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A study into the optoelectronic property of $Bi_{2+\delta}Cr(TM)O_{6+X}$ (TM = Fe, Mn) on prospective of photovoltaic application

Summary

Here, we synthesized $Bi_{2+\delta}Cr\ TM\ O_{6+X}$ (TM = Fe, Mn) thin films on fluorine-doped tin oxide (FTO) coated glass substrate by spin coating. $Bi_{2+\delta}CrFeO_{6+X}$ (BCFO) and $Bi_{2+\delta}CrMnO_{6+X}$ (BCMO) thin films exhibit a monoclinic crystal structure with an indirect band gap of 1.34 eV and 1.43 eV, respectively, exhibiting a significant reduction in the band gap in contrast to single perovskite oxides such as $BiFeO_3$, $BiCrO_3$, and $BiMnO_3$. Furthermore, solar cells (SCs) were fabricated with suitable hole- and electron- transfer layers based on band alignment. Albeit small, both BCFO and BCMO based SCs show photovoltaic (PV) conversion efficiencies, 0.09 % and 0.24 %, respectively.

Keywords: Perovskite Solar Cells, BCFO, BCMO, Double-perovskites

1. Introduction

ABO_3 perovskite oxides have attracted significant attention due to their diverse functional properties, such as ferroelectricity, magnetism, and metal-to-insulator transition, to name a few (Nechache et al, 2014). Certain ferroelectric (FE) oxides, mostly perovskites have been also shown to demonstrate anomalous photovoltaic response with beyond bandgap photovoltage (Chakrabartty et al, 2018). Unlike conventional p–n junction based photovoltaic devices, where charge separation occurs by intrinsic built-in field due to asymmetric device structure, in FE-based PV devices, intrinsic polarization induced electric field (Chen et al., 2015) is thought to be responsible for the separation of the photo-induced charge carriers. However, the photovoltaic conversion efficiency in traditional FE-based PV device is typically very small, presumably due to wide bandgap vis-à-vis tiny photocurrent. Therefore, tailoring bandgap by combining multiple transition metals stabilized in double perovskite oxide structure could be a viable option to realize a new class of photovoltaic materials.

The search for different compositions of bismuth-based double perovskite has led to combinations such as Bi_2FeCrO_6, Bi_2MnCdO_6, Bi_2FeMnO_6, Bi_2MnMoO_6, Bi_2CrCoO_6, Bi_2CrNiO_6, Bi_2FeNiO_6, Bi_2FeZnO_6, Bi_2CrZnO_6, and Bi_2CoZnO_6 (Kumar et al., 2023; Parsad et al., 2024; Ravi et al., 2017; Lin et al., 2019). Indeed, BCFO demonstrated early promise showing more than 1 % conversion efficiency (Meng et al. 2020). However, most other oxide-double perovskite materials have remained unexplored for prospective photovoltaic applications.

Here, we study the structural, optical, and photovoltaic response of bismuth-based oxide double-perovskites, specifically BCFO and BMCO, synthesized via solution processing. Film deposition for device fabrication uses spin coating on an FTO-coated glass substrates. The intermediate layers, SnO_2 and Spiro-OMeTAD, act as electron transport layer (ETL) and hole transport layer (HTL), respectively. Meanwhile, FTO and a thin silver film function as the anode and cathode, respectively.

2. Results and discussions

Fig. 1(a) shows the powder X-ray diffraction (p-XRD) patterns of BCFO and BCMO indexed using monoclinic crystal symmetry bearing the space group of *P2* (#3). For the (211) planes, two prominent reflections are observed at 27.66˚ and 28.79˚. Field-emission scanning electron microscopy (FESEM) images reveal that BCFO films consist of densely packed rod-like structures, whereas BCMO films exhibit a network-like morphology. Datta et. al. (2023) reported that the addition of an additive improved the

morphology of $MAPbI_3$ films, transforming a relatively less dense structure into a denser and less pinhole one, significantly enhancing their photovoltaic performance. The Energy-dispersive X-ray spectroscopy (EDX) analysis confirms that the elemental compositions of Bi: Fe: Cr in BCFO and Bi: Mn: Cr in BCMO are approximately 2.1:1:1, respectively.

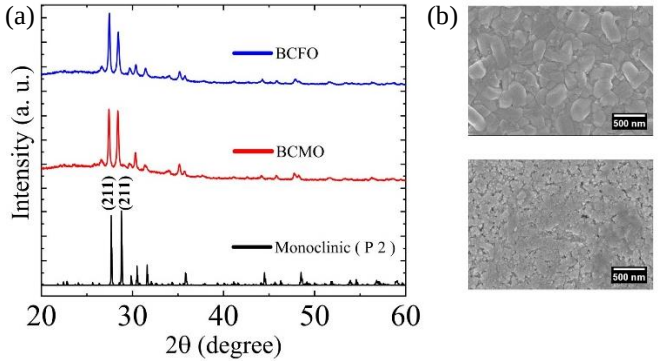

Fig. 1: (a) p-XRD pattern of BCFO and BCMO, (b) FESEM image of BCFO and BCMO, respectively

The optical properties of the films were studied using UV-Visible spectroscopy. The band gap energy was determined based on the Tauc relations.

$$\alpha h\nu = B\,(h\nu - E_g)^n \tag{1}$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, B is a constant, E_g is the band gap energy, and n is ½ or 2 for direct and indirect excitation, respectively. The band gap energy was determined from the x-intercept of the tangent to the linear region of the $(\alpha h\nu)^n$ vs. $h\nu$ plot.

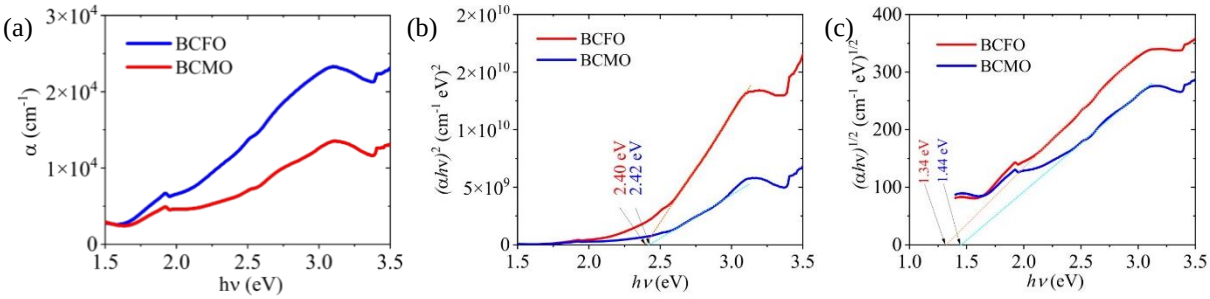

Fig. 2: (a) The absorption coefficient of BCFO and BCMO, (b) the direct band gap energy, and (b) the indirect band gap energy using Tauc's plot

As shown in Fig. 2, the absorption coefficient for both materials is ~10^4 cm^{-1}, comparable with perovskite solar cells having better performance (Targhi et al., 2018). The band gap of BCFO and BCMO are 1.34 eV and 1.44 eV, respectively, comparable to the band gap (~1.4 —1.5 eV) of lead-based perovskites which are known for their high photovoltaic conversion efficiency (Targhi et al., 2018). Contrastingly, the band gap of pristine $BiCrO_3$ (~2.4 eV), is significantly reduced by doping with Fe and Mn atoms (Nie et al., 2016), thereby enhancing solar absorption in the visible region and potentially improving the photovoltaic conversion efficiency of the device.

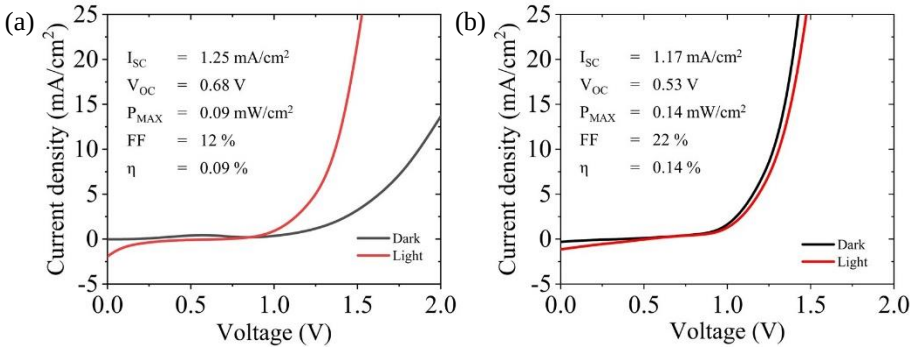

Fig. 3: current density-voltage plot of photovoltaic cell based on (a) BCFO and (b) BCMO as light absorbing layer

Fig. 3 shows the current density-voltage (J-V) characteristics of FTO/SnO2/BCFO/Spiro-OMeTAD/Ag and FTO/SnO2/BCMO/Spiro-OMeTAD/Ag devices. For the BCFO (BCMO) devices, the short circuit current density (J_{SC}), open circuit voltage (V_{OC}), and fill factor (FF) are 1.25 (1.43) mA/cm^2, 0.68 (0.54) V, and 0.12 (0.31) %, respectively. The corresponding photovoltaic conversion efficiencies are 0.09 % for BCFO and 0.24 % for BCMO.

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