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Structural and Optical Constants of Ba doped Fe_2O_3 Thin Films Deposited by Chemical Spray Pyrolysis Method

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Abstract

Ba-doped Fe_2O_3 thin films are grown employing spray pyrolysis technique (SPT). XRD reveal that the high peak matched (113) plane . The effects of Ba (1 and 3% volumetric concentration) content was obtained .The Grain size of the grown films was (11.69- 13.63) nm, the microstrian increased from 2.96 to 2.54. The optical properties were determined with various Ba content (0, 1 and 3). AFM images indicate dependence of surface morphology upon doping. The UV-Vis spectra revealed that the transmittance of all samples was over 65% and the energy bandgap offer a decrement from 2.52 to 2.44 eV with increment of Ba. Results of optical constants for undoped and Fe_2O_3:Ba films was studied. The absorption coefficient increases by Ba doping, whilst refractive index and extinction coefficient increases with Ba content. This result is very useful for transparent thin films that are used for optoelectronic devices applications.

Keywords: Fe_2O_3 thin film, Ba, structural, topography, Optical Properties, bandgap.

Introduction

Semiconductor thin films have gained high attention because of their huge use in the fabrication of optoelectronic devices [1]. Iron oxide thin film was employed in many fields, due to its high refractive index and chemical stability. Besides they employed in dehydration, oxidation and Fischer– Tropsch synthesis [2-9]. Several methods for depositing Fe_2O_3 like; sol-gel [10-11], thermal evaporation method [12], CVD [13], sputtering [14] and DC reactive magnetron sputtering [15] PLD [16,47-67]. , and spray pyrolysis method [17-21], In this work, Fe_2O_3:Ba films were deposited via SPT to study their characterization.

Experimental

Thin films of Fe_2O_3 :Ba were deposited utilizing SPT. A glass atomizer was employed for spraying the solution. Films were grown on glass bases at a temperature of 400 °C. 0.1 M of $BaCl_2$ and $FeCl_3$ ressolved in redistilled water. Volumetric percentage of 2% and 4% Ba was used. the optimized conditions were; spray time was 8 s and stopping time between two sprayers was 1 min. The transporter gas (air) was put at compressing of 10^5 Pa, and distance between spout and base was 28 cm.

Film thickness was found gravimetrically to be about 325 nm. Structural coefficients were utilized by XRD (Shimadzu XRD-6000 Japan). AFM is employed to study surface topography , Optical transmittance were done employing spectrophotometer (Schimadzu).

Results and Discussions

Fig. 1 displays XRD styles of grown Fe_2O_3 thin film (thickness325 nm) is 31.20°, 39.12°, 53.62°, and 63.31° correspond to anatase (113),(207), (300) and (233) planes, respectively. High peak at (113) was seen that fit with ICDD card no 40-1139. There is no peak correspond to Ba ,but the shift in 2θ may indicate the existence of dopant

The grain size *D* was obtained from Scherrer formula [22-25]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where β is the FWHM, and θ is Bragg angle .

Table 1 shows that the crystallite sizes are (11.69 nm) and (13.63 nm) for Fe_2O_3 and Fe_2O_3: 3% Ba thin films respectively, The increase in Ba content lead to grain growth and enhance the order of crystallinity.

The dislocation density (δ) was obtained employing the equation [26-29]:

$$\delta = \frac{1}{D^2} \qquad (2)$$

The microstrain (ε) was obtained employing the equation [30-33]:

$$\varepsilon = \frac{\beta cos\theta}{4} \qquad (3)$$

It can be seen that the value of *ε* (Table 1) increases with increasing Ba content. The structural coefficient are displayed in Table. 1.

Figure (2) offers, FWHM, D, δ and ε as a function of Ba content.

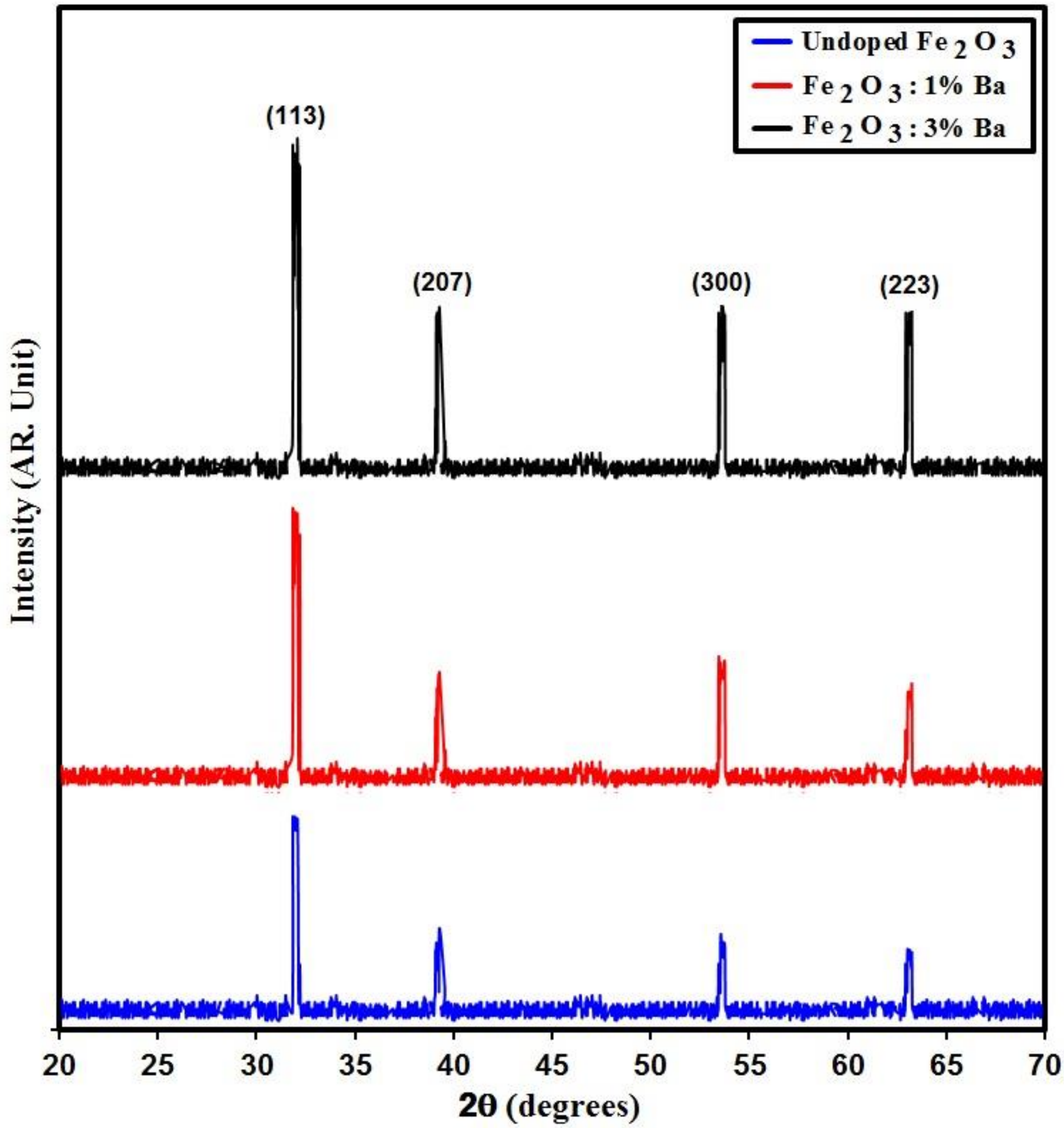

Fig.1. XRD styles of grown films.

Table 1. *D*, E_g and structural parameters of the intended films.

Sample	(hkl) Plane	2 □ (°)	FWHM (°)	Optical bandgap (eV)	Grain size (nm)	Dislocations density ($\times 10^{15}$) (lines/m^2)	Strain ($\times 10^{-3}$)
Undoped Fe_2O_3	113	31.20	0.56	2.52	11.69	7.31	2.96
Fe_2O_3: 1% Ba	113	31.00	0.52	2.48	12.77	6.13	2.71
Fe_2O_3: 3% Ba	113	30.80	0.47	2.44	13.63	5.38	2.54

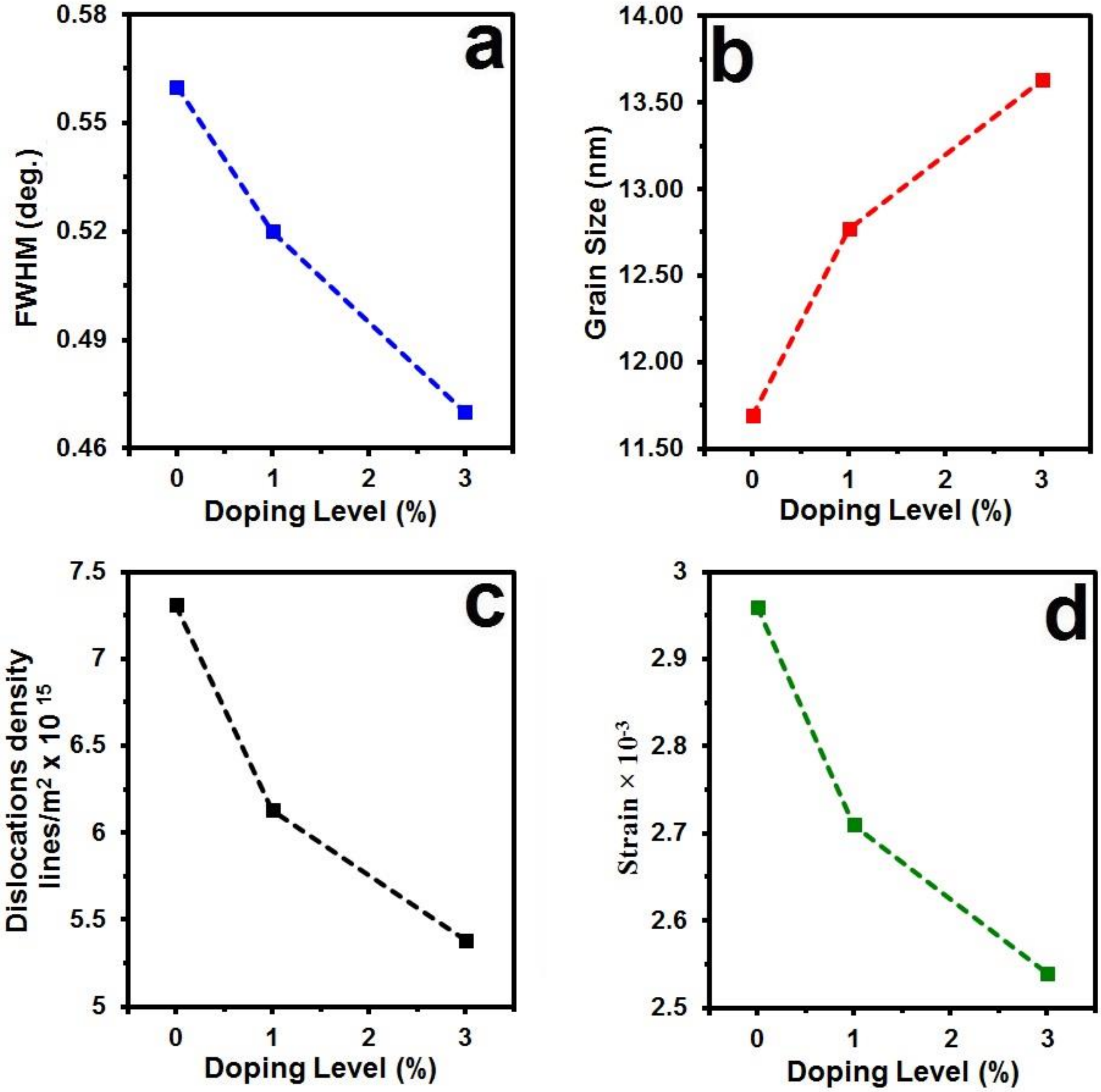

Fig.2. FWHM (a) *D* (b) δ (c) ε (d) of the grown films.

Topography Films Undoped Fe_2O_3 and Fe_2O3: 1% Ba were obtained via AFM. Figure 3. Displays the granules ,which exist in films suffer scattered in some zones. surface morphology can be estimated via roughness (Ra) and root mean square roughness (rms). From Figure 3 (a_3, b_3 and c_3). Average Particle size and rms values of (69.51, 65.19 and 62.51) nm and (6.33, 4.73 and 3.63) nm, respectively, which strongly affected by Ba dopant.

Table (2) shows that the average roughness and average particle size P_{av} increases of the intended films.

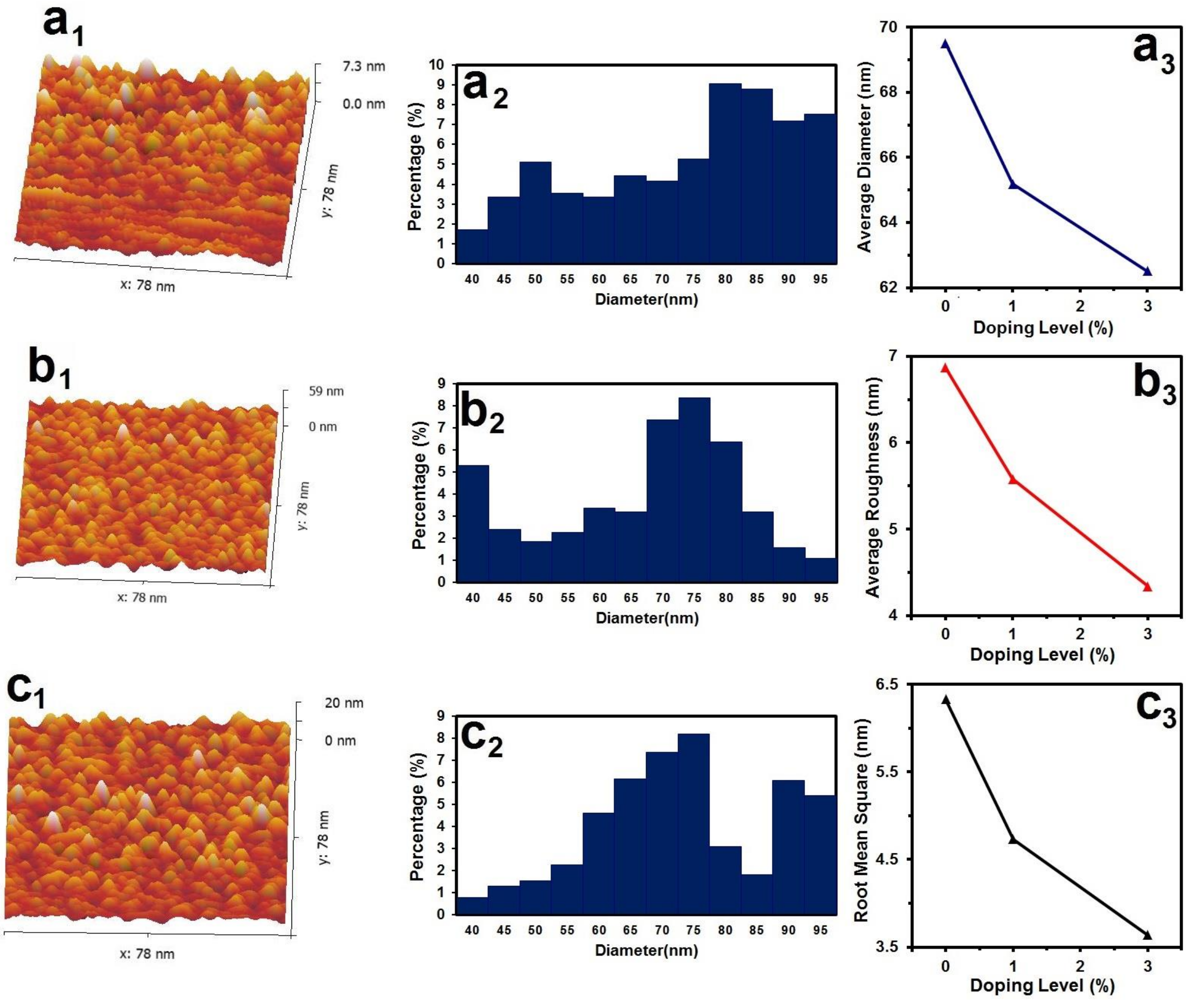

Fig. 3. AFM information of the intended films.

Table 2. AFM parameters

Specimen	P_{av} nm	Ra (nm)	rms (nm)
Undoped Fe_2O_3	69.51	6.87	6.33
Fe_2O_3: 1% Ba	65.19	5.58	4.73
Fe_2O_3: 3% Ba	62.51	4.33	3.63

Fig. 4 represents the transmittance spectra Fe_2O_3:Ba. It is noted from the shape that the percentage transmittance decreases with the increases in Ba and the reason is due to the reduction of the areas of dispersion of the incident rays on which reduces the crystal limits the Fe_2O_3 due to the increase of crystallization and the increase of the crystal size.

The absorption coefficient α is estimated via relation [34-37]:

$$\alpha = (2.303\times A)/t \quad (4)$$

Where (t) is film thickness. Figure (4) offers α versus photon energy (hν) (From figure 5 we can conclude that α of Fe_2O_3 thin films depends on the Ba-content and E_g increase as BA increase.

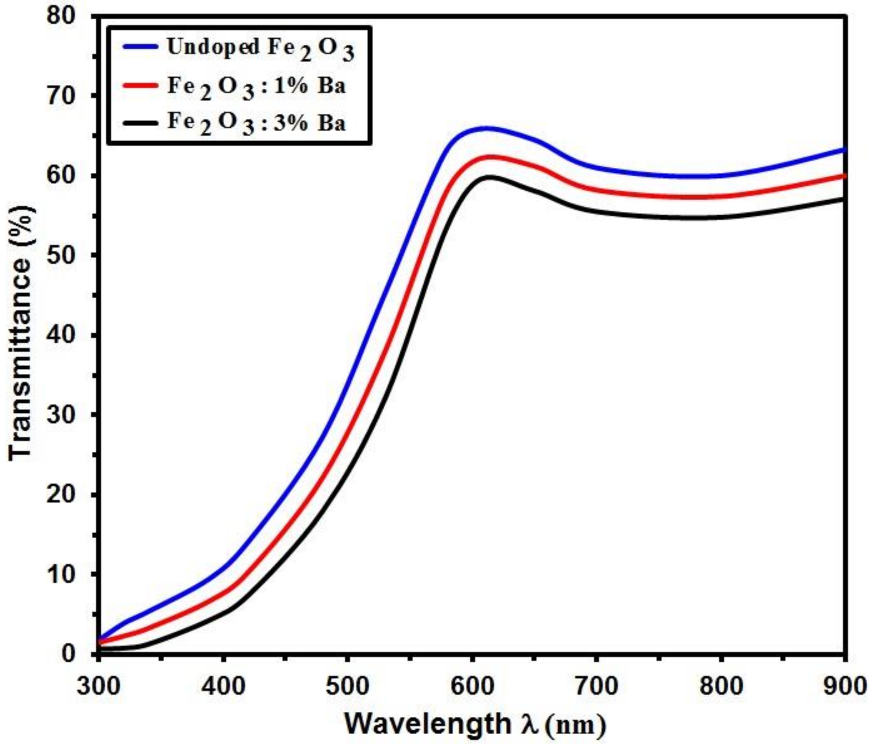

Fig. 4: Transmittance with wavelength of the grown films.

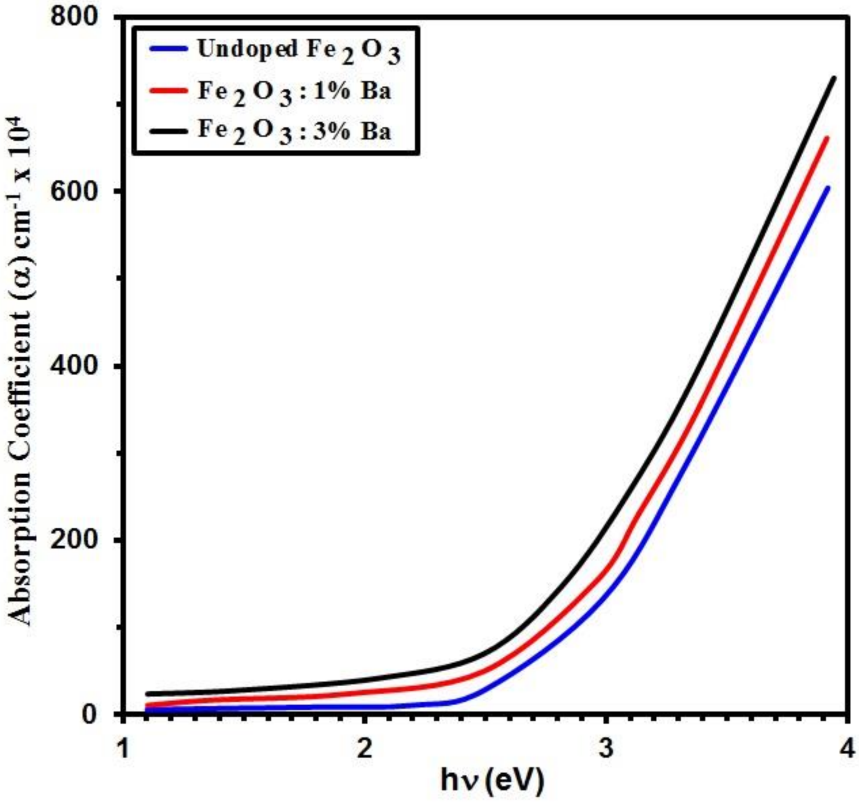

Fig. 5: α against wavelength of the grown films.

The bandgap energy E_g can be estimated by Tauc's relation [38-41]:

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (5)$$

where A is a constant, The relation between $(\alpha h\nu)^2$ and hν is plotted, From figure 6 it can be concluded that Fe_2O_3 bandgap depends on Ba-content and E_g decreases as doping increase. The band gap values of the synthesized nanocrystalline Fe_2O_3 and Fe_2O_3: 3% Ba thin films are 2.52 and 2.44 eV, respectively.

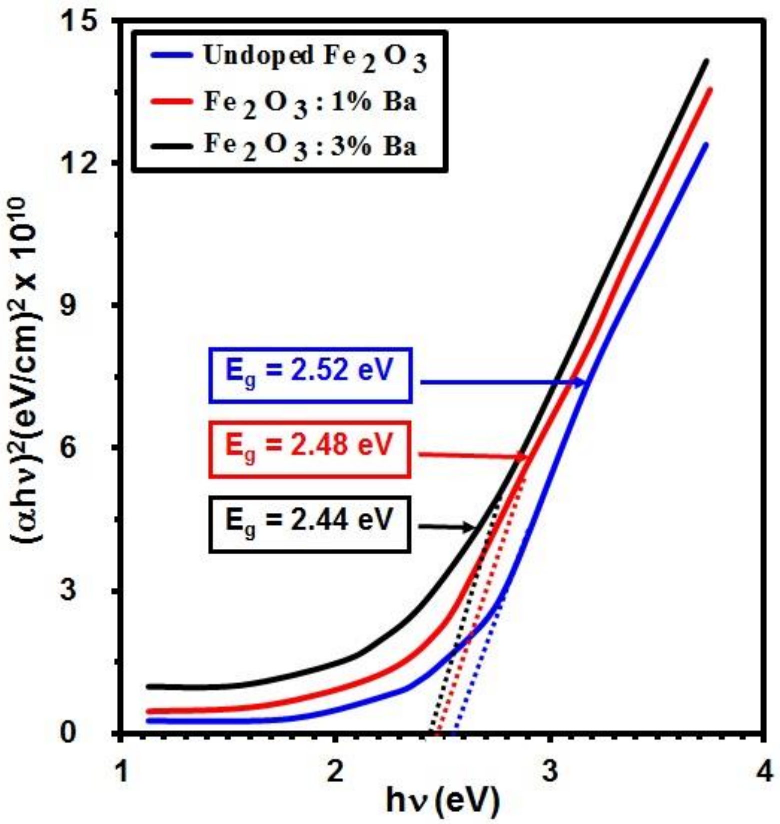

Fig.6: $(\alpha h\nu)^2$ versus hν of the intended films

Fig. (7) displays extinction coefficient *K* of Fe_2O_3 : Ba thin films calculated. *K* decreases sharply with the increment of wavelength until 600 nm.

The refractive indices (n) were obtained from equation(6) [42-46]. It can be seen from Fig. (8), that n are affected by Ba content, as n decrease with Ba content increase

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (6)$$

Where

$$k = \frac{\alpha\lambda}{4\pi} \quad (7)$$

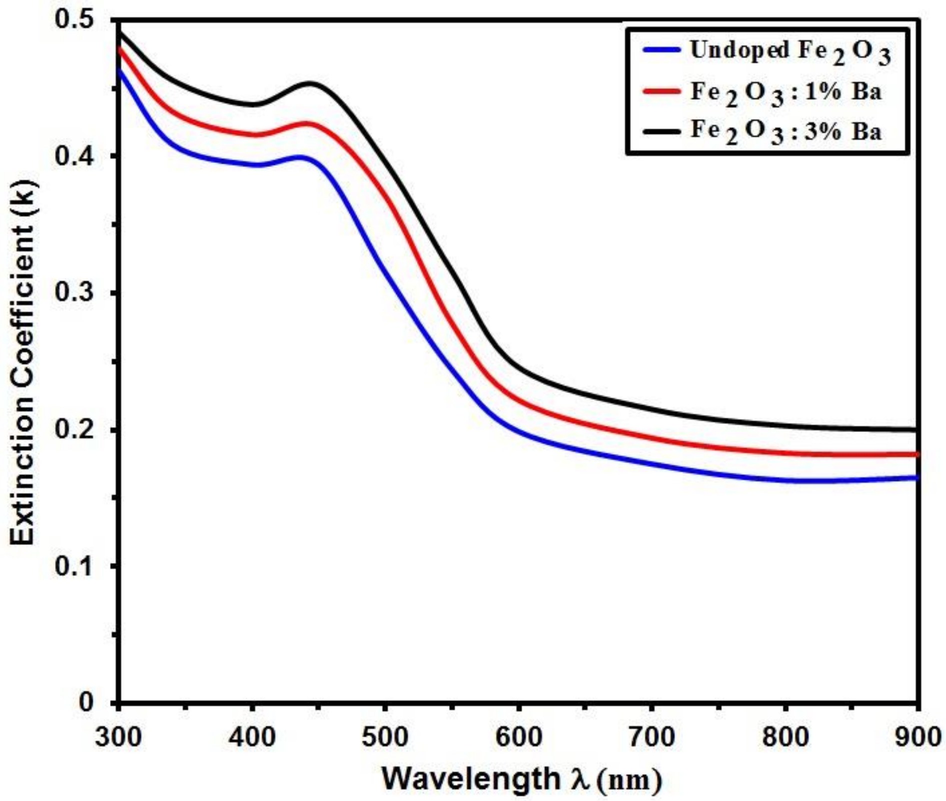

Fig.7: k of intended films.

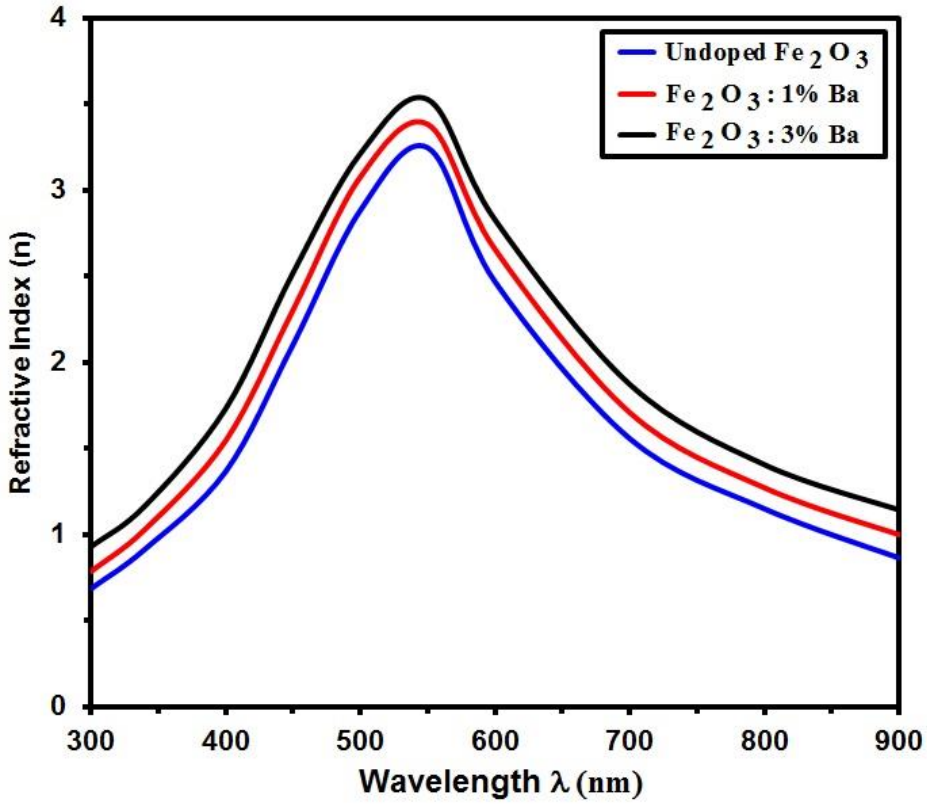

Fig. 8. n of intended films

Conclusion

Fe_2O_3 films are deposited under various Ba dopants. From the XRD analysis we inferred that the obtained Fe_2O_3 films have a pure rhombohedral crystalline structure with the preferential orientation along the plane (113), Structural investigations showed that average grain size increased from 11.69 nm to 13.63 nm with increase in Ba content . AFM images indicate that average particle size were in the area of 69.51 nm to 62.51 nm with Undoped Fe_2O_3 and Fe_2O_3: Ba with 1% and 3% concentrations respectively, The transmittance spectra was decrease upon Ba content. Optical bandgap was decreased from (2.52 to 2.44) eV with Ba doping, whilst n and k increase with Ba content. This result is very useful for transparent thin films that are used for applications in optoelectronic devices.

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