EFFECT OF Zr AND Bi DOPANTS ON THE ENERGY EFFICIENCY OF dssc TiO_2 SOLAR CELLS

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ABSTRACT

Research into alternative energy sources has gained popularity in recent years due to the increasing demand for energy as the world's population grows and fossil fuels become scarcer. For this reason, energy has become one of the most important areas of scientific research in recent times. Although studies have been carried out on this subject in our country, more comprehensive research is needed to bring it to an adequate level. This study, which was carried out to increase the use of renewable energy, is aimed to contribute to the protection of the world and the environment.The aim of this study is to obtain doped TiO_2 dye-sensitised solar cells to obtain high-efficiency, low-cost solar cells that generate electrical energy using solar energy, which is an important resource . Bismuth and Zirconium were doped at 1% and 3% in the study. Characterisations were carried out by XRD, SEM, EDS. Band gap and efficiency measurements of photo anodes were performed. The band gap increased with the addition of Bi and Zr.

Keywords: effect, Zr, Bi, dopants, energy, dssc TiO_2, solar cells.

INTRODUCTION

With the increase in the world population, industrial development and technological advancement, the demand for energy worldwide is increasing. Meeting this energy demand is important for economic, political and environmental stability (Lewis, 2005). The gradual decline in oil production poses an enormous challenge that affects economic outcomes due to increasing energy demand (Hamann et al, 2008; Hirsch, 2008). In addition, the world has focused on carbon-free energy due to environmentally damaging gases from the combustion of fossil fuels and global warming (Al Dahoudi et al., 2013). Graphic 1 shows the projection of world energy demand until 2028 (IEA, 2023). Renewable energy capacity additions will continue to grow over the next five years, with solar PV and wind accounting for a record 96% of the total, as their generation costs are lower than both fossil and non-fossil alternatives in most countries and policies continue to support them. Solar PV and wind additions are forecast to more than double by 2028 compared to 2022, breaking records throughout the forecast period to reach nearly 710 GW.

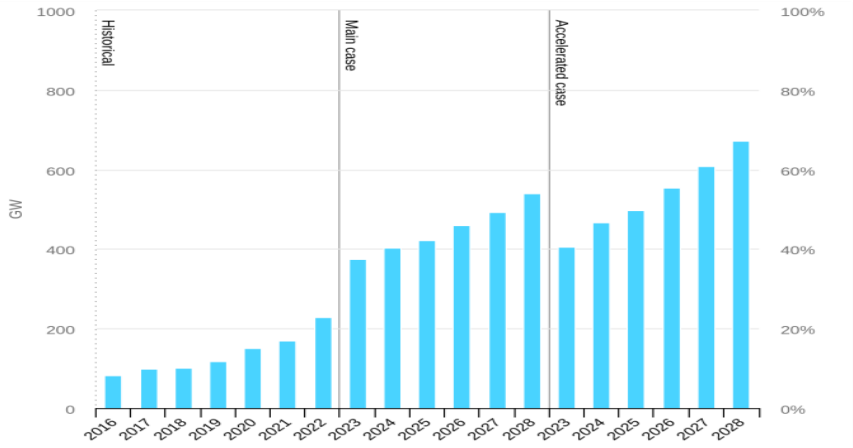

Figure 1. Renewable Solar PV electricity capacity additions by technology and segment, 2016-2028 (www.iea.org)

Energy consumption is one of the most effective indicators of a country's level of development. Today, when energy resources (oil, coal and natural gas) are limited, research into alternative or sustainable energy sources has increased in recent years. Among the sustainable energy sources, solar energy attracts the most attention. There is an energy of 3X1024 joules/year coming from the sun to our world. This energy is 10000 times more than the energy consumed in the world so far. A solar cell covering 0.1 per cent of the Earth's surface and operating at only 10 per cent efficiency has the potential to meet all current energy needs (Ajder, 2011).

The fact that sunlight is an infinite, ideal, clean and unlimited source of energy will make it possible to increase the use of solar energy through the effective, efficient and cost-effective conversion of solar energy into electricity using advanced technology (Lewis, 2007).

Solar energy attracts the most attention among sustainable energy sources. There is a 3X1024 joule/year energy coming from the sun to our world. This energy is 10000 times more than the energy consumed so far in the world. A solar cell that will cover 0.1 per cent of the Earth's circumference and operate with only 10 per cent efficiency has the potential to meet all current energy needs (Ajder, 2018).

Large-scale utilisation of photovoltaic devices for electricity generation is currently very expensive, with production from existing commercial devices being about ten times more expensive than conventional methods. In 1991, O'Regan and Grätzel were the first to produce a photovoltaic cell formed from low to medium purity materials by low-cost processes that exhibited a commercially realistic energy conversion efficiency. The device is based on a 10 µm thick, optically transparent film of titanium dioxide particles several nanometres in size, which is coated with a charge transfer dye layer to sensitise the TiO2 film for solar light harvesting. Due to the high surface area of the semiconductor film and the ideal spectral properties of the dye, the device collects a high proportion of the incident solar energy flux (46 %) and converts the incident photons into electric current (more than 80 %). The overall light-to-electricity conversion efficiency is 7.1-7.9% in simulated sunlight and 12% in diffuse daylight. The resulting dye-sensitised (DSSC) solar cells have large current densities (greater than 12 mA cm-2) and exceptional stability. DSSC have been shown to enable low-cost, practical applications (O'Regan and Grätzel, 1991).

Dye Sensitised Solar Cells (DSSC)

A dye-sensitised solar cell (DSSC) is a semiconductor-based photovoltaic device that converts both artificial and natural (solar) radiation directly into electric current. Unlike conventional systems where the semiconductor takes on both light absorption and charge carrier separation and transport tasks, the two functions are separated in a DSSC. In a conventional DSSC, light is absorbed by a sensitiser fixed on the surface of a wide bandgap semiconductor. This hybrid device, often referred to as a Grätzel cell, was first reported in 1991 with the seminal publication by Brian O'Regan and Michael Grätzel, who presented to the scientific community a device made of sensitised nanocrystalline TiO2 with a power conversion efficiency of 7.1%. DSSCs are probably the cheapest photovoltaic technology available today and their efficiency has been continuously improved over the last 25 years.

In general, the conversion of visible light into electricity by DSSCs is inspired by the plant's photosynthesis process (Abdel-Latif et al., 2015). The dye applied in DSSCs absorbs light and provides electron excitation, similar to the function of chlorophyll in plants. The mobile electrons are then captured by an electron acceptor before emission

(Hug et al., 2014). However, the insufficient efficiency and stability of DSSCs make their widespread commercialization difficult (Fakharuddin et al., 2014). The maximum achievable energy efficiency has been reported as 32% and 13% for theoretical and practical results, respectively (Snaith, 2010; Mathew et al., 2014).

MATERIALS AND METHOD

Production of dye sensitized solar cells : Within the scope of the experimental studies, DSSC solar cells were fabricated using TiO_2 photoanode and TiO2 photoanodes doped with Zr, Bi, (1% and 3%) and Ruthenizer 535-bisTBA (C58H86O8N8S2Ru) as dye sensitizer. FTO (fluorine-doped tin oxide coated glass) electrodes were used in solar cell production. FTO conductive glass substrates were first washed with ethanol, distilled water and acetone in an ultrasonic bath and dried in an oven at 100ºC. The properties of the electrodes are as in the table.

Table 1. Properties of FTO (fluorine doped tin oxide coated glass).

Glass Substrate (Conductive)	FTO
Thickness of glass (mm)	2,2
Transmittance (%)	80
Conductivity (ohm.m)	7

In the preparation of TiO_2-based pastes, the pechini method was used with starting materials of oxides related to hydroxyl acids. In the first stage, the starting materials (Titanium (IV) isopropoxide) were dissolved in 10 ml ethylene glycol, which reached 70 ˚C on a magnetic stirrer, for 15 minutes by adding slowly at 70 ˚C. The temperature of the solution was increased to 90 ˚C and citric acid was added. 0.5 ml of acetyl acetone was added as surfactant to the solution obtained by stirring for 15 minutes. Then oxides used in pastry making (Degussa P25 TiO2) were added. The mixture was stirred for approximately 1 hour to obtain a homogeneous consistency (Figure 3.51). Then ZrO_2 for Zr additive and BiI_3 for Bi additive dissolved in 2 ml of ethyl alcohol were added to the TiO2 paste prepared at 1% and 3% as given in Table 3.18 and stirred at room temperature for 24 hours in a magnetic stirrer . The paste was coated on the active surface of the microscope glass and FTO glass covering an area of 6x6 mm by spin coating at 1000 rpm for 30 s. The process was repeated until a homogeneous surface was obtained. Spin coating method was preferred for the production of homogeneously dispersed thin films. With this method, the film thickness can be produced in desired dimensions by adjusting the density of the solution used. In the study, the coating process of TiO2 and doped solutions was carried out with POLOS Spin 150 Rotational Coating Device. At 100 °C for 15 minutes , the masks were removed and dried on the heating surface. The photoanodes were heat treated at 500°C for 30 minutes in order to gain strength and remove the organics.

RESULTS

In this section, the characterisation of the photoanode part of the solar cells produced and the measurement results of the solar cells will be discussed.

XRD Phase Analyses : X-ray diffraction (XRD) is used for phase analyses of powder and solid materials to determine structural properties such as the amounts of these phases. The crystal structures of the photoanodes produced in this study were analysed by PANalytical EMPYREAN model X-Ray Diffractometer.

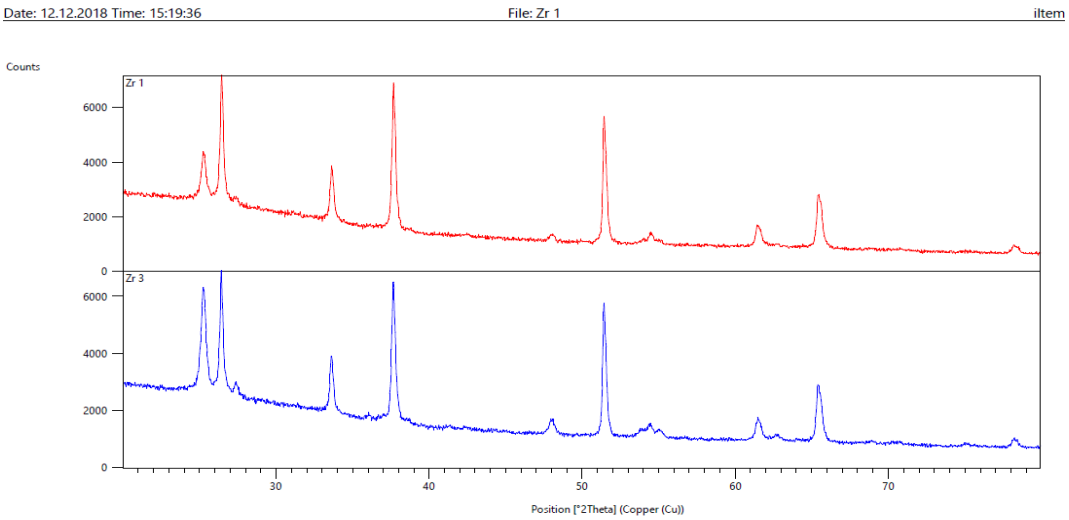

Figure 2. XRD analyses of TiO2 photoanode doped with 1% Zr and 3% Zr.

XRD phase analysis of TiO_2 thin films showed TiO_2 phases formed as seen XRD results in figüre 2 and 3.

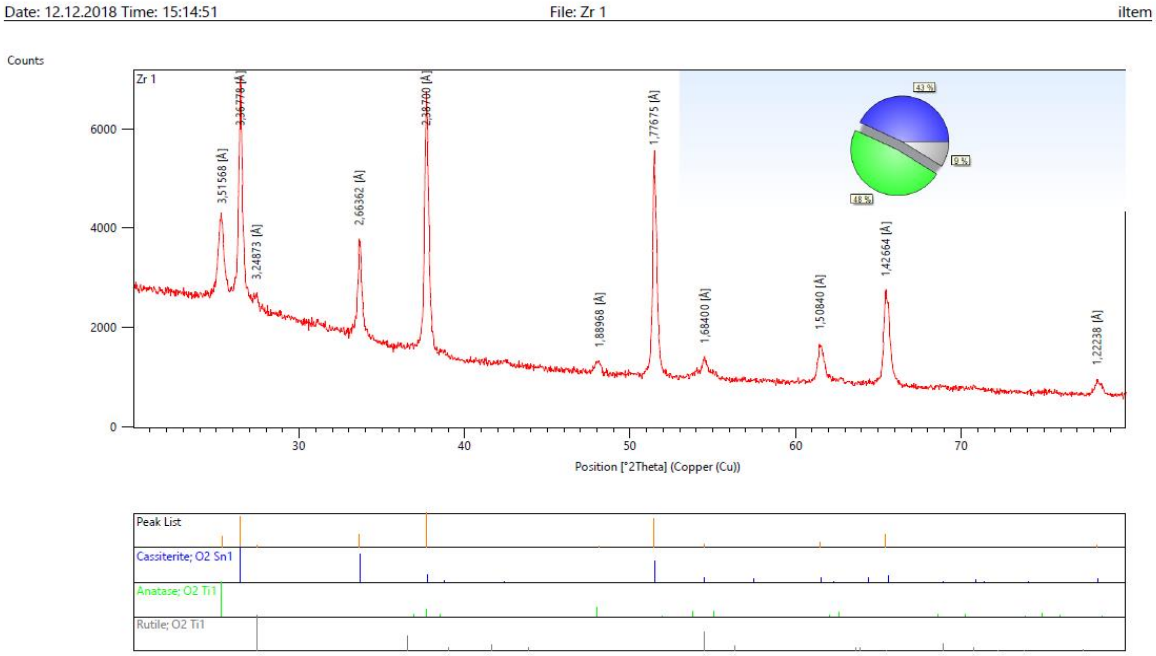

Figure 3. %1 Zr doped fotoanot TiO_2 XRD.

We observe that the anatase phase is the dominant phase with about 90% of TiO2 and the rutile phase is formed at a rate of 7%. SnO2 phases come from FTO glass. The doping elments and doping level have an effect on the peak size. In the case of Zr doping, we noticed that the peak size for the anatase phase did not change; however, the peak size decreased in the case of Bi doping. 1% and 3% are very low ratios, so no distinct peaks are -observed.

SEM Microstructure Analyses

Microstructure images of the produced photoanodes were taken at Kütahya Dumlupınar University ILTEM with FEI NovaNano SEM650 and EDAX Tridient chemical analyser. The elements in the structure were determined by energy scattering x-ray (EDS) spectroscopy as the basic chemical analysis technique.

The SEM surface image of Bismuth doped TiO2 thin films spin coated with Spin Coating is shown in Figure 4. SEM images show that the films can be produced homogeneously and the surface quality is good. In the SEM image taken at 400 nm, it is observed that the particles are in nano size .

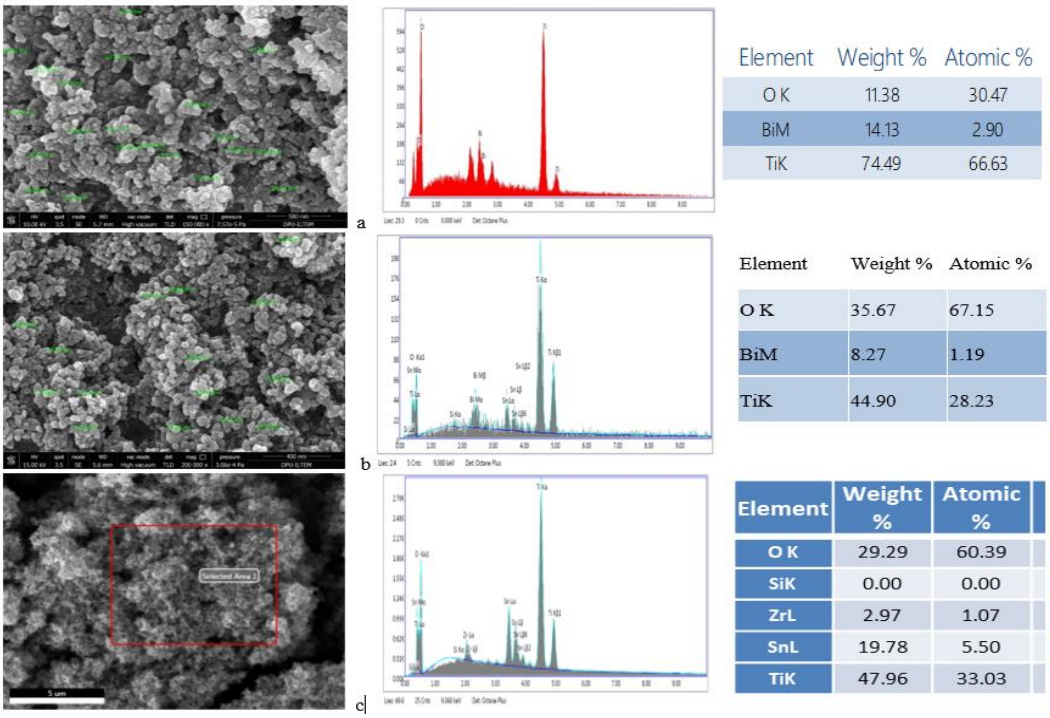

Figure 4. EDS - SEM for a) 3% Bi,b)1 % Bi and 1 % Zr Doped TiO_2.

Bandgap Analysis

Optical properties such as transmittance, absorption and reflection are very important parameters in determining the basic working principle of photovoltaic devices. The optical absorption spectra (400-700 nm) of TiO2 films were performed at room temperature with the Jasco brand V-730 model UV-Visible/NIR Spectrophotometer . Band gaps were measured according to tauc formula. Ti atomic radius is 1.45 angstrom; Zr atomic radius is 1.6 angstrom. The atomic radius of bismuth is 1.7 Angstrom. The bandgap of TiO2 has widened with the addition of Bi and Zr dopants that have shown in Figure 5-6-7.

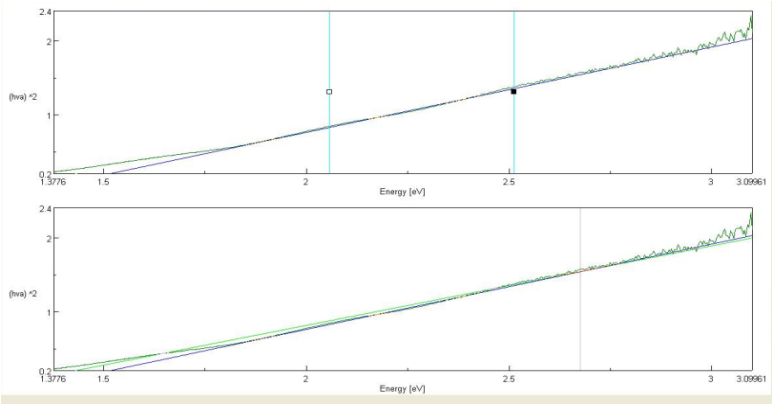

Figure 5. Band gap measurement value of TZ1 (2,67504eV).

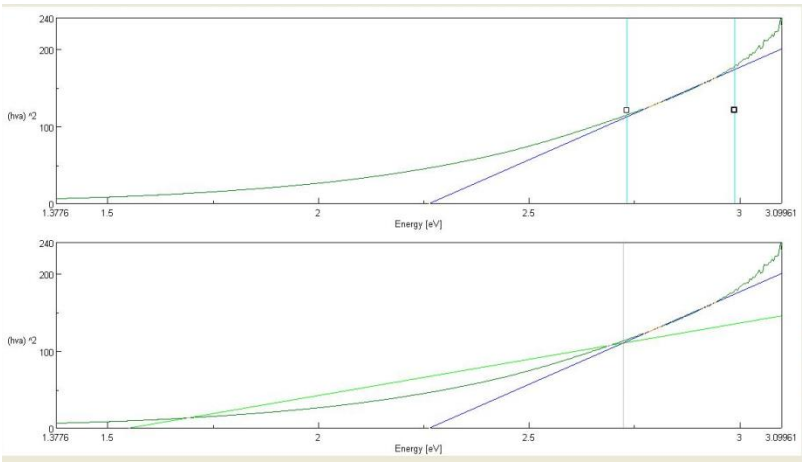

Figure 6. Band gap measurement value of TB1 (2,7228).

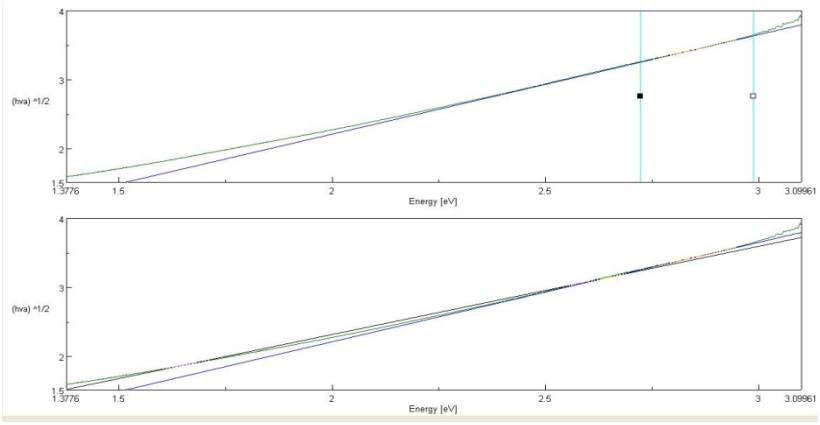

Figure 7. Band gap measurement value of TB1 indirect band gap (1,5).

The table shows the band gap measurement values of the experimentally produced doped TiO2 samples. Although the theoretical band gap of TiO2 is 3.2V, the band gap value obtained by the production method here is 2.48V. Band gap increased with Zr and Bi dopants as shown in table 2.

Table 2. Band Gap Measurement Values.

Sample		Band Gap (eV)
T/ Saf TiO_2	indirect	2,48803
%1 Zr doped TiO_2	direct	2,67504
%1 Bi doped TiO_2	direct	2,72194
%3 Bi doped TiO_2	indirect	2,97879

Current-Voltage (I-V) Measurements: DSSC photovoltaic performance

For the efficiency calculations of DSSC TiO2 solar cells, current-voltage (I-V) values were measured with the Keithley 2400 device shown in Table3. As shown in the table the short circuit current, I sc, and open circuit voltage, V oc, are measured at 0 V and 0 A, respectively. The overall solar-to-electrical energy conversion efficiency is also known as the power conversion efficiency, η, of the solar cell. It is calculated as follows (Hagfeldt et al., 2010)

η=JscVocFFPin (3.2)FF=PmaxJscVoc (3.3)Pmax=Imp×Vmp, where J sc is a short circuit photocurrent density, V oc is the open circuit voltage, FF is a fill factor of the cell and P in is the incident light intensity. FF is defined as the

ratio of the maximum power output per unit area solar cell, P max divided by V oc and J sc and the value is between 0 and less than 1. Whereas P max is defined as the product of the maximum current power, I mp , and voltage, V mp . The performance of the DSSC can be characterised using a photocurrent-voltage (IV) and power-voltage (PV) curves as shown in Table3 and 4 .

Table 3. 3% doped TiO2 current, voltage, FF% and efficiency values.

Dop	Voc(V)	Isc (A)	FF %	ŋ
Zr %3	0,6441	3,360 E-3	51,16	1,23
Bi%3	0,6571	3,512 E-3	53,65	1,38
TiO_2	0,5705	4,7520E-3	74,30	5,60

Table 4. 1% doped TiO2 current, voltage, FF% and efficiency values.

Dop	Voc(V)	Isc (A)	FF %	Ɒ
Zr %1	0,6534	2,958 E-3	44,91	0,96
Bi%1	0,4987	3,5408 E-3	36,63	0,72
TiO_2	0,5705	4,7520E-3	74,30	5,60

CONCLUSION AND RECOMMENDATIONS

According to these results, TiO2 phase was formed according to xrd results. It is seen in the SEM images that photoanode parts were formed at nanoscale and dopants have been incorporated into the system. Tthe addition of bismuth and zirconium decreases TiO2 efficiency. However, bandgap measurements show that the bandgap has also widened. It is known that the decrease in the band gap of the semiconductor will facilitate transmission for photovoltaic solar cells. With the addition of Bi and Zr dopant, the bandgap is widened. The reason for the decrease in efficiency is the band gap widening. he results of this study can be used in the studies of solar cells to be produced in order to utilise solar energy more efficiently. The bandgap of TiO2, which has a theoretical bandgap of 3.2 ev, has widened with the addition of Bi and Zr dopants. Ti atomic radius is 1.45 angstrom; Zr atomic radius is 1.6 angstrom. The atomic radius of bismuth is 1.7 Angstrom. The efficiency decreased as the atomic radius of the dopant increased.

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