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# Influence of transition metal doping (X = Co, Fe) on structural, optical properties of Ferroelectric $Bi_{3.25}La_{0.75}X_1Ti_2O_{12}$

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## Abstract

Studies of the photoelectric properties of complex oxides have recently focused on materials with a narrow band gap because the wide band gap of complex oxides is one of the major obstacles limiting their use in photovoltaic cells. To tune the band gap of complex oxides, this study examined the effects of cobalt and iron doping on lanthanum-modified $Bi_4Ti_3O_{12}$-based oxides (BLT) synthesized using a solid reaction method. The structural, optical and electrical properties of the synthesized powers were examined by x-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible spectroscopy. Doping with both atoms affected the tunability of the band gap dramatically without breaking symmetry. On the other hand, the transition region in the band gap from the iron-doped sample was much sharper than that from the cobalt-doped sample. Control of the band gap chemical doping can be applied to other complex oxides materials and provides a new tool for manipulating oxide optoelectronics.

**Keywords:** Bismuth titanate; Band gap; Chemical doping

## 1 Background

Ferroelectric oxides are used widely in the microelectronic, ferroelectric, optoelectronic, and refrigerated cooling fields on account of their high dielectric constant, and large spontaneous polarization [1,2]. For several decades, many studies of ferroelectric materials have been conducted because of their excellent physical properties suitable for devices based on piezoresponse. For example, ferroelectric thin films and ceramics have a strong effect on a large number of technological applications [3,4].

Recently, novel opto-electronic systems have attracted considerable attention [5]. Among the many classes of materials, ferroelectric complex oxide materials are emerging as promising candidates for opto-electronic device applications, such as photovoltaic devices and photo detectors [6,7]. Complex oxides have excellent characteristics including ferroelectricity and excellent stability at high temperatures and high humidity. On the other hand, they have a much wider band gap than the materials available commercially for photovoltaic cells. Therefore, reducing the band gap without losing the useful characteristics is a key factor for achieving significant scientific and technological applications.

Among the range of complex oxides, Aurivillius phases are good alternative materials for solving the wide band gap problem. The Aurivillius family is a class of complex bismuth titanate-based oxides with a number of layered perovskite structures. These compounds, $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, are generally good insulators. In addition, unlike other classes of ferroelectric materials, the electrical and structural properties of Aurivillius phases have strong sustainability, even after extensive chemical doping because of their layered structure with alternating $Bi_2O_2$ and $Bi_2Ti_3O_{10}$ layers [8,9].

To achieve the large bandgap tunability, W. S. Choi et al. suggested superlattice films by allying $Bi_4Ti_3O_{12}$ and $LaTMO_3$ (TM = Ti, V, Cr, Mn, Co, Ni, Al) [10]. They concluded that cobalt atoms might be the best candidate for reducing the band gap of BiT but they did not provide information on the substitution of Ti with Fe for tuning the bandgap in BiT.

A simple alloying method is used widely to reduce the bandgap of oxide materials. According to reference [11],

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lanthanum doping of $BiFeO_3$ films induces a decrease in the band gap due to compositional changes in the host network. The substitution may also create localized states in the band gap, which will lead to a shift in the absorption edge towards a lower photon energy, and thus a decrease in the optical energy gap.

Recently, the optical bandgap of $Bi_4Ti_3O_{12}$ (BiT) could be controlled using a simple alloying method without a superlattice structure [12]. This shows that the site specific substitution of layered ferroelectric BiT with La and Co could reduce the band gap of BiT considerably, while maintaining their original properties. Doping BiT with La enhances the ferroelectricity of samples, and cobalt atoms in BLT would contribute the most to modifying the electronic structure of BiT-based powder [13,14]. In this reference, the bandgaps ($E_g$) of $Bi_{3.25}La_{0.75}CoTi_2O_{12}$ (Co-BLT), $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), and $Bi_4Ti_3O_{12}$ (BiT) samples were estimated. The BLT sample did not show a remarkable change in the optical bandgap, whereas the $E_g$ value of the Co-BLT sample decreased dramatically. On the other hand, the absorption edge of the optical band gap in cobalt-doped lanthanum bismuth titanate (Co-BLT) was not defined clearly in both alloying methods, superlattice and simple alloying method, even though cobalt doping induced band-gap narrowing and enhanced the visible light activity of bismuth titanate.

Iron atoms in the BLT structure could induce significant bandgap tunability like other 3d metals, but alloying has not been considered. Therefore, ferroelectric BLT powder was doped with Fe to identify more a useful candidate for accurately controlling the bandgap than doped cobalt.

In this study, pure BLT was synthesized and doped chemically using a simple solid reaction method. The structural and optical properties of the Fe or Co-doped lanthanum-modified bismuth titanate samples were examined. The synthesized powders were characterized structurally by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical properties of the synthesized powers were determined by ultraviolet–visible (UV–vis) absorption spectroscopy. As a result, the optical bandgap of iron-doped lanthanum bismuth titanate (Fe-BLT) powders were similar to Co-BLT powders without breaking the orthorhombic structure of bismuth titanate.

## 2 Methods

The BLT-based powders had the following compositions: $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), $Bi_{3.25}La_{0.75}CoTi_2O_{12}$ (Co-BLT) and $Bi_{3.25}La_{0.75}FeTi_2O_{12}$ (Fe-BLT). The levels of Co or Fe substitution for Ti ranged from 0 to 1. Figure 1 summarizes the entire procedure.

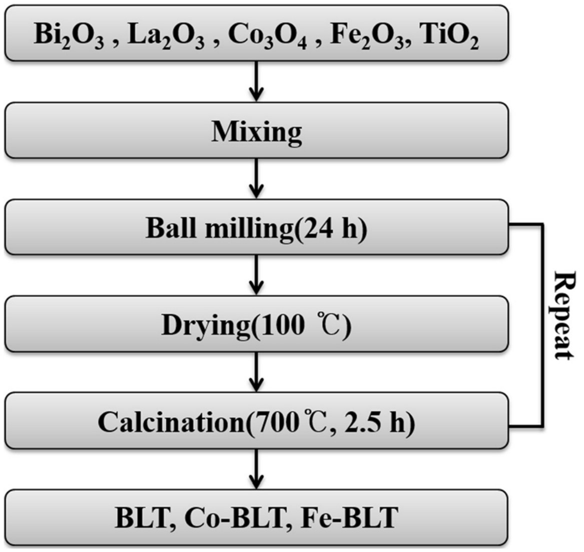

**Figure 1** Procedure to synthesize BLT, Co-BLT and Fe-BLT powders.

The samples were synthesized by a solid-state reaction with the following starting binary oxide powders as the raw materials: $Bi_2O_3$ (99.9%, Kojundo), $TiO_2$ (99.99%, Kojundo), $La_2O_3$ (99.99%, Kojundo), $Co_3O_4$ (99.9%, Kojundo) and $Fe_2O_3$ (99.9%, Kojundo). The powders blended at the stoichiometric ratio were mixed thoroughly in a ball mill for 24 hours, dried in an oven at 100°C and calcined at 700°C for 2.5 hours in air. The resulting calcined powders were milled and calcined again under the same conditions.

The samples were characterized structurally by XRD (Rigaku, D/MAX 2200) using Cu K$\alpha$ radiation over the range, 20 to 60° $2\theta$, with an angular step of 0.02°/min. The microstructure of the synthesized powers was examined by scanning electron microscopy (SEM, Hitachi, S-4700). To estimate the optical band-gap, the optical properties were measured using a UV–vis spectrometer (Agilent, 8453).

## 3 Results and discussion

Figure 2 shows the XRD patterns of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), $Bi_{3.25}La_{0.75}CoTi_2O_{12}$ (Co-BLT), and $Bi_{3.25}La_{0.75}FeTi_2O_{12}$ (Fe-BLT). The XRD patterns of all samples agreed well with that of lanthanum-modified bismuth titanate with an orthorhombic structure (ICSD No. 150091) [12,15,16]. The positions of the peaks with an orthorhombic structure remain unchanged for all samples, indicating that the Aurivillius structure had been sustained without breaking symmetry, despite the doped-BLT containing a small amount of secondary phase, as shown in the XRD pattern in Figure 2. The XRD result confirmed that the cobalt and iron atoms have been incorporated successfully into the BLT unit cell with a negligible amount of secondary phases. The secondary phase in Co-BLT was the expected cobalt-based phase because Co easily forms cobalt

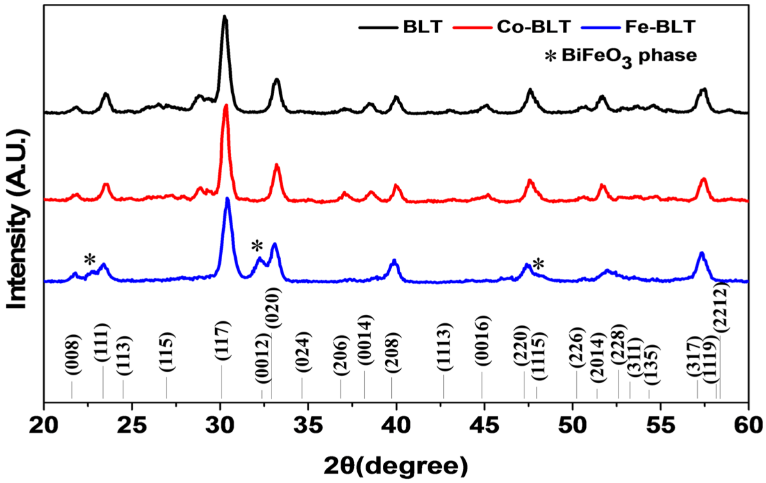

**Figure 2 The XRD patterns of BLT, Co-BLT and Fe-BLT powders.** The vertical lines indicate the position of ICSD No. 150091.

oxide phases (typically $Co_3O_4$ or CoO). The secondary phase in Fe-BLT confirmed that the $BiFeO_3$ phase had formed, which is similar to the data previously reported [17]. This phenomenon was attributed to the formation of a $BiFeO_3$ phase synthesized from Bi and Fe.

The morphological and microstructural properties of all samples were examined by SEM. Figure 3 (a), (b), (c) show the microstructures of the BLT, Co-BLT, and Fe-BLT. All the specimens consisted of plate like grains with a random orientation of plate-like grains because they have an almost anisotropic crystal structure. The plate-like grain organization was reported to be the typical properties of bismuth layer-structured ferroelectrics. The microstructure is dominated by the presence of polygonal edges grains. As expected from XRD, SEM confirmed that the grain size and shape in a series of samples were identical to each other.

UV–vis absorption spectroscopy was used to determine the band gap of the samples. Figure 4 shows the optical band gap ($E_g$) of the samples (BLT, Co-BLT, Fe-BLT) evaluated by UV–vis absorbance spectroscopy at wavelengths from 200 to 800 nm. The optical band gap is related to the absorbance and photon energy according to the following equation:

$$\mathrm{h}\nu\alpha \propto \left(\mathrm{h}_{\nu} \text{-} \mathrm{E}_{\mathrm{g}}\right)^{\mathrm{m}}$$

where α is the absorbance, h is the Planck constant, ν is the frequency of the incident photon, $E_g$ is the optical bandgap, and m is a constant associated with the different types of electronic transitions. The $E_g$ values of the samples were measured by extrapolating the linear portion of the curve or tail towards the x-axis [18].

As a result, the optical band gap of the BLT, Co-BLT and Fe-BLT samples were 2.75 eV, 1.85 eV and 2.02 eV, respectively. Although both doped BLT samples showed a dramatically decrease in the optical bandgap, the optical bandgap of the undoped BLT samples agreed well with the reported values. The band gap tuning due to the transition from O 2p to transition metal 3d state were suggested in Co doped BLT [19] and similar analogy can be applied to Fe doped BLT. Cobalt atoms are better for the tunability of the optical bandgap in BLT than iron. On the other hand, Fe-BLT shows much sharper transition in the absorption spectra than Co-BLT, as shown in Figure 4. This dispersive transition of the optical bandgap in Co-BLT was observed, even in the superlattice form. Although the nominal bandgap was narrower in Co-BLT than Fe-BLT, this dispersive transition of the bandgap of Co-BLT can be an obstacle to realizing an actual device.

XRD revealed secondary phase in the Co-BLT sample. On the other hand, the secondary phase did not contribute to the reduction of the optical bandgap. This is because the bandgap tuning could not be realized with a significant amount of cobalt-rich secondary phases from Bruggenman EMA simulation [19], and formed a negligible amount. The amount of secondary phases in Fe-BLT was higher than Co-BLT. On the other hand, the secondary $BiFeO_3$ phases did not have a direct effect on the reduction of the optical bandgap in the Co-BLT sample. Indeed, reports of the optical band gap of $BiFeO_3$ (2.67 eV) are similar to BLT [20]. Therefore, the decrease in band gap was attributed to Fe doping in BLT.

Consequently, the substitution of BLT by Fe and Co affects the optical properties dramatically. Cobalt and iron atoms are responsible for the modification of the electronic structure in the BLT based oxides. These conditions can be correlated with the renormalization of the electronic band structure and band-gap energy. In the case of BLT, the band structure is generally defined by the Ti 3d level (conduction band) and O 2p level (valence band) [21], and the incorporated dopants of Co, Fe are

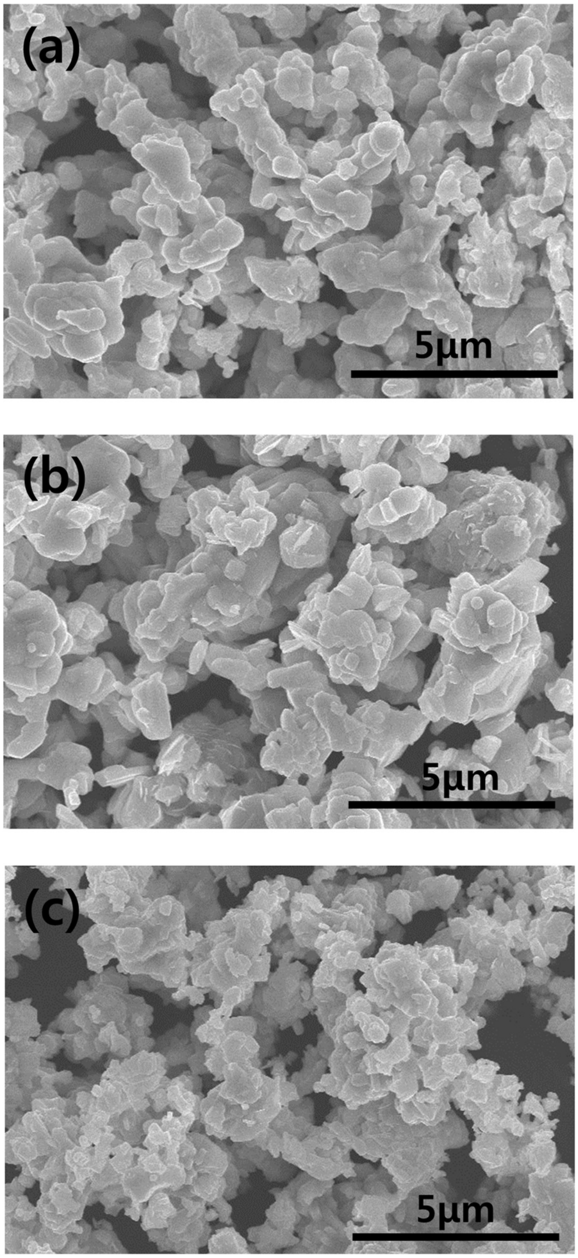

**Figure 3** SEM images of (a) BLT, (b) Co-BLT, (c) Fe-BLT samples.

more electronegative than Ti, whose energy level is lower than that of Ti 3d, thus leading to a lowering of conduction band and narrowing of band gap. In addition, it was reported that the Fe-doped ferroelectric system showed a promising magnetoelectric effect for this material. For example, V. R. Palkar et al. reported the conversion of ferroelectric $PbTiO_3$ to a magnetoelectric system by partly substituting Ti with Fe [22]. Moreover, ferrimagnetism were observed on $LaFeO_3$ doped BLT structure [23]. It implies that this approach might lead to similar magnetic properties in doped BLT.

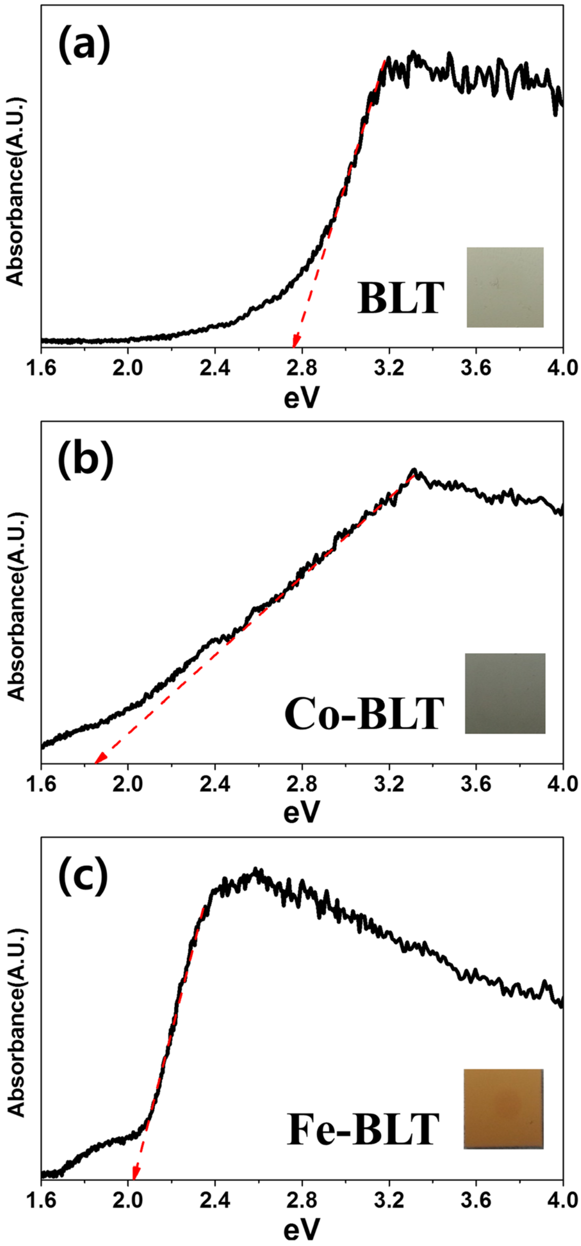

**Figure 4 UV–vis absorbance spectra of the BLT-based powders, (a) BLT, (b) Co-BLT, (c) Fe-BLT.** The extrapolation lines (dashed lines) indicates the optical band gap. The $E_g$ value can be obtained by extrapolating the linear segments of the curves towards the x-axis. The optical images of the the doped powers showed clear change of the color with the changes of bandgap energy (inset).

## 4 Conclusion

The substitution of Ti with Co or Fe atoms was used for chemical doping in the Co-BLT and Fe-BLT powders to control the bandgap. As a result, the band gaps of BLT, Co-BLT and Fe-BLT powder were approximately 2.75 eV, 1.85 eV and 2.02 eV, respectively. Both doped atoms in the

BLT samples showed a comparable reduction of the optical bandgap, but Fe-BLT showed a much sharper absorption transition in the UV–vis measurements than Co-BLT. Band gap control by chemical doping is expected to be applicable to other complex oxide materials, and will provide a new tool for manipulating oxide optoelectronics.

### Competing interests
The authors declare that they have no competing interests.

### Authors' contributions
JYH carried out the growth of sample, the sturcutral and optical measrements, drafted the manuscript. CWB conceived of the study, and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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