

## **Synthesis and Morphology Study of Nano-Indium Tin Oxide (ITO) Grains**

**Majid Farahmandjou**

*Assistant Professor, Department of Physics, Varamin Pishva Branch, Islamic Azad University, Varamin, Iran*

*Electronic and Computer Department, Qazvin Branch, Islamic Azad University, Qazvin, Iran*

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### **ABSTRACT**

In this paper, indium tin oxide (ITO) nanoparticles has been prepared by chemical methods under given conditions with solution of indium chloride ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ), tin chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) in ammonia solution. The samples were characterized by X-ray Diffraction (XRD) and scanning electron microscopy (SEM) analyses after heat treatments. The SEM results showed that, the size of the ITO particles prepared by co-precipitation route decreased to 46 nm whereas the size of the ITO prepared by hydrothermal and pechini sol-gel methods increased to 1 micron. The XRD patterns revealed that, the size of crystallite ITO particles prepared by sol-gel and hydrothermal methods increased. Finally the intensity ratio of  $I_{400}/I_{222}$  had a decrease of 21.67 percent for ITO prepared by hydrothermal method.

**Keyword:** Liquid phase; Hydrothermal; ITO nanoparticles; Pechini sol-gel; Co-precipitation.

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### **1. INTRODUCTION**

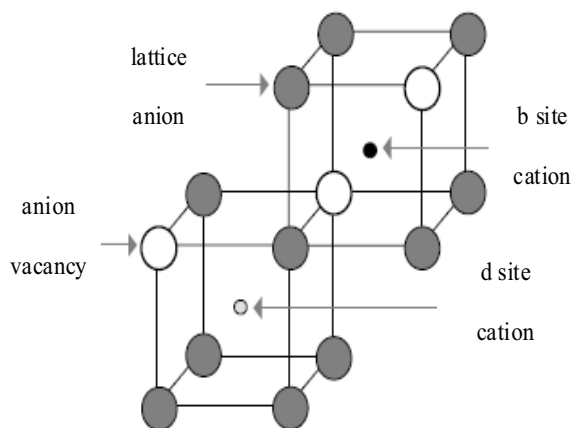
Sn-doped  $\text{In}_2\text{O}_3$  is an n-type transparent conducting oxide (TCO) with extensive commercial applications, including flat-panel displays, solar cells, and energy efficient windows [1]. Although indium tin oxide (ITO) is a widely used TCO, knowledge about its defect structure is limited. ITO and  $\text{In}_2\text{O}_3$  crystallize in the cubic bixbyite or  $\text{Ia}_3$  space group. The bixbyite structure is similar to the fluorite structure, but one-fourth of the anions are vacant, allowing for small shifts of the ions [2].  $\text{In}_2\text{O}_3$  has two nonequivalent six-fold coordinated

cation sites. Figure 1 shows the two cation sites, which are referred to as equipoints "b" and "d" [3]. The b site cations have six equidistant oxygen anion neighbors at 2.18 Å that lie approximately at the corners of a cube with two anion structural vacancies along one body diagonal [4]. The d site cations are coordinated to six oxygen anions at three different distances: 2.13, 2.19, and 2.23 Å. These oxygen anions are near the corners of a distorted cube, with two empty anions along one face diagonal. Indium tin oxide exhibits higher con-

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(\*) Corresponding Author - e-mail: farahmandjou@iauvaramin.ac.ir

ductivities and carrier concentrations than pure  $\text{In}_2\text{O}_3$  because of the electron compensation of the Sn species. An existing model of the defect chemistry of Indium tin oxide has been inferred from measured electrical properties of the material [5], following the anion interstitial model for doped  $\text{In}_2\text{O}_3$  structures [2, 6].



**Figure 1:** Nonequivalent cation sites in ITO

The tradition deposition techniques of indium tin oxide film are DC sputtering, RF sputtering, or electron beam evaporation. It is the first step to fabricate indium and tin alloy target or indium tin oxide ceramic target. Afterwards the target is sputtered to glass substrate by the controlled electron beam. These techniques need costly equipments, and the utilization rate of the target materials is low [7-10]. Because indium is a rare metal, it is necessary to explore a new route to deposit indium tin oxide thin film with high-Indium utilization rate. The synthesis nanoparticles of metal oxide from aqueous solutions and deposition thin films at low temperatures are an important way for preparation of transparent conductive film [11]. Dip-coating or spray deposition of light transparent, good conductive and low-membrane resistant indium tin oxide film has been studied by the researchers [12-14]. The fabrication of indium tin oxide nanoparticle is important in emulsion preparation for spray deposition or dip-coating ITO film. The indium tin oxide thin film's quality is related to the size and morphology of the nanoparticles. With the development of nanometer

material research, several kinds of preparation methods for nanosized ITO emerged. The current methods for nanometer indium tin oxide preparation mainly include solid-phase method, liquid-phase method, and gas-phase method [15-17]. The liquid-phase method, with the advantages of simple operation and controllable granularity, can realize the atomic scale level of mixing. The doping of components achieves easily, and the nanoscale powder material has high-surface activity. The liquid-phase methods include liquid phase precipitation, hydrothermal (high temperature hydrolysis), sol-gel (colloidal chemistry), radiation chemical synthesis, and so forth [18, 24].

In this paper, the indium tin oxide nanoparticles are first fabricated by liquid-phase co-precipitation, hydrothermal and pechini sol-gel method and the nanoparticles' structure is then compared by these methods. The morphology of indium tin oxide nanoparticles is studied by scanning electron microscopy and X-ray diffraction.

## 2. MATERIALS AND METHODS

### 2.1. Liquid phase co-precipitation synthesis

The synthesis of indium tin oxide nanoparticles was carried out by liquid phase co-precipitation as follows. A certain quality of indium chloride ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  99%, Aldrich) and tin chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  99%, Aldrich) was dissolved in pure de-ionized water or ethanol, keeping the ratio of  $\text{In}_2\text{O}_3 : \text{SnO}_2 = 9 : 1$ . Certain concentrations (5%) of ammonia solutions were made by mixing certain amount of ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 25%) with pure water. The prepared  $\text{InCl}_3$  solution (0.3 mol/L) was transferred into fixed three-neck flask, keeping in  $60^\circ\text{C}$  temperatures under electromagnetic agitation. The ammonia solution was added to the flask, controlling the stirring speed and testing the pH value till the required pH value was added as dispersant. The precipitate precursor of indium tin oxide was aged a certain time and washed with deionized water and absolute alcohol for three times, respectively. After washing, the precipitates were dried at  $110^\circ\text{C}$  for 1 hour. The dried samples

were calcinated at 650°C for 1 hour to get the indium tin oxide nanopowder.

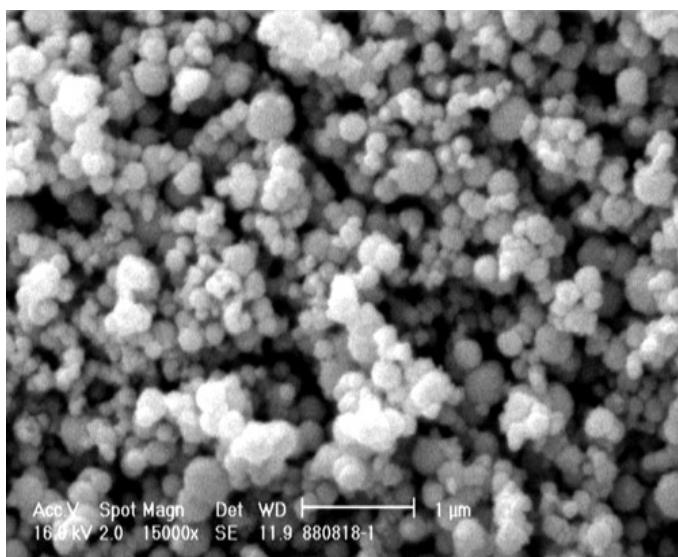
### 2.2. Hydrothermal method

In this method, the acidity of indium ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ) and tin chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) were first controlled by ammonia and then hexamethylenetetramine was added to the solution as precipitant agent. The reaction was transferred into fixed three-neck flask, keeping in 120°C temperatures under electro-

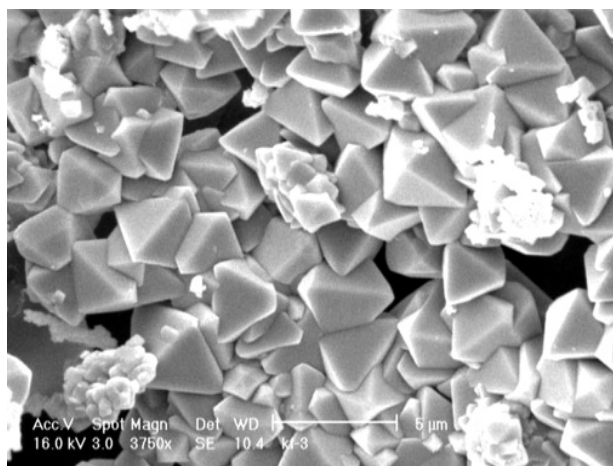
magnetic agitation for 6 hours and then the solution filtered and calcinated. The product was finally annealed at 550°C for 2 hours.

### 2.3. Pechini Sol-gel method

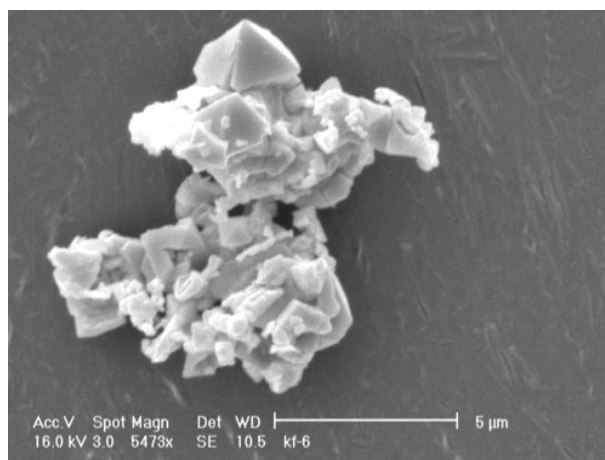
In Pechini sol-gel method, ethylene glycol was first added to the solution of a certain quality of indium chloride ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  99%, Aldrich) and tin chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  99%, Aldrich) in citric acid. The solution was then dried at 80°C for 2 hours to



**Figure 2:** The SEM images ITO nanoparticles prepared by co-precipitation method.



(a)



(b)

**Figure 3:** SEM images of ITO prepared by (a) hydrothermal and (b) pechini method.

remove the solvent. Finally, the ITO particles were annealed at 600°C for 2 hours after purification.

The morphology and structure of the prepared nanoparticles were characterized by means of scanning electron microscopy and X-ray diffraction. The microstructure of the indium tin oxide samples were characterized by a KYKY-Ammray 2800 type SEM with 200 kV acceleration voltages. To determine the nanoparticles' structure, the X-ray diffraction (XRD) measurement of the samples were performed using a Seifert with Cu-K $\alpha$  radiation (wavelength = 1.54 Å).

### 3. RESULTS AND DISCUSSION

Figure 2 shows the scanning electron microscopy image of indium tin oxide nanoparticles prepared by liquid phase coprecipitation method in the presence of ammonia solution. The size ITO nanoparticle is about 46 nm after 600°C calcination. As you can see the particles are in good uniformity in size.

Figure 3 shows the SEM images of indium tin oxide particles prepared by hydrothermal and sol-gel pechini methods. It is realized that the particle size of ITO is more than 1 micron for both of methods. But for the particles prepared by hydrothermal method (Figure 3a) the uniformity and crystallinity is better than pechini method (Figure 3b).

From the width of X-ray diffraction broadening, the mean crystalline size has been calculated using Scherer's equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

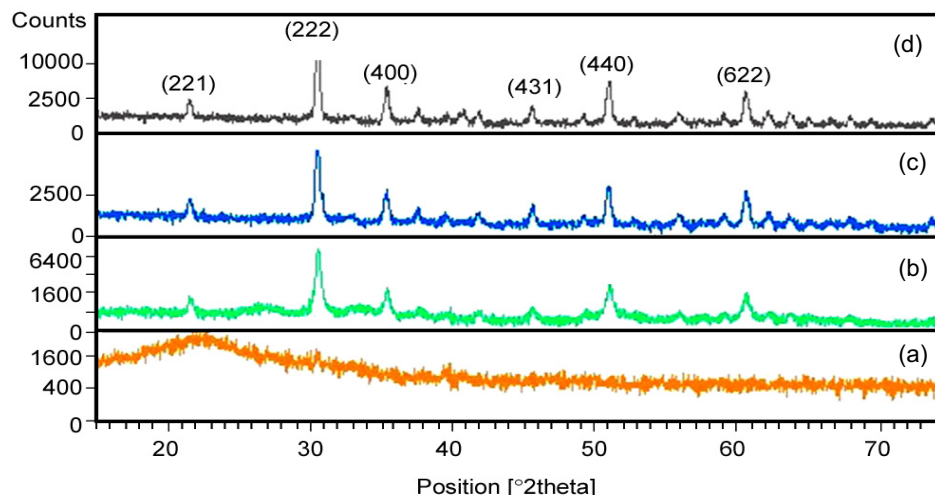
Where D is the diameter of the particle, K is a geometric factor taken to be 0.9,  $\lambda$  is the X-ray wavelength,  $\theta$  is the diffraction angle and  $\beta$  is the full width at half maximum of the diffraction main peak at  $2\theta$ , is a function of the crystalline size.

In Table 1, the lattice parameters according to XRD patterns are listed, including the size of nanocrystals, D(nm), atomic planar distance  $d_{222}$  (Å), the intensity of diffraction peak,  $I_{222}$ , and the intensity ratio  $I_{400}/I_{222}$ . In 1998, Quaas and co-workers reported that if tin oxide penetrates into the indium oxide by 5%, the atomic planar distance will decrease, and for penetration more than 5%, the atomic planar distance will increase [25]. Comparing the atomic planar distance for the  $In_2O_3$  sample  $d_{222} = 2.92$  (Å), it is realized that the penetration of Sn atoms into indium oxide is more than 5% for indium tin oxide prepared by co-precipitation, hydrothermal and sol-gel methods with atomic planar distance  $d_{222} = 2.917$  (Å),  $d_{222} = 2.923$  (Å) and  $d_{222} = 2.929$  (Å) respectively. By comparison of the  $I_{400}/I_{222}$ , it is found that the ratio  $I_{400}/I_{222}$  for ITO particles prepared by three methods is less than 29.3%. The results show that

**Table 1:** The data of lattice parameters for  $In_2O_3$  and ITO nanoparticles.

Sample name*	Preparation Method	D(nm)	$d_{222}$ (Å)	$I_{222}$	$I_{400}/I_{222}$
$In_2O_3$	Actual value	----	2.921	----	29.3
ITO	Pechini sol-gel	>100	2.929	14112	28.2
ITO	Hydrothermal	>100	2.923	8653	21.67
ITO	Co-precipitation	46	2.917	8747	29.07

\* D=crystallite size,  $d_{222}$  =atomic planar distance of 222



**Figure 4:** X-ray diffraction pattern of  $\text{SnO}_2$  and ITO nanoparticles.

the crystallite indium tin oxide particles have more growth in  $\langle 400 \rangle$  preferential orientation. In fact, the ITO crystal growth is increased at the preferential orientation with more atoms at higher temperatures. Therefore, the penetration of Sn atoms into the indium oxide prepared by hydrothermal and sol-gel approaches is more than indium tin oxide prepared by the co-precipitation method.

Figures 4 shows the X-ray diffraction patterns of  $\text{SnO}_2$  and indium tin oxide nanoparticles are calculated for 1 hour at  $650^\circ\text{C}$ . The large wide of the picks for  $\text{SnO}_2$  pattern indicate that this particles have the amorphous structure (Figure 4a), while the ITO prepared by co-precipitation (Figure 4b), pechini sol-gel (Figure 4c) and hydrothermal (Figure 4d) were intensively crystallized after annealing and sharp picks indicate the body centered cubic structure. The XRD results also indicate that the intensity ratio of  $I_{400}/I_{222}$  is increased to 29.07 percent by co-precipitation method.

#### 4. CONCLUSIONS

In conclusion, indium tin oxide nanoparticles were successfully synthesized by liquid phase co-precipitation, hydrothermal and sol-gel methods. The results indicate that the size of ITO prepared by

co-precipitation method is about 46 nm while the size of indium tin oxide nanocrystals prepared by hydrothermal and sol-gel methods is more than 100 nm, because of temperature. The X-ray diffraction results indicated that the ITO particles are finely crystallized body centered cubic structure. The penetration of Sn atoms into indium oxide is more than 5% for the indium tin oxide prepared by co-precipitation, hydrothermal and sol-gel methods. Finally, the preferential growth and orientation of the indium tin oxide prepared by the hydrothermal and pechini sol-gel methods is the  $\langle 400 \rangle$  orientation.

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