

Cu-DOPED BiFeO₃ THIN FILM MATERIALS FOR SOLAR SUPERCAPACITOR DEVICE

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Abstract

BiFeO₃ (BFO) has attracted much research attention as the material has variety of properties, including multiferroic effect, photovoltaic effect and high specific electrical capacitance. In this work, we have measured the photovoltaic effect and electrical capacitance of Cu-doped BiFeO₃ synthesized by the simple solution method. Then we construct a so-called “solar supercapacitor” which can both generate electricity and store energy in one single device. This provides a conceptual guideline which help reducing the cost of components for the solar cell system with energy storage. It also demonstrates a new type of simple device which can measure accumulated solar energy as a function of time.

Keywords: Bismuth ferrite, BiFeO₃, photovoltaic effect, energy storage, solar supercapacitor

Introduction

Multiferroic BiFeO₃ (BFO) has attracted much research interest as electrode materials for supercapacitors with high specific capacitance (Suzuki *et al.*, 2002; Imoto *et al.*, 2003; Murakami *et al.*, 2006; Ramasamy *et al.*, 2008). Wide range of interesting properties such as high Neel temperature of 370°C and strong ferroelectric order at high Curie temperature of 830°C have been observed in BFO which are suitable for potential applications spanning spintronics, magnetoelectric sensors and photovoltaic devices (Baek *et al.*, 2010; Yang *et al.*, 2010b; Yang *et al.*, 2009). The atomic structure of BFO is rhombohedral with R3c space group. It possesses high electrical conductivity which is a result of carrier hopping between Fe³⁺ and Fe²⁺

upon dielectric relaxation process. Moreover, various metal oxides (i. e. Co (Khajonrit *et al.*, 2018), La (Reddy *et al.*, 2018), and Cu (Khajonrit *et al.*, 2016)) have been substituted into BFO structure to improve its electrical and electrochemical properties. Recently, Cu-doped BFO (BiFe_{0.95}Cu_{0.05}O₃ electrode) has been reported with high specific capacitance up to 568.13 F/g at current density 1 A/g and retention of 77.13% after 500 cycles (Khajonrit *et al.*, 2016). This is attributed to the mixed oxidation states of Fe and Cu in the structure resulting in the observed pseudocapacitive behavior. Numbers of preparation techniques on BFO-based-supercapacitor such as solid state synthesis and electrodeposition have been reported

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with high specific capacitance and retention of up to 72.7 F/g and 82.8% after 1500 cycles, respectively (Jadhav *et al.*, 2016; Han *et al.*, 2017) which emphasize the use of BFO in energy storage applications.

There are reports that metal oxides can generate some voltage through light irradiation (Ruhle *et al.*, 2012; Kupfer *et al.*, 2015; Chatterjee *et al.*, 2016). This is due to the photovoltaic effects which have recently received much interest in solar cell application. Particularly, ferroelectric oxide solar cells constructed from (Sharma and Singh, 2016) ferroelectric materials are one of the interesting topics motivated by the intrinsic photovoltaic due to their spontaneous polarization. Investigation of ferroelectric photovoltaic effect was originally explored in several perovskite oxides such as BaTiO₃ (Brody and Crowne, 1975), PbTiO₃ (Windsch, 1980). Essential properties such as band gap and its conductivity can be tuned through chemical substitution making them a suitable candidate for thin film ferroelectric photovoltaic (Basu *et al.*, 2008). Recently, very large photo responses in BFO up to 15 V have been discovered which is vitalized the third generation solar cells (Yang *et al.*, 2010b).

In this work, we are interested in combining both of these interesting effects into one single device which we call “solar supercapacitor” device. We will show that each of our BFO devices can either have photovoltaic effect by looking at the power-conversion-efficiency measurement or store electrical energy from the charge-discharge measurement. Then, we will demonstrate that both of these two effects can co-exist in one single device.

Experimental Setups and Sample Preparations

5% Cu-doped BiFeO₃ powder was prepared following the method reported in the literature (Khajonrit *et al.*, 2016). The Cu/BFO nanopowders were synthesized by using a simple solution method.

The obtained powders were calcined at 600°C for 3 h in air with heating rate 10°C/min. The calcined powders were pressed into the pellets having diameter of 2 inch and sintered at 800°C for 3 h then obtain the Cu/BFO sputtering target. After that, Cu doped BFO thin film was coated onto FTO-glass substrates (sheet resistance of 8 Ω/sq, Solaronix) with an active area of 1 cm², using RF-magnetron sputtering technique. The thickness of BFO film is approximately 700 nm. Then a thin layer of Cu with thickness of around 40 nm was added for surface protection. For activated carbon (AC) electrode, we made a solution mixing 9 g activated carbon, 2 g carbon black, 2 g Styrene-Butadiene Rubber/Sodium Carboxyl Methyl Cellulose (SBR/CMC, Targray) binder and 115 ml deionized water together. The solution was ball-milled for 24 h. Then, the AC solution was coated on FTO-glass substrate by doctor blade technique and heated at 80°C for 30 min. Both types of these electrodes were then used for creating solar-supercapacitor devices. For photovoltaic measurement, the light sources were a 450 nm laser with 28 mW power and AM 1.5G solar simulator (PhotoEmission Tech model SS100AAA). Galvano-statics charge discharge measurements were performed by using Metrohm Autolab model PGSTAT302N with FRA32M module. The voltage and current measurements were performed using Agilent sourcemeter model B2901A.

Results and Discussion

To demonstrate the properties of BiFeO₃ solar supercapacitor, we measure a) the photovoltaic effect, b) the electrical capacitance from the charge-discharge measurement and c) then both of the two effects in one single device as described in the following. To measure the photovoltaic effect, we create a simple device by firstly sputtering BiFeO₃ with approximate 0.7 micron thickness on transparent F-doped tin oxide (FTO) glass and then putting aluminum (Al) electrode on the other side of BFO film (Figure 1(c)). These act as two electrodes

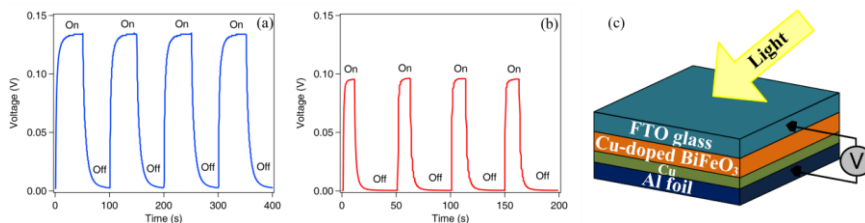


Figure 1. Voltage versus time of Cu-doped BFO device as a function of a) violet laser b) simulated solar irradiations. c) Schematic diagram of Cu-doped BFO device and measurement setup

where one side is transparent, allowing the light to pass through. By shining the 450 nm laser with power of 28 mW through the FTO electrode, the observed voltage difference across the two electrodes is shown in Figure 1(a) and the highest voltage is around 0.13 V after exposure of 50 sec. Note that because the bandgap of BFO is around 2.61 eV (Agrawal *et al.*, 2014) which corresponds to wavelength of 475 nm, so we select the wavelength of our laser to be 450 nm which is slightly below this value to excite the BFO films. Similar effect is observed when using the light from solar simulator where the highest voltage difference is around 0.10 V after exposure of 10 sec. To measure the photocurrent and solar cell efficiency, the measurement diagram is shown in the inset of Figure 2. In Figure 2 (a), when the light is off, the I-V curve is shown in black line and when the laser is on, the I-V curve (blue line) moves up showing the character of solar cell where some photocurrent is generated with maximum current I_{sc} of 0.28 mA ($J_{sc} \sim 7 \text{ mA/cm}^2$). The power conversion efficiency (PCE) is calculated to be around $1.6 \times 10^{-5}\%$. Similar effect is observed in the case that uses the light from solar simulator; the maximum current I_{sc} is measured to be 0.24 mA ($J_{sc} \sim 0.24 \text{ mA/cm}^2$) and the PCE is calculated to be around $0.26 \times 10^{-5}\%$. These results show that our BFO samples can exhibit the property of solar cell similar to previous studies (Yang *et al.*, 2009; Yang *et al.*, 2010b). This pronounce voltage difference may be further enhanced that the depolarization field causes charge separation in ferroelectric BFO sample (Pilch and Molak, 2014). Then, to show that BFO itself can store some electrical energy, we construct a supercapacitor device (see the inset of Figure 3) using BFO film on FTO glass as one electrode and activated carbon film on FTO glass as the other electrode where the two electrodes are separated by parafilm and the electrolyte is 6M KOH solution. We then perform the galvanostatic charge-discharge measurement of this supercapacitor device with charging current of 0.15 mA for 1 min and discharging current of 0.07 mA. The capacitance of

the device with area of 1 cm^2 is measured to be approximately 0.4 mF from the charge-discharge data as shown in Figure 3. Although leakage current is observed, similarly to previous reports (Yang *et al.*, 2010a), this charge-discharge curve clearly shows that some energy can be stored into this device, as previously shown in (Jadhav *et al.*, 2016; Khajonrit *et al.*, 2018). Then for the last step, to demonstrate that the device can exhibit the property of solar supercapacitor, we shine the laser on the supercapacitor device from the BFO side (see the diagram in the inset of Figure 4) and observe the change in voltage across the two electrodes of the supercapacitor device as a function of time. As shown in Figure 4(a), when the laser is on, the

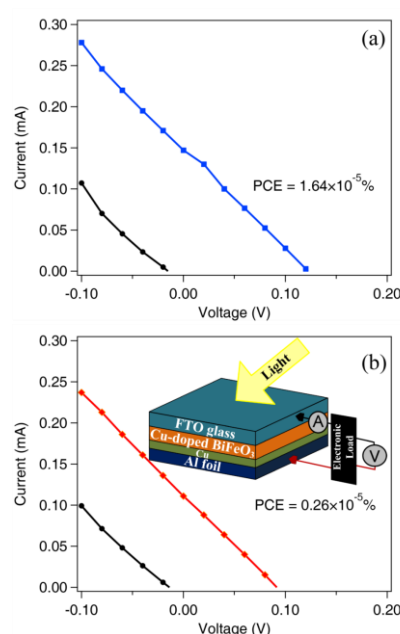


Figure 2. Photocurrent versus voltage (I-V) curves of Cu-doped BFO device a) violet laser (blue curve) and b) simulated solar (red curve) irradianations compared to the dark condition (black curves). The solar efficiency measurement is represented in the inset

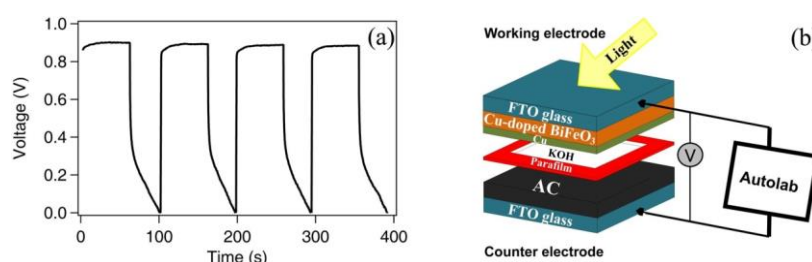


Figure 3. Galvanostatic charge-discharge of the Cu-doped BFO/AC cell a) Schematic illustration of Cu-doped BFO/AC cell b)

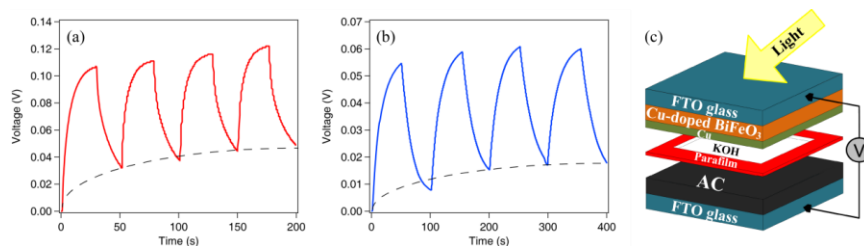


Figure 4. Voltage versus time of the Cu-doped BFO/AC cell with a) violet laser b) simulated solar irradiations. Dashed lines indicate the remnant voltage in the absent of light irradiations

voltage difference becomes higher, similar to the first case in Figure 1. However, after several on-off exposures of laser, the voltage curve becomes different from Figure 1 as the remnant voltage becomes higher every time after each on-off cycle; this is shown by the dash line in Figure 4(a). Similar effect is also observed when changing the light source to the solar simulator. The higher value of this remnant voltage indicates that more energy can be stored in the solar supercapacitor device every time when exposed to either the laser or the solar simulator. Hence, this has then unambiguously demonstrated that our BFO device can act as a solar supercapacitor which can both generate electricity and store energy in one single device.

Summary

In this work, we have shown that the 5% Cu-doped BiFeO₃ sample can exhibit photovoltaic effect with maximum voltage difference of 0.13 V and 0.10 V when exposed to the 450 nm laser and the AM 1.5G solar simulator, respectively and can also store electrical energy as a supercapacitor. By constructing the supercapacitor device whose one side of electrode is transparent, allowing the light to reach BFO film, we can demonstrate that this can exhibit the property of a solar supercapacitor which can act both as a solar cell and supercapacitor energy storage. Although the performance of the device is still limited, this provides a new conceptual design which can combine both photovoltaic effect and energy storage property in one single and simple device. It may also find application as a solar-powered sensor or a new type of sensor which can measure the *accumulated* solar energy through the increasing voltage.

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