

Preparation and Study of Bismuth Oxide Doped and co-Doped with Cobalt(III) and Holmium(III) via Sol-Gel Method

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ABSTRACT: In this research work the solid-solutions of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Co}_2\text{O}_3)_x$, [$x= 0.05, 0.1$] (1), $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Ho}_2\text{O}_3)_x$, [$x= 0.025, 0.05$] (2), and $(\text{Bi}_2\text{O}_3)_{1-x-y}(\text{Co}_2\text{O}_3)_x(\text{Ho}_2\text{O}_3)_y$, [$x=0.05$] ; [$y= 0.01, 0.02$] (3) have been synthesized using sol-gel method. The effects of transition metal oxides doping on the crystallization and phase transition of the Bi_2O_3 were discussed by X-Ray Diffraction (XRD). The XRD pattern showed that 1 and 3, have Body Center Cubic (bcc) single phase; similar to $\gamma\text{-Bi}_2\text{O}_3$. While 2, has phase transition from bcc to tetragonal phase. The surface morphology of the samples was assessed by Scanning Electron Microscopy (SEM). Furthermore electrochemical properties of electrodes modifying by these new synthesized ceramics were studied by Cyclic Voltammetry (CV).

KEY WORDS: Solid-solution, Sol-gel method, X-ray diffraction, Body center cubic, Tetragonal phase.

INTRODUCTION

Bi_2O_3 easily forms solid solutions with many other metal oxides. The chemistry of bismuth oxide is very interesting research area in solution and solid works. Bismuth oxide is strongly polymorphic, α , β , γ , δ forms are known [1-6]. Phase diversity in bismuth oxide is valuable area for doing different research in the base of phase transformation in bismuth oxide base structure. So the chemistry of bismuth oxide as solid solution is interesting for finding different composition between

bismuth oxide and other metal oxides (transition and lanthanide elements).

Bismuth oxide is as a component finds use in wide applications in varistors, catalysts, gas sensors, and as an additive in paints [7]. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, co-precipitation, sol-gel, hydrothermal and colloid emulsion techniques

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have been confirmed to efficiently control the morphology and chemical composition of prepared powders [8-11]. Among oxygen ion conducting materials, oxide phases derived from Bi_2O_3 deserve special emphasis owing to their high ionic conductivity with respect to other well-known solid electrolytes [12]. The doped systems of Bi_2O_3 exhibit a complex array of structures and properties dependent on the type of dopant, the dopant concentration.

In this work, we used sol-gel method for synthesis of the compounds and they were characterized by XRD, SEM and CV.

EXPERIMENTAL SECTION

Materials

All starting materials $\text{Bi}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ho_2O_3 , mono hydrated citric acid, and ethylene glycol purchased from Merck chemical company and used without further purification. All synthesis were done using double distilled water.

Sample preparation

preparation of 1 and 2

The powder samples were prepared by sol-gel method. Starting materials $\text{Bi}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for synthesis of 1 and $\text{Bi}(\text{NO}_3)_3$, Ho_2O_3 for synthesis of 2 were dissolved in 20 mL water and 5 mL nitric acid. Then 2.7 g mono hydrated citric acid and 6 mL ethylene glycol were added to the solution. The result solution was stirred for 2 hours at 100°C . The produced gel was heated at 400°C in furnace. The resulting powder ground and homogenized in agate mortar and it was again kept for second heating at 780°C for 6 hours and cooled to room temperature slowly.

preparation of 3

At the first $(\text{Bi}_2\text{O}_3)_{0.95}(\text{Co}_2\text{O}_3)_{0.05}$ was synthesized using method described in preparation of 1. Then it was used as one starting material with Ho_2O_3 for synthesis of co-doped product (3) by using the same method described in preparation of 1, 2.

Cyclic voltammetry study

Preparation of bare carbon ceramic electrode

The Carbon Ceramic Electrode (CCE) was prepared according to the procedure described by Lev et al. [13].

0.3 mL Methyltrimethoxysilane, 0.45 mL of methanol, and 0.5 mL of hydrochloric acid (0.5 M) catalyst were mixed for 3 minutes and 0.3 g of carbon powder was added and the resultant mixture was shaken for an additional 1 minutes. A piece of Teflon tube with 7 mm length and ca. 4 mm inner diameter was filled with the sol-gel carbon mixture, and the mixture was then dried overnight under ambient conditions. The electrode was polished with polishing paper and subsequently rinsed with double distilled water. Electric contact was made with a copper wire through the back of the electrode.

Preparation of Bi_2O_3 and $(\text{Bi}_2\text{O}_3)_{1-x}(\text{M}_2\text{O}_3)_x$ [$\text{M}=\text{Co}(x=0.1)$, $\text{Ho}(x=0.05)$] modified electrodes

Preparation of modified electrodes were as follow: 1mg of Bi_2O_3 or $(\text{Bi}_2\text{O}_3)_{1-x}(\text{M}_2\text{O}_3)_x$ [$\text{M}=\text{Co}(x=0.1)$, $\text{Ho}(x=0.05)$] powders were vigorously dispersed with ultrasonic irradiation for about 10 min in 1 ml deionized water. Subsequently, 15 μL of obtained colloid solution was coated on carbon ceramic electrode with micro sampler and dried in room temperature.

Characterization techniques

X-Ray Diffraction (XRD) patterns of the samples were recorded by a Bruker AXS model D8 advance diffractometer using Cu K_α radiation ($\lambda=1.54 \text{ \AA}$) at 40 kV, 35 mA with Bragg angle ranging from 20° to 70° . The Thermo Gravimetric Analysis (TGA) was carried out on a Mettler-Toledo TGA 851e apparatus at a heating rate of 10°min^{-1} under a nitrogen atmosphere. The morphologies of the samples were observed by a Scanning Electron Microscope (SEM) (Model VEGA/Tescan, 15.00 kV). The adsorption values were measured with a Scinco UV-Vis spectrometer model S4100. The electrochemical experiments were carried out using an AUTOLAB PGSTAT-100 (potentiostat/galvanostat). The utilized three-electrode system was composed of a Saturated Calomel Electrode (SCE) as the reference electrode, a platinum wire as the auxiliary electrode and carbon ceramic modified electrodes as working electrodes.

RESULTS AND DISCUSSION

Characterization of crystalline structures

The powder XRD patterns of samples are shown in Fig. 1(a-f). The Characteristics of X-ray patterns are reported in Tables (1-6). All samples were characterized

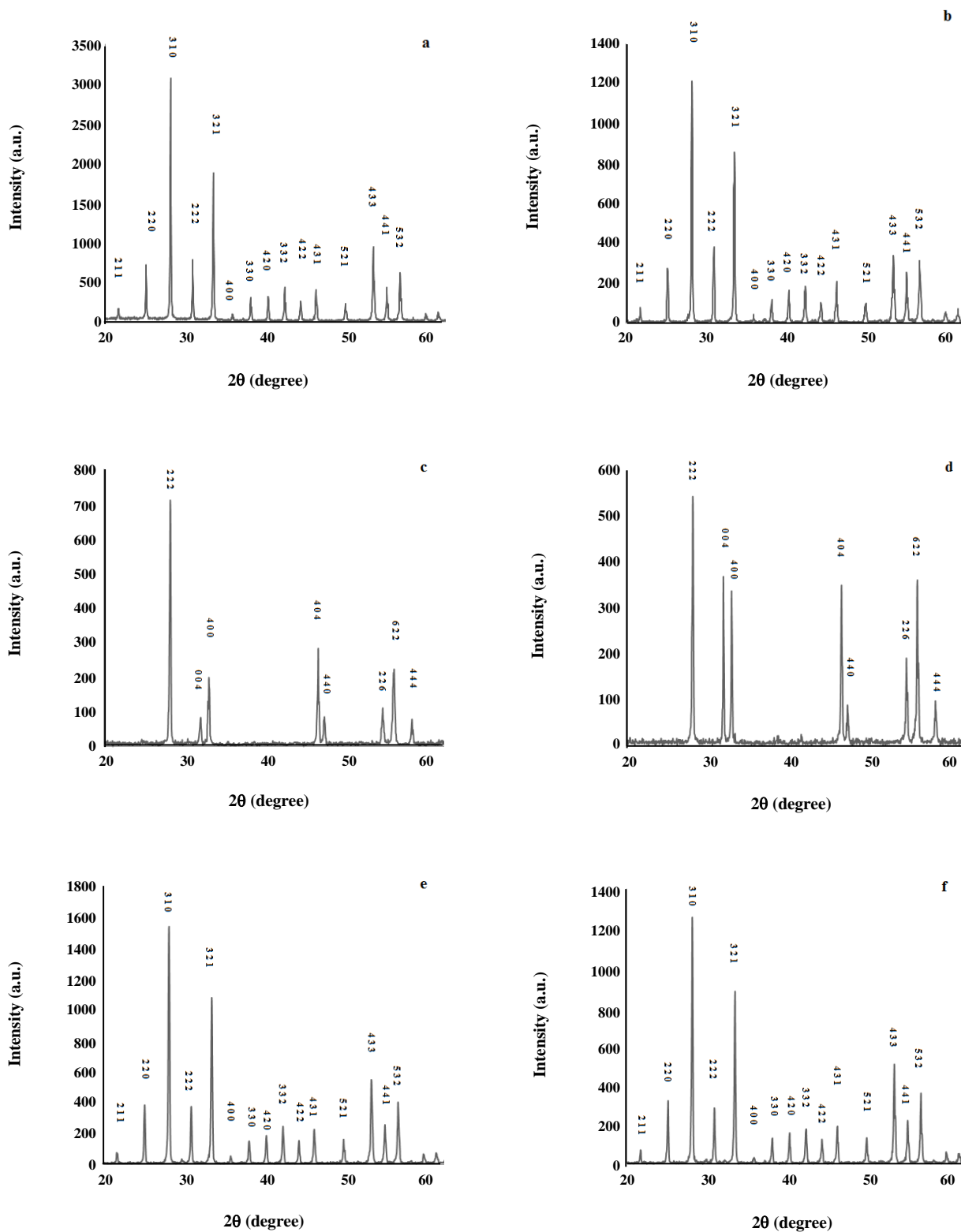


Fig.1: X- ray pattern of a= $(\text{Bi}_2\text{O}_3)_{0.95}(\text{Co}_2\text{O}_3)_{0.05}$, b= $(\text{Bi}_2\text{O}_3)_{0.9}(\text{Co}_2\text{O}_3)_{0.1}$, c= $(\text{Bi}_2\text{O}_3)_{0.975}(\text{Ho}_2\text{O}_3)_{0.025}$, d= $(\text{Bi}_2\text{O}_3)_{0.95}(\text{Ho}_2\text{O}_3)_{0.05}$, e= $(\text{Bi}_2\text{O}_3)_{0.94}(\text{Co}_2\text{O}_3)_{0.05}(\text{Ho}_2\text{O}_3)_{0.01}$, f= $(\text{Bi}_2\text{O}_3)_{0.93}(\text{Co}_2\text{O}_3)_{0.05}(\text{Ho}_2\text{O}_3)_{0.02}$.

Table 1: X- ray pattern Characteristics of a= (Bi₂O₃)_{0.95} (Co₂O₃)_{0.05} .

Peak number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(h k l) miller indices	2 1 1	2 2 0	3 1 0	2 2 2	3 2 1	4 0 0	3 3 0	4 2 0	3 3 2	4 2 2	4 3 1	5 2 1	4 3 3	4 4 1	5 3 2
2θ	21.56	24.98	27.96	30.70	33.22	35.58	37.80	39.95	41.97	43.90	45.80	49.42	52.86	54.45	56.12

Table 2: X- ray pattern Characteristics of b= (Bi₂O₃)_{0.9} (Co₂O₃)_{0.1}

Peak number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(h k l) miller indices	2 1 1	2 2 0	3 1 0	2 2 2	3 2 1	4 0 0	3 3 0	4 2 0	3 3 2	4 2 2	4 3 1	5 2 1	4 3 3	4 4 1	5 3 2
2θ	21.93	25.12	28.12	30.83	33.31	35.73	37.90	40.03	42.07	44.03	45.92	49.54	52.96	54.59	56.23

Table 3: X- ray pattern Characteristics of c= (Bi₂O₃)_{0.975} (Ho₂O₃)_{0.025} .

Peak number	1	2	3	4	5	6	7	8
(h k l) miller indices	2 2 2	0 0 4	4 0 0	4 0 4	4 4 0	2 2 6	6 2 2	4 4 4
2θ	28.12	31.92	33.14	46.52	47.29	54.21	55.64	57.93

Table 4: X- ray pattern Characteristics of d= (Bi₂O₃)_{0.95} (Ho₂O₃)_{0.05} .

Peak number	1	2	3	4	5	6	7	8
(h k l) miller indices	2 2 2	0 0 4	4 0 0	4 0 4	4 4 0	2 2 6	6 2 2	4 4 4
2θ	28.21	31.81	32.88	46.39	47.10	54.35	55.67	57.93

Table 5: X- ray pattern Characteristics of e= (Bi₂O₃)_{0.94} (Co₂O₃)_{0.05} (Ho₂O₃)_{0.01} .

Peak number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(h k l) miller indices	2 1 1	2 2 0	3 1 0	2 2 2	3 2 1	4 0 0	3 3 0	4 2 0	3 3 2	4 2 2	4 3 1	5 2 1	4 3 3	4 4 1	5 3 2
2θ	21.70	25.07	28.05	30.79	33.32	35.66	37.90	40.03	42.05	44.01	45.89	49.51	52.92	54.59	56.19

Table 6: X- ray pattern Characteristics of f= (Bi₂O₃)_{0.93} (Co₂O₃)_{0.05} (Ho₂O₃)_{0.02} .

Peak number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(h k l) miller indices	2 1 1	2 2 0	3 1 0	2 2 2	3 2 1	4 0 0	3 3 0	4 2 0	3 3 2	4 2 2	4 3 1	5 2 1	4 3 3	4 4 1	5 3 2
2θ	21.75	25.14	28.13	30.85	33.38	35.73	37.97	40.10	42.12	44.08	45.97	49.54	52.96	54.63	56.23

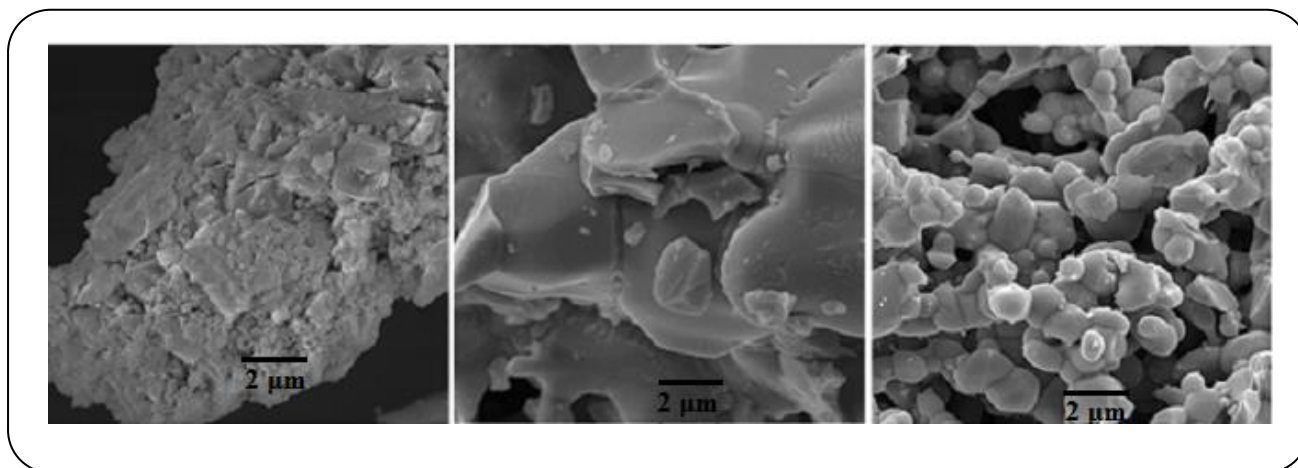


Fig. 2: Scanning electron microscopy (SEM) of $a = (\text{Bi}_2\text{O}_3)_{0.9} (\text{Co}_2\text{O}_3)_{0.1}$, $b = (\text{Bi}_2\text{O}_3)_{0.95} (\text{Ho}_2\text{O}_3)_{0.05}$, $c = (\text{Bi}_2\text{O}_3)_{0.93} (\text{Co}_2\text{O}_3)_{0.05} (\text{Ho}_2\text{O}_3)_{0.02}$.

at room temperature by using XRD technique. The X-ray analysis indicated that all samples of the solid solution series; 1 and 3 were crystallized in body-centered cubic structure, bcc phase (JCPDS Card File No. 45-1344), the same phase of $\gamma\text{-Bi}_2\text{O}_3$, whereas the samples of the solid solution series; 2 were undergone phase transformation from cubic to tetragonal (JCPDS Card File No. 22-0515). The results of present study reveal that the bcc phase is not stabilized in Ho_2O_3 doped samples within the range of dopant concentrations studied. From the consideration of the cationic radius of the dopant oxides, it is expected that the oxide ion conductive phase in the system $(\text{Bi}_2\text{O}_3)_{1-x} (\text{M}_2\text{O}_3)_x$ is tetragonal in the case of a relatively large ionic radius of M^{3+} and is bcc in the case of comparatively small ionic radius of M^{3+} . The tetragonal phase is formed in the system doped with Ho_2O_3 , the cationic radius of Ho^{3+} (0.90 Å) ions are comparatively large. The bcc phase is stabilized by doping with oxides with relatively small cationic radius Co^{3+} (0.67 Å) than Bi^{3+} (1.03 Å). The deviation in structural stabilization is due to the difference in electronic configuration of Co (3d) and Ho (5f).

Characterization of morphology

Scanning Electron Microscopy (SEM) images are shown in Fig. 2(a-c). The morphology of 1(x=0.1) revealed aggregation in structure with high density grading. Comparing 1 and 2 revealed that by changing Co_2O_3 to Ho_2O_3 in solid solutions, the size of particles is increased which it is related to the size of doped elements. The particles of 3 were more homogenized

in comparison to 1 and 2. Furthermore the shape of particles in 3 is spheroid. We guess that this interesting change in morphology (3 compared to 1, 2) can be related to their synthesis method. As mentioned in sample preparation section, 1, 2 are prepared in one step heat treatment while 3 is prepared during two steps.

Electrochemistry studies

To recognize the electrochemical properties of modified electrode, Cyclic Voltammograms (CVs) of bare CCE, Bi_2O_3 modified CCE, 1 (x=0.01) and 2 (x=0.05) modified CCE were studied in phosphate buffer solution, (0.1 M, pH=7), scan rate was 100 mV/S. Fig. 3 shows the CVs of bare CCE (a), Bi_2O_3 modified CCE (b) and cobalt oxide doped Bi_2O_3 modified CCE (c). As can be seen, there is no redox peak for CCE in the range -1.7 to 1.5 V (Fig. 3, curve a). However Bi_2O_3 modified CCE shows some anodic and cathodic peaks in -0.3 to 0.2 V and -0.69 to -1.26 V corresponding to Bi_2O_3 redox reactions [14-17]. Fig. 3 (curve c) shows the CVs of $(\text{Bi}_2\text{O}_3)_{0.9} (\text{Co}_2\text{O}_3)_{0.1}$ modified CCE. As can be seen, the anodic peaks of Bi_2O_3 were shifted to less positive potential (140 mV) showing the feasibility of the redox reaction of Bi_2O_3 in the presence of cobalt. Also the peak currents of $(\text{Bi}_2\text{O}_3)_{0.9} (\text{Co}_2\text{O}_3)_{0.1}$ were increased dramatically compared with Bi_2O_3 . The results show that the electrochemical behavior of $(\text{Bi}_2\text{O}_3)_{0.9} (\text{Co}_2\text{O}_3)_{0.1}$ was improved in comparison with Bi_2O_3 . The broad anodic peaks at 0.31 V and 0.69 V are attributed to the Co_2O_3 electrochemical reactions [18-20].

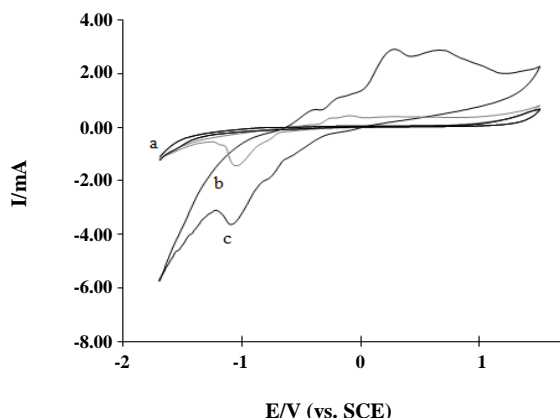


Fig. 3: Cyclic voltammograms (CV) of bare a=CCE, b= Bi_2O_3 modified CCE, and c= $(\text{Bi}_2\text{O}_3)_{0.9} (\text{Co}_2\text{O}_3)_{0.1}$ modified CCE .

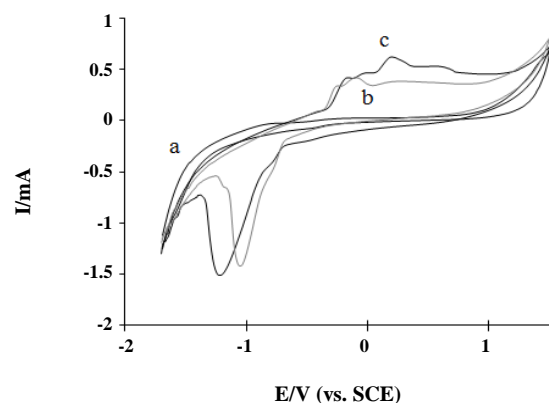


Fig. 4: Cyclic voltammograms (CV) of a= bare CCE, b= Bi_2O_3 modified CCE (b), c= $(\text{Bi}_2\text{O}_3)_{0.95} (\text{Ho}_2\text{O}_3)_{0.05}$ modified CCE.

Fig. 4 shows the CVs of bare CCE (a) in comparison with Bi_2O_3 modified CCE (b) and Holmium oxide doped Bi_2O_3 modified CCE (c). CVs show that the anodic peaks of Bi_2O_3 were shifted to positive potential (97 mV) showing that Ho_2O_3 decreased the electrochemical reactivity of the Bi_2O_3 . The anodic peaks at 0.24 V and higher potential can be attributed to the Ho_2O_3 [21-22].

Thus Co_2O_3 is an appropriate material for doping in to Bi_2O_3 compared with Ho_2O_3 for improving the electrochemical behavior of Bi_2O_3 . The cause of voltage shifts at anodic and cathodic peaks in the voltammetric curves in comparison with references can be attributed to factors such as the type and concentration of electrolyte [23].

CONCLUSIONS

The new compounds of $(\text{Bi}_2\text{O}_3)_{1-x} (\text{Co}_2\text{O}_3)_x$, [$x= 0.05, 0.1$] (1), $(\text{Bi}_2\text{O}_3)_{1-x} (\text{Ho}_2\text{O}_3)_x$, [$x= 0.025, 0.05$] (2), and $(\text{Bi}_2\text{O}_3)_{1-x-y} (\text{Co}_2\text{O}_3)_x (\text{Ho}_2\text{O}_3)_y$, [$x=0.05$] ; [$y= 0.01, 0.02$] (3) have been synthesized and characterized. The analysis of the XRD patterns showed that the lattice symmetry of system 1, 3 is body-centered cubic structure but it changed to Tetragonal for system 2. The results of SEM revealed that by changing of the doped transition metals, the shape and size of particles change more. The cyclic voltammetric experiments demonstrated that the electrochemical behavior of 1 modified CCE acceptability improves as compared to Bi_2O_3 modified CCE but electrochemical behavior of 2 modified CCE was unlike.

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