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Synthesis and characterization of structural and intergrain nanocrystallites in chemically prepared BaS :Ce^{+3}-ions thin films

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Abstract:
*BaS: Ce^{+3}-ions matrix thin films were synthesized in doping ranges 2,4,6,8 and 10 at.% onto ultrafine Silicon wafer substrates using Successive Ionic Layer Adsorption and Reaction (**SILAR**) technique and reports the structural lattice parameters, nanocrystallite sizes, microstress, strains and dislocation densities in the films. Field Emission Scanning Electron Microscope (FESEM) and XRD- techniques were used in the characterization works. XRD results showed b.c.c. cubic zinc blend structure with preferential reflections along (100) plane at 2 at.%, (110) planes at 4 at.%, 6 at.% and 8 at.% and (200) plane at 10 at.%of Ce^{+3}-ion concentrations.The particle sizes at 100% relative intensity of X-ray lines profile were found between 80-100nm in diameter. The observed lattice parameters a- and d- values were found in close agreement to the standard values. The microstress between crystallites, and average intergrain dislocation density in the films were found to decrease while microstrains randomized with increasing Ce^{+3} – ion concentrations in the BaS thin films.*
***Key words**: BaS thin films, doping, FESEM, XRD*

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I. Introduction:

Extensive researches on chemically synthesized BaS doped with rare earth activators are rare cases in national and international level. Barium sulphide (BaS) is an inorganic compound semiconductor having indirect wide energy gap of E_g = 4.0eV in bulk state that belongs to metal chalcogenite group of II-VI. BaS can be synthesized by different deposition techniques- (i) electrodeposition, (ii) chemical bath deposition (iii) photoelectrochemical (iv) spray pyrolysis (v) thermal evaporation (vi) successive ionic layer adsorption and reaction (SILAR). Among these, SILAR technique has been proven most cost effective and less man power and time consumption[1].Such a metal chalcogenide crystallizes new phase transition from the rock salt crystal structure to the CsCl-crystal structure under pressure[2-4] particularly in one of two motives-(i) zinc blend structure where the sulphide ions (S^{+2}) occupy half of the tetrahedral holes, which results a dimondered frame work and (ii) other motive is the wurtzite structure wherein the atomic arrangement are similar tetrahedral but the crystal symmetry is hexagonal. Basically, II-VI compounds have attracted greater interest due to their potential applications in the fields of light emitting diodes (LEDs), laser diodes (LDs) and other photoelectronic devices.[5-7] BaS is moderately water and acid soluble compound.

II. Experimental details :

The synthesis of BaS doped Ce^{+3} ions nanocrystalline thin films was carried out by **Successive Ionic Layer Adsorption And Reaction** (**SILAR**) technique. In this process, high purity (i) Barium acitate, $Ba(CH_3COO)_2$ $2H_2O$(AR Grade),was used as Ba^{+2} – cation source (ii) Thiourea, $CS(NH_2)_2$ (AR Grade) as S^{-2} - anion source (iii) Cerium nitrate, $Ce(NH_3)_3$ as doping agent, (iv) Ammonia solution to adjust the pH of the precursor solution (v) Polyvinyl alcohol (PVA) was used as matrix for controlling the growth and stabilization of BaS thin films on the substrates.

The synthesis of BaS thin films was carried out at doping ranges *2,4,6,8* and *10 at.%* of *Ce^{+3}*-ions at 0.2M equimolar solutions in the following steps:

(i) *Preparation of 0.2M $Ba(CH_3COO)_2$ solution*:
We prepared 0.2M $Ba(CH_3COO)_2$ by dissolving 5.11gms of it in 500ml DI water and stirred thoroughly for 30mins for reserved solution.

(ii) *Preparation of 2wt.% PVA solution*:

We dissolved 2gms. of PVA in 100ml DI water and the resultant solution was stirred for 1hr. till PVA dissolved. The precursor was divided into two beakers.

(iii) *Preparation of 2 at.% Ce^{+3}-ion solution*:

By calculation, 0.34gm of $Ce(NO_3)_3$ was dissolved in 50ml DI water to obtain *2at.% Ce^{+3}*-ionic solution.

Now, 50ml of $Ba(CH_3COO)_2$ solution was mixed with 50ml PVA solution and 50ml of *2at.% Ce^{+3}*-ionic solution and the resultant solution was refluxed for 5mins. The properly cleaned silicon wafer substrates (5nos.) were fully immersed vertically in the precursor solution for 24hrs when Ba^{+2}-cations were adsorbed onto the substrates. The substrates were removed gently, stabilized for 10mins and then rinsed in running DI water for removal of unwanted course Ba^{+2} –ions.

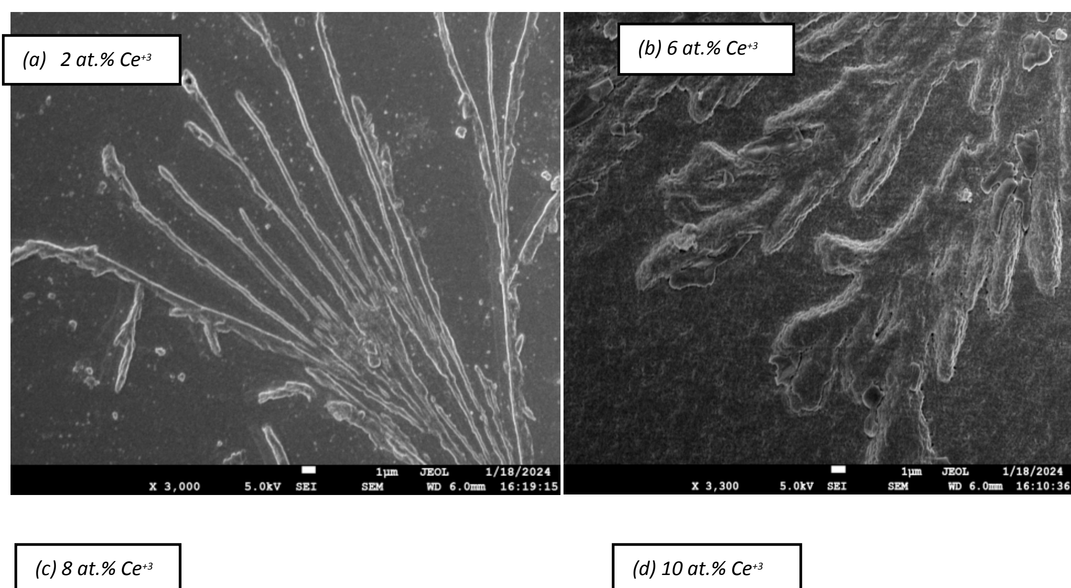
(iv) *Preparation of 0.2M $CS(NH_2)_2$ solution*:

We prepared 0.2M $CS(NH_2)_2$ solution by dissolving 1.5gms of it in 500ml DI water with constant stirring for 30mins. Then, a few drops of ammonia solution were added to yield alkalinity at pH-10. The precursor was heated to 70^{0}C for 1hr. with constant stirring till $CS(NH_2)_2$ dissolved completely and finally cooled down to room temperature.

The substrates were immersed again vertically into the precursor solution for 24hrs when S^{-2}-anions were adsorbed onto the Ba^{+2}-ions pre-deposited substrates.The two opposite Ba^{+2} and S^{-2}-ions reacted to form BaS (0.2M)equimolar thin films doped Ce^{+3} at *2 at.%.* The substrates were gently removed then finally rinsed in running DI water and stabilized at room temperature and then annealed at 50^{0}C for 24hrs. Similar procedures were carried out for synthesis of *4,6,8* and *10at.% Ce^{+3}* ions doped BaS thin films.

III. Results and discussion:

3.1. *Surface morphology and structural characterization:* The as synthesized doped BaS thin films were taken FESEM for surface imaging and characterization. Figure 1 (*a, b, c & d*) showed the microstructures of surface morphology of BaS thin films doped Ce^{+3} –ions at *2, 6, 8 & 10 at.%* concentrations. The morphological micrographs reveal the rode-like microstructures at lower Ce^{+3}-doping concentrations and uniform leaf or petal -like network structures at higher dozes. The particle sizes in the structures lie between 80-100nm in diameter.



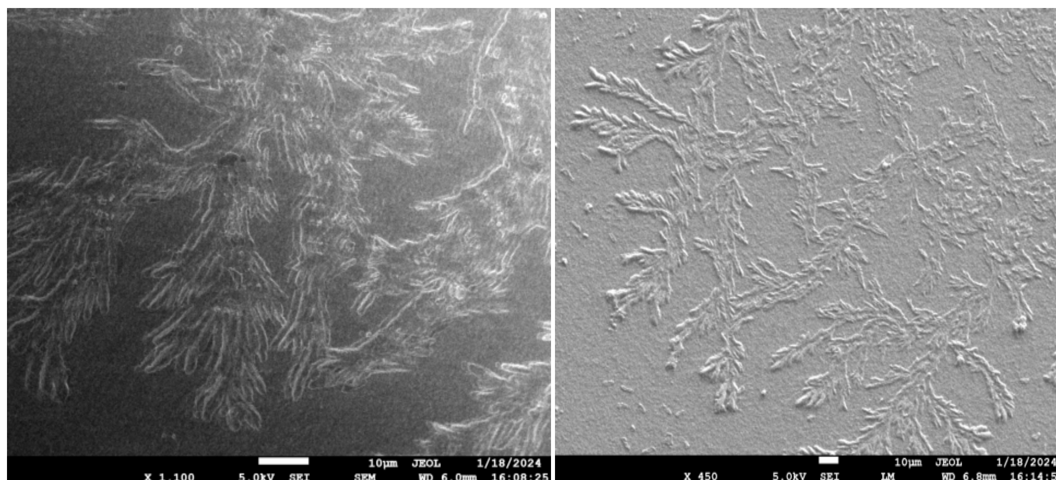


Figure 1. FESEM –surface morphology of BaS : Ce^{+3}- ions.

The characterization of crystal structure, lattice parameters, particle sizes and other correlated parameters of the BaS doped films were done with the help of X-ray diffraction line profiles of the films. Therefore, XRD- spectra were taken with low angle X-ray diffractometer (**Phillips X'pert Pro-Automated X-ray** (**model APD 1700**) diffractometer with CuK_α *– radiation* (λ = 1.572Å) as shown in Figures 2 (*a,b,c,d & e*) respectively. The crystal lattice parameters and the phase structures of the films at the doping concentrations of Ce^{+3}-ions were calculated using Bragg's relation

$$2d\sin\theta = n\lambda \quad (1)$$

where n is the order of X-ray diffraction and the phase structures were calculated from the relation

$$\sin^2\theta = (\lambda^2/4a^2)N \quad (2)$$

where $N = h^2 + k^2 + l^2$ and

$$d_{cal} = a/\sqrt{h^2 + k^2 + l^2} \quad (3)$$

The calculated (*hkl*) phase structures, and the lattice parameters in the doped BaS thin films have been shown in Table-2.

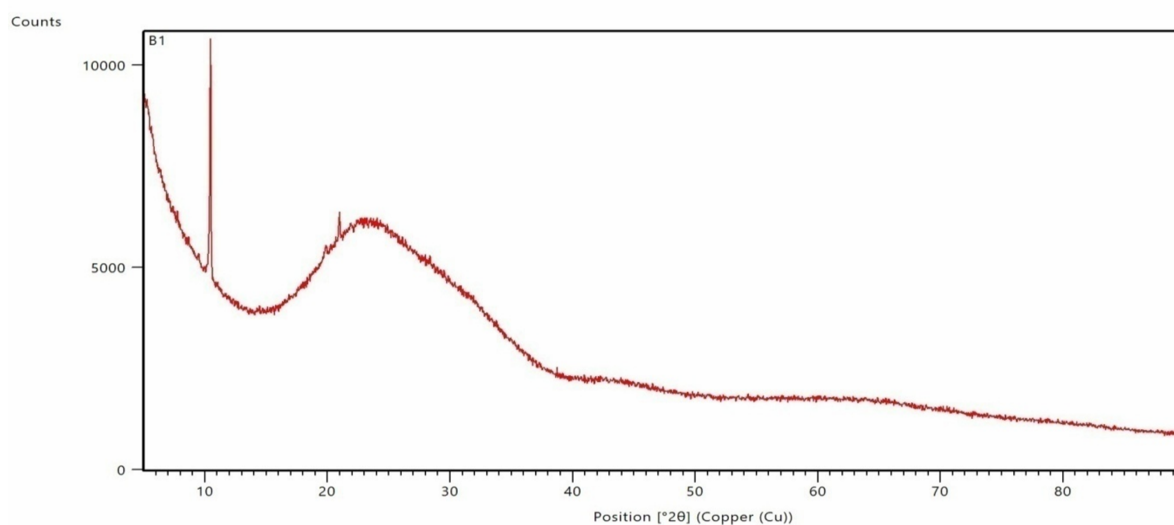
Table-1. X-ray diffraction line profile data of BaS:Ce^{+3} films

Quantum of Ce^{+3}	*Re.In. (%)*	*2θ (degree)*	*Height (cts)*	*FWHM Left (°2θ)*	*d-spacing (Å)*
2 at.% (BaS)	100.00	10.451	5940.00	0.1023	8.465
	32.56	19.812	1934.12	0.3070	4.481
	49.84	20.972	2960.64	0.1023	4.236
4.at% (BaS)	1.34	5.124	660.90	0.512	1,340
	100.00	20.798	49449.21	0.1023	100.00
	0.72	42.280	354.38	0.1535	0.720
	0.89	65.387	438.47	0.1872	0.890
	0.61	69.589	299.74	0.0936	0.610
6at.% (BaS)	28.90	19.881	2241.17	0.1023	4.465
	100.00	20.757	7753.79	0.0768	4.279
	28.46	28.356	2206.59	0.3070	3.148
8 at.% (BaS)	6.79	5.166	797.53	0.4093	17.108
	6.50	10.494	764.16	0.1023	8.430
	100.00	20.815	11748.68	0.0768	4.268
10 at.%(BaS)	100.00	28.007	2797.44	0.0936	3.184

(100)

(a) 2 at.% Ce^{+3}

(110)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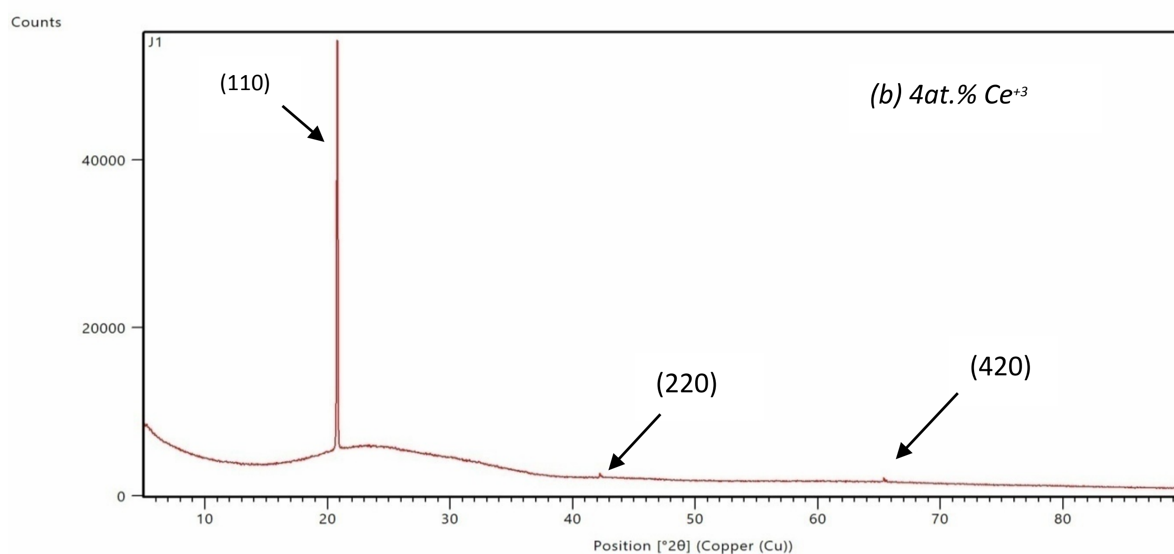
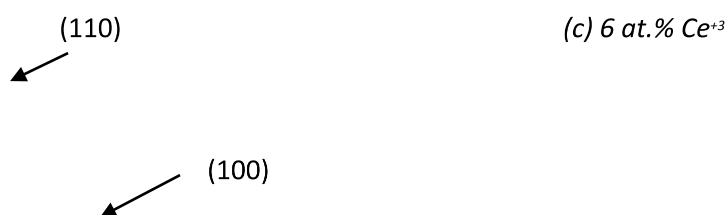
B1
10000
5000
0
10
20
30
40
50
60
70
80
Position [°2θ] (Copper (Cu))


Counts
J1
(110)
(b) 4at.% Ce+3
40000
20000
0
(220)
(420)
10
20
30
40
50
60
70
80
Position [°2θ] (Copper (Cu))


(110)
(c) 6 at.% Ce+3
(100)

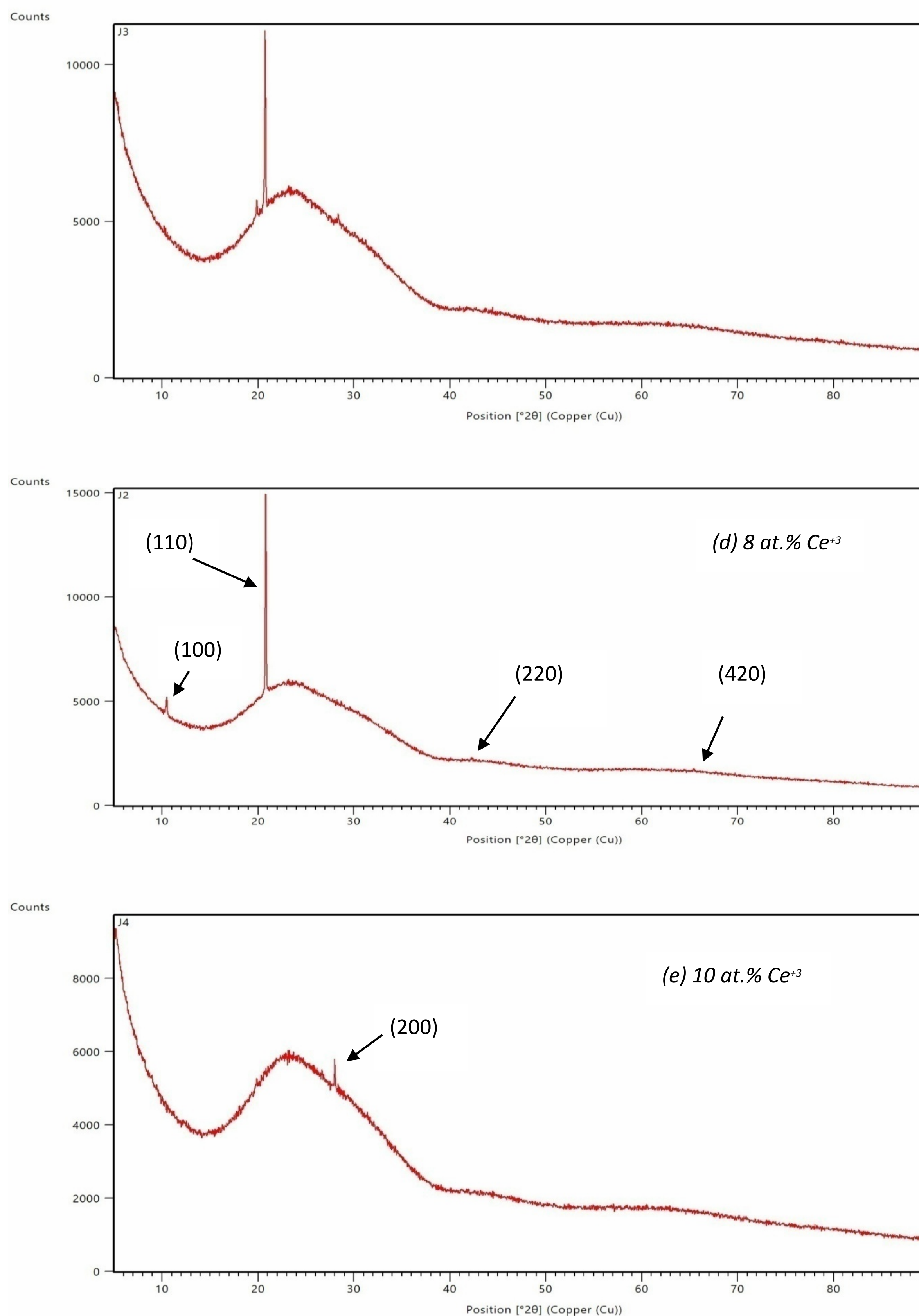


Figure 2. X-ray diffraction line spectra of BaS : Ce^{+3}-ions thin films.

Table-2. Phase structures and lattice parameters in BaS:Ce^{+3} –ions.

Quantum of Ce^{+3}-ions	*Rel.Int (I/I_0) %*	*2θ-value (degree)*	*Phase parameters (hkl)*	*Standard a-value (Å)*	*a_{cal}-value (Å)*	*Standard d-value (Å)*	*d_{cal}-value (Å)*
2at.%	100	10.451	(100)		8.448		8.465
	32.56	19.813	(110)		6.329		4.481
	49.84	20.972	(110)		6.329		4.236
4at.%	1.34	5.124					17.247
	100	20.798	(110)		6.033		4.271
	0.72	42.280	(220)		6.039		2.138
	0.89	65.387	(420)		6.375		1.426
	0.61	65.589	(420)		6.325		1.426
6at.%	28.90	19.881	(110)		6.308		4.466
	100.00	20.757	(110)	6.450	6.050	4.778	4.279
	28.46	28.356	(200)		6.287		2.148
							3.143
8at.%	6.79	5.166					17.108
	6.50	10.494	(100)		6.287		8.480
	100.00	20.815	(110)		6.028		4.268
10 at.%	100.00	28.007	(200)		6.364		3.183

*3.2***.** Grain *size, , micro-strains and stress and dislocation density:*

The grown BaS :Ce^{+3} films consist of grains of different sizes depending on the ionic doping concentrations**.** The grains or crystallite sizes were calculated using the Scherrer relation [8,9]

$$D_{hkl} = k\lambda/\beta_{2\theta}\cos\theta \quad (4)$$

where the value of the shape factor k is taken as 0.94, $\beta_{2\theta,}$ the full width of half maximum intensity (100%) of the sample are taken from the XRD data (Table- 1) and θ the Bragg angle. The values of the grain sizes at different doping are shown in Table-3. The crystallite sizes of the grown BaS doped Ce^{+3} - ions are found lying nearly between 80 – 100nm.

The chemically synthesized BaS doped nanocrystalline thin films grown under suitable experimental conditions were observed under various micro-strains on account of some factors likevariations of lattice parameters, oxygen vacancies. The micro-strains were calculated using the relation [10]

$$\varepsilon = \beta_{2\theta} [\cot\theta/4] \quad (5)$$

The stresses caused by some thermal expansion co-efficient of the films and haphazard grain size orientations were calculated using the relation [11,12]

$$S = E/2\gamma(a_0 - a)/a_0 \quad (6)$$

where $a_0$and a are lattice parameters of BaS bulk and thin film materials, γ the Poisson ratio taken as 0.28 and E the Young's Elastic Moduli as 67.2GPa.[13] The value of a is the average of a_{cal}-values of the films corresponding to sets of Ce^{+3}--ion doping. The dislocation density in the films on account of oxygen vacancies were calculated using Willamson and Smallman's relation [14 -16]

$$\delta = 1/D_{hkl}^2 \quad (7)$$

where D_{hkl} is the grain or particle size. The values of particle sizes, micro-strains, stress and dislocation density are shown in Table-3..

Table-3. Observed grain sizes, micro-strains, stress and dislocation density

Sample (BaS)	*Max. Int. (%)*	*FWHM Left (^{0}2θ)*	*Grain size (nm)*	*Micro-strains (ε) x 10^{-2}*	*Stress (GPa)*	*Dislocation density(δ) x10^{14} (linesm^{-2})*	*Bulk a_0 (Å)*	*Sample a_{av} (Å)*
2 at.%		0.1023	81.28	50.01	12.30	1.51		7.035
4 at.%		0.1023	81.28	50.01	5,41	1.51		6.149
6 at.%	100	0.0768	108.13	5.00	4.22	0.86	6.450	6.215
8 at.%		0.0768	108.13	5.00	5.25	0.86		6.158
10 at.%		0.0936	88.74	50.01	1.54	1.27		6.364

*E = 67.2GPa and *γ = 0.28

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Table-4. Determination of BaS doped crystal structure

BaS: Ce^{+3}	*At intensity 100%*				*$Sin^2\theta_1/sin^2\theta_2$*	*$(h_1^2+k_1^2+l_1^2)/(h_2^2+k_2^2+l_2^2)$*	*Cr.struc.*
	$(h_1k_1l_1)$	*$(h_2k_2l_2)$*	*Θ_1*	*Θ_2*			
2 at.%	100	110	5.23^0	9.91^0	0.28	0.50	b.c.c
4at.%	110	220	10.39^0	21.14^0	0.25	0.25	trans.
6at.%	110	200	10.38^0	28.36^0	0.54	0.50	b.c.c
8at.%	100	110	5.25^0	10.41^0	0.26	0.50	b.c.c
10at.%	200		14.00^0				

It is observed that the host BaS :Ce^{+3}-nanocrystal thin films consist of 2 atoms per unit cell with unit cell dimensions *8.448Å (2at.%), 6.329Å (4at.%), 6.050Å, (6at.%), 6.028Å (8at.%)* and *6.364Å (10at.%)* corresponding to *(100), (110), (100), (110)* and *(200)* reflection planes respectively.The $Sin^2\theta_1/Sin^2\theta_2$ values corresponding to the first to second reflection planes at maximum intensity yielded ≤ 0.50 and confirms the b.c.c. cubic zinc blend structure [17] as shown in Table-4.

IV. Conclusion

Successive Ionic Layer Adsorption and Reaction (SILAR) technique is found to be the economically and less time easiest method for synthesis of doped or undoped semiconducting thin films. The XRD of the as synthesized Ce^{+3} - ions doped BaS thin films showed exclusively b.c.c. cubic zinc blend structures as confirmed with $sin^2\theta$ ratio. FESEM imaging surface morphology in the BaS films revealed uniform rode like at lower dopings and leaf or petal like at heigher doping concentrations. The nanoparticle sizes range down from 80 – 100nm in diameter. Some localized crystalline dislocation density were observed in the films growing up relatively with increase of Ce^{+3} -ion concentrations. The dislocation density on account of oxygen vacancies attributed micro lattice stress and strains in the chemically synthesized BaS doped thin films.

Acknowledgements

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References

[1]. Okoli Donald Nuanyere**,,** IOSR Journal of Applied Physics (IOSR-JAP) Vol. 7, Issue 4 Ver.11 (Jul.-Aug., 2015), 10-15
[2]. Mohammed Ameri, Amina Touia, Houari Khachai, Zoubir Mahdjoub, Mohamed Zoheir Chekroun, Amei Slamani, Materials Science and Applications, Sept., 2012, 3,612-618
[3]. K Syassen, N E Christenssen, H Winzen, K Fischer and J Evers, Physical Review B, Vol. 35, No.8, 1987, 4052-4059
[4]. G. Kalpane, B. Palanivel and M. Rajagopalan, Physical Review B, Vol. 50, No. 17, 1994, 12318-12325.
[5]. Cotvin V. I., Schlamp, M. C. And Alivisatos, A.P., (1994) : Nature, 370, 354.
[6]. Okoli Donald Nuanyere**,** IOSR Journal of Applied Physics (IOSR-JAP) Vol. 7, Issue 4 Ver.11 (Jul.-Aug.,2015),10-15.
[7]. Subra Misra, D.S. Kshatri, Ayush Khare and Sanjay Tiwari**,** Proceeding of BITCON-2015 Innovations for National Development National Conference on Nanostructural Materials and their Characterization,
[8]. H. P. Klug, L. E Alexander, X-Ray Diffraction Procedures, (New York : John Willey & Sons, Inc.) (1954) Chap 9, 491
[9]. K.Kunjabali Singh and H.L.Das, Indian J. Phys, **82**(6),(2008) 685-693
[10]. Suchitra Sen, S. K. Halder and S. P. Sengupta, J. Phys. Soc. Jpn. **38** (1975)1644
[11]. C. K. Dey, N. K. Misra and T. B. Ghosh, Indian j. Phys., 69A (2) (1995), 261
[12]. C. K. Dey, N. K. Misra and T. B. Ghosh, Indian j. Phys., 71A (5) (1997)530
[13]. Marvin J. Weber, Hand Book of Optical Materials, CRC Press LLC, New York Sec. 1 (2003)117
[14]. Mahalingam T, Thanikaikarasan S, and Chandramohan R, Mater,Sci Eng B,174 (2010)236
[15]. M. Rasmani Devi and K. Kunjabali Singh, International Journal of Engineering and Technical Research (JETR) Vol.-9, Issue-12,Dec., 2019,1-4
[16]. K. Manikandan, P. Mani, P. Fermi Hilbert Janbaraj, T. Dominic Josheph, V. Thangaraj, C. Surendra Dilip and J. Josheph Prince, Indian Journal of Pure & Applied Physics Vol. 52, May 2014, 354-359
[17]. N. Gupta and R. C. Gupta, Principle of Material Sci. and Eng (New Delhi : Dhanapati Rai & Co. Ltd.) (2001)79