Optical properties of BiCr$_x$Fe$_{1-x}$O$_3$ films grown by sol-gel method

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Abstract. The BiCr$_x$Fe$_{1-x}$O$_3$ thin films were fabricated on Si substrate by sol–gel method with $x$ range from 0 to 0.05. X-ray diffraction analysis shows that both pure BiFeO$_3$ thin film and Cr-doped BiFeO$_3$ thin films have rhombohedral structure with space group R3c. Moreover, the influence of different values of $x$ on the extinction coefficient and refractive index were investigated in order to exploit their possible application in optoelectronic devices. The optical constants of the Cr-doped BiFeO$_3$ thin films in the wavelength range 500-1100 nm were obtained by spectroscopic ellipsometry, and the band-gap energy of BiCr$_{0.03}$Fe$_{0.97}$O$_3$ was found to be 2.40 ±0.02 eV, and that of BiCr$_{0.05}$Fe$_{0.95}$O$_3$ was 2.30 ±0.02 eV.

1. Introduction
Multiferroic materials are currently attracting extensive attentions due to their potential applications and fascinating physical phenomena. However, single-phase multiferroic materials are rare because of contradictory requirement of d-electron occupancy in the A and B metal sites of ABO$_3$ type perovskite structure. BiFeO$_3$ (BFO) is a multiferroic material in which ferroelectricity is due to the presence of lone pair of electrons present in Bi$^{3+}$ ions and (anti) ferromagnetism is due to the occupancy of unpaired $d$-orbital electrons. BFO is a rare single phase material which gives multiferroic characteristics at room temperature. BFO was discovered to show ferroelectric order with high Curie temperature ($T_C$~850 °C) and G-type antiferromagnetic order with Neel temperature ($T_N$~370 °C). The structure of BFO is rhombohedrally distorted perovskite, which belongs to the space group R3c. However, the optical properties of the Cr-doped BFO materials were seldom investigated.

In this paper, The BiCr$_x$Fe$_{1-x}$O$_3$ (BCFO) thin films were fabricated on silicon substrates by sol–gel method, and the optical properties of the films were investigated.

2. Experimental details
Fe(NO$_3$_3)·9H$_2$O, Bi(NO$_3$_3)·5H$_2$O and Cr(NO$_3$_3)·9H$_2$O were adopted as raw materials. Cr(NO$_3$_3)·9H$_2$O was dissolved into the ready precursor solution, which was prepared by mixing Bi(NO$_3$_3)·5H$_2$O solution with Fe(NO$_3$_3)·9H$_2$O solution, and then the catalyst acetic acid was added. The solutions with Cr$^{3+}$ concentrations of 0 %, 3 %, and 5 % were prepared. These solutions were stirred for 2 hrs at room

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temperature. All solutions were prepared with excess 5 % Bi to compensate the bismuth loss during annealing process. The concentration of the precursor solution was adjusted to approximately 0.2 mol·L⁻¹. The BCFO thin films were spin-coated on Si substrate at 4000 rpm for 25 s. Each layer was dried at 200 °C for 2 min and then pyrolyzed at 350 °C for 3 min in a rapid thermal annealing in air. After deposited two layers, the amorphous films were annealed at 600 °C for 10 min. The above process was repeated four times to obtain the desired thickness.

The structural properties were examined by x-ray diffraction (XRD, Rigaku D/max-2200), and the influence of different values of $x$ to the extinction coefficient and refractive index were investigated using spectroscopic ellipsometry.

3. Results and discussions

Figure 1(a) shows XRD patterns of pure BFO film, 3 % Cr-doped BFO film (Cr 3 %, BCFO-3 %), and 5 % Cr-doped BFO film (Cr 5 %, BCFO-5 %). The diffraction peaks were identified by PDF cards[^4]. As can be seen in figure 1a, there are typical peaks of BFO in the XRD pattern, such as [012], [104], [110], [202], [024], [116], [300]. However, with increasing the concentration of Cr some additional peaks were observed in BCFO that might be due to some impurity phase. It is clear that impurity phases around 32° are observed in the films with Cr doping concentration varying from 3 % to 5 %, it might belong to Fe₂O₃. There are also some other impurity phase of Cr₂O₃ and Bi₂O₂Fe₉, as shown in figure 1(a).

Figure 1(b) shows the diffraction peaks corresponding to (104) and (110) of the pure and Cr-doped BFO films. In the present case, the prominent splitting around 32° for the 104/110 reflections were clearly visible for the pure and Cr-substituted BFO films, suggesting invariance of structural change upon Cr substitution. The XRD patterns indicate the rhombohedral structure of BFO with space group R3c, that is because the radii of Cr³⁺ (0.0615 nm) is similar to Fe³⁺ (0.0645 nm)[^5] and the BFO structure could be less affected by light doping.

![Figure 1](image-url)

**Figure 1.** (a) XRD patterns of Cr 0%, Cr 3%, and Cr 5% doped BFO films, (b) the diffraction peaks corresponding to (104) and (110) of Cr 0%, Cr 3%, and Cr 5% doped BFO films.
Figure 2. The refractive index \( n \) (a) and the extinction coefficient \( k \) (b) of Cr 0%, Cr 3% and Cr 5% doped BFO thin films deposited on Si.

Spectroscopic ellipsometry (SE) is a powerful technique to investigate the optical constants of the materials. It has been used to measure the refractive index \( n \) and extinction coefficient \( k \). Figure 2 presents the optical constants \((n, k)\) of the samples with the wavelength in the range 500–1100 nm. The refractive index of the pure BFO thin films reduces over 500 nm, however, the curves of BCFO-3% and BCFO-5% rise during short wavelength. The maximum refractive index of BCFO-3% and BCFO-5% is 2.20 at 515 nm (2.41 eV) and 1.94 at 534 nm (2.32 eV), respectively. Moreover, with increasing the amount of Cr, the refractive index decreases and the extinction coefficient increases, and the extinction coefficient curves showing a bunching behavior towards higher wavelengths.

Figure 3 displays absorption coefficient of Cr 0%, Cr 3% and Cr 5% doped BFO thin films deposited on Si. We assigned the observed excitations based on recent first-principles calculations\(^{6-8}\). Although the overall absorption profiles are similar, the absorption coefficient increases with the Cr doping from 0 to 5% at the same photon energy.

Figure 3. Absorption coefficient of Cr 0%, Cr 3% and Cr 5% doped BFO thin films deposited on Si.
Figure 4. The plot of $\alpha \nu$ versus photon energy for Cr 0%, Cr 3% and Cr 5% doped BFO thin films deposited on Si, and direct band gap analysis of Cr 3% and Cr 5% doped BFO thin film (inset).

The direct optical band gap energy $E_g$ of the BFO thin films was deduced from the spectral dependence of the absorption coefficient $\alpha$. The energy $E_g$ of the BCFO-3% is about 2.40±0.02 eV and that of BCFO-5% is 2.30±0.02 eV, which were estimated from the inset of figure 4 by extrapolating the linear portion of the plot to $(\alpha \nu)^2 = 0$. The values are smaller than that of pure BFO films\cite{10}, which was 2.67±0.02 eV.

4. Conclusions
In summary, the prominent splitting around 32° for the 104/110 reflections were clearly visible for the pure and Cr-substituted BFO films, suggesting the rhombohedral structure of BFO with space group R3c. The maximum refractive index of BCFO-3% and BCFO-5% is 2.20 at 515 nm and 1.94 at 534 nm, respectively. Moreover, the absorption coefficient increases with the Cr doping from 0 to 5% at the same photon energy, and the extinction coefficient curves show a bunching behavior towards higher wavelengths. The energy $E_g$ of the BCFO-3% is about 2.40±0.02 eV and that of BCFO-5% is 2.30±0.02 eV, whereas that of pure BFO thin films was 2.67±0.02 eV.

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