

# Photo-Catalytic Activity of $\text{Ca}_{1-x}\text{Ni}_x\text{S}$ Nanocrystals

Rupali Sood, Barinder Singh, Dinesh Kumar, H. S. Bhatti\*, Karamjit Singh

Department of Physics, Punjabi University, Patiala, India

Email: [\\*drhsbhatti03@yahoo.co.in](mailto:drhsbhatti03@yahoo.co.in)

Received 24 March 2015; accepted 13 July 2015; published 16 July 2015

Copyright © 2015 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

---

## Abstract

$\text{Ca}_{1-x}\text{Ni}_x\text{S}$  ( $0 \leq x \leq 0.05$ ) nanocrystals have been synthesized by facile solid state reaction method. Synthesized nanocrystals are further etched with mild acid solutions to reduce the particle size, which augments the surface to volume ratio and confinement of carriers. Crystallographic and morphological characterizations of synthesized nanomaterials have been done by X-ray diffraction and electron microscopy, respectively. Comparison of the diffraction and electron microscopy studies reveal the formation of single crystalline nanostructures. Optical characterization of synthesized nanomaterials has been done by UV-vis. absorption spectroscopic studies. The photo-catalytic activity of synthesized nanomaterials under UV irradiation has been tested using methylene blue (MB) dye as a test contaminant in aqueous media. Photo-catalytic behaviour dependence on dopant concentration and etching has been thoroughly studied to explore the potential of synthesized nanomaterials for next era optoelectronic industrial applications as well as polluted water purification.

## Keywords

$\text{Ca}_{1-x}\text{Ni}_x\text{S}$  Nanocrystals, Crystallography, Morphology, Photo-Catalytic Activity

---

## 1. Introduction

Semiconductor nanostructures due to their size tunable photo-physical and photo-chemical properties caused by enhanced surface to volume ratio and quantum confinement effects on nanoscale, establish as competent materials for smart optoelectronic industrial applications as well as efficient photo-catalysts [1]-[5]. Efficiently luminescing intrinsic and extrinsic semiconductor nanocrystals have received considerable attention during the last three decades [6]-[10]. The changes in the electronic structure as a function of particle size due to quantum size

---

\*Corresponding author.

effects are intriguing and have stimulated fundamental research on various types of nanocrystalline semiconductors. Intrinsic and extrinsic semiconductor nanostructures are generally used as heterogeneous photo-catalysts due to their high oxidizing power and non-requirement of oxidizing reagents. Heterogeneous photo-catalytic processes are widely utilized to oxidize or mineralize organic/inorganic substances that could not be degraded with biological techniques. Semiconductor photo-catalysts offer the potential for completing elimination of toxic chemicals through their efficiency and potentially broad applicability.

Doped calcium sulfide (CaS) nanophosphor has a great potential for its applications as a phosphor in CRTs, fluorescent screen, displays panels and even in thermoluminescence dosimetry [11]-[13]. Numerous researchers have studied the irradiation effects in doped CaS during last several decades [14]-[16]. Potential of doped CaS nanocrystals as UV dosimeters has been also reported [17] [18]. But to the best of our knowledge, nobody has tried to explore the potential of intrinsic and extrinsic CaS nanocrystals for photo-catalytic applications.

In the present investigations emphasis has been given to explore the photo-catalytic activity potential of  $\text{Ca}_{1-x}\text{Ni}_x\text{S}$  ( $0 \leq x \leq 0.1$ ) nanocrystals synthesized via facile solid state reaction method. The photo-catalytic behavior of synthesized nano photo-catalysts has been studied by recording MB dye degradation in aqueous media under UV radiation exposure. Photo-catalytic activity dependence on the nanocrystals morphology and dopant concentration has been thoroughly studied.

## 2. Experimental

$\text{Ca}_{1-x}\text{Ni}_x\text{S}$  ( $0 \leq x \leq 0.1$ ) nanocrystals have been synthesized by the solid state diffusion method [19] [20]. Analytical reagent (AR) grade chemicals; calcium sulphate, nickel nitrate, sodium thioisulphate, carbon powder and ethanol were used as the starting materials without further purification. All these chemicals were purchased from Sigma Aldrich and purity content of all these chemicals was 99.9%. Carbon acts as a reducing agent for the reduction of sulphate to sulphide at high temperature, and nickel acts as an activator. Sodium thioisulphate acts as flux for the reaction. The calculated quantities of calcium sulphate, carbon powder, nickel nitrate and flux were mixed thoroughly with the help of agate pestle and mortar. For the uniform distribution of dopant, initially dopant precursor was dissolved in small volume of ethanol, and then this solution was mixed with the entire charge. Then, the resulting mixture was transferred to a clean graphite crucible (which was already baked at the firing temperature) and a thin layer of carbon powder spread over it. The charge in the crucible was covered with another similar crucible. The thin layer of the carbon over the charge created a reducing environment at high temperature. This whole arrangement was placed in the muffle furnace, and the charge was fired at  $950^\circ\text{C}$  for two hour. Firing at high temperature causes the incorporation of nickel in the host lattice. After two hour, the red hot charge was taken out and rapidly crushed. Finally, the prepared powder sample was collected in dry sample tubes for further studies. For the further reduction of the particle size, the synthesized samples were etched with dilute hydrochloric acid. The particles were dispersed in etching solution (HCl aqueous solution) using mechanical stirring. The solution was allowed to settle for a couple of minutes. Then, the etched nanoparticles were collected by centrifugation and redispersed in ethanol. Then these particles were dried in vacuum oven at ambient temperature for further studies.

Analytical's (Netherlands) X 'Pert Pro Powder X-ray diffractometer with  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) was used to record diffraction patterns of the synthesized samples in the  $2\theta$  range  $20^\circ - 80^\circ$ . Average crystallite size has been calculated from the line broadening of the X-ray diffraction (XRD) diffractograms using Scherrer formula [21]. Hitachi, [(H-7500), Japan] transmission electron microscope (TEM) was used to record the electron micro-graphs for average particle size determination. For TEM studies, a drop of well ultrasonicated ethanol dispersed nanocrystals was placed on the carbon coated copper grid.

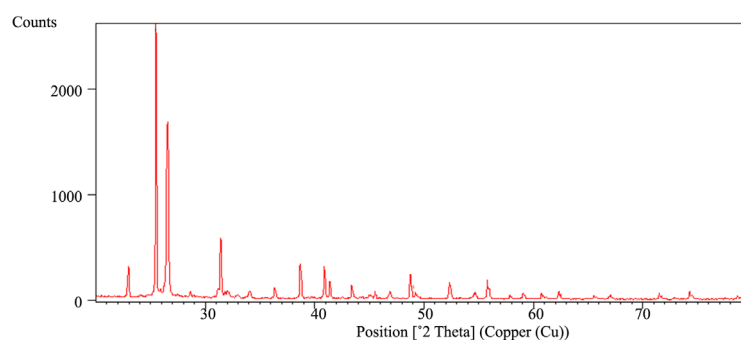
The photo-catalytic activity of synthesized  $\text{Ca}_{1-x}\text{Ni}_x\text{S}$  ( $0 \leq x \leq 0.1$ ) nanocrystals was studied by monitoring the degradation of methylene blue (MB) ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 2\text{H}_2\text{O}$ ) dye in an aqueous suspension containing nanocrystals under the UV-radiation exposure with continuous magnetic stirring. A 350 ml of aqueous suspension was prepared by completely dissolving 1.1322 mg of the MB dye and then dispersing 140 mg of the  $\text{Ca}_{1-x}\text{Ni}_x\text{S}$  nanocrystals in the de-ionized water. The resulting suspension was equilibrated by stirring in the dark for 1 h to stabilize the adsorption of MB dye on the surface of nanocrystals. The stable aqueous suspension was then exposed to the UV-radiation with continuous magnetic stirring, using the home made photoreactor containing two 18-W tubes as the UV-source ( $\lambda = 200 - 400 \text{ nm}$ ). Following the UV-radiation exposure, 10 ml sample of aqueous suspension was taken out after every 10-min interval for the total 80 min of the UV-radiation exposure. Suspen-

sion sample was centrifuged to filter out the nanophoto-catalyst particles, then nanophoto-catalyst free aqueous dye solution was examined using UV-vis absorption spectrophotometer (Hitachi U-2900) to study the photo-degradation of the MB dye.

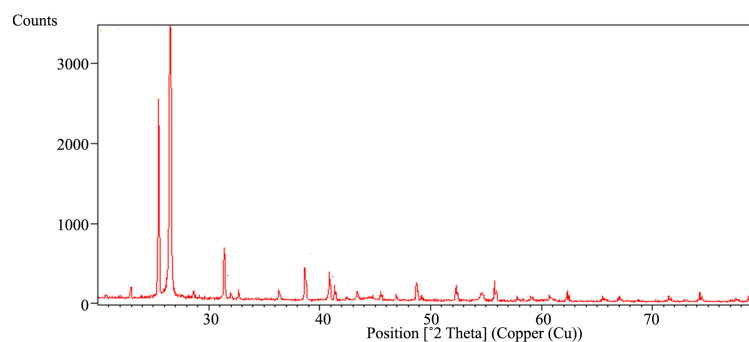
### 3. Results and Discussion

Nominally broadened XRD patterns have been recorded for all the synthesized  $\text{Ca}_{1-x}\text{Ni}_x\text{S}$  samples. **Figures 1-3** show X-ray diffractograms recorded for pristine CaS, etched CaS and  $\text{Ca}_{0.95}\text{Ni}_{0.05}\text{S}$  nanocrystals, respectively. Recorded diffractograms confirm the formation of nanocrystallites having average crystallite size extremely larger than Bohr exciton radius of the calcium sulphide. Crystallographic characteristics are strongly dependent on the synthesis conditions and hence the morphology. In case of pristine CaS nanocrystals, major diffraction peak has been observed at  $25.3^\circ$ , on the other hand, major diffraction peak at  $26.5^\circ$  has been observed for the etched CaS and Ni doped CaS samples. It can be clearly observed from the recorded diffractograms that the addition of nickel ions in the host lattice augments the crystalline texture of synthesized nanocrystals.

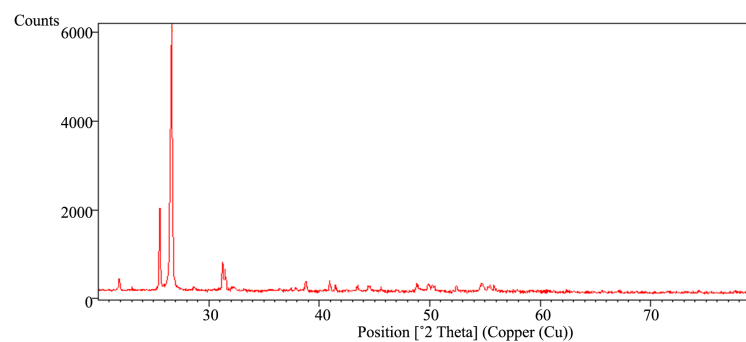
**Figure 4** shows the TEM micrograph recorded for synthesized CaS nanocrystals. Although, synthesized



**Figure 1.** XRD pattern of CaS nanocrystals.



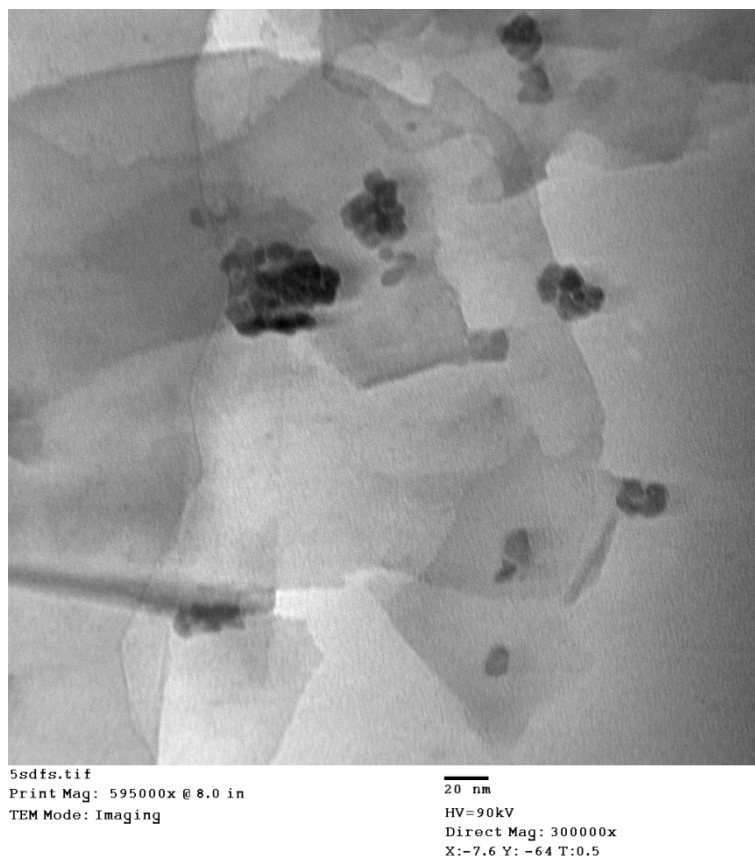
**Figure 2.** XRD pattern of etched CaS nanocrystals.



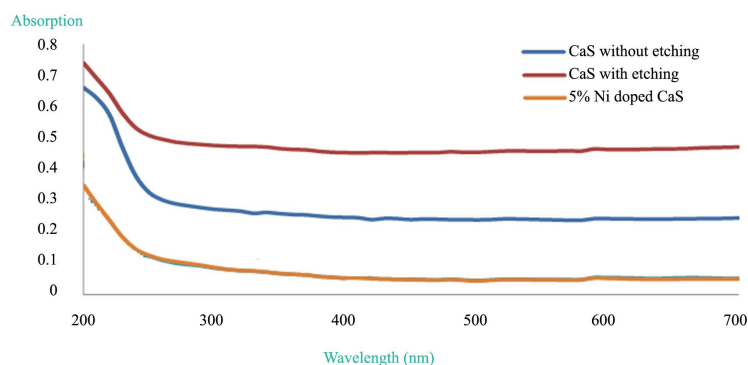
**Figure 3.** XRD pattern of  $\text{Ca}_{0.95}\text{Ni}_{0.05}\text{S}$  nanocrystals.

nanoparticles appear in the form of agglomerates due the absence of capping agents, but average size of the fundamental units of agglomerates are less than 20 nm.

**Figure 5** shows the UV-Vis. absorption spectra of synthesized nanocrystals dissolved in aqueous media. Recorded spectra show the blue shift in the absorption edge of the etched samples compared to the pristine samples. The blue shift in the etched samples reveals the reduction in the particle size, which is also confirmed by the XRD results. All the synthesized samples have sturdy absorption in UV region.

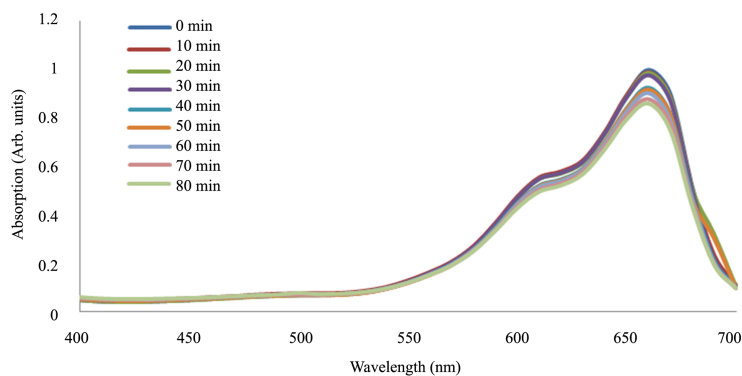


**Figure 4.** TEM micrograph of CaS nanocrystals.

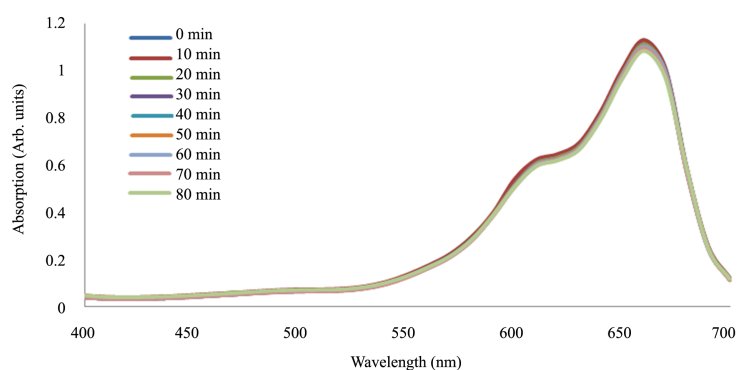


**Figure 5.** Absorption spectra of synthesized nanocrystals.

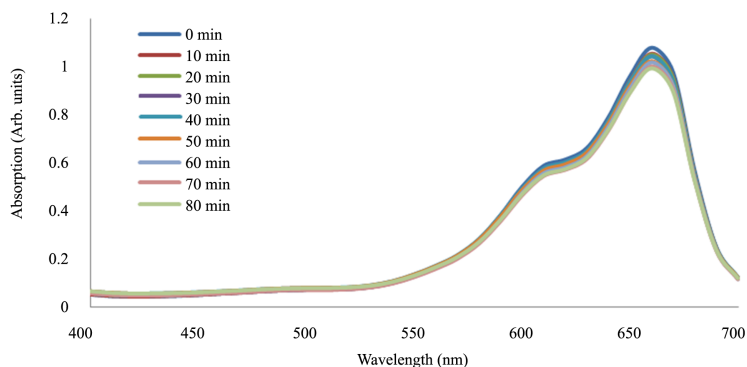
**Figure 6** shows the absorption spectra of the MB dye solution in the presence of CaS nanocrystals for different durations of UV radiation exposure. **Figure 7** & **Figure 8** show the absorption spectra of dye solution for different durations of UV-radiation exposure in the presence of etched CaS and  $\text{Ca}_{0.95}\text{Ni}_{0.05}\text{S}$  nano-photocatalysts.



**Figure 6.** Absorption spectra of dye solution for different durations of UV-radiation exposure in the presence of pristine CaS nanocrystals.



**Figure 7.** Absorption spectra of dye solution for different durations of UV-radiation exposure in the presence of etched CaS nanocrystals.



**Figure 8.** Absorption spectra of dye solution for different durations of UV-radiation exposure in the presence of  $\text{Ca}_{0.95}\text{Ni}_{0.05}\text{S}$  nanocrystals.

Decrease of absorbance with increasing irradiation time shows the efficient degradation of MB dye, hence the synthesized nanocrystals have excellent photo-catalytic activity potential to purify the dye contaminated water. But, comparative study of the recorded results shows that the pristine CaS nanocrystals have high photo-catalytic activity than the etched and doped CaS nanocrystals. Etching may enhance the surface defect states, which may act as charge carrier recombination centers and thus diminishes the probability of charge carrier's participation in oxidation and reduction reactions. Initially, addition of nickel in CaS causes decline in the photo-catalytic activity, as these dopant ions may introduce ladder like levels in the forbidden gap of the host material for the non-radiative relaxation of charge carriers, but increasing dopant concentration slightly boost the

photo-catalytic activity.

#### 4. Conclusion

Solid state reaction method is an efficient method, which gives high yield of good quality  $\text{Ca}_{1-x}\text{Ni}_x\text{S}$  ( $0 \leq x \leq 0.05$ ) nanocrystals. Crystallographic and morphological characteristics of the synthesized nanomaterials are tunable with synthesis reaction parameters. Dilute hydrochloric acid acts as an efficient nanomaterial etchant, although the nanomaterial morphology can easily altered with etching, but etching enhances the surface defect states, which may act as charge carrier recombination centers to reduce the photo-catalytic activity. Pristine CaS nanocrystals have high photo-catalytic activity than etched and doped CaS nanocrystals. These eco-friendly nanocrystals can be used for purification of polluted water.

#### References

- [1] Ranfagni, A., Fabeni, P., Pazzi, G.P. and Mugnai, D. (1993) Anomalous Pulse Delay in Microwave Propagation: A Plausible Connection to the Tunneling Time. *Physical Review E*, **48**, 1453. <http://dx.doi.org/10.1103/PhysRevE.48.1453>
- [2] Bol, A.A., Beek, R.V. and Meijerink, A. (2002) On the Incorporation of Trivalent Rare Earth Ions in II-VI Semiconductor Nanocrystals. *Chemistry of Materials*, **14**, 1121-1126. <http://dx.doi.org/10.1021/cm011195s>
- [3] Singh, K., Kumar, S., Verma, N.K. and Bhatti, H.S. (2009) Photoluminescence Properties of  $\text{Eu}^{3+}$ -Doped  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  Quantum Dots. *Journal of Nanoparticle Research*, **11**, 1017-1021. <http://dx.doi.org/10.1007/s11051-009-9586-1>
- [4] Chitkara, M., Singh, K., Sandhu, I.S. and Bhatti, H.S. (2011) Photo-Catalytic Activity of  $\text{Zn}_{1-x}\text{Mn}_x\text{S}$  Nanocrystals Synthesized by Wet Chemical Technique. *Nanoscale Research Letters*, **6**, 438. <http://dx.doi.org/10.1186/1556-276X-6-438>
- [5] Kumar, D., Singh, K., Kaur, G., Verma, V. and Bhatti, H.S. (2015) Synthesis and Optical Characterization of Pure and Cobalt Doped Gallium Nitride Nanocrystals. *Journal of Materials Science: Materials in Electronics*. <http://link.springer.com/article/10.1007/s10854-015-3184-z>
- [6] Rossetti, R., Hull, R., Gibson, J.M. and Brus, L.E. (1985) Excited Electronic States and Optical Spectra of ZnS and CdS Crystallites in the  $\approx 15$  to 50 Å Size Range: Evolution from Molecular to Bulk Semiconducting Properties. *Journal of Chemical Physics*, **82**, 552. <http://dx.doi.org/10.1063/1.448727>
- [7] Brus, L. (1986) Electronic Wave Functions in Semiconductor Clusters: Experiment and Theory. *Journal of Physical Chemistry*, **90**, 2555-2560. <http://dx.doi.org/10.1021/j100403a003>
- [8] Henglein, A. (1989) Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. *Chemical Reviews*, **89**, 1861-1873. <http://dx.doi.org/10.1021/cr00098a010>
- [9] Wang, Y. and Herron, N. (1991) Nanometer-Sized Semiconductor Clusters: Material Synthesis, Quantum Size Effects and Photophysical Properties. *Journal of Physical Chemistry*, **95**, 525. <http://dx.doi.org/10.1021/j100155a009>
- [10] Alivisatos, A.P. (1996) Perspectives on the Physical Chemistry of Semiconductor Nanocrystals. *Journal of Physical Chemistry*, **100**, 13226-13239. <http://dx.doi.org/10.1021/jp9535506>
- [11] Pham-Thi, M. (1995) Rare-Earth Calcium Sulfide Phosphors for Cathode Ray Tube Displays. *Journal of Alloys & Compounds*, **225**, 547-551. [http://dx.doi.org/10.1016/0925-8388\(94\)07060-1](http://dx.doi.org/10.1016/0925-8388(94)07060-1)
- [12] Marwaha, G.L., Singh, N., Vij, D.R. and Mathur, V.K. (1979) CaS: Bi as U.V. Dosimeter. *Materials Research Bulletin*, **14**, 1489-1495. [http://dx.doi.org/10.1016/0025-5408\(72\)90217-6](http://dx.doi.org/10.1016/0025-5408(72)90217-6)
- [13] Marwaha, G.L., Singh, N. and Mathur, V.K. (1980) Spectral Variations and Retrapping Processes in CaS: Bi Dosimeter. *Radiation Effects*, **53**, 25-31. <http://dx.doi.org/10.1080/00337578008207092>
- [14] Marwaha, G.L., Singh, N., Nagpal, J.S. and Mathur, V.K. (1981) Operational Importance of Some Physical Parameters of TL Phosphor CaS: Bi. *Radiation Effects*, **55**, 85-90. <http://dx.doi.org/10.1080/00337578108225469>
- [15] Hutt, G. and Jaek, I. (1996) Optically Stimulated Luminescence Materials Based on CaS for Gamma and Fast Neutron Dosimetry. *Radiation Protection Dosimetry*, **65**, 297-300. <http://dx.doi.org/10.1093/oxfordjournals.rpd.a031645>
- [16] Kumar, V., Kumar, R., Lochab S.P. and Singh, N. (2007) Swift Heavy Ion Induced Structural Modification and Photo-Luminescence in CaS: Bi Nanophosphors. *Journal of Nanoparticle Research*, **9**, 661-667. <http://dx.doi.org/10.1007/s11051-006-9189-z>
- [17] Kumar, V., Kumar, R., Lochab, S.P. and Singh, N. (2006) Thermoluminescence and Dosimetric Properties of Bismuth Doped CaS Nanocrystalline Phosphor. *Radiation Effects & Defects in Solids*, **161**, 479-485. <http://dx.doi.org/10.1080/10420150600800597>

- 
- [18] Kumar, V., Singh, N., Kumar, R. and Lochab, S.P. (2006) Synthesis and Characterization of Bismuth Doped Calcium Sulfide Nanocrystallites. *Journal of Physics: Condensed Matter*, **18**, 5029.  
<http://dx.doi.org/10.1088/0953-8984/18/22/003>
- [19] Sharma, G., Chawla, P., Lochab, S.P. and Singh, N. (2009) Thermoluminescence Characteristics of CaS: Ce Nanophosphors. *Chalcogenide Letters*, **6**, 705.
- [20] Singh, V., Rao, T.K.G., Zhu, J.J. and Tiwari, M. (2006) Luminescence and Defect Studies of Ce<sup>3+</sup> Doped CaS Phosphor Synthesized via Solid State Diffusion Method. *Material Science and Engineering: B*, **131**, 195-199.  
<http://dx.doi.org/10.1016/j.mseb.2006.04.015>
- [21] Cullity, B.D. (1978) Elements of X-Ray Diffraction. Addison-Wesley Publishing Company, Boston, 102.