$	orthorhombic	$a = 0.55306$[f]	*a*[g]	curved walls	0.069
		$b = 0.55344$		granular[h,i]	
$SrBi_2Nb_2O_9$	orthorhombic	$a = 0.55094(4)$[c]	*a*[g]	...	<0.0018
		$b = 0.55094(4)$			

(a) *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1981), New Series, Group III, Vol. 16, Part a, p. 360.
(b) *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by T. Mitsui and E. Nakamura (Springer-Verlag, Berlin, 1990), New Series, Group III, Vol. 28, Part a, p. 74.
(c) A. D. Rae, J. G. Thompson, R. L. Withers, and A. C. Willis, Acta Crystallogr. Sec. B: Struct. Sci. B**46**, 474 (1990).
(d) Polarization lies almost entirely along a (8% along c). S. E. Cummins and L. E. Cross, J. Appl. Phys. 39, 2268 (1968).
(e) X. Q. Pan, J. C. Jiang, C. D. Theis, and D. G. Schlom, submitted to Appl. Phys. Lett. (Feb. 27, 2001).
(f) A. D. Rae, J. G. Thompson, and R. L. Withers, Acta Crystallogr., Sect. B **48**, 418 (1992).
(g) Follows directly from A21am space group.
(h) Y. Ding, J. S. Liu, and Y. N. Wang, Appl. Phys. Lett. **76**, 103 (2000).
(i) X. Zhu *et al.*, Appl. Phys. Lett. **78**, 799 (2001).

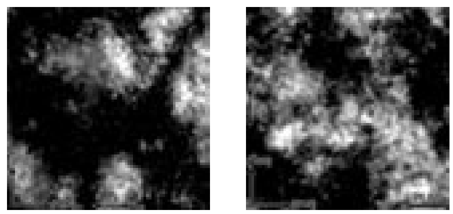
FERROELECTRIC DOMAIN STRUCTURE

The growth of single crystals of $SrBi_2Nb_2O_9$ large enough for domain structure studies is difficult, so we have used (001) $SrBi_2Nb_2O_9$ epitaxial films (*c* axis perpendicular to the substrate surface) for our domain studies.

Because of the absence of ferroelastic distortion, standard strain-based techniques for imaging ferroelectric domains are not feasible with this material. Instead, we utilized Fourier processing of high-resolution transmission electron microscopy (HRTEM) images to form a series of orthogonal polar-domain maps, generated from unique superlattice reflections associated with individual domain orientations.

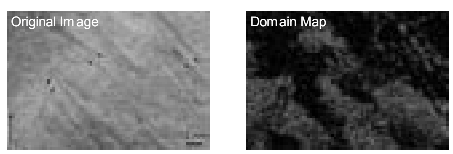
Domain walls in $SrBi_2Nb_2O_9$ are found to be highly curved, indicating that the highly faceted 90° domain morphology found in typical oxide ferroelectrics is dominated by strain energy. The curved walls also indicate that $SrBi_2Nb_2O_9$ is fairly tolerant of the space charge associated with divergence of the normal component of the polarization at such walls.

c-plane morphology

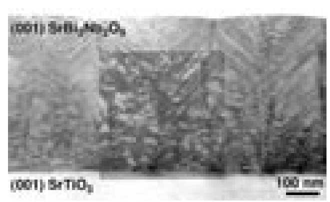


These two images show the two 90° ferroelectric domain types in the same area of a $SrBi_2Nb_2O_9$ film. Bright areas correspond to regions with remanent polarization axes as indicated by P_s in each image. Imaging along the non-polar *c*-axis (plan view) reveals a complementary 90° domain morphology controlled by electrostatic and dipole-dipole interactions. Some overlap between the bright regions exists due to through-thickness variation of the ferroelectric domain structure, visible in the images below.

a/*b*-plane morphology



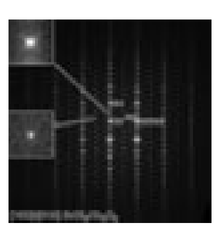
Imaging along the polar *a*/*b*-axis (cross-section) reveals a 90° domain morphology controlled by electrostatic interactions alone (in *c* direction). Bright areas in the domain map correspond to regions with a spontaneous polarization vector perpendicular to the plane of the image.



Cross-section image of the full thickness of a (001) $SrBiNb_2O_9$ film, with an *a*/*b* ferroelectric domain map superimposed over the center of the image. This film has a high density of OPBs, visible as wavy diagonal bands of contrast.

OPBs: FERROELECTRICALLY INACTIVE VOLUMES OF MATERIAL

OPBs, visible in the cross-section HRTEM images above, are dark in the corresponding domain map. As planar defects, the OPBs give rise to streaking in the diffraction pattern. Additionally, only certain reflections in the diffraction pattern are streaked. Indexing of the plane group of the streaked regions shows that any potential ordering at the OPBs would not support a remanent polarization. Taken together, this evidence indicates that OPBs are ferroelectrically inactive.

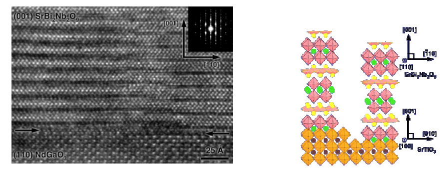


The direction of the streaking also indicates a $(111)_{perovskite\ subcell}$ habit for OPBs.

OUT-OF-PHASE BOUNDARY NUCLEATION MECHANISMS

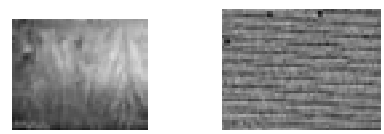
OPBs are nucleated by two mechanisms in $SrBi_2Nb_2O_9$ epitaxial films: physical and chemical. Terraces on the surface of the substrate cause *c*-direction misregistry of neighboring nuclei, resulting in the generation of OPBs with ~3.9 Å offsets. Bismuth desorption from an otherwise perfect film results in the generation of OPBs with ~4.5 Å offsets.

Physical - step-edge nucleation



HRTEM image of a (001) $SrBi_2Nb_2O_9$ / $(001)_{subcell}$ $NdGaO_3$ film, showing the nucleation of an OPB by a single step edge in the substrate surface. This is shown schematically on the right

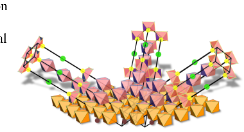
Chemical - bismuth desorption

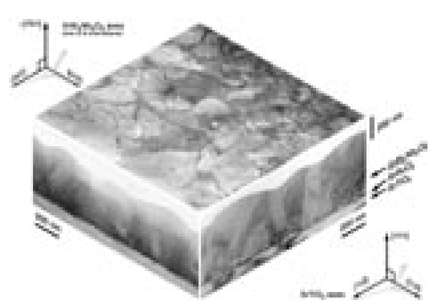


These cross-sectional TEM images show a film that was thermally annealed after growth, resulting in massive bismuth loss through evaporation. Groups of OPBs formed "chimneys" (left image) as the bismuth percolated up through the epitaxial film. The HRTEM image on the right shows three individual OPBs in the same film.

GROWTH TWIN DOMAINS

We have also investigated variation in ferroelectric properties with orientation. Films grown on differently-oriented substrate surfaces adopt non-*c*-axis orientations. Epitaxy results from local continuation of the perovskite sublattice, shown schematically on the right. The image below is an isometric montage composited from three TEM images taken along three orthogonal viewing directions of the same film, grown on a (111) $SrTiO_3$ substrate. This is an epitaxial film with three orientational variants, each identically-oriented with respect to the cubic perovskite sublattice of the substrate.





FUTURE WORK

Our goal is now to correlate the observed domain structures with the lack of fatigue in this system. Of particular interest is the extent to which space-charge and its compensation influences domain wall mobility. Future experiments to address these issues will be accomplished using *in-situ* methods to observe polarization dynamics. These experiments will utilize electron microscopy, as well as x-ray microprobe/nanoprobe techniques under development at the Advanced Photon Source.

ACKNOWLEDGEMENTS

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