# Composition dependence of dielectric function in ferroelectric $BaCo_xTi_{1-x}O_3$ films grown on quartz substrates by transmittance spectra

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Near-infrared-ultraviolet optical properties of $BaCo_xTi_{1-x}O_3$ (BCT) ($x$ from 1.0% to 10%) films have been investigated by the transmittance spectra. The dispersion functions in the photon energy range of 1.24–6.2 eV have been extracted by fitting the experimental data with Adachi's model. It was found that the oscillator and dispersion energies linearly increase with the Co composition and the maximum optical transition occurs near the energy range of 4.3–5.0 eV for the BCT materials. The absorption coefficient at the visible region linearly increases with the composition due to grain boundaries and disorder induced band tail into the forbidden gap. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2870094]

For several decades, much effort has been made on the studies of ferroelectric materials with regard to the ferroelectics, dielectrics, and optical properties. Recently, perovskite ferroelectric film materials have received much attention in view of their wide applications in dynamic random access memories, electro-optic switches, pyroelectric detectors, optical modulators, and mixers.[1–3] Among these materials, $BaTiO_3$ is a typical ferroelectric material and considered to be very promising compound for optics information process and storage.[4] On the other hand, optimal cation doping ($Ti^{4+}$) is a widely accepted approach to tailor the physical properties, such as transition temperature, ferroelectric characteristics, and dielectric properties. There has been an increased interest in transition metals (TMs) doped wide band gap materials, which was amplified by theoretical predictions suggesting that ferromagnetism of diluted magnetic compounds with Curie temperatures above room temperature (RT) could be obtained.[5] Cobalt (Co) element is one of typical TMs and its doping can produce some perturbation on the physical properties in the ferroelectric materials, such as ferroelectricity and electronic transitions. Therefore, it is interesting and significant to investigate the optical properties of Co-doped $BaTiO_3$ films due to the unique characteristics by the replacement of $Ti^{4+}$.[6,7]

It is well known that macroscopical dielectric function above reststrahlen frequencies can be related to the electronic band structure of material. Recently, it was found that the optical band gap $E_g$ of the $BaCo_xTi_{1-x}O_3$ (BCT) films decreases with increasing Co composition by the extrapolation method with ultraviolet transmittance spectra.[4] However, Co-doping effects on the dielectric function, i.e., optical constants remain as an open issue. Note that transmittance spectra can directly provide optical band gap, optical constants, absorption characteristics, band tail state behavior, and optical phonon modes.[8–11] In this letter, the optical properties of the BCT films with different Co compositions are studied in detail.

BCT films were grown on quartz substrates by the sol-gel technique.[4] Barium acetate, cobalt acetate, and titanium *n*-butoxide were used as the starting materials. The Co content in the precursor solution was matched to 1%, 2%, 5%, and 10%, respectively. It should be emphasized that all chemical materials and organic reagents are analytically pure. Therefore, the effects from impurities in the solution could be neglected, as compared to the Co doping concentration in the present work. The films were fabricated by spin-coating and the thermal treatments were carried out in a rapid annealing processor. In order to avoid the influences from the hydroxyl (OH) in the atmosphere, the BCT growths were processed under a dry ambient in the clean room. Moreover, the OH defects can be removed in the inorganic ferroelectric compounds, which were suffered from the high temperature post-annealing procedure (up to 700 °C).

The crystalline structure of the BCT films was analyzed by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. There are the diffraction peaks (100), (110), (111), and no impurity phases observed, which further confirms the above discussion about the impurity effects.[4] The optical transmittance at RT were recorded with a double beam ultraviolet-infrared spectrophotometer (PerkinElmer UV/visible Lambda 2S) at the photon energy from 1.24 to 6.2 eV (200–1000 nm).

A three-phase layered structure (air/film/substrate) was used to calculate the transmittance spectra of the BCT films.[12,13] At the normal incidence configuration, the following form describes the transmittance coefficient $t=t_{01}t_{12}e^{-i\delta}/(1+t_{01}t_{12}e^{-2i\delta})$. Where, the partial transmittance coefficient $t_{01}$ (vacuum film) and $t_{12}$ (film substrate) are written as $t_{i,i+1}=2\sqrt{\tilde{\varepsilon}_i}/(\sqrt{\tilde{\varepsilon}_i}+\sqrt{\tilde{\varepsilon}_{i+1}})$ and the phase factor for the film with thickness $d$ is described by $\delta=2\pi d\sqrt{\tilde{\varepsilon}_1}/\lambda$. Here, $\lambda$ is the incident wavelength, and the dielectric functions of vacuum, the film, and the substrate are $\tilde{\varepsilon}_0(=1)$, $\tilde{\varepsilon}_1$, and $\tilde{\varepsilon}_2$, respectively. Thus, the spectral transmittance can be readily obtained from $T=\mathrm{Real}(\sqrt{\tilde{\varepsilon}_2})tt^*$. It should be noted that the absorption from the substrate must be taken into account to calculate the transimittance of the film-substrate system.[14] For wide band gap ferroelectric materials, the dielectric response, which can be described by the contribution from the

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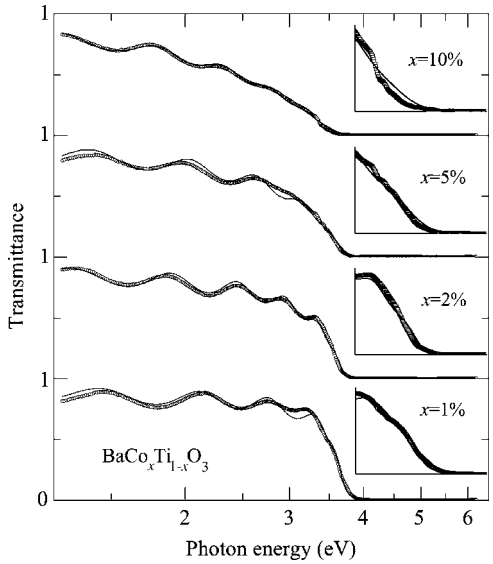


FIG. 1. Experimental (dotted lines) and best-fit (solid lines) transmittance spectra of the $BaCo_xTi_{1-x}O_3$ films from near-infrared to ultraviolet photon energy region. The horizontal coordinate is the logarithmic unit to enlarge the transparent region. The insets show an enlarged fitting fundamental band gap region of 3.2–4.2 eV.

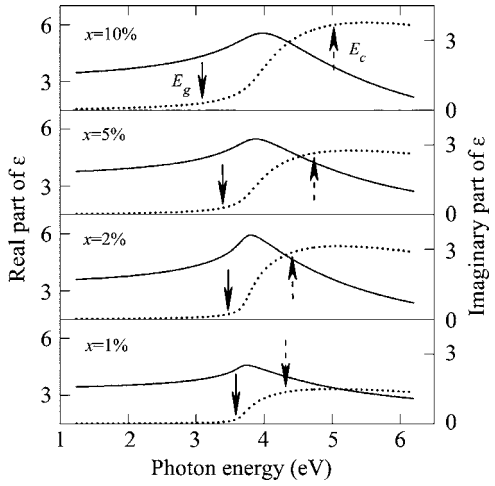


FIG. 2. Composition dependence of the dielectric function for the $BaCo_xTi_{1-x}O_3$ films in the photon energy range of 1.24–6.2 eV. The solid and dotted lines represent the real and imaginary parts, respectively. The solid and dashed arrows indicate the optical band gap $E_g$ decreases and the oscillator energy $E_c$ increases with increasing Co composition, respectively.

lowest three-dimensional $M_0$ type critical point (CP), is written as

$$\tilde{\varepsilon}(E) = \varepsilon_\infty + \frac{A_0}{E_0^{3/2}} \frac{2 - (1+\chi_0)^{1/2} - (1-\chi_0)^{1/2}}{\chi_0^2}. \quad (1)$$

Here, $\chi_0 = (E + i\Gamma)/E_0$, $\varepsilon_\infty$ is the high-frequency dielectric constant, $E_0$ the optical transition energy, $E$ the incident photon energy, and $A_0$ and $\Gamma$ the strength and broadening parameters of the $E_0$ transition, respectively.[14,15] The above Adachi's model is successfully applied in many semiconductor and dielectric materials.[16–18] It should be emphasized that the dielectric function with the Adachi's model abides by the Kramers–Krönig transformation in the entirely measured photon energy region.[15]

The experimental transmittance spectra of the BCT films are shown in Fig. 1 with the dotted lines. The Fabry–Pérot interference patterns have been observed below the photon energy of 3.0 eV, indicating that the films are transparent in the wavelength region. Note that the interference oscillation intensity decreases with increasing Co composition, showing that the transparency of the BCT films decreases and the optical absorption in the subgap region increases. The fundamental absorption edge becomes much sharper with decreasing Co composition. It suggests that the Co addition can contribute to the valance and conduction bands, which extend into the forbidden gap and form the stronger Urbach tail absorption characteristics.[6,19] The fitted parameter values in Eq. (1), and thicknesses are summarized in Table I and the simulated transmittance data are also shown in Fig. 1 by the solid lines. A good agreement is obtained between the experimental and calculated spectra in the entirely measured photon energy range, especially near the fundamental band gap region (see the insets of Fig. 1). The fitting standard deviations are less than $4.6 \times 10^{-3}$ for all four BCT layers. Beyond the fundamental optical band gap $E_g$, there are high-energy CP transitions. For $BaTiO_3$ material, they are far away from 6.0 eV (Ref. 20) and cannot be detected by the present transmittance measurements due to the spectral limitation and sensitivity.[11] Nevertheless, it confirms the ability of the Adachi's model to express the dielectric function of the present BCT films near the fundamental band gap region.

From Table I, Adachi's model parameters except for the $\varepsilon_\infty$ increase with increasing Co composition. It indicates that the contribution from the $E_0$ transition increases with the composition, which can be described to the electronic structure variations of the BCT material.[6,7] The evaluated dielectric functions of the BCT films are shown in Fig. 2. The evolution of $\tilde{\varepsilon}$ with the photon energy is a typical optical response behavior of dielectric and/or semiconductors.[15,18,20] Generally, the real part $\varepsilon_1$ increases with the photon energy and approaches the maximum, then decreases with further increasing photon frequency due to the known Van Hove singularities.[15,20] The $\varepsilon_1$ value was approximately varied from 2.2 to 6.0 for all doping contents. Note that there is a sharper feature in $\varepsilon_1$ near the maximum for the films with two lower Co compositions due to much smaller broadening values (about 0.09 eV). In the wide

TABLE I. The parameter values of Adachi's model for the BCT films with different Co compositions are determined from the fitting of transmittance spectra in Fig. 1. The 90% reliability of the fitting parameters is given in parentheses.

| Samples | $x$ (%) | Thickness $d$ (nm) | $\varepsilon_\infty$ | $A_0$ ($eV^{3/2}$) | $E_0$ (eV) | $\Gamma$ (eV) |
|---|---|---|---|---|---|---|
| A | 1 | 465.6 (5.0) | 2.21 (0.14) | 33.6 (3.1) | 3.67 (0.01) | 0.08 (0.01) |
| B | 2 | 508.4 (4.7) | 0.99 (0.18) | 72.6 (4.8) | 3.73 (0.01) | 0.09 (0.01) |
| C | 5 | 460.1 (6.3) | 1.38 (0.35) | 67.8 (9.5) | 3.78 (0.02) | 0.19 (0.02) |
| D | 10 | 545.3 (4.7) | 0.12 (0.34) | 99.1 (9.8) | 3.87 (0.02) | 0.28 (0.03) |

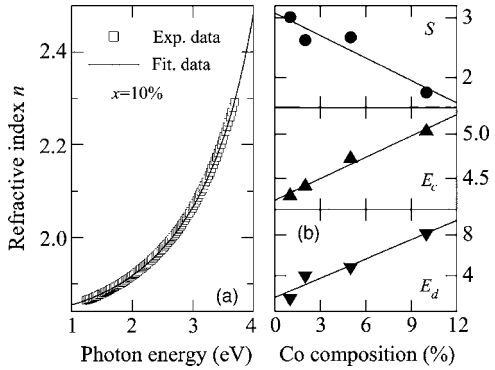


FIG. 3. (a) A single oscillator function model in the transparent region for the film with the Co composition of 10%. (b) Composition dependence of the oscillator parameters for the $BaCo_xTi_{1-x}O_3$ films. Note that the solid lines are the linear fitting results to guide the eyes.

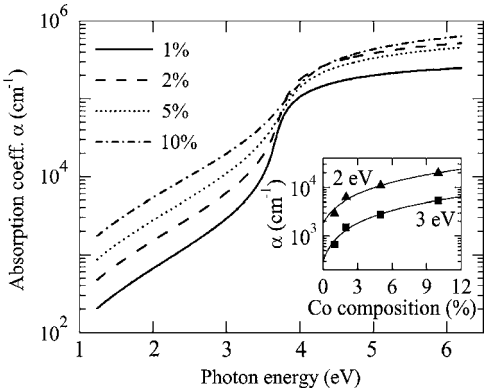


FIG. 4. Evolution of absorption coefficient for the $BaCo_xTi_{1-x}O_3$ films with the photon energy. The inset shows the linear variations of $\alpha$ with the Co composition at the photon energies of 2 and 3 eV, respectively.

transparent region, the imaginary part $\varepsilon_2$ is down to zero and $\varepsilon_1$ increases slowly with the photon energy. With the photon energy further increasing, the $\varepsilon_2$ sharply increases and strong photon absorption appears, showing the interband transition behavior.

In order to give an insight on the electronic structure of the BCT films, we have fitted the refractive index $n$ obtained below the fundamental band gap with a dispersion formula corresponding to a single oscillator function, $n^2=S+E_cE_d/(E_c^2-E^2)$. Here, $S$ is the contribution from high-energy CP transitions, $E_c$ the oscillator energy, and $E_d$ the dispersion energy. The fitting quality from the $BaCo_{0.1}Ti_{0.9}O_3$ film and parameter values have been shown in Figs. 3(a) and 3(b), respectively. The single oscillator model gives a relatively good description to the optical dispersion in the transparent range. Note that the $S$ value linearly decreases with increasing Co composition, which indicates that the effects from high-frequency electronic transitions becomes less in the $BaCo_{0.1}Ti_{0.9}O_3$ film. It can be found that the maximum optical transition occurs near the energy range of 4.3–5.0 eV from the fitted oscillator energy, which agrees well with the $\varepsilon_2$ observed (see Fig. 2). It indicates that the optical dispersion in the transparent region is mainly ascribed to the higher CP virtual transitions ($A_1$-$A_2$) and not by the band gap energy of $E_g$, which is similar to the result from $BaTiO_3$.[20] In the BCT films, the electronic transitions are due to the crystal field and electrostatic interaction between O ($2p$) ionic orbitals, which play an important role in the band structure.[6] In particular, the conduction band comes mainly from Co $3d$ hybridized with O $2p$ orbitals. Therefore, the replacement of Ti with Co cation can affect the hybridization strength between the Ti $3d$ (Co $3d$) and O $2p$ orbitals and further its covalent bond energy of Ti–O (Co–O) bond. It will result in the band structure variations of the BCT films.

The absorption coefficient is the basic parameters for optoelectronic device designs.[21] The absorption coefficient $\alpha$ of the BCT films is presented in Fig. 4 and these values approach a magnitude order of $10^4$–$10^6$ $cm^{-1}$ beyond the $E_g$. The data agree with those from wide band gap insulators $BaTiO_3$ and $SrTiO_3$.[20] Moreover, the $\alpha$ values linearly increase with increasing Co composition at the visible region, as shown in the inset of Fig. 4. It indicates that the Co addition can result in the larger subgap absorption. This absorption can be ascribed to electronic states introduced by grain boundaries, dangling bond states, and disorder induced band tailing into the forbidden gap for the polycrystalline BCT films. This observation can be explained by the fact of the *sp-d* exchange interactions between the band and localized $d$ electrons of the TMs cation.[19]

In conclusion, the cobalt composition dependence of the dielectric function in the BCT films has been determined from near-infrared to ultraviolet region by spectral transmittance technique.

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