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Characterization of Mg, Ce Co-Doped CdO Nanostructured Material Using Statistical Image Analysis

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Abstract:- Structural and Morphological properties are the two fundamental tasks involved in the physical characterization newly synthesized nanostructured material. In this paper, Statistical image analysis of SEM images is employed for the characterization of Mg, Ce co-doped CdO nanosystems. Statistical parameters: Mean, Energy, Homogeneity and Edge density of the SEM images are computed using MATLAB software. The formation of crystalline grains and grain boundaries of SEM images are used as key features for the characterization of CdOnanosystems with increasing concentration of dopants Mg and Ce. Molecular structure of the material was elucidated using X- ray diffraction studies.Results obtained from this methodology are compared with the X-rd studies and are in good agreement with each other.

Keywords:- *Nano Materials, Scanning Electron Microscopy, X-Ray Diffraction, Statistical Image Analysis, Morphological Properties, MATLAB.*

I. INTRODUCTION

The high conductivity and transparent properties of CdO nanocrystalline materials make them as promising candidates for the various applications of Opto electronic devices. Such as displays, Solar cells, Transistors,electrodes etc [1-4]. In view of nanosclae dimension also, CdOnano structured materials have also great technical importance due to their extensive application in thinfilm technology as nano rods, nano needles, nano fibers etc [5-8]. All these applications are depend on the structural and optical properties of the CdO.But, alow band gapCdO (approximately 2.5 e.V) is not widely useful in the applications of opto electronics and photovoltaics. This remarkable property can be achieved by changing the physical and optical properties of the material by adding the some other suitable elements to the CdOwithout altering the structural properties. Many authors reported the single compound doping of CdO to modify the optical properties and thus optical band gap [1],[5],[9],[10]. But,the singleelement doping could not improve thestructuraland optical propertiessimultaneously. Therefore, Co-doping is considered an alternative and effective technique to improve the performance of CdO which is useful for the opto electronic applications.Traditionally, the elements of group (III) and group (IV) are used for the co-doping technique[11]. Here in this paper Mg and Ceare considered for the co-doping process. Dopant Mg modifies the optical properties of CdObychanging its bandgap without changing the CdO structure [1],[5],[9],[10],[12]. Appropriate amount of Cecataions will stabilize the oxygen octahydron that helps to decrease the voltalization and improves the crystallization and the ionic radii of Ce^{3+}(1.01A^0), Ce^{4+} (0.78A^0) are closer to the ionic radii of Cd^{2+}(0.97A^0) [11-14]. All the above, motivated authors to prepare Mg:Ce co-doped CdOnano systems. Most of the research work reported on the co-doped nano structured materials, by fixing the one dopant concentration and varies the second dopant concentration. But, in our studies equimolar ratio of (Mg : Ce = 1:1) is considered, Such ratios are Mg:Ce=1.5:1.5, 3:3,4.5:4.5 percentages are co-doped in the CdOnanopatricles.

Generally, the basic thing involved in the newlysynthesizednanocrystaiilne material is characterization of structural and morphological properties. This can be done by the X-ray diffraction analysis,Scanning Electron Microscopy (SEM) .Here, Statistical image analysis of SEM images is employed for the characterization of Mg,Ce co-doped CdOnanosystems.Satistical image analysis is a technique which is useful to extract the meaningful informationfrom the images by means of applying some computational algorithms on image data or intensity values.Statistical parameters: Mean, Energy, Homogeneityand Edge density of the SEM images are computed using MATLAB software[15-19]. The formation of crystalline grains and grain boundaries of SEM images are used as key features for the characterization of CdOnanosystems with increasing concentration of dopants Mg and Ce.The results of the present study are to be compared with those being made with other methods like X-ray diffraction. In extension to this work, Image analysis method has a wider scope of studying the optical properties of the nano crystals in addition to structural and morphological investigation. However, the investigated results are compared with other standard techniques to confirm our results.

II. EXPERIMENTAL

Mg and Ce co-doped Cadmium oxide nano materials at different concentration percentages (Mg:Ce – 1.5:1.5,3:3,4.5:4.5) were synthesized by simple chemical precipitation route [20]. The precursor materials used in this work were cadmium acetate -$Cd(CH3COO)_2.2H_2O$ magnesiumnitrate hexahydrate-$MgN_2O_6.6H_2O$and cerium nitrate hexahydrate- $Ce(NO_3)_3.6H_2O$ and sodium hydroxide as a precipitator material. All purchased from PSL CHEMICALSand used without further purification. The formed hydroxideswere washed with de-ionized water and ethanol.X-ray diffraction patterns of synthesized samples are obtained from the X-ray diffractometer(PANalytical PW 340/60 X'pert PRO) which was operated at 40Kv and 40mA with CuKα (λ=1.5406A^0) radiation.Scanning electron microscopy observations observed are recorded using Zeiss E|VO 18Scanning electron microscope at room temperature.The recorded gray color images have resolution of1024 x 768with intensity values ranges from 0 to 255 is used for the analysisIn the present work, the translated gray scale imageis used for analysis. The dimensions of the image are selected to be 256. The program has been coded using MATLAB (R2013) software (implemented on P5 1.6GHz with 2GB RAM computer) for analysis of SEM images which is an efficient tool for computational analysis [19],[21].

III. THEORETICAL CONSIDERATIONS

A. Computation of stastical parameters

The computations of statistical parameters are based on gray level intensities of image pixels. They analyze the spatial distribution of gray levels by computing the local and global features at each pixel in the image and derive a set of statistical parameters from the distribution of the image features [15],[16],[17,[18],[19].

An image or texture *I(i ,j)* is of size *m*-by-*n* is a two dimensional function composed of *m* pixels in the vertical direction and *n* pixels in the horizontal direction, *i, j* are horizontal and vertical co - ordinates of the image. The total number of pixels in the image is $m*n = N$, $0 \le i \le m, 0 \le j \le n$. The defined statistical parameters are explained below.

➢ *Mean:*

The mean (μ) is defined as the average level of intensity values of the image or texture *I (i, j).*

$$\mu = \frac{1}{N}\sum_{i=1}^{m}\sum_{j=1}^{n} I(i, j) \qquad (1)$$

➢ *Energy:*

Energy measures the textural uniformity, i.e pixel pair repetitions. Maximum energy of the texture or image occurs when the gray level distribution of given image is either constant or a periodic uniform.

$$Energy = \sum_{i=1}^{m}\sum_{j=1}^{n}(GLCM(i, j))^2 \qquad (2)$$

Where GLCM is Gray level co-occurrence matrix of the image. The elements of the GLCM represent the relationships between pixel intensity and its neighboring pixels [22],[23].

➢ *Homogeneity:*

Homogeneity measures the closeness of the distribution of values in the GLCM. Homogeneous texture will contain only a limited range of gray levels, giving a GLCM with only a few values but relatively high probability (*P(i,j)*) for the GLCM values. Thus the sum of squares will be high. Energy and Homogeneity are similar measures; the only difference is that energy considers the elements of the GLCM and homogeneity considers the probability of GLCM values.

$$Homogeneity = \sum_{i=1}^{m}\sum_{j=1}^{n}(P(i, j))^2 \qquad (3)$$

➢ *Edge density:*

Edges are the discontinuity in the intensity values and edge density measures the gradient magnitude of edges over a neighborhood. It is defined as [19,24]

$$Edgedensiy = \frac{\sum \mathrm{W}}{\mathrm{N}} \qquad (4)$$

Where W is white pixels and N gives the total number of pixels (width*height).

All the defined parameters are extremely sensitive to changes in the textural features of SEM images as a function of doping concentration.

B. Structural parameters from X-rd

The following are the structural parameters obtained from the X-rd patterns of given samples and are calculated from the equations given below.

➢ *Grain size:*

The grain size (D) is calculated using the Scherrer formula [12],[25],[26]

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (5)$$

Where β is FWHM and λ is the wavelength of the X-ray used (1.5406 A^0) and θ is bragg angle.

➢ *Lattice constant:*

The lattice constant was calculated using the following formula [27]:

$$a = d\sqrt{h^2 + k^2 + l^2} \qquad (6)$$

Where d is the interplaner distance,h kl : miller indices, a is lattice constant .

➢ *Dislocation density:*

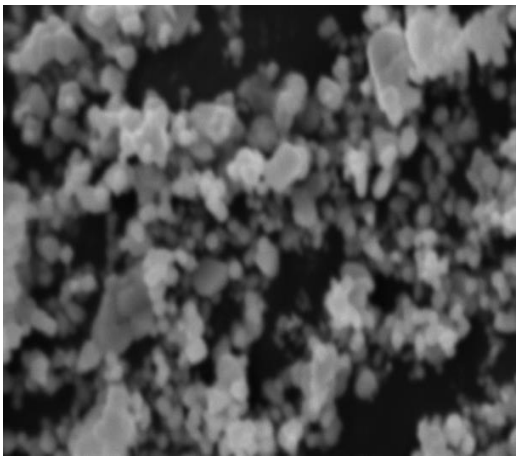
The dislocation density (δ) measures the length of dislocation lines or number of dislocations per unit volume of the crystal and was calculated from the equation [28].

$$\delta = \frac{1}{D^2} \qquad (7)$$

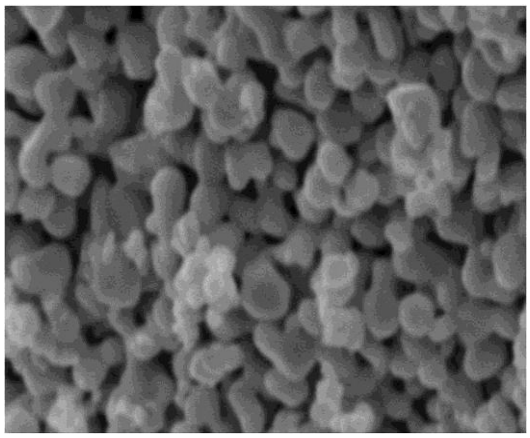
Here *D* is grain size calculated from the sherrer formula.

IV. RESULTS AND DISCUSSION

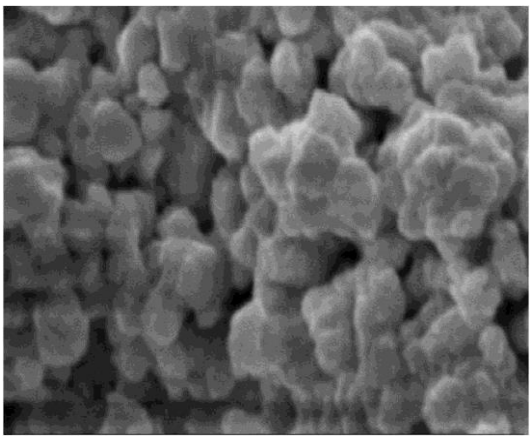
The recorded Scanning electron microscopic images of Mg, Ce co-doped CdOnano systems at different concentrations (0% – 4.5%) are shown in Fig1. Theserecorded observations are used to study the morphology of the synthesized systems. For thesynthesized co-doped systems, the surface morphology changes clearly with increasing concentration and was shown in Fig1.The spherical grains and traces of empty sites also evident from the pure sample of CdO was shown in Fig1(a) . At concentration of Mg:Ce – 1.5:1.5 the surface of the material modifies with loosely packed grains and few empty sites. This was shown Fig1(b). With further doping of Mg:Ce – 3:3, the surface modifies with closely packed dense structure of different grains and grain boundaries.This was shown Fig1(c). As the doping concentration increased further (4.5:4.5), the surface is fully modified asclosely packed dense structure with inter connected tiny grains of different sizes and was shown in Fig1(d). It is an indication of improved crystallinity of Mg, Ceco-doped CdOnano system with increasing concentration.



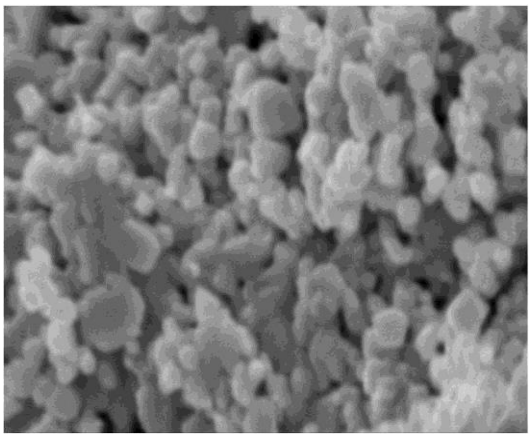
(a)



(b)



(c)



(d)

Fig 1:- SEM iimages of Mg,Ce co-doped CdO nano systems with magnification of 200nm at differennt concentrations.(a);Pure or (0:0) (b) 1.5:1.5;(c) 3:3;(d) 4.5:4.5.

The explained morphological properties ofMg, Ce co-doped CdOnano systems are further confirmed by the statistical image analysis using MATLAB software. Statistical parameters of SEM images are computed from (1)-(4).The plotsaredrawn for the statistical parameters as a function of concentration and ae shown in Figs 2,3,4,5.

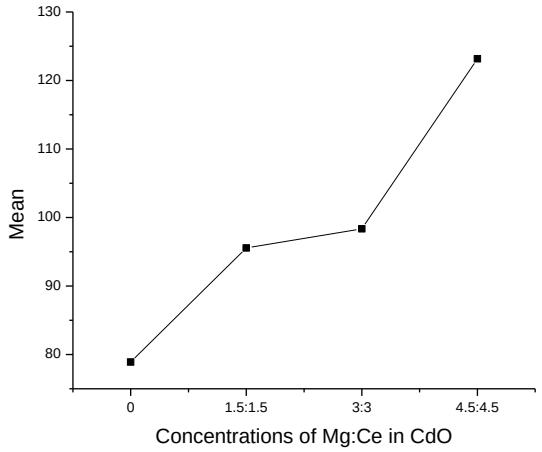


Fig 2:- Statistical parameter Mean of SEM images as a function of concentration.

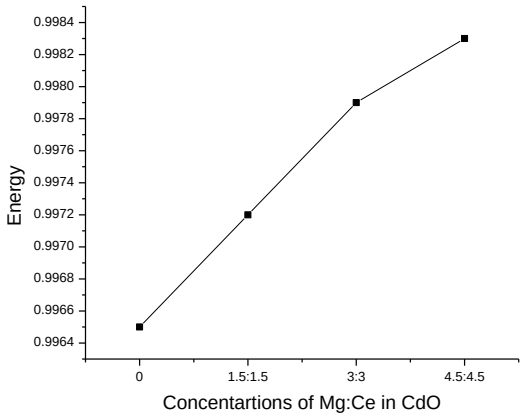


Fig 3:- Statistical parameter Energy of SEM images as a function of concentration.

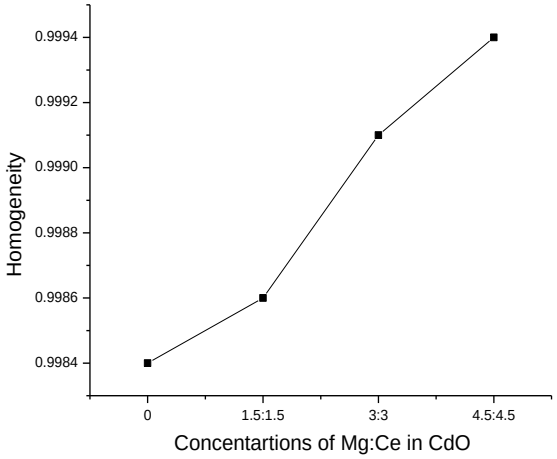


Fig 4:- Statistical parameter Homogeneityof SEM images as a function of concentration.

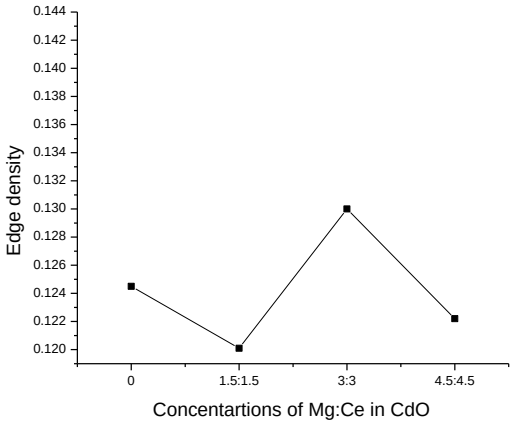


Fig 5:- Statistical parameter Edge density of SEMimages as a function of concentration.

Fig 2 shows that; Mean intensity of the SEM images is increases with increasing concentration of co-doping Mg and Ce in CdOnano systems.At the concentrations Mg, Ce 0 - 1.5, the image appears with small grains and empty sites and the average transmittance of the image is less. The concentration increases from 3% to 4.5%, different grains are interconnected with each other without empty siteswhich results the high surface recombination. Therefore, average transmitted intensityof the SEM images also increases. This is due to the fact that, Transmittance is high for the images withoutdefects compared to the other.This confirms the improved crystallinity of the newly synthesized system [29].The statistical measures Homogeneity and Energy measure the surface uniformity. They increase with increasing concentration of co-doping and was shown in Fig3 &Fig4. The surface recombination of different sizes of grains and grain boundaries results the low surface roughness with uniform intensity values for the newly synthesizednano systems [30]. One more important statistical parameter which is used to study the morphological properties of SEM images of nano systems is Edge density. Edges are nothing but the discontinuities in the intensity values and called as defects.Edge density in nothing but the gradient of the edges defined from the grain boundaries. For the newly synthesizednano systems, Edge density decreases with increasing concentration of co-doping except at 3% (shown in Fig 5). This is due to the fact that, surface recombination oflarge size grains and grain boundaries increases discontinuities in the intensity values results the higher edge density (shown in Fig1(c)). Surface recombination with small size grains and grain boundaries decreases the discontinuities in the intensity values and lowers the edge density (shown in Fig1(d)) [30]. This indicates the improved crystallinity of the Mg, Ceco-doped CdOnano system with increasing concentration.

Results obtained from the statistical image analysis methodology are very well acknowledged by the X-ray diffraction studies of the Mg ,Ce co-doped CdOnano systems.X-ray diffraction patterns of Mg, Ce co-doped CdOnano systems at different concentrations are shown in Fig 6.

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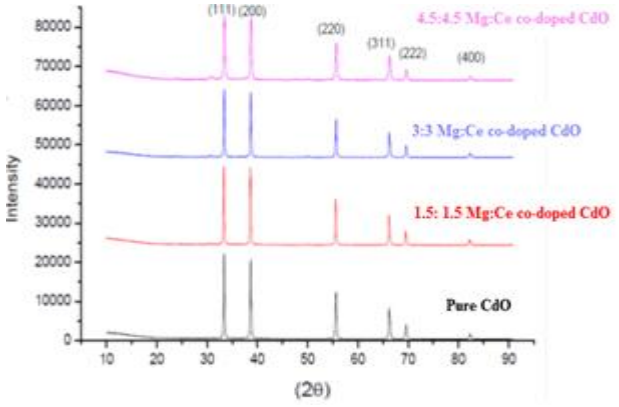

Fig 6:- XRD patterns of Mg, Ce co-doped nanosystems at different concentrations.

Fig 6 reveals that, the synthesized systems are polycrystalline in nature with diffraction peaks at 2θ values of33.358^0, 38.633^0, 55.594^0, 66.217^0, 69.5468 and 82.314^0 were indexed as (111), (200), (220), (311), (222) and (400)planes of Cubic CdO (JCPDS card No: 73-2245). Further, there are no additional peaks are identified. This indicates that the structure of CdOnano system was not altered by the co--doping of Mg and Ce [9],[10],[12]. The high diffraction peak intensities are observed for the planes (1 1 1) (2 0 0) at the Bragg angles33.358^0, 38.633^0. This indicates the co-doping systems have preferred orientation along the (1 1 1) and (2 0 0) direction. With increasing the concentration of co-doping, the diffraction angles of(1 1 1) and (2 00) planes are slightly shifted towards the higher angle 2θ from the pure CdO. This shift indicates the incorporation of Mg and Ce dopants in the CdO lattice without changing the structure.The defined structural parameters calculated from ((5).(6), (7)) the X-rd patterns of synthesized systems are shown in Table 1.

Mg:Ce co-doped CdOnano sysytemss	Grain size D (nm)	dislocation density (δ) *10^{16}	Lattice Constant (a) A^0	Interatomic spacing (A^0) (standard -2.7129)
Pure Cdo (0:0)	70.83	1.99	4.6483	2.6838
1.5:1.5	84.49	1.41	4.6570	2.6888
3:3	65.09	2.36	4.6376	2.6759
4.5:4.5	72.15	1.92	4.6448	2.6818

Table 1:- Structural parameters calculated from the X-rd patterns of Mg, Ce co-doped CdOnano systems

From Table 1, it was observed that the grain size is in the range of 70nm - 84nmand there is only slight variation in the grain size with Mg,Ce co-doping concentration from pure CdO.The decrease in grain is due to the smaller ionic radius of Mg (0.72A^0), Ce (0.78A^0) compared to Cd (0.97A^0).Relatively, the small grain size gives the low surface roughness (more smooth ness) for the materials which increases the efficiency of material.The same also proved from the statistical parameters of the SEM images, such as energy and homogeneity since they both measures the uniformity of the images. The low surface roughness enhances the usage of the material in different device applications like photovoltaic solar cells. Table 1 gives the values of inter atomic spacing and lattice parameter. They decrease with increasing concentration of co-doping.The slight shrinkage of lattice parameter from the pure CdO is due to the decrease of interatomic spacing with increasing concentration. The decrease of interatomic spacing results from the substitutionofsmallerMg^{2+} ions (0.72A^0)and Ce^{4+}(0.78A^0)intolargerCd^{2+} ions (0.97A^0).The slight increase of lattice parameter value observedat the concentration of 1.5%might be dueto Mg^{2+} ions and Ce^{4+}ions placed in the grainboundaries or the surface of the material not successful in replacing the Cd^{2+}ions in the host CdO lattice. The other structural parameter like lattice defect calculated from the X-ray diffraction patterns is dislocation density.

Table 1 showed that a decreasing trend was observed for the dislocation density of synthesizednano systems with increasing concentration of co-doping except at 3%.This is due to the fact that, Surface recombination with large grains gives the more dislocation lines results the high value of dislocation density and surface recombination with small grains lowers the dislocation density. It was similar to the statistical measure of SEM images called edge density and is shown in Fig7. Decrement of dislocation density and edge density with increasing concentration leads to the improvement of crystallinity of the Mg,Ce co-doped CdO nano systems. However, the computed statistical parameters of SEM images are very well acknowledges the structural parameters of X-ray diffraction patterns.

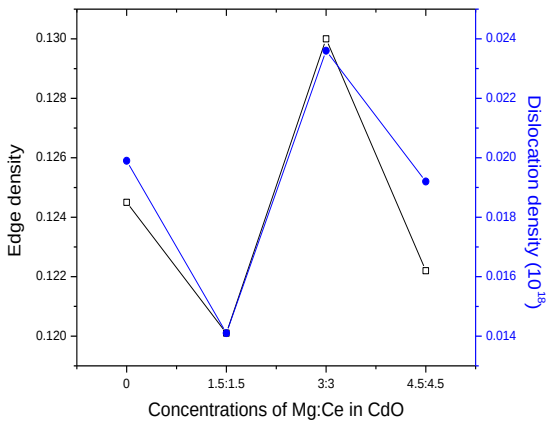

Fig 7:- Statistical parameter Vs Structural Parameter.

Results obtained from the both methods infer that the structural and morphological properties of the CdOnano systems are strongly influenced by the Mg,Ce co-doping.

V. CONCLUSION

Statistical image analysis method was successful in characterizing the structural and morphological properties of Mg,Ce co-doped CdOnanosystems. Results obtained from the statistical image analysis ,X-ray analysis are in good agreement with each otherand confirms the improvement of crystallinity of the nano systems with Mg,Ce co-doping in CdOnano systems. And also, the results infer that structural and morphological properties of the CdOnano systems are strongly influenced by the Mg,Ce co-doping without changing the structure.

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