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Araştırma Makalesi - Research Article

Co Katkılı SnO_2 Numunelerinin Sentez ve Karakterizasyonu

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ÖZ

Yüksek kristalleşmeye sahip katkısız ve Co katkılı SnO_2 numuneleri başarılı bir biçimde hazırlandı. Co içeriğinin SnO_2'nin termal ve morfolojik özellikleri üzerine etkileri araştırıldı. Co ilavesiyle Kristal büyüklüğünde ve birim hücre parametrelerinde değişimler tespit edildi. Co ilavesiyle faz bileşimi değişmedi. Hem X-ışını kırınımı hem de Fourier dönüşümlü kızılötesi sonuçları her bir numune için SnO_2 fazının oluşumunu doğruladı. Üretilen numunelerin oda sıcaklığından 900 °C'ye kadar termal kararlılığı gözlendi. Morfoloji Co içeriğinden etkilendi ve enerji dağılımlı X-ışını sonuçları SnO_2 yapısı içerisine Co'ın nüfuz ettiğini doğruladı.

Anahtar Kelimeler- Kristal yap, Elektron mikroskobu, IR, X-ışını difraksiyon

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Synthesis and Characterization of Co-Doped SnO_2 Samples

ABSTRACT

The un-doped and Co-doped SnO_2 samples having high crystallinity were successfully prepared. The effects of Co content on the structural, thermal and morphological properties of SnO_2 were investigated. Changes in the crystallite size and unit cell parameters were detected with adding of Co. The phase composition did not alter with the addition of Co. Both X-ray diffraction and Fourier transform infrared results confirmed the formation of the SnO_2 structure for each sample. The thermal stability of the as-produced samples from room temperature to 900 °C was observed. The morphology was affected by Co content, and energy dispersive X-ray results verified the introduction of Co into the SnO_2 structure.

Keywords- Crystal structure, Electron microscopy, IR, X-ray diffraction

I. INTRODUCTION

Metal oxide structures have been gained great importance in optoelectronic, magnetic, and sensing applications for long years [1,2]. Among these structures, tin (IV) oxide or stannic oxide (SnO_2) is, without a doubt, one of the most popular ones. As known, SnO_2 is an n-type metal oxide semiconductor, having a high carrier concentration, and has a wide optical bandgap, ranging from 3.6 to 4.0 eV, and high transmittance in the visible region [3,4]. SnO_2 is a very stable material both chemically and thermally [5]. SnO_2 has been used in the gas sensing applications (especially in the detection of the flammable, toxic and corrosive gases), lithium-ion batteries, anti-refractive coatings, transparent conducting electrodes, light-emitting diodes, solar cells, transistors, flat panel displays, catalysts, supercapacitors, memristors and so on due to its superior electrical, optical and electrochemical properties [6-16].

The previous studies show that doping of materials with foreign atoms is an effective approach to modify the structural, thermal, and morphological properties for consequent tuning of their characteristic properties [17-19]. In this context, the doping of some elements, such as Ni, B, Fe, Au, Ca, and Co, into the SnO_2 structure has been carried out for improving its characteristic properties. In this way, some properties, such as the gas sensing and/or lithium storage abilities, of SnO_2 can be controlled and improved for its further applications [20,21]. Co-doped SnO_2 was used as lithium-ion anode material by Ma *et al.* [22]. A theoretical study on the magnetic properties of Co-doped SnO_2 was done by Luo and Sun [23]. The effect of the surfactant of cetyltrimethylammonium bromide (CTAB) on the magnetic and optic properties of Co-doped SnO_2 prepared by the co-precipitation route as studied by Jiang *et al.* [24]. The catalytic performances of Co-doped SnO_2 synthesized via an eco-friendly KA oil (mixture of cyclohexanol and cyclohexanone) synthesis were investigated by Silva *et al.* [25].

In the present study, we aimed to synthesize the pure and Co-doped SnO_2 samples at various amounts (e.g., 0, 0.25, 0.50 and 1.00 at.%) and determine the effects of the Co content on the structural, thermal properties and morphology of the SnO_2 structure using the experimental techniques of X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential thermal analysis (DTA), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX). For this purpose, with a different method than the above-mentioned ones reported in the literature, we produced four SnO_2 samples via using a facile wet chemical method. All the characterization results were reported in detail.

II. MATERIALS AND METHOD

All the chemicals were purchased from Sigma-Aldrich and were used without any further purification. 100 mL of (25.00-*x*) mmol of tin (IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) and *x* mmol of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) were dissolved in ethanol, where *x* is 0, 0.25, 0.50 and 1.00. Hereafter, the samples were called as the pure SnO_2, 0.25Co-SnO_2, 0.50Co-SnO_2 and 1.00Co-SnO_2, respectively. Each solution was stirred without heating for 1 h and dried in an oven at 60 °C for 70 h. The as-dried powders were calcined in an electric furnace under an ambient atmosphere at 900 °C for 2.5 h.

The characterization of the samples was carried out using X-ray diffraction (XRD, Rigaku RadB-DMAX II) analysis, Fourier transform infrared (FTIR, Perkin Elmer Spectrum One) spectroscopy, differential thermal analysis (Shimadzu DTA 50), thermogravimetric analysis (Shimadzu TGA 50), scanning electron microscopy (SEM, LEO EVO 40xVP) and energy dispersive X-ray (EDX, Röntech xflash) spectroscopy techniques.

III. RESULTS AND DISCUSSION

A. XRD Results

Fig. 1 shows the XRD patterns of the as-manufactured samples. For all the samples, the single-phase distribution of polycrystalline SnO_2 (JCPDS PDF No: 41-1445) structure with the tetragonal crystal system is observed. No secondary phase formation is detected with an increasing amount of Co. The peaks belonging to the planes of (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202) and (321) were observed

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for each sample. With the addition of Co, some variations in the intensity of the as-mentioned peaks were seen, and this indicates the introduction of Co into the SnO_2 structure [26].

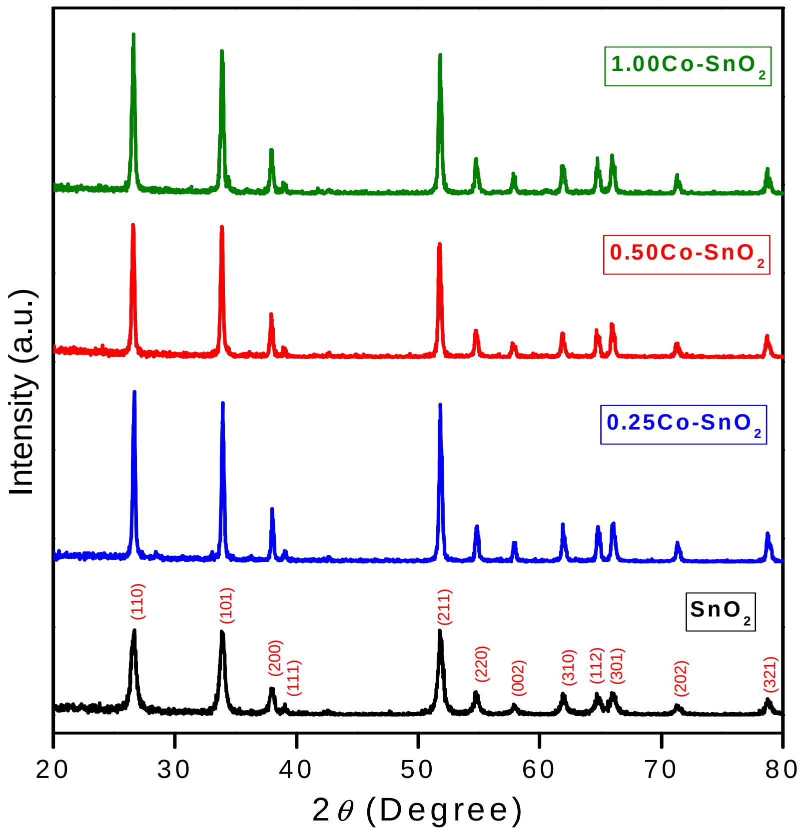

Fig. 1. XRD patterns of the samples

The lattice parameters (*a* and *c*), unit cell volume (*V*) and crystallite size (*D*) were calculated from the following equations, respectively [27]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

$$V = a^2 c \tag{2}$$

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

where *h*, *k*, and *l* are the Miller indices, *d* is the distance for two adjacent planes, β is the full width at half maximum (FWHM), θ is the Bragg angle and λ is the X-ray wavelength, which is equal to 0.15406 nm for CuK_α radiation. The significant variations in the lattice parameters, unit cell volume, and crystallite size values are clearly seen in Table 1. The changes in the peak intensities and calculated parameters may be related to the charge imbalance between Co^{2+} and Sn^{4+} ions and their ionic radii (0.058 nm for Co^{2+} and 0.069 nm for Sn^{4+}) [28].

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Table 1. The calculated values of the *D*, *a*, *c* and *V* for each sample.

	Pure SnO_2	0.25Co-SnO_2	0.50Co-SnO_2	1.00Co-SnO_2
D **(nm)**	21.80	34.59	30.46	28.74
a **(nm)**	0.473146	0.473332	0.473909	0.473666
c **(nm)**	0.318424	0.318471	0.318878	0.318666
V **(nm^3)**	0.071285	0.071351	0.071617	0.071496

B. FTIR Results

FTIR spectra of the pure and Co-doped SnO_2 samples are shown in Fig. 2. The as-detected bands and their assignments are given as follows: Two sharp bands observed at 463 and 604 cm^{-1} are related to the vibration modes of O-Sn-O bonds belonging to the SnO_2 structure [29]. The as-observed bands confirm the formation of the SnO_2 structure for each sample.

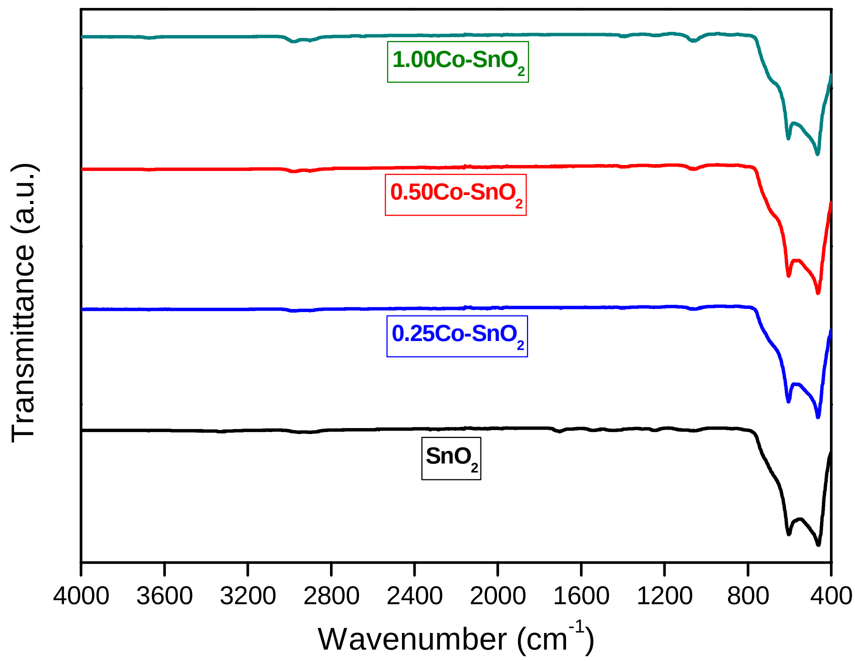

Fig. 2. FTIR spectra

C. Thermal Analysis Results

DTA and TGA curves of the as-obtained samples are shown in Figs. 3 and 4, respectively. From 25 to 800 °C, no peak was observed, and all the samples are thermally stable in this temperature range. In addition, the mass gain for each sample was seen in this temperature interval. The net mass gains, which are possibly due to oxidation, at 800 °C are found to be 1.03, 1.00, 1.10 and 1.38% for SnO_2, 0.25Co-SnO_2, 0.50Co-SnO_2 and 1.00Co-SnO_2, respectively (Fig. 4).

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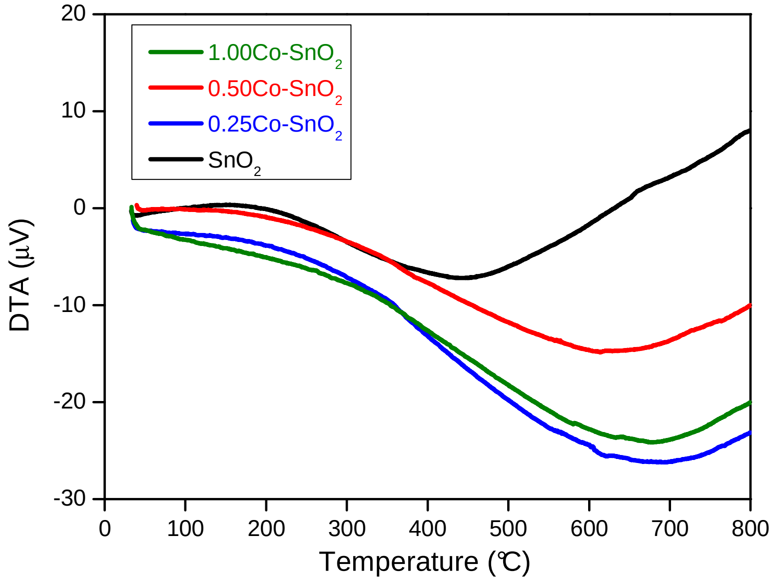

Fig. 3. DTA curves of the samples

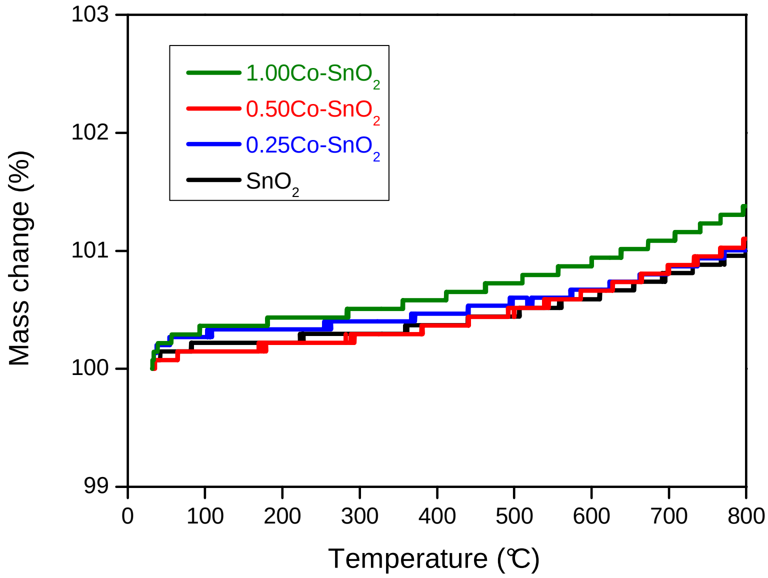

Fig. 4. TGA curves of the pure and Co-doped SnO_2 samples.

D. Morphological investigation

By investigating the SEM images of the samples shown in Fig. 5, it is seen that all the samples have porous microstructure. This can be considered as an advantageous feature, leading to a fast response and quick recovery, to the use of each sample in the gas sensing applications [30]. Furthermore, the EDX reports confirm the introduction of Co-ions into the SnO_2 structure.

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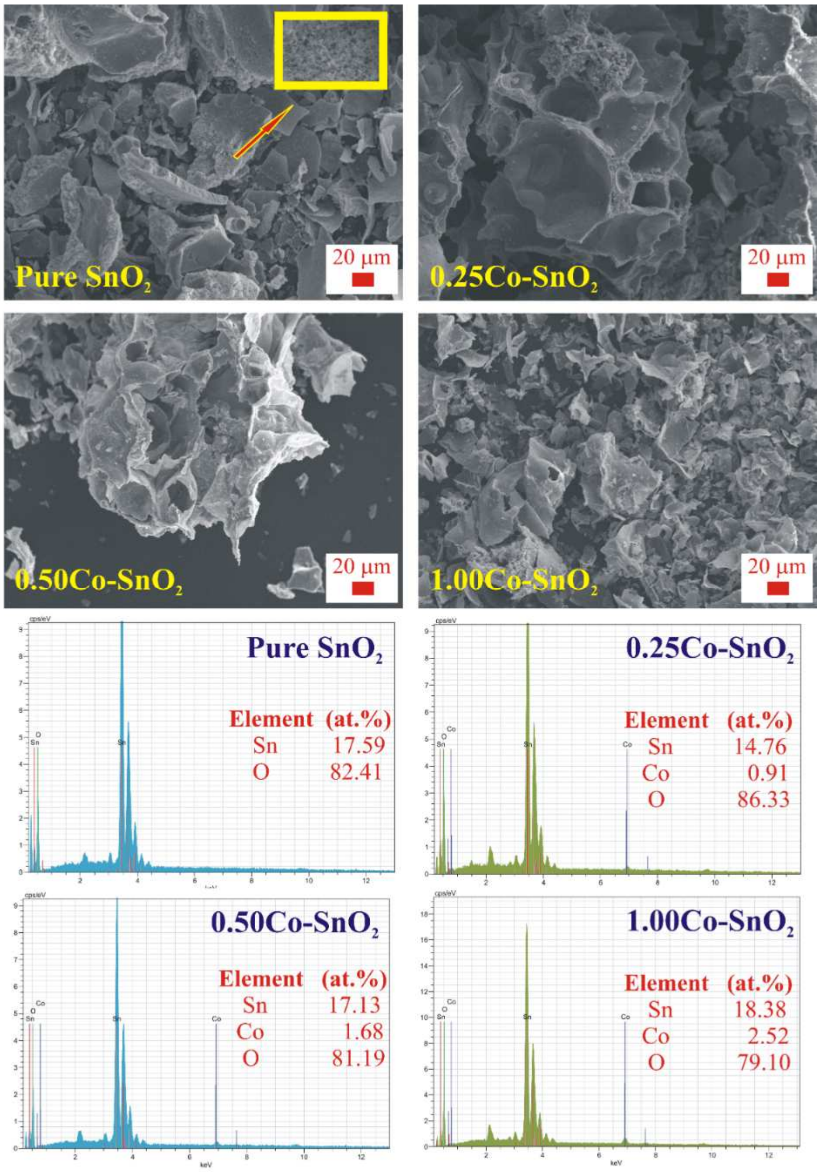

Fig. 5. SEM images and EDX reports of the as-produced SnO_2 samples.

IV. CONCLUSION

The pure and Co-doped SnO_2 samples with high crystallinity were easily produced at 900 °C via wet chemical synthesis. The effects of the amount of Co on the structural, thermal and morphological properties of SnO_2 were investigated using XRD, FTIR, DTA, TGA and SEM techniques. Last, the following results were observed. Single-phase distribution of SnO_2 for each sample is seen and no secondary phase formation is detected with adding of Co, but small changes in the peak intensities are observed from the XRD patterns of the as-manufactured samples. Moreover, the values of the crystallite size, lattice parameters, and volume of the unit cell are significantly affected by Co content. All the samples are thermally stable in the temperature range from 25 to 800 °C. No mass loss is observed within this temperature interval. The negligible mass gains, which are not exceeded the value of % 1.38, are detected for all the samples. The morphology is affected by Co content, and EDX data confirm the influence of Co into the SnO_2 structure. Additionally, the morphological observations also support that all the samples can be good nominates for gas sensing applications.

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