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Multiple optical impacts of anion doping in epitaxial barium titanate films

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ABSTRACT

Multiple strong impacts of anion doping Λ (Λ = oxygen vacancy, nitrogen, or hydrogen) on the optical properties in the near-infrared to vacuum ultraviolet spectral range are experimentally revealed in cube-on-cube-type epitaxial perovskite BaTiO$_3$-$_\delta$Λ$_\delta$ films ($\delta \leq 0.01$) grown on (001)SrTiO$_3$ substrates. Compared to the reference undoped films and bulk crystal, the anion-doped films exhibit massive changes of the index of refraction in the transparency range $\Delta n$ of $\sim 0.1$ to $0.2$, a profound bandgap widening $\Delta E_g$ of $\sim 0.3$ eV to $0.4$ eV, a dopant-specific near-edge absorption, and doping-induced interband transitions. Both the conduction-band uplift and the changes in the index of refraction are ascribed to the internal stress and electric field, which result from epitaxially controlled dopant locations in the [Ba–O](001) planes. The dopant-induced in-gap states are responsible for the near-edge absorption, whereas the dopant-induced conduction-band states are suggested to modify the interband transitions and the intrinsic elasto- and electro-optic coefficients.

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Barium titanate (BaTiO$_3$, BTO) is one of the best studied optical perovskite oxide ferroelectrics (FEs). Owing to a wide bandgap $E_g > 3$ eV, FEs are transparent in the spectral range from the mid-infrared to the ultraviolet. In the transparency range, the index of refraction of an FE is a function of electric field (electro-optic effects) and stress (elasto-optic effect) and can be modified by light (photorefractive effect). These optical properties, especially the strong Pockels effect (linear electro-optic effect), are a basis for various optoelectronic and photonic applications of FEs. Although bulk translucent optical FE crystals and ceramics have been and continue to be developed, their utilization in modern devices is limited by synthesis and integration issues. These limitations can be overcome, thanks to progress in the growth of single-crystal-type epitaxial FE films, in particular those on commercial substrates. Devices that use the Pockels effect in such films have also been demonstrated. Despite the many remarkable technological achievements, the reported optical properties of epitaxial FE films are strongly scattered and poorly understood. This disparity creates a bottleneck for future developments.

In heteroepitaxial FE films, film–substrate mismatches in crystal symmetries, lattice parameters, and thermal expansion coefficients can lead to lattice strain, strain-induced phases, and point defects, which have no analogues in bulk crystals. We note that depending on the method of growth, unintentional point defects may form in FE films. In BTO, the most probable native point defects are oxygen vacancies, whose formation energy is generally low and decreases under oxygen-deficient conditions (e.g., in ultrahigh-vacuum molecular beam epitaxy). Additionally, incorporation of hydrogen or nitrogen at an oxygen site is also possible (e.g., in metalorganic and other chemical deposition processes). Because FE properties are intrinsically related to oxygen BO$_6$-octahedra (TiO$_6$ in BTO), substitution of oxygen may principally produce changes in both the electronic band structure and the interband transitions, affecting the optical behavior in FEs. However, whereas controlling strain and further modeling strain-induced FE properties are treated with scrutiny, the optical impact of anion vacancies/dopants is tracked only in an increased absorption due to the corresponding in-gap states.
Here, we report on experimental evidence of multiple strong optical effects induced by anion substitution in epitaxial BaTiO$_3$, where $\Lambda$ stands for an oxygen vacancy, nitrogen, or hydrogen and the doping level is $\delta \leq 0.01$. Compared to the reference undoped films and bulk crystal, such anion-doped films exhibit unexpected $>10\%$ changes in the index of refraction and the bandgap energy, in addition to an expected dopant-induced absorption. It is suggested that epitaxy-controlled positions of the dopants produce strong tetragonal and internal field, which can lead to conduction-bundle uplift and changes in the index of refraction through elasto- and electro-optic effects. Concurrently, it is revealed that dopant-induced conduction-bundle states modify the interband transitions, which can lead to intrinsic changes in the elasto- and electro-optic coefficients.

BTO films of $\sim 200$ nm in thickness were grown by pulsed laser deposition at a temperature of 973 K on single-crystal (100) SrTiO$_3$ (STO) substrates. Undoped and anion-doped films were obtained by varying gas ambience during deposition and post-deposition cooling: 20 Pa oxygen for undoped films ("films" here), 2 Pa oxygen for oxygen-vacancy-doped films (marked by "O" here), 2 Pa nitrogen for nitrogen-doped films (marked by "N"), and 2 Pa hydrogen for hydrogen-doped films (marked by "H"). Inspections of the films’ elemental composition by x-ray photoelectron spectroscopy (XPS) did not reveal stoichiometric deviations (see Fig. S1 of the supplementary material). The BTO films are perovskite-type and oriented with tetragonality $\sim 0.9$–0.4 $\pi$, index of refraction $n = 2.5$–2.2, and critical-point energies for different phase angles $\phi$ in the reference crystal, undoped film, and anion-doped films. Consequently, the theoretical compressive misfit strain increases to $\kappa_{\text{STO}} = (a_{\text{STO}}/(V_{\text{STO}})^{1/3}) - 1$ for doped BTO films on STO. The relaxation of the large strain $s_{\text{BTO}}$ in the doped films is expected to be at least as efficient as that in the undoped film. In contrast to this expectation, the doped films exhibit concurrently very strong out-of-plane tetragonality $t > 2\%$ and lattice expansion $\Delta V > 2\%$. This anomalous anisotropic expansion indicates the compression-induced selective formation of oxygen vacancies in the (001) [Ba–O] planes parallel to the substrate surface (see Fig. S4 of the supplementary material). The vacancy formation partly releases the lattice strain. It is also likely that anion dopants (H or N) are preferably located in the (001)[Ba–O] planes in the result of incorporation at the oxygen vacancy site (see Fig. S4 of the supplementary material). Compared to regular misfit-strained films, the doped films experience peculiar dopant-induced strains.

To elucidate optical impacts of anion doping, we investigated the optical constants (index of refraction $n$, extinction coefficient $k$, and absorption coefficient $\alpha$) and dielectric functions ($\varepsilon$) for the doped and undoped films, as well as a polycrystal BTO crystal. The optical constants and dielectric functions were determined by variable angle spectroscopic ellipsometry on a J.A. Woollam VUV ellipsometer at room temperature and wavelengths $\lambda = 140$ nm–1600 nm (see Fig. S5 of the supplementary material).

The films are transparent at wavelengths of $\lambda > 350$ nm (see Fig. S6 of the supplementary material). Compared to the reference undoped film and crystal, the index of refraction is significantly diminished in the doped films for the wavelengths $\lambda = 350$ nm–1500 nm in the transparency range (Fig. 1a). The extinction coefficient of the doped films is $k \approx 0.01$–0.02 at $\lambda = 350$ nm–600 nm but increases to $k \approx 0.05$–0.15 for $\lambda > 800$ nm. We note that the increased $k$ can explain the wavelength dispersion and relative increase in $n$ at $\lambda > 800$ nm, but not the global decrease in $n$ in the doped films. The constants $n$ and $k$ at $\lambda = 500$ nm for the films and crystal are listed in Table I.

When anion vacancies/dopants are introduced into BTO, the unit-cell volume increases to $V_{\text{BTO}} = V_{\text{B}}$, where the chemical expansion factor $B$ can reach $B \approx (1-2) \times 10^{-7}$ for the vacancy/dopant concentration of several atomic percent in bulk BTO. Consequently, the theoretical compressive misfit strain increases to $\kappa_{\text{STO}} = (a_{\text{STO}}/(V_{\text{STO}})^{1/3}) - 1$ for doped BTO films on STO. The relaxation of the large strain $s_{\text{BTO}}$ in the doped films is expected to be at least as efficient as that in the undoped film. In contrast to this expectation, the doped films exhibit concurrently very strong out-of-plane tetragonality $t > 2\%$ and lattice expansion $\Delta V > 2\%$. This anomalous anisotropic expansion indicates the compression-induced selective formation of oxygen vacancies in the (001) [Ba–O] planes parallel to the substrate surface (see Fig. S4 of the supplementary material). The vacancy formation partly releases the lattice strain. It is also likely that anion dopants (H or N) are preferably located in the (001)[Ba–O] planes in the result of incorporation at the oxygen vacancy site (see Fig. S4 of the supplementary material). Compared to regular misfit-strained films, the doped films experience peculiar dopant-induced strains.

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| $t$ (%) | $\Delta V$ (%) | $s_{\text{out}}$ (500 nm) | $n$ (500 nm) | $k$ (500 nm) | $\alpha$ (eV) | Critical points $E_{\text{cr}}$ (eV) |
|--------|--------------|------------------|-------------|-------------|-------------|----------------|
|        |              |                  |             |             |             | $\varphi, \pi$   |
| Crystal| 1.1          | 2.521            | 0.088       | 3.22        | 3.8         | 4.2           | 4.5           | 4.9           |
| Film   | −0.9         | 0.4              | −1.1        | 2.564       | 0.029       | 3.12          | 3.8           | 4.3           | 4.8           | 5.1           |
| O      | 2.2          | 2.2              | 1.45        | 2.369       | 0.006       | 3.54          | 4.1           | 4.8           | 5.4           |
| N      | 2.3          | 2.6              | 1.70        | 2.398       | 0.013       | 3.62          | 4.2           | 4.4           | 5.3           |
| H      | 2.5          | 2.5              | 1.80        | 2.347       | 0.009       | 3.52          | 4.1           | 4.8           | 5.4           |
\[ \Delta (n^{-2}) = ps, \]  

where \( p \) and \( s \) are the effective elasto-optic coefficient and strain, respectively. Considering the films’ out-of-plane lattice strain \( s = 5 \text{nm} \) as related to the room-temperature tetragonal cell of bulk BTO and assuming a maximum coefficient \( p = 0.37 \) reported for BTO, \( \Delta (n^{-2}) \) the index \( n_s \) of the strained films is estimated as:

\[ n_s = \left( n_{cr}^{-2} + ps \right)^{-1/2}. \]  

The estimated index \( n_s \) is close to the measured one in the undoped film but exceeds the measured values by \( \Delta n_s \approx 0.1 \)–0.2 in the doped films (see Fig. S7 of the supplementary material). The difference \( \Delta n_s \) can be ascribed to the electro-optic effect caused by an internal out-of-plane electric field \( F \):

\[ \Delta (n^{-2}) = rF. \]  

Here, \( r \) is the electro-optic coefficient and the field \( F \) is equal to:

\[ F = r^{-1} \left( n^{-2} - n_{cr}^{-2} - ps \right). \]  

For the measured values of \( n \) and \( s \), the field \( F \) tends to zero if the coefficients \( p \) are assumed to be giant, up to \( \sim 1.5 \). Although the coefficients may be enhanced in the films compared to bulk, their fourfold increase is unrealistic that points to the presence of the field \( F \). As an example, the suggested internal field was estimated for \( \lambda = 500 \text{nm} \) using bulk coefficients \( p \approx 0.37 \) and \( r \approx 1300 \) in BTO.\(^{36} \) The optically estimated field is approximately \( F \approx 12 \text{MV/m} \). The near-edge absorption humps evidence the presence of deep in-gap states [Fig. 2(b)]. In the vacancy-doped O-film, the states are located at approximately \( \Delta E \approx 2.3 \text{eV} \) below the conduction band and are likely related to electron polarons trapped at doubly charged oxygen vacancies.\(^{44} \) In addition to the vacancy-related traps, there are states at \( \Delta E \approx 1.5 \text{eV} \) in the N-doped film and states at \( \Delta E \approx 1.2 \text{eV} \) and \( \Delta E \approx 3.1 \text{eV} \) in the H-doped films. Although the electronic structure of a nitride ion in BTO is not exactly known, the achieved perovskite BaTiO\(_3\) phase points to a stable oxygen-site occupation for nitride to which the states at \( \Delta E \approx 1.5 \text{eV} \) may be assigned in the N-doped film.\(^{22} \) In the H-doped film, a small polaron at a positively charged hydride ion in the oxygen-vacancy site, [H\(_2\)]\(^+\), and a neutral center containing two H\(^+\) ions in the vacancy site, [(2H\(^+\))\(_0\)], can both be stable and responsible for the two types of the in-gap states.\(^{22,45} \) Notably,

In the doped films, the near-edge absorption humps evidence a giant electro-optic effect caused by an internal out-of-plane electric field \( F \) in the films compared to bulk, their fourfold increase is unrealistic that points to the presence of the field \( F \). As an example, the suggested internal field was estimated for \( \lambda = 500 \text{nm} \) using bulk coefficients \( p \approx 0.37 \) and \( r \approx 1300 \) in BTO.\(^{36} \) The optically estimated field is approximately \( F \approx 12 \text{MV/m} \). The near-edge absorption humps evidence the presence of deep in-gap states [Fig. 2(b)]. In the vacancy-doped O-film, the states are located at approximately \( \Delta E \approx 2.3 \text{eV} \) below the conduction band and are likely related to electron polarons trapped at doubly charged oxygen vacancies.\(^{44} \) In addition to the vacancy-related traps, there are states at \( \Delta E \approx 1.5 \text{eV} \) in the N-doped film and states at \( \Delta E \approx 1.2 \text{eV} \) and \( \Delta E \approx 3.1 \text{eV} \) in the H-doped films. Although the electronic structure of a nitride ion in BTO is not exactly known, the achieved perovskite BaTiO\(_3\) phase points to a stable oxygen-site occupation for nitride to which the states at \( \Delta E \approx 1.5 \text{eV} \) may be assigned in the N-doped film.\(^{22} \) In the H-doped film, a small polaron at a positively charged hydride ion in the oxygen-vacancy site, [H\(_2\)]\(^+\), and a neutral center containing two H\(^+\) ions in the vacancy site, [(2H\(^+\))\(_0\)], can both be stable and responsible for the two types of the in-gap states.\(^{22,45} \) Notably,

### Fig. 1
(a) Index of refraction \( n \) and (b) extinction coefficient \( k \) as a function of wavelength in the anion-doped films (O, N, and H) compared to those in the undoped film (film) and reference crystal (crystal).

### Fig. 2
(a) Absorption coefficient as a function of photon energy in the BTO crystal (marked by “crystal”), undoped film (“film”), and anion-doped films (marked by O, N, and H).
the polaronic trapping at the vacancies/dopants, which are preferably located in the [Ba-O](001) planes, can produce the out-of-plane internal electric field \( F \) discussed above (see Fig. S4 of the supplementary material). We note that because of their peculiar nature, the dopant-related lattice strains cannot directly lead to electric fields through the macroscopic piezoelectric effect. We also note that the macroscopic flexoelectric origin of the field is unlikely.\(^{42,43}\)

Importantly, the observations in Fig. 2(b) evidence the presence of different dopant-specific in-gap states and thus prove anion doping, which is difficult to detect by composition analysis in thin films.

Compared to the undoped film and crystal, the broad absorption peaks in the doped films are not only blueshifted but also possess different shapes [Fig. 2(a)], which indicate changes in the interband transitions contributing to the peaks. To detect the changes, the interband transitions are identified using critical-point (CP) analysis.\(^{44,45}\) For a two-dimensional CP, the second derivative of the dielectric function takes the following form:

\[
d\epsilon /dE^2 \propto A \exp(i\phi) / (E - E_0 + i\Gamma)^2.
\]

Here, \( A, E_0, \Gamma, \) and \( \phi \) are the amplitude, energy, width, and phase angle of the CP line, respectively. The derivatives \( d^2\epsilon /dE^2 \) and \( d^2\epsilon_i /dE^2 \) (Fig. 3 and Fig. S9 of the supplementary material) reveal the strongest main CP, whose energy is \( E_0 \approx 3.8 \) eV in the crystal and noticeably larger (blueshifted) in the doped films [Fig. 3(a)]. This blueshift of the main CP is consistent with the bandgap widening and confirms the uplift of the conduction bands in the doped films. However, when the derivatives’ spectra are normalized and moved along the energy axis so that the main CPs coincide at \( \sim 3.8 \) eV for all BTO samples, more complex changes become obvious: the adjusted spectra for \( E > 4 \) eV in the films clearly differ from those in the crystal and from each other [Figs. 3(b)–3(d) and Fig. S10 of the supplementary material].

To quantify the changes, the energies \( E_0 \) from the second derivatives of the dielectric functions assuming the phase angles \( \phi = 0\pi, 0.5\pi, 1\pi, \) or 1.5\pi for simplicity (Table I). Besides the blueshift of the bulk CP at \( \sim 3.8 \) eV, the fine structure (CPs at \( \sim 4.2 \) eV and \( \sim 4.5 \) eV) that is observed in the crystal disappears from the films’ spectra. Instead, a new CP at \( \sim 4.3 \) eV to 4.4 eV is found in the undoped and N-doped films, but not in the O- and H-films. The bulk CP at \( \sim 4.9 \) eV is practically unchanged in the undoped and O- and H-doped films, but absent in the N-doped film. A well-expressed CP at \( \sim 5.1 \) eV to 5.4 eV in the films has no a clear analogue in the crystal. Thus, the CP analysis unveils the dopant-specific alterations of the band structure, in addition to the strain- and field-induced ones, in the films. The dopant-specific band structure behavior complies with the theoretically predicted possibility for conduction-band states that are related either to oxygen vacancies or to nitrogen or hydrogen dopants in oxygen-vacancy positions.

Whereas trapping of electron polarons at the vacancy/dopant sites creates the in-gap states that are responsible for the near-edge absorption and have no influence on the interband transitions [Fig. 2(a)], the vacancy/dopant-induced conduction-band states modify the interband transitions [Fig. 3(a)]. Considering the semi-empirical models of elasto- and electro-optic effects in perovskite oxide ferroelectrics,\(^{44,45}\) these modifications imply intrinsic changes in the effective polarization potential and quadratic electro-optic coefficients and, consequently, intrinsic changes in the linear elasto- and electro-optic coefficients. We note that modern theory of ferroelectric polarization does not discard the conclusions of the semi-empirical approach, whereas it clarifies the physical meaning of the quadratic electro-optic coefficients therein.\(^{56,58}\)

Thus, the revealed optical impacts of anion doping are manifold:

- The polaron trapping at the dopant sites produces dopant-specific in-gap states that are manifested in the near-edge absorption.
- The internal epitaxy- and dopant-induced stresses and electric fields raise the bottom conduction bands. Correspondingly, the bandgap widens and the optical spectra blueshift. The index of refraction in the transparency range decreases.
- The dopant-induced conduction-band states modify the interband transitions, which can lead to intrinsic changes in the elasto- and electro-optic coefficients.

We note that here, the concentration of dopants/vacancies is smaller than the quantification accuracy of XPS, i.e., \(<1\) at. %. However, being combined with epitaxial strain, such a relatively weak doping produces strong impacts on the optical properties. Likewise, even minor unintentional anion doping, which is difficult (if not impossible) to trace by many methods of compositional analysis, may have surprisingly large influence on the index of refraction and the elasto- and electro-optical coefficients in epitaxial FE films. Concurrently, knowledge-based anion doping can enable

![FIG. 3. (a) Spectra and [(b)–(d)] adjusted spectra of the second derivative of the real part of the dielectric function in the crystal and doped films.](https://scitation.aip.org/content/aip/journal/apm/8/71107-4)
efficient tuning of the technologically important optical and electronic properties of FEs. To bring this possibility to its full fruition, more detailed experimental investigations and comprehensive theoretical modeling remain a necessity.

In summary, cube-on-cube epitaxial BaTiO$_3$–δAs films (A = V, O, N, H; δ ≤ 0.01) were grown on compressive (001)SrTiO$_3$ substrates. The observed strong tetragonality and internal field are ascribed to the epitaxially controlled location of the dopants in the (001)[Ba–O] planes. Compared to the reference undoped films and bulk crystal, the anion-doped films exhibit strong changes in the index of refraction, the bandgap energies, the near-edge absorption, and the interband transitions.

It is shown that the lattice strain and internal field lead to the conduction-band uptake and changes in the index of refraction through elasto- and electro-optic effects. The in-gap states responsible for the near-edge absorption are explained by polaron trapping at the dopant sites. It is suggested that anion-induced conduction-band states modify the interband transitions and the intrinsic elasto- and electro-optic coefficients.

See the supplementary material for (I) XPS spectra, (II) XRD scans, (III) schematics of oxygen vacancies, (IV) details of ellipsometric analyses, (V) absorption spectra, (VI) estimated index of refraction, and (VII) critical-point analyses.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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