Theoretical estimation of the linear electro-optic effect in compressively strained c-domain (Ba, Sr)TiO₃ thin films using a phenomenological thermodynamic model

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The influence of compressive strain on the linear electro-optic (EO) effect in c-domain (Ba,Sr₁₋ₓ)TiO₃ (BST) thin films was theoretically investigated using a phenomenological thermodynamic model. We considered that the c-domain BST thin films were grown on cubic substrates and an electric field was applied parallel to the direction of spontaneous polarization. To estimate the EO coefficients, we considered not only the intrinsic EO effect but also the elasto-optic effect by converse piezoelectric response. We found that the EO response is mostly determined by the difference in temperature from the ferroelectric-to-paraelectric phase transition boundary modified by the strain, and the elasto-optic effect appreciably affects the overall EO coefficient when the intrinsic EO effect is weak.

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1. Introduction

Integrating epitaxial functional oxide thin films with semiconductors, especially Si, is a key for developing various applications.¹ For optical applications, the electro-optic (EO) effect in ferroelectric films such as BaTiO₃ (BTO) is expected to be applied in small, energy-saving photonic and plasmonic modulators.²⁻⁵ The EO effect in ferroelectric thin films and their corresponding device performance have been reported.³⁻⁵ However, it is observed that the EO properties in ferroelectric films are sensitive to the specific fabrication processes, conditions, substrates, and film thicknesses.⁶⁻¹⁰ Recently, Fredrickson et al. and Hamze et al. reported a theoretical prediction of a strain effect in BTO and SrTiO₃ (STO) thin films based on first-principles calculations. They found that the EO effect can be enhanced by softening of the phonon via strain engineering.¹¹,¹² Indeed, we recently observed such an effect in (Ba,Sr₁₋ₓ)TiO₃ (BST) thin films experimentally.¹³ These results show that strain engineering of ferroelectric thin films is a valid approach to enhancing EO properties and thus to realizing advanced thin-film-based EO devices.

In this paper, we theoretically estimate the linear EO effect in compressively strained c-domain BST thin films with different Ba/Sr compositions based on a phenomenological thermodynamic theory. Unlike similar approaches by Qiu et al. and Liu et al.,¹⁴⁻¹⁶ the elasto-optic effect is taken into account in addition to the intrinsic EO effect.

2. Method

The refractive index of nonmagnetic materials, the square of which is proportional to the permittivity, is often expressed by the optical indicatrix or index ellipsoid.¹⁷ In the cubic paraelectric phase, the inverse permittivity can be expressed by a quadratic function of the polarization. DiDomenico and co-workers proposed that the linear EO effect in the ferroelectric phases was described as a quadratic effect biased by the spontaneous polarization, and later Bernasconi et al. estimated the temperature dependence and wavelength dispersion of the EO properties, including not only the intrinsic effects but also the mechanical contribution.¹⁸⁻¹⁹ By applying this relationship to strained ferroelectric thin films, the influence of strain on the linear EO effect is modeled in the present study.

The inverse permittivity of the cubic phase at optical frequencies under the influence of polarization and strain can be expressed as:

\[ \varepsilon_{ij}^{-1} = \delta_{ij}\varepsilon_{C}^{-1} + \sum_{ijkl}^{\text{ijkl}} P_k P_l + P_l^{\text{ijkl}} \delta_{kl}, \tag{1} \]

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to which the dummy suffix summation rule is applied. Here, \( \delta_{ij} \) and \( \delta_{ijl} \) are the Kronecker delta (\( \delta_{ij} = 1 \) for \( i = j \), and \( \delta_{ij} = 0 \) for \( i \neq j \)), the permittivity of the cubic state, the quadratic polarization-optic tensor at constant strain, and the elasto-optic-optic tensor at constant polarization, respectively, and \( P_{ijkl} \) and \( d_{ijkl} \) are the polarization and strain of the material.

When an electric field, \( E_m \), is applied to the material, the inverse permittivity is modified to become,

\[
e_{ij}^{-1}(E_m) = e_{ij}^{-1}(0) + \Delta e_{ij}^{-1},
\]

where \( e_{ij}^{-1}(0) \) and \( \Delta e_{ij}^{-1} \) are the inverse permittivity before application of the electric field and the variation after application of the electric field, respectively. From Eq. (1), \( e_{ij}^{-1}(0) \) of a ferroelectric thin film having spontaneous polarization can be written as

\[
e_{ij}(0)^{-1} = \delta_{ij}e_{c}^{-1} + g_{ijkl}^{S}P_{S,k}P_{S,l} + p_{ijkl}^{\psi}u_{0,kl}, \tag{3}
\]

where \( P_{S,k} \) is the spontaneous polarization and \( u_{0,kl} \) is the lattice deformation caused by spontaneous polarization and mismatch with the substrate. Assuming a linear dependence of polarization and strain on the electric field, \( \Delta e_{ij}^{-1} \) in Eq. (2) can be written as,

\[
\Delta e_{ij}^{-1} = (2g_{ijkl}^{S}P_{S,k}\chi_{lm} + p_{ijkl}^{\psi}d_{ijkl})E_{m},
\]

where \( \chi_{lm} \) and \( d_{ijkl} \) are the electric susceptibility and the piezoelectric coefficient, respectively. The parenthesis corresponds to the linear EO coefficient \( r_{ijm} \) in which the first term describes the intrinsic EO effect and the second term describes the elasto-optic effect arising from the converse piezoelectric response.

In the present study, we focus on the paraelectric phase and ferroelectric \( c \)-domain phase in compressively strained (001)-epitaxial BST films, where the \( e_{ij} \) is diagonal. We also assume that the electric field \( E_{3} \) is applied parallel to the spontaneous polarization \( P_{S,3} \) (see Fig. 1); thus, \( E_{3} \) does not affect the diagonality of \( e_{ij} \). Namely, \( E_{3} \) does not cause any rotation of optical indicatrix. In such a situation, \( e_{11}(0)^{-1} = e_{22}(0)^{-1} \) and \( e_{33}(0)^{-1} \) are

\[
e_{11}(0)^{-1} = e_{22}(0)^{-1} = e_{c}^{-1} + \frac{g_{1333}^{S}P_{S,3}P_{S,3} + p_{1111}^{\psi}+ p_{1112}^{\psi}u_{0,11} + p_{1133}^{\psi}u_{0,33}}{1 + p_{3333}^{\psi}u_{0,33}}, \tag{5}
\]

\[
e_{33}(0)^{-1} = e_{c}^{-1} + \frac{g_{3333}^{S}P_{S,3}P_{S,3} + 2p_{1311}^{\psi}u_{0,11} + p_{3333}^{\psi}u_{0,33}}{1 + p_{3333}^{\psi}u_{0,33}}, \tag{6}
\]

and \( \Delta e_{11}^{-1} = (\Delta e_{22}^{-1}) \) and \( \Delta e_{33}^{-1} \) are

\[
\Delta e_{11}^{-1} = \Delta e_{22}^{-1} = (2g_{1333}^{S}P_{S,3}\chi_{33} + p_{1113}^{\psi}d_{333}E_{3}), \tag{7}
\]

\[
\Delta e_{33}^{-1} = (2g_{3333}^{S}P_{S,3}\chi_{33} + p_{3333}^{\psi}d_{333}E_{3}),
\]

respectively. The principal refractive indices under the electric field \( E_{3} \) are expressed as

\[
n_{1}(E_{3}) = n_{2}(E_{3}) = \frac{1}{\sqrt{e_{11}^{-1}(0) + \Delta e_{11}^{-1}}}, \tag{9}
\]

\[
n_{3}(E_{3}) = \frac{1}{\sqrt{e_{33}^{-1}(0) + \Delta e_{33}^{-1}}}, \tag{10}
\]

Therefore, the change in the principal refractive indices by \( E_{3} \) can be described as

\[
\Delta n_{1} = \Delta n_{2} = -\frac{1}{2}e_{11}(0)^{2}\Delta e_{11}^{-1} = -\frac{1}{2}n_{1}(0)^{2}r_{13}E_{3}, \tag{11}
\]

\[
\Delta n_{3} = -\frac{1}{2}e_{33}(0)^{2}\Delta e_{33}^{-1} = -\frac{1}{2}n_{3}(0)^{2}r_{33}E_{3}, \tag{12}
\]

where \( r_{13} \) and \( r_{33} \) are the linear EO coefficients in Voigt notation. As explained above, the linear EO coefficients contain the intrinsic EO effect and the elasto-optic effect arising from the converse piezoelectric response. In the considered situation, the latter is the function of piezoelectric constant \( d_{33} \) in Voigt notation. Since the film is clamped by the substrate, \( d_{33} \) can be modified by \( d_{31} \) and the elastic compliances \( s_{11} \) and \( s_{12} \) as

\[
d_{33}^{*} = d_{33} - \frac{2s_{12}}{s_{11} + s_{12}}d_{31}. \tag{13}
\]

The parameters \( P_{S,3}, \chi_{33}, d_{33}, \) and \( d_{31} \) required for the numerical estimation of \( r_{13} \) and \( r_{33} \) in \( c \)-domain BST thin films for different strains and temperatures can be calculated by using the modified thermodynamic potential, \( G \), as

\[
G = \alpha_{3}^{*}P_{S,3}^{3} + \alpha_{33}^{*}P_{S,3}^{3} + \alpha_{111}^{*}P_{S,3}^{3} + \frac{u_{m}^{2}}{s_{11} + s_{12}}, \tag{14}
\]

where \( \alpha \) is the dielectric stiffness and \( u_{m} \) is the biaxial parent misfit strain. The coefficients used in our calculations are listed in Table 1. Some of the coefficients for BST are interpolated from the values for bulk BTO and STO single crystals. One should be also aware that the position of the \( c \)- and \( r \)-domain boundary (see Fig. 3) can be slightly modified by the renormalization of the sixth-power polarization term taking into account high-order electromechanical couplings.

3. Results and discussion

Figure 2 shows the dependences of out-of-plane spontaneous polarization, \( P_{S,3} \), electric susceptibility, \( \chi_{33} \), and effective piezoelectric constant, \( d_{33}^{*} \), on the compressive misfit strain, \( u_{m} \), for \( c \)-domain BST (\( x = 0.5, 0.7, \) and 1.0) thin films at 300 K. As has already been reported, \( 22,23,27,28 \) the paraelectric-to-ferroelectric phase tran-
sition temperature significantly increases with increasing compressive strain (also see Fig. 3). Therefore, when \( x = 1.0 \), i.e., BTO, the paraelectric-to-ferroelectric phase transition temperature is far above room temperature regardless of the strain, which results in a weak strain dependence of \( P_{\text{S,3}} \), \( \chi_{33} \), and \( d_{33}^{\text{eff}} \) at 300 K. On the contrary, when \( x = 0.5 \) and 0.7, the transition temperature either is close to room temperature without strain or meets room temperature by a compressive strain; thus, \( P_{\text{S,3}} \), \( \chi_{33} \), and \( d_{33}^{\text{eff}} \) showed larger strain dependences, and \( \chi_{33} \) and \( d_{33}^{\text{eff}} \) diverged at a particular strain at 300 K.

Figure 3 shows a temperature–strain map of the linear EO coefficient, \( r_{33} \), of \( c \)-domain BST \((x = 0.5, 0.7, \text{and} \ 1.0)\) thin films. As can be predicted from Eq. (8) and Fig. 2, the largest \( r_{33} \) was obtained near the paraelectric-to-ferroelectric phase transition temperature modified by the strain, the tendency of which also agrees with recent reports of first-principles calculations for BTO and STO thin films.\(^{11,12}\) In addition, regardless of the magnitude of the strain, the EO response was mostly determined by the difference in temperature from the paraelectric-to-ferroelectric phase transition boundary. On the other hand, the EO response was not enhanced at the boundary between \( c \)- and \( r \)-domain structures as \( \chi_{33} \) and \( d_{33}^{\text{eff}} \) did not diverge.

It is also worth mentioning that the single domain state, which is desired for developing modulators, can be only achieved in \( c \)-domain (001)-BST thin films. Although a single \( r \)-domain was also predicted in our simple model at zero strain (or weak

![Table 1. Coefficients used in the calculation for BST thin films in SI units (temperature, \( T \), in K). Except for \( \alpha_{1} \), the values for \( x = 0.5 \) and 0.7 were interpolated by using the values reported for BTO and STO](image)

### Table 1.

| BST \((x = 1.0)\) | BST \((x = 0.7)\) | BST \((x = 0.5)\) |
|-------------------|-------------------|-------------------|
| \( \alpha_{1} \) \((\text{m}^{2} \text{N}^{-1} \text{C}^{-2})\) | 4.69 \((T - 381)\) | 4.86 \((T - 310)\) |
| \( \beta_{11} \) \((\text{m}^{6} \text{N}^{-2} \text{C}^{-2})\) | 5.31 \((T - 250)\) | 5.87 \((T - 200)\) |
| \( \alpha_{12} \) \((\text{m}^{2} \text{N}^{-1} \text{C}^{-2})\) | 7.54 | 9.30 |
| \( \beta_{111} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.60 | 4.62 |
| \( \beta_{12} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.30 | 4.33 |
| \( \beta_{121} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.20 | 4.33 |
| \( \beta_{13} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.10 | 4.33 |
| \( \beta_{131} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{132} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{1321} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{1322} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{13221} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{13222} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{132221} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{132222} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{1322221} \) \((\text{m}^{10} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
| \( \beta_{1322222} \) \((\text{m}^{8} \text{N}^{-3} \text{C}^{-2})\) | 6.00 | 4.33 |
thin compressive strain), complex multi domain structures will be appeared in such a condition to minimize the energy of the system.\textsuperscript{30} It is also known that any single domain be appeared in such a condition to minimize the energy (compressive strain), complex multi domain structures will be appeared in such a condition to minimize the energy of the system.\textsuperscript{30} It is also known that any single domain structures are not formed with tensile strain.\textsuperscript{30,33} Therefore, the use of compressive strain will be important for practical applications.

**Figure 4** shows the contribution of the intrinsic EO effect and the elasto-optic effect to $r_{33}$ as a function of misfit strain, $\mu_{\text{m}}$, for BST ($x = 0.5$, 0.7, and 1.0) thin films at 300 K. As can be seen in the figures, the contribution of the elasto-optic effect is generally quite minor. Nevertheless, it becomes appreciable when the intrinsic EO effect is weak, as shown in Fig. 4(a) for $x = 1.0$, i.e., BTO. The ratio of the elasto-optic effect to $r_{33}$ for different compositions is listed in **Table 2**, together with the values measured for unclamped BTO bulk single crystals$^{32,33}$ and predicted by first-principles calculation for clamped STO thin films.\textsuperscript{12} As can be seen, the contributions of the elasto-optic effect in the clamped $c$-domain BST thin films estimated in this study are similar to those in the clamped STO thin films estimated by first-principles calculations. In contrast, these contributions are smaller than the values measured for unclamped bulk BTO, which basically supports our scenario for the influence of substrate clamping on the thin films. Although the reduction of the elasto-optic effect is unavoidable in thin films, its contribution becomes negligible when $r_{33}$ is maximized.

### 4. Conclusions

We developed a model to simulate the effect of compressive strain on the linear EO response of $c$-domain BST thin films considering both the intrinsic EO effect and the elasto-optic effect. By using the quadratic relationship between the polarization and the inverse permittivity at optical frequencies, the EO coefficient $r_{33}$ was calculated for a wide range of strains and temperatures. We found that the magnitude of the EO response is mostly determined by the difference in temperature from the paraelectric-to-ferroelectric phase transition boundary modified by misfit strain. Although the contribution of the elasto-optic effect to the overall EO response is relatively minor, it becomes appreciable when the intrinsic EO effect is small. The method proposed here can be also applied to other materials including solid solutions, for which first-principles calculations are computationally expensive.

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**Table 2.** Contribution of the elasto-optic effect to the linear EO coefficient, $r_{33}$, for BST thin films. The values measured for unclamped BTO bulk single crystals$^{32,33}$ and predicted for STO thin films by first-principles calculations$^{12}$ are also listed in parentheses.

| Composition $x$ | Contribution of elasto-optic effect to $r_{33}$ |
|-----------------|-----------------------------------------------|
| 1.0             | 0.141 (0.613$^{32}$, 0.787$^{33}$)             |
| 0.7             | 0.106                                          |
| 0.5             | 0.0846                                         |
| 0               | (0.076, 0.122)$^{12}$                         |

a) Value is for the contribution to $r_c$.
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