Materials Research Express

PAPER

Raman modes and dielectric relaxation properties of epitaxial BaBiO₃ thin films

M Talha and Y W Lee

Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
E-mail: mtalha@postech.ac.kr

Keywords: epitaxial growth, pulsed laser deposition, octahedral breathing, octahedral tilting, Raman spectroscopy, soft phonon modes, dielectric relaxation

Abstract

Perovskite BaBiO₃ films are grown on MgO (100) substrate and SrTiO₃ (001) and (110) substrates using pulsed laser deposition. The thickness of the films ranges from ~10 nm up to 200 nm. X-ray diffraction and reciprocal space mapping show that the thin films are grown epitaxially but relaxed considerably particularly for the films on SrTiO₃. The topography of the film surfaces are obtained with AFM and found to be atomically flat with the step and terrace structure of unit cell step height. Raman spectroscopy is performed on the BaBiO₃ films in the temperature range from 50 K to 300 K. The phonon modes related to octahedral breathing, bond bending, and bond stretching are detected in the Raman spectra, and the distinctive features are found in the phonon modes below and above a structural transition around 140 K. Out-of-plane dielectric measurements are also carried out from 10 K to 400 K for the films on SrTiO₃ with different orientations. In particular, the dielectric measurements demonstrate frequency as well as orientation dependent anisotropic dielectric relaxation behaviors in BaBiO₃ films.

1. Introduction

In transition metal perovskites ABO₃ with rare earth ions at A sites and transition metal ions at B sites, extremely diverse physical properties arise depending particularly on which transition metal ions occupy the B-sites [1]. In contrast, BaBiO₃ is a perovskite with nontransition metal ion Bi at B sites and it still possesses interesting properties [2]. This compound is rather well known as the parent material of superconducting Ba₀.₆K₀.₄BiO₃ and BaPbₓBi₁₋ₓO₃ (x = 0.3) with transition temperature (Tₜ) at 30 K and 13 K, respectively [3, 4]. Note that the nominal valence of Bi ions in BaBiO₃ would be 4⁺; however, Bi ions in this compound have a tendency to take the valence value of either 3⁺ (6s²6p⁰) or 5⁺ (6s⁰6p⁶) rather than 4⁺ (6s¹6p⁶) [5]. This phenomenon of multiple valence states for a single cation is called charge disproportionation (CD), and CD would induce three dimensional charge density wave (CDW) with octahedral BiO₆ of 3⁺ Bi valence expanding (breathing out) and the octahedron of 5⁺ Bi valence contracting (breathing in). Thus, the octahedral breathing (OB) accompanies naturally the CD and CDW [6]. It is noted that there exists another type of distortion, called octahedral tilting (OT), in BaBiO₃ in addition to OB. OT occurs because in perovskites, depending on the relative sizes of A and B cations, the BO₆ octahedra undergo rigid rotations to remove the empty space in the structure. The OT about the different crystallographic axes in BaBiO₃ induces structural phase transitions as a function of temperature [7]. In addition, BaBiO₃ has recently become an object of particular interest because Bi atoms, being the B-site cation, possess large spin–orbit coupling (SOC) for 6s and 6p electrons and strong SOC would allow BaBiO₃ to manifest the properties of topological nature [8]. In fact, BaBiO₃ would become a topological insulator (TI) in the electron doped region according to the calculation of [8]. On the other hand, superconductivity (SC) appears in the hole doped region of BaBiO₃ as mentioned above [3]. Thus, the BaBiO₃ system suggest an exciting possibility of combining SC and TI in a single heterostructure by integrating BaBiO₃ layers of different doping successively.
which could then be used as quantum devices. For this purpose, of course, a high quality thin film in double gated configuration is required [8].

As BaBiO$_3$ undergoes an OT-driven structural transition as a function of temperature, there would be a change in Raman spectra around the structural transition temperature. It is noted that different structural phases of BaBiO$_3$ would have different number of vibrational normal modes that are Raman active. It is further noted that OT is related to low frequency modes while OB goes with higher energy modes [9]. Due to the displacement of atoms from their equilibrium positions, localized modes would be modified around the structural transition. Electron hoping processes through these modified states, for example, would result in Raman responses on applying electromagnetic field. BaBiO$_3$ in CD would also absorb electric energy and then relax depending on applied electric field frequency and temperature [10]. It is accordingly expected that for different orientations the hoping processes for 6s electrons in BaBiO$_3$ may be different and would lead to orientation dependent dielectric relaxation properties. In short, the electromagnetic and dielectric investigations of this material are expected to provide an insight on the system not available in other kinds of measurements.

In polycrystalline bulk samples, however, one would not be able to see the orientational variation in electronic properties in the absence of anisotropy in the samples. For the purpose of varying the orientation of the system, we have grown BaBiO$_3$ films on substrates with different orientations and studied the Raman and dielectric responses of the films. In particular, the dielectric relaxation property variation depending on the orientation is of interest and unknown at present. Thus, thin films are used as a means to measure the physical properties of the system for varying orientations, which would not be possible for bulk samples. In addition, for a thin film the properties of the system can be tuned using in-plane strain arising from a film-substrate lattice parameter mismatch [11] as well as film thickness variation [12]. In the case of BaBiO$_3$, epitaxial films would be particularly useful because strain may have effects on the suppression of tilting or breathing distortions [13, 14]. We have studied the dynamics of the soft phonon modes in BaBiO$_3$ as a function of temperature using the thin films of different orientations.

2. Experimental procedures

A Nd–YAG laser, of wavelength 266 nm and 10 Hz repetition rate, was used to ablate a target at 20 mTorr background oxygen pressure in a pulsed laser deposition (PLD) chamber. As for the target for PLD, BaBiO$_3$ was first synthesized via calcination from BaCO$_3$ and Bi$_2$O$_3$, a ceramic pellet of disk type was formed, and then the pellet was sintered at 750 °C in air for 24 h. Films were deposited at substrate temperature 550 °C. As-received SrTiO$_3$ (001) and (110) substrates were treated using buffered hydrogen fluoride (NH$_4$F: HF = 7:1) solution with pH = 4.5 for 30 s followed by heat treatment at 1000 °C for two hours in order to obtain unit cell step height and terrace features [15]. MgO (100) substrates were heat treated in situ inside the PLD chamber at 850 °C for 2 h in vacuum [16]. Film surfaces were scanned using an atomic force microscope (AFM) XE-100 and room temperature x-ray diffraction (XRD) were performed using the Cu $\alpha$ line with RIGAKU. Reciprocal space mapping (RSM) was carried out with $\times$-ray synchrotron radiation from Pohang Light Source. Raman spectra were taken using 535 nm laser light. In-plane resistance was measured adopting a Keithley 6517B high resistance meter, and dielectric measurements were taken with an Agilent E4980A precision LCR meter. For out-of-plane dielectric measurements, films were deposited on conducting substrates, 5 wt% Niobium–doped SrTiO$_3$ (001) and (110). Samples were placed in Quantum Design PPMS environment for temperature variation from 10 K to 400 K.

3. Structure characterization of epitaxial BaBiO$_3$ films

The quality of the films deposited on atomically smooth substrates may be quickly judged by the surface morphology inspection. When atomically flat SrTiO$_3$ substrates of low miscut angle $\theta$ $\sim$ 0.1° with unit cell step height are used, the grown films on them retrace the step and terrace features of the underlying substrates. In figure 1(a) the AFM image of a 16 nm thick BaBiO$_3$ film on a SrTiO$_3$ (001) substrate is shown and the surface roughness turns out to be $\sim$0.459 nm. The line profile of a designated area of the film shows the step–terrace structure in figure 1(b). The step height is equal to one unit cell length of SrTiO$_3$ $\sim$ 0.3905 nm. Figure 1(c) is an AFM image of a 17 nm thick BaBiO$_3$ film on a SrTiO$_3$ (110) substrate with surface roughness $\sim$0.475 nm. Figure 1(d) shows the height variation along the line indicated in figure 1(c), and the average step height is equal to the (110) lattice spacing $d_{110}$ $\sim$ 0.276 nm.

We next analyze the crystalline structure of various BaBiO$_3$ thin films on MgO and SrTiO$_3$ substrates; the XRD patterns of the films are displayed in figure 2. (BaBiO$_3$ and SrTiO$_3$ are designated as BBO and STO, respectively, in this figure and the following ones.) It may be noted that there exists an overall mismatch of
about 10% in the lattice constant of BaBiO$_3$, 0.4337 nm for bulk[17], to that of SrTiO$_3$, 0.3905 nm while there is only a 3% difference in the case of MgO with 0.4210 nm. Nevertheless, it is seen from the XRD data that the films are well in epitaxy with the underlying substrates. In figure 2(a) the XRD pattern of a 16 nm thick film on SrTiO$_3$ (001) is shown; the film thickness is obtained from low angle x-ray reflection (XRR) measurements. The inset is the theta rocking curve measured at the (001) peak with FWHM $= 0.077^\circ$ from a Gaussian line fit. Similarly, figure 2(b) is the XRD pattern of a 9 nm thick film on a SrTiO$_3$ (110) substrate and figure 2(c) is for a 88 nm thick film on MgO (100). Reciprocal space mapping (RSM) is also carried out at Pohang Light Source; figures 2(d) and (e) are the detailed RSM results for a 44 nm film on SrTiO$_3$ around the SrTiO$_3$ (103) peak and for a 88 nm film on MgO measured at the MgO (113) peak, respectively. X-ray energy is calibrated with substrate peak with relative energy resolution of $dE/E \sim 10^{-4}$ under the assumption that bulk substrate is an infinite ideally perfect crystal. It is seen from figure 2(e) that the peaks from the film and the underlying substrate are in close proximity and thus the film on MgO (100) is in registry with the substrate. For the BaBiO$_3$ film on SrTiO$_3$ (001), on the other hand, it appears relaxed due to the lattice constant mismatch and the film peak in the reciprocal space are not at all in proximity. In this case, two separate measurements were needed to cover the relevant reciprocal space region as shown in figure 2(d).

4. Physical properties of epitaxial BaBiO$_3$ films

4.1. Raman scattering measurements

Our main interest towards BaBiO$_3$ epitaxial thin films is how their physical properties would differ as orientation as well as strain vary. For this purpose, we first resorted to light scattering measurements of the thin films because the Raman modes of BaBiO$_3$ would be sensitive to strain variation. Structural distortion, which connects the ideal cubic structure to the observed distorted structure, can be identified as a symmetry breaking element of displacive nature, either polar or non-polar, leading to distinct electromagnetic responses. For BaBiO$_3$ the most distorted structure is monoclinic with symmetry group $P2_1/n$; for the transition from ideal cubic $Fm3m$ to monoclinic $P2_1/n$, two symmetry modes, $\Gamma^4^{+}$ and $X^3^{+}$, are involved[9]. $\Gamma^4^{+}$ corresponds to out-of-phase tilting along the pseudo-cubic [110] axis while $X^3^{+}$ is the mode responsible for in-phase tilting.
along the pseudo-cubic [010] axis. Both of these modes are non-polar, and the distortion can be understood in terms of the octahedral tilting only. At room temperature BaBiO$_3$ belongs to another monoclinic I2/m (a - a - c$^0$) with out-of-phase tilting along the [110] direction; in the monoclinic phase, Raman active optical phonon modes are $I_{\text{Raman}} = 7A_g \oplus 5B_g$ [18, 19].

Figure 3 shows Raman scattering spectra for the films on MgO (001) and SrTiO$_3$ (001) substrates. With the help of the reported optical data [20], we are able to assign the peaks in the Raman spectra as the OT modes (Bi–O bending and Bi–O stretching) and the OB (BiO$_6$ breathing) mode from low to high energy values. Specifically, the strongest Raman peak at 565 cm$^{-1}$ is due to the BiO$_6$ breathing with Ag symmetry [21], the peak at 492 cm$^{-1}$ is assigned to the Bi–O stretching mode, and the one around 300 cm$^{-1}$ is the superposition of the multiple Bi–O bending modes as designated in figure 3(a). 2nd order peak also appears around 1130 cm$^{-1}$. For the multiply superposed bond bending peak in the vicinity of 300 cm$^{-1}$ whose details are displayed in figures 3(b) and (c), the spectral line at 298 cm$^{-1}$ would be due to the out-of-phase Bi–O bending with $A_g$ symmetry while the mode at wave number 314 cm$^{-1}$ may be assigned to the $A_g$ symmetric in-plane mixed vibrations of Bi and O atoms. The peaks at 342 cm$^{-1}$ and 347 cm$^{-1}$ are due to the out-of-phase bond bending with $B_g$ symmetry. From figure 3(b) for the relaxed film on SrTiO$_3$ (001), it is of interest to note that the $A_g$ symmetric in-plane vibrational mode at 314 cm$^{-1}$ has a higher intensity and a narrower width than the out-of-phase bending mode at 298 cm$^{-1}$. In addition, a broad spectral line with $B_g$ symmetry appears at 342 cm$^{-1}$. It is also noted from figure 3(c) that the strained film on MgO (001) gives rise to a narrower linewidth and a higher intensity at 299 cm$^{-1}$ than at 314 cm$^{-1}$ and only a very small $B_g$ mode at 347 cm$^{-1}$ is seen. These results would imply that in-plane bond bending is restricted in strained films and thus a shortened phonon lifetime and a broader linewidth would follow. Again it is recalled that BaBiO$_3$ with lattice constant $a = 0.4338$ nm has 3% lattice mismatch with MgO ($a = 0.421$ nm) whereas 10% with SrTiO$_3$ ($a = 0.395$ nm). In particular, a large mismatch between BaBiO$_3$ and SrTiO$_3$ would cause relaxation; indeed, BaBiO$_3$ films grown on SrTiO$_3$ (001) are fully relaxed while the films on...
MgO (100) are strained. It is mentioned in passing that Inumaru et al. claimed a partial suppression of the OT modes for BaBiO$_3$ films grown on MgO substrates [13], and, in contrast, local breathing and tilting distortions were reported even for superconducting Ba$_{1-x}$K$_x$BiO$_3$ and BaPb$_{1-x}$Bi$_x$O$_3$ films on SrTiO$_3$ substrates [22].

To monitor the changes in the tilt pattern of BaBiO$_3$ in association with the structural transition around 140 K, Raman scattering measurements were performed, as a function of temperature ranging from 50 K to 300 K, on the films on SrTiO$_3$ substrates with (001) and (110) orientations. The broad peak in the vicinity of 300 cm$^{-1}$ is analyzed in terms of the superposition of multiple Lorentzian lines and the results are displayed at various temperatures in figures 4(a) and (b). As can be seen from the figures, there is a significant change in the superposition contents of the modes below and above the transition temperature. The structural transition from monoclinic P2$_1$/n (a$^-$a$^-$c$^\parallel$) to monoclinic I2/m (a$^-$a$^-$c$^\parallel$) occurring at temperature 140 K upon raising temperature is known to be an octahedral tilt-driven continuous transition [7]. From figures 4(a) and (b), it is immediately obvious that the vibrational modes of A$_g$ symmetric 306 cm$^{-1}$ and B$_g$ symmetric 352 cm$^{-1}$ appear only in the low temperature phase; in-phase rotation of the BiO$_6$ octahedra around the c-axis would induce such modes. In figure 4(c), there is not too much change in the energy shift for the observed Raman modes except for A$_g$ symmetric in-plane vibrational mode at 314 cm$^{-1}$ which shows hardening on cooling. The peak intensity of the A$_g$ symmetric 306 cm$^{-1}$ mode increases with lowering temperature for the film grown on SrTiO$_3$ (110) substrate as can be seen from figure 4(d). The intensity of all other modes decreases with decreasing temperature. The spectral width of a line in the Raman spectrum is a measure of the phonon lifetime. With the in-phase rotation around c-axis at transition temperature 140 K, the width of the B$_g$ modes at 342 cm$^{-1}$ broadens with decreasing temperature. It is also seen from figure 4(d) that there is a difference in the spectral features depending on the orientation; the film with (001) orientation shows low scattering intensity for the 314 cm$^{-1}$ mode compared to the film with (110) orientation in the low temperature phase. It may be recalled that a BaBiO$_3$ film grown with (001) orientation was reported to have a tetragonal structure [14]; an elongation in the c-axis would release the out-of-phase octahedral tilting along the [110] axis, corresponding to the in-plane
vibrational mode at 314 cm$^{-1}$, and this could be a reason for the lower intensity of the 314 cm$^{-1}$ mode for the film on SrTiO$_3$ (001) compared to the film with (110) orientation.

4.2. Dielectric constant measurements

We next turn to dielectric measurements of BaBiO$_3$ films. BaBiO$_3$ is considered to be a semiconducting material because it has a band gap arising from the CDW [10, 23]; using the 2-probe method, we measured the surface resistance of a BaBiO$_3$ film and found it to be 16 MΩ at 300 K. In general, disorder inevitable even in crystalline samples causes the occurrence of localized states, and electrons could be trapped in the localized states. Random thermal fluctuations would then give electrons enough energy to get out of a localized state and move to a near one by hopping, that is, electrons move, for a brief amount of time, before relaxing into another localized state. For BaBiO$_3$, conduction would be possible due to hopping of 6s electrons on the localized states and this behavior could lead to relaxation phenomena. Furthermore, charge disproportionation in two adjacent B-site Bi ions in distorted BaBiO$_3$ might give rise to a local electric dipole that can absorb electromagnetic energy depending on measuring field frequency and temperature.

We grew BaBiO$_3$ films on conducting substrates, 5 wt% Niobium doped SrTiO$_3$ in (001) and (110) orientations, and out-of-plane dielectric measurements were taken in a vertical capacitor arrangement as sketched in figure 5(a). Top electrodes were deposited with gold in a thermal evaporation chamber. For quantitative analyses with regard to the orientation dependence, we covert the raw data to complex dielectric constant of intrinsic nature without geometric dependence of measuring devices. In the vertical configuration as in the present case, it is straightforward to obtain $\varepsilon'$; real part and $\varepsilon''$; imaginary part of the complex dielectric constant from the raw data [24]:

\[ \varepsilon' = \frac{\Delta \varepsilon}{\Delta \varepsilon' + \sqrt{\Delta \varepsilon^2 + \Delta \varepsilon''^2}}, \quad \varepsilon'' = \frac{\Delta \varepsilon''}{\Delta \varepsilon' + \sqrt{\Delta \varepsilon^2 + \Delta \varepsilon''^2}} \]

Figure 4. Temperature effects on the Raman modes around 300 cm$^{-1}$ for BaBiO$_3$ films grown on SrTiO$_3$-substrates. (a) Raman spectra at various temperatures for 200 nm thick BaBiO$_3$ film on SrTiO$_3$ (001). The broad peak is decomposed into constituent Raman modes. (b) For 200 nm BaBiO$_3$ film on SrTiO$_3$ (110). (c)–(e): The energy shift, intensity, and spectral line width of the decomposed Raman modes are plotted as a function of temperature.
where $C_x$ is the measured capacitance value for material, $\tan \delta$ is the loss tangent, $d$ is the thickness of a film, $A$ is the area of the electrode, and $\varepsilon_0$ is the permittivity of free space. For 200 nm thick BaBiO$_3$ films on Nb-doped SrTiO$_3$ (001) and (110), $\varepsilon'$ and $\varepsilon''$, obtained from the data measured at applied signal frequencies of 50 and 500 Hz, are plotted against temperature in figures 5(b)–(e). The structural transition of BaBiO$_3$ from monoclinic-I (P2$_1$/n) to monoclinic-II (I2/m), occurring around 140 K on increasing temperature, is associated with a large abrupt change in dielectric constant $\varepsilon'$ from a low value to a large value [7]. In figures 6(a) and (c) imaginary part of dielectric constant $\varepsilon''$ is plotted against temperature for BaBiO$_3$ film on Nb-doped SrTiO$_3$ (001) measured at frequencies of 50 and 500 Hz, respectively, with a fitting curve. Only one broad relaxation peak is observed here, and the fitting curve is from a Gaussian distribution of relaxation times. In contrast, for a 200 nm thick film on Nb-doped SrTiO$_3$ (110), $\varepsilon''$ again obtained at measuring frequencies of 50 and 500 Hz, behave quite differently from the case of the (001) orientation as can be seen from figures 6(b) and (d). The imaginary part $\varepsilon''$ in particular can be considered to consist of two broad relaxation peaks, one peak around 140 K and another one around 180 K. The fitting curves in figures 6(b) and (d) are again from the Gaussian distribution of relaxation times. In BaBiO$_3$, Bi 6s and O 2p orbitals form an electronic band near the Fermi level, i.e., the conduction band. Lattice distortions in the perovskite structure would modify the conduction properties of BaBiO$_3$; the breathing distortion opens the charge gap while the tilting distortion causes an overall band narrowing [25]. To hybridize with Bi 6s orbitals, only O 2p$_{\delta}$ orbitals with $A_{1g}$ symmetry
are allowed. For low energy electronic excitations in BaBiO$_3$, Khazraie et al estimated effective hopping integrals for nearest neighbor and next nearest neighbor using a single orbital tight binding model [26]. They showed that with the breathing distortion of $A0.1\text{\AA}$ and no external electric field, the size of the hopping integral $t_1$ between nearest neighbors involving oxygen atoms with $A_{1g}$ symmetry is four times larger than that of the next nearest neighbor hopping integral $t_2$ between two Bi ions sit at a distance $\sqrt{2}a$ as shown in figure 6(e). The difference in the relaxation behaviors of BaBiO$_3$ films with orientations (001) and (110) may be due to the difference in the relative contributions of hopping integrals, i.e., $t_1$ alone vs both $t_1$ and $t_2$ depending on the direction of an applied electric field. When an applied electric field is parallel to the [001] axis, only $t_1$ contributes whereas both hopping integrals, $t_1$ and $t_2$, contribute when $E// [110]$, leading to two relaxation peaks as observed experimentally. It is also noted that the relaxation peak height due to $t_2$ in figures 6(b) and (d) is about $1/4$ less than that due to nearest neighbor hoping $t_1$; in fact, this quantitative difference was already demonstrated by the calculation in 26.

5. Conclusion

We have grown BaBiO$_3$ films epitaxially on MgO (100) and SrTiO$_3$ (001) and (110) substrates using pulsed laser deposition. X-ray diffraction and reciprocal space mapping show that the thin films are grown epitaxially but

![Figure 6.](image)
relaxed considerably particularly for the films on SrTiO$_3$. The topography of the film surfaces is found to be atomically flat with the step and terrace structure of unit cell step height. Raman spectroscopy measurements on strained BaBiO$_3$ films grown on MgO (100) substrates reveal the restriction effect on in-plane Bi–O bond bending. In the temperature range from 50 K to 300 K, it is observed that the number of the vibrational modes is different for the two phases below and above the structural transition temperature around 140 K. The broad peak in the Raman spectra of BaBiO$_3$ is decomposed into the multiple vibrational modes. Dielectric measurements reveal the frequency and orientation dependence of the dielectric constant and loss of BaBiO$_3$ for strained BaBiO$_3$ atomically.

Acknowledgments

We thank Eun Soo Ahn, and Sang Woo Kim for the assistances in measurements and Abhijit Biswas and Alireza Kashir for helpful discussion. We would like to thank Prof. Yoon H Jeong for the guidance in carrying out the whole experiment. Reciprocal Space Mapping (RSM) measurements were performed at beam line 3A of the Pohang Light source (PLS). This work was supported by National Research Foundation (NRF) of Korea (2015R1D1A1A02062239 and 2018R1A6075964).

ORCID iDs

M Talha https://orcid.org/0000-0003-2351-367X

References

[1] Roth R S 1957 Classification of perovskite and other ABX$_3$-Type compounds Journal of Research of the National Bureau of Standards 58 2736
[2] Li G, Yan B, Thomale R and Hanke W 2015 Topological nature and the multiple Dirac cones hidden in Bismuth high-Tc superconductors Sci. Rep. 5 10435
[3] Cava R J, Batlogg B, Krajewski J J, Farrow R, Rupp L W Jr, White A E, Short K, Peck W F and Kometani T 1988 Superconductivity near 30K without copper: the Ba$_{0.8}$ K$_{0.2}$ Bi$_2$O$_5$ perovskite Nature 332 814–6
[4] Sleight A W, Gillson J L and Bierstedt P E 1975 High-temperature superconductivity in the BaPb$_{1-x}$Bi$_x$O$_3$ System Solid State Commun. 17 27–8
[5] Cox D E and Sleight A W 1976 Crystal structure of Ba$_2$ Bi$^{3+}$ Bi$^{4+}$ O$_6$ Solid State Communications 19 969–73
[6] Balachandran P V and Rondinelli J M 2013 Interplay of octahedral rotations and breathing distortions in charge-ordering perovskite oxides Phys. Rev. B 88 054101
[7] Kennedy B J, Howard C J, Knight K S, Zhang Z and Zhou Q 2006 Structures and phase transitions in the ordered double Perovskites Ba$_2$Bi$^{3+}$Bi$_x$O$_3$ and Ba$_2$Bi$^{3+}$Sb$_x$O$_6$ Acta Cryst. B 62 537–46
[8] Yan B, Jansen M and Feller C 2013 A large-energy-gap oxide topological insulator based on the superconductor BaBiO$_3$ Nature Physics 9 709–11
[9] Islam M A, Rondinelli J M and Spanier J E 2013 Normal mode determination of perovskite crystal structures with octahedral rotations: theory and applications J. Phys. Condens. Matter 25 175902
[10] Lee S H, Jung W H, Sohn J H, Lee J H and Cho S H 1999 Dielectric loss anomaly of BaBiO$_3$ Journal of Appl. Phys. 86 6351–4
[11] Biegalski M D et al 2009 Influence of anisotropic strain on the dielectric and ferroelectric properties of SrTiO$_3$ thin films on DyScO$_3$ substrates Phys. Rev. B 79 224117
[12] Matthews J W, Blakeless A E and Mader S 1976 Use of misfit strain to remove dislocations from epitaxial thin films Thin Solid Films 33 253–66
[13] Inumaru K, Miyata H and Yamanaka S 2008 Partial suppression of structural distortion in epitaxially grown BaBiO$_3$ thin films Phys. Rev. B 78 132507
[14] Kim G, Neumann M, Kim M, Le M D, Kang T D and Noh T W 2015 Suppression of three-dimensional charge density wave ordering via thickness control Phys. Rev. Lett. 115 266402
[15] Biswas A, Yang C H, Ramesh R and Jeong Y H 2017 Atomically flat single terminated oxide substrate surfaces Prog. Surf. Sci. 92 117–41
[16] Bonholzer M, Lorenz M and Grundmann M 2014 Layer–by–layer growth of TiN by pulsed laser deposition on in situ annealed (100) MgO substrates Phys. Status Solidi Appl. Mater. Sci. 211 2621–4
[17] Pei S, Jorgensen J D, Dabrowski B, Hinks D G, Richards D R and Mitchell A W 1990 Structural phase diagram of the Ba$_{1-x}$ K$_x$ BiO$_3$ system Phys. Rev. B 41 4126
[18] Uchida S, Tajima S, Masaki A, Sugai S, Kitazawa K and Tanaka S 1985 Infrared Phonons in semiconducting phase of BaPb$_{1-x}$Bi$_x$O$_3$ J. Phys. Soc. Jpn. 54 4395
[19] Sugai S, Uchida S, Kitazawa K, Tanaka S and Katsui A 1985 Lattice vibrations in the Strong electron-phonon-interaction system BaPb$_{1-x}$Bi$_x$O$_3$ studied by Raman Scattering Phys. Rev. Lett. 55 426
[20] Khorossabdi H, Miyasaka S, Kobayashi J, Tanaka K, Uchiyama H, Baron A Q R and Tajima S 2011 Softening of bond-stretching phonon mode in Ba$_{1-x}$K$_x$BiO$_3$ at metal insulator transition Phys. Rev. B 83 224325
[21] Tajima S, Yoshida M and Koshizuka N 1992 Raman-scattering study of the metal–insulator transition in Ba$_{1-x}$ K$_x$ BiO$_3$ Phys. Rev. B 46 1232–5
[22] Harris D T et al Charge density wave modulation in superconducting BaPbO$_3$/BaBiO$_3$ Superlattices arXiv:1812 08589
[23] Cox D E and Sleight A W 1979 Mixed-valent Ba$_2$Bi$_2$$^{3+}$Bi$_5$$^{5+}$O$_{6}$: structure and properties versus temperature Acta Cryst. B 35 1–10
[24] Yadav V S, Sahu D K, Singh Y and Dhubkarya D C 2010 The effect of frequency and temperature on dielectric properties of Pure Poly Vinyldene Fluoride (PVDF) thin films Proc. of the Int. MultiConference of Engineers & Computer Scientists (IMECS) 3
[25] Khamari B, Kashikar R and Nanda B R K 2018 Topologically invariant double dirac states in bismuth-based perovskites: Consequence of ambivalent charge states and covalent bonding Phys. Rev. B 97 045149
[26] Khazraie A, Foyevtsova K, Elfinov I and Sawatzky G A 2018 Oxygen holes and hybridization in the bismuthates Phys. Rev. B 97 075103