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Colorization of 1-D photonic crystals with rare-earth element doping

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Abstract **–** Nowadays, nature-inspired structural colorization takes increasing attention due to its exceptional optical properties. One-dimensional (1-D) photonic crystals are new kind of optical materials which can be used to obtain structural colorization. In recent years many studies carried out about 1-D photonic crystals because of its simplicity and cost effectiveness. In this study, CuO/TiO_2 multilayer thin films were prepared by the sol-gel spin coating technique on the boron silicate substrate. To understand the effect of rare-earth element doping on structural colorization, Cerium and Europium ions doped CuO layers were prepared with different dopant concentrations. Structural and morphological properties of 1-D photonic crystals were investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and optical microscopy. Obtained results show that CuO/TiO_2 multilayer thin films with different Cerium and Europium concentrations were successfully prepared. Additionally, red and green colorization was achieved with different type and concentrations of dopant elements and more vivid colors were obtained as a result of the increment in dopant concentration.

Keywords *– Photonic Crystal, Thin film, Sol-gel, Rare-earth Doping, Structural Color*

I. Introduction

Colors can be obtained from chemical pigments or photonic structures. Structural colorization is a physical phenomenon that originates from refraction, scattering, diffraction of light with designed structures [1-3]. Due to properties like nonfading, pigment-free and brilliant colors, structural colorization will replace chemical pigments [4]. One of the main research topics about structural colorization is photonic crystals. Photonic crystals are arranged structures that can manipulate and control light throughout its structure and they can be produced different dimensions (1-dimensional (1D), 2- dimensional (2D) and 3-dimensional (3D)). Among them, due to practicality and production easiness 1-D photonic crystals have been much more studied in recent years [5]. 1-D photonic crystals consist of stacks of layers in periodicity with high refractive index contrast which generates photonic bandgap. Within the photonic bandgap, some frequencies in incident light are inhibited, reflected and these reflected frequencies form color [6-8].

The one-dimensional photonic crystals can be fabricated with different types of production techniques like electrodeposition [9], sputtering [10], chemical vapor deposition [11] and sol-gel processes [12]. Because of its advantages like cost-effectiveness, control over fabrication, and easiness make the sol-gel process an attractive method to produce 1-D photonic crystals. [13].

In this study one dimensional CuO/TiO_2 photonic crystals fabricated by the sol-gel process. In order to investigate the effect of rare-earth doping on colorization, copper oxide layer doped with Eu and Ce with different concentrations (0.30-0.45-0.60 wt%). The optical properties of 1-D photonic crystal heavily depend on the refractive index contrast between layers [14]. Therefore, copper oxide with n= 0.86 and titanium dioxide with n= 2.46 was chosen for the preparation of photonic crystals.

Materials and Method

Preparation of TiO_2 and CuO layers were prepared by the sol-gel process. Titanium (IV) isopropoxide (TTIP) and Copper (II) Acetate precursors were used as titanium and copper sources, respectively. Cerium (III) chloride hexahydrate and Europium(III) acetate hexahydrate were used as Ce (0.30-0.45-0.60 wt%) and Eu (0.30-0.45-0.60 wt%) doping source, respectively Ethanol and isopropanol were used as a solvent for the preparation of TiO_2 and CuO solution, respectively. Prepared solutions were coated on the borosilicate glass substrate by spin coating technique. Each sample was prepared by the sequential deposition of 5 layers and the first layer was started with the CuO layer in all samples.

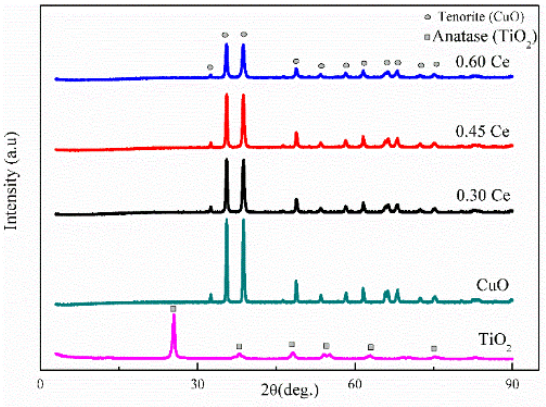
A. Characterization

The crystal structures and phase analysis of samples were investigated with X-ray diffraction (XRD) using Rigaku D/Max-2200/PC X-ray diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm) at 40 kV and 30 mA over 2θ range of 3-90º. The morphology of samples was examined with Scanning electron microscope (SEM) (JEOL-JSM 6060) and structural colors of samples were observed with the optical microscope. In order to investigate the optical properties of coatings UV-

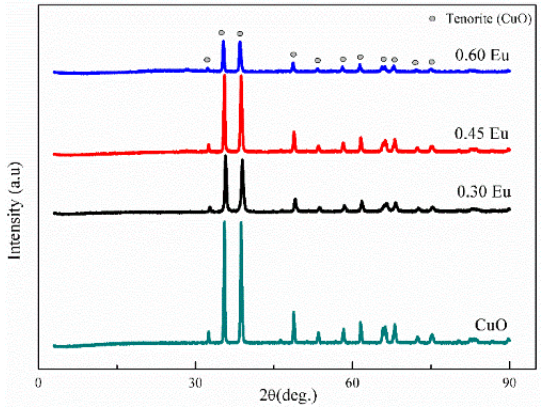
Vis Spectroscopy (Thermo Scientific Evolution 600 UV-VIS) was conducted in the visible range (400-700 nm).

II. Results And Discussion

In order to investigate phase structure, XRD analyze was conducted. XRD pattern of undoped, Ce and Eu doped CuO and TiO_2 samples is given in Fig.1. As seen from fig.1, CuO shows characteristic peaks at 32.5°, 35.5°, 38.7°, 46.28°and 48.84° corresponding to (110), (002), (111), (112) and (202) planes, respectively, which can be indexed as Tenorite phase in accordance with JCPDS card No. 41-0254. Also, The diffraction peaks located at 25.2°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, 74.0°, and 76.1° corresponding to (101), (004), (200), (105), (211), (204), (116), (220), (107), and (301), respectively observed which indicate Anatase phase in accordance with (JCPDS card No. 21-1272).



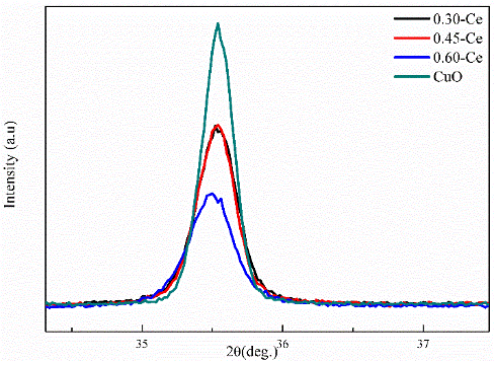
(a)



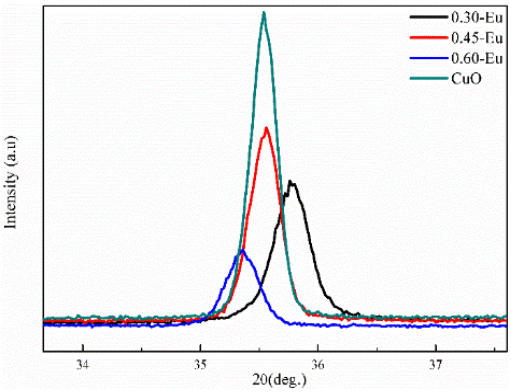
(b)

Fig 1. XRD pattern of (a) Ce and (b) Eu doped CuO samples.

In order to investigate the effect of doping on the crystal structure of CuO, the main peak of CuO of all samples were given in Fig. 2. The positions of (002) plane for the undoped CuO film shifted to small diffraction angles because of Eu and Ce doping process. The shift in diffraction angle indicating some change in the crystal structure of CuO due to the distortion effect of doping elements.



(a)



(b)

Fig.2. Main peak (002) of CuO samples doped with different rare-earth elements ((a)Ce and (b) Eu) and concentrations (0.30-0.45-0.60 wt%).

Fig. 3 shows SEM images of 0.45 wt% Eu (a-b) and 0.30 wt% Ce (c-d) doped coatings. It can be seen that from the images, some cracks observed on the surface of the Eu doped CuO coating. The presence of cracks in the structure is thought to be caused by the stress that occurs during the heat-treatment process. Besides, it can be seen from SEM images that Ce doping did not cause a significant change in coating morphology compared to Eu doping, even if it caused crack formation in the coating structure.

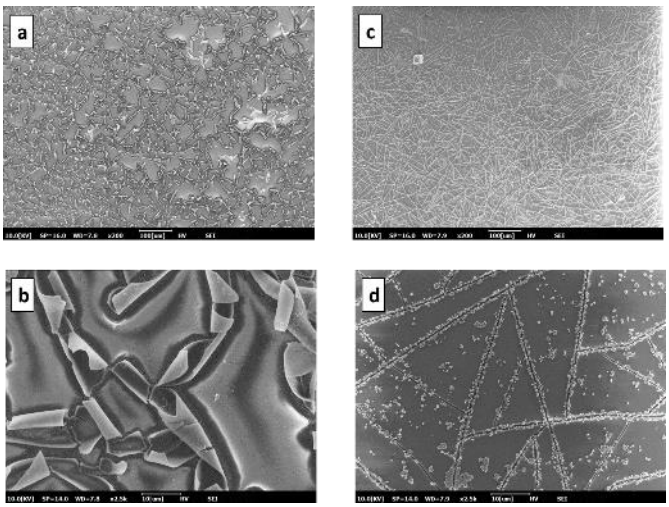


Fig.3. SEM images of (a-b) 0.45 wt% Eu doped and (b-d) 0.30 wt% Ce doped Coatings

Optical images of undoped and Ce doped samples are given in Fig. 4. In order to confirm the colorization of samples UV-Vis spectroscopy was conducted in the visible region (400-750 nm) and the reflectance spectrum of undoped and Ce doped samples is given in fig. 5.

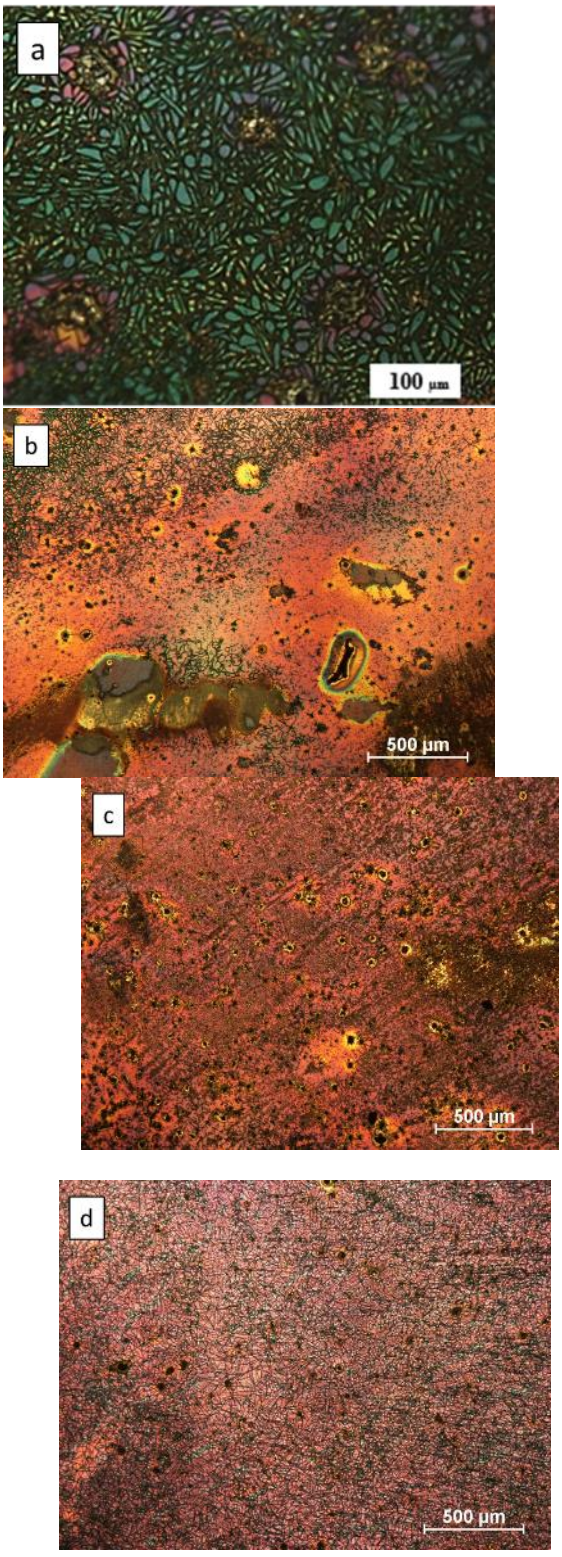


Fig.4. Optical images of (a) undoped, (b) 0.30 wt%, (c) 0.45 wt%, (d) 0.60 wt% Ce doped samples

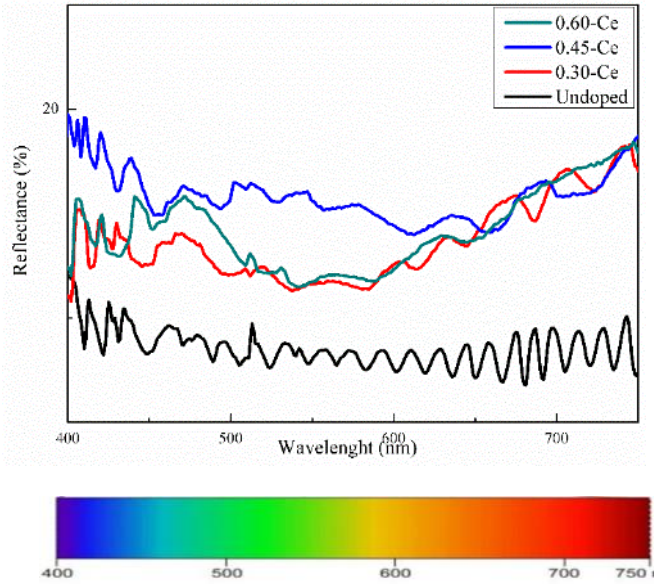


Fig.5. Reflectance spectrum of Ce doped 1D photonic crystals.

According to optical images of samples, green color is dominant in the undoped sample. Ce doped CuO coatings with various Ce concentrations led to the colorization of the coating. While the undoped sample show green color with 0.30 wt% Ce addition color of the coating changed from green to yellow and orange color. It is observed from the optical microscope images that the color of the coating changes from yellow to orange and red with increasing Ce doping. Full red colored surface was obtained with a 0.60 wt% Ce doped sample.

Also, in order to demonstrate the colorization of coating reflectance measurements were carried out. As seen in Fig. 5 the undoped sample shows a reflectance of about %10, while the reflectance value increased with increasing Ce doping. Additionally, with increasing Ce dopant concentration reflectance percentage of samples increased between 600 and 700 nm comparing to the undoped sample. When comparing this increase which takes place at 600-700 nm with the electromagnetic spectrum, it is seen that the increase in 600-700 nm matches up with orange and red colorization. Results of the reflectance spectrums of samples are consistent with optical microscopy in terms of colorization of coatings.

Similarly, the colorization of Eu doped samples was investigated with optical microscopy and to prove the colorization of coatings Uv-Vis Spectroscopy was conducted. Optical images of Eu doped samples were given in fig. 6. No significant color change was observed in the Eu doped sample compared to the undoped sample. 0.30 wt% Eu doped sample shows green and indigo color, on the other hand, the indigo color disappeared with an increase in Eu concentration and the green color was dominant in other Eu doped samples.

On the other hand, the reflectance spectrum of Eu doped samples in accordance with the colorization of samples which demonstrated in optical images (Fig. 6). As seen in fig.7, the reflectance percentage of samples increased with increasing Eu dopant concentration and more green and vivid colors

obtained. Decrement can be observed at the reflectance value of 0.60 wt% Eu doped coating due to the presence of some defect in the coating structure.

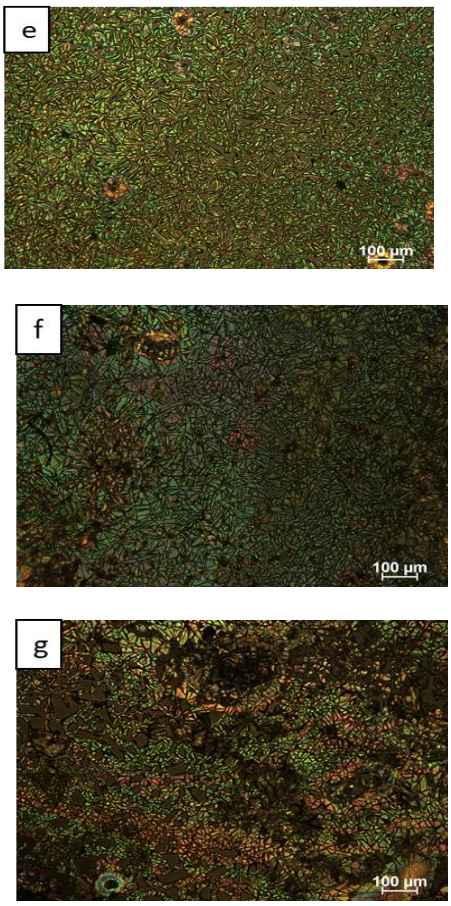


Fig.6. Optical images (e) 0.30 wt%, (f) 0.45 wt%, (g) 0.60 wt% Eu doped Coatings.

Consequently, different dopant elements and concentration affected the colorization of coating differently. While increasing Ce concentration caused change color of coatings from green to red and orange, Eu doping did not change the color of the coating significantly but more vivid colors were obtained.

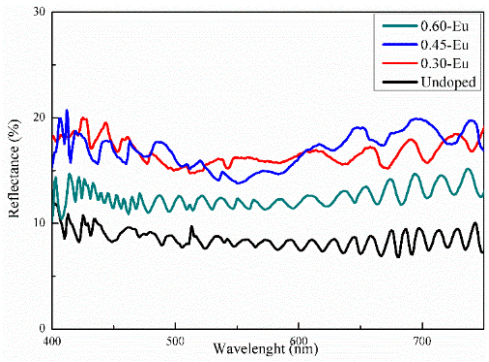
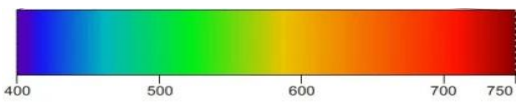


Fig.7. Reflectance spectrum of Eu doped 1-D photonic crystals.



III. CONCLUSION

1-D photonic crystals for structural colorization successfully produced by the sol-gel method. The Ce and Eu ions successfully doped into CuO crystal structures. With increasing dopant concentration, shifts in the diffraction angle of the (002) plane was observed. SEM images show that some crack formations observed in Eu doped samples due to increasing layer number or thermal treatment of samples. In contrast, the surface of Ce doped samples contain less crack compared to Eu doped samples. The rare-earth element doping for structural colorization shows an affirmative effect on colorization. With Ce ions doping into CuO crystal structure color change observed and completely red surface obtained with increasing dopant concentration. Also with Eu doping to CuO crystal structure, increasing reflectance value observed. UV-Vis spectrums of Ce and Eu doped photonic crystals compatible with the colorization of coatings.

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