

A Review on Synthesis of Nanophosphors – Future Luminescent Materials

Harish Chander

Luminescent Materials and Devices Group, Electronic Materials Division
National Physical Laboratory,
Dr K S Krishnan Road, New Delhi-110012 (INDIA)
hchander@mail.nplindia.ernet.in

Abstract: *Nanophosphors have been extensively investigated during the last decade due to their application potential for various high-performance and novel displays and devices. Synthesis of nanophosphors is generally done by chemical methods. Under chemical methods, different routes such as colloidal, capping, cluster formation, sol-gel, electrochemical etc., are being followed. Physical methods widely used are molecular beam epitaxy, ionised cluster beam, liquid metal ion source, consolidation, sputtering and gas aggregation of monomers are much sophisticated. Chemical precipitation in presence of capping agents, reaction in microemulsions, sol gel reaction and auto-combustion are commonly used techniques for synthesis of nanophosphors. Particle size must be less than twice of Bohr radii of exciton as quantum confinement regime is limited to that size. A brief review of different synthesis techniques employed all over the world for the development of industrially important nanophosphors and extent of particle size reduction achieved is discussed. The approach being followed by us at NPL shall also be given.*

Introduction

Semi-conductors in nano-crystallized form exhibit markedly different electrical, optical and structural properties as compared to those in the bulk form. Out of these, the ones suited as phosphor host material show considerable size dependent luminescence properties when an impurity is doped in a quantum-confined structure. The impurity incorporation transfers the dominant recombination route from the surface states to impurity states. If the impurity-induced transition can be localized as in the case of the transition metals or the rare earth elements, the radiative efficiency of the impurity-induced emission increases significantly. The emission and decay characteristics of the phosphors are, therefore, modified in nanocrystallized form. Also, the continuous shift of the absorption edge to higher energy due to quantum confinement effect, imparts these materials a degree of tailorability. Obviously, all these attributes of a doped nanocrystalline phosphor material are very attractive for optoelectronic device applications.

Nanoparticles, in general, are supposed to have nearly half of their atoms contained in top two monolayers, which make optical properties highly sensitive to surface morphology. Blue shift of band gap and strong non-linear response of nanoparticles of CdS and CdSe

in glass samples were first reported² in the early 1980s. Enhanced quantum properties were further confirmed with study of other semiconductor nanoparticles of ZnS, PbS, ZnSe and CdSe³. Metal nanoparticles⁴ were also synthesized with a view to prepare better catalysts. The size has to be less than twice of Bohr radii of exciton (3-5 nm) for quantum confinement regime.

In the present talk, I shall review different nano luminescent materials, their preparation strategy, crystalline phase, size and luminescent property. What is the future of nanophosphors and related devices? Are nanoscale display devices, detectors and light sources going to be reality?

Preparation Strategies and Results

Chemical Precipitation

In this strategy we control the size by arrested precipitation technique. The basic trick has been to synthesis and studies the nanomaterial in situ i.e. in the same liquid medium avoiding the physical changes and aggregation of tiny crystallites. Thermal coagulation and Oswald ripening were controlled by double layer repulsion of crystallites using non-aqueous solvents at lower temperatures for synthesis. The first report on nanosize luminescent materials was by Bhargava et al¹ in 1994. They synthesized manganese-doped nanocrystals of zinc sulfide. The nanomaterials had external photoluminescence quantum efficiency of 18 %. The synthesis involved reaction of diethyl zinc with hydrogen sulfide in toluene. The dopant manganese is added as ethylmanganese in tetrahydrofuran solvent to the parent solution of zinc salt before precipitation reaction. Surfactant methacrylic acid was used to maintain separation between the particles formed. The dried material was further subjected to UV curing for possible polymerization of surfactant methacrylate capping film on the surface of Mn doped ZnS nano cluster for imparting true quantum confinement. The enhancement of efficiency has been explained on the basis of surface passivation of the nanocrystals due to photopolymerization of the surfactant. The photoluminescent (PL) and photoluminescence excitation (PLE) spectra of the nanophosphor have been compared with bulk ZnS:Mn. The PL is slightly shifted and there is a larger linewidth in the nanophosphor as compared to bulk.

Following the encouraging results of Bhargava et al on Mn doped ZnS nanophosphor Khosravi et al⁵ reported synthesis of manganese doped ZnS nanoparticles by aqueous method. Aqueous solution of zinc chloride

H. Chander

with required amount of dopant manganese chloride is mixed slowly with mercaptoethanol under constant agitation and then reacted drop wise with sodium sulfide solution. The reaction was carried under nitrogen gas to avoid oxidation of freshly formed highly reactive nanoparticles. They observed PLE and PL peaks at 312 and 600 nm respectively. Mn concentration of 12 at wt % was found to be optimum. Khosravi et al⁶ with slightly different team reported synthesis of copper doped zinc sulfide quantum particles. Synthesis was carried out in presence of sodium hexametaphosphate at pH 8-9. On a growing metal sulfide cluster, phosphate chains get attached through metal ions. These chains separate the clusters due to their length and avoid coalescence. Luminescence decay times were determined for both Cu doped and undoped ZnS. Two exponential decay times of 2.9, 54.2 and 1.62, 22.12 ns were observed. Undoped sample obviously had shorter decay times.

A large amount of work⁷⁻²⁸ is reported on preparation by the strategy and interesting results have been obtained. For details one should refer to Development of Nanophosphors-A Review⁶³.

Karar et al²⁹ in 2004 synthesized and reported studies on ZnS:Mn nanophosphor capped with ZnO. The nanophosphor was prepared by reacting acetates of zinc and manganese with sodium sulfide. Thereafter, in the same reaction medium zinc acetate along with ammonia solution were reacted leading to formation of zinc hydroxide i.e. ZnO on drying on zinc sulfide. Capping was confirmed by TEM micrography and XPS with sputtering. PL spectra of samples with different level of ZnO coating have been recorded.

Sol-gel Strategy

Stanic et al³⁰ reported in 1997 sol-gel synthesis of nanosize ZnS. Zinc tert-butoxide in butanol and water free toluene was taken and high purity hydrogen sulfide gas bubbled through the solution till complete gelation occurred. Gel was aged and dried in vacuum. Formation of ZnS was confirmed by X-ray diffraction (XRD) and IR absorption spectra.

Many other phosphors have been made by the strategy. Park et al³¹ in 2000 made YAG – $Y_3Al_5O_{12}$:Tb phosphor in nanocrystallized form; Yu et al³² in 2001 synthesized nanostructured Al_2O_3 by sol-gel process; Ishizaka et al³³ in 2002 prepared Tb^{3+} and Eu^{3+} doped alumina films by gel technique and studied their luminescence properties; Lu and Jagannathan³⁴ in 2002 synthesized $Y_3Al_5O_{12}$: Ce^{3+} (YAG) nanophosphor by sol-gel pyrolysis; Yang et al³⁵ in 2002 reported lowering of synthesis temperature of doped $SrAl_2O_4$ solid-state reaction if the precursor was made in nanophase by sol-gel method; Pan et al³⁶ in 2003 reported synthesis of Pr^{3+} -doped $CaTiO_3$ nanophosphor and Wang et al³⁷ in 2003 synthesized cubic nanocrystalline Y_2O_3 :Tb phosphor by combustion technique followed by sol-gel synthesis of organo compound. Gu et al³⁸ in 2003 prepared SnO_2 :Dy nanophosphor; Morita et al³⁹ in 2004 prepared metal ion doped silica glasses by sol-gel

technique; In other sample of ZnS:Cu,Al in sol-gel matrix; Yan and Zhou⁴⁰ in 2004 prepared $Y_xGd_{2-x}O_3$: Eu^{3+} nanophosphor via sol-gel technique.

Haranath et al⁴¹ in 2004 reported controlled growth of ZnS nanophosphor in porous silica matrix in an effort to replace organic capping agents with inorganic ones which are more stable and robust. Synthesis involved preparation of silica alcogel from tetraethylorthosilicate with ethanol and water as diluents and hydrochloric acid as catalyst. Aqueous solutions of zinc and manganese were added in colloidal solution of silica before gelling followed by addition of Na_2S solution. Samples with varying ratios of ZnS and SiO_2 were prepared and their annealing at different temperatures was studied. It is found that ZnS goes to wurtzite phase after annealing at 900 C, which has been reported for the first time.

Hydrothermal Strategy

Xu et al⁴² in 1998 synthesized impurities-activated ZnS nanocrystals in microemulsion with hydrothermal treatment. They used petroleum ether as oil phase and mixture of poly(oxyethylene)5nonyl phenol ether (NP-5) and poly(oxyethylene)nonyl phenol ether as surfactant phase. Two reverse microemulsions of the system with aqueous solutions of $ZnCl_2$ along with dopant and sodium sulfide were prepared separately and mixed with continuous stirring. The microemulsion system was also treated under hydrothermal conditions for surface passivation. ZnS:Cu, ZnS:Eu and ZnS:Mn nanocrystals were prepared and particle size found to vary from 3 to 18 nm. Emission intensity enhancement of sixty times as compared to Mn doped ZnS nanocrystals synthesized by conventional aqueous reaction method has been reported. Another significant observation of the workers is increase of integrated PL intensity with increasing atomic number of dopant.

Haase et al⁴³ in 2000 synthesized colloidal lanthanide doped nanophosphors of YVO_4 and $LaPO_4$ in high boiling coordinating solvents or by hydrothermal means. Qiao et al⁴⁴ in 2002 reported a route to synthesis Wurtzite ZnS and CdS nanorods.

Ultrasonic Assisted Strategy

Xu and Ji⁴⁵, 1999 gave an interesting new route for preparation of nanoparticles of ZnS. The new route is via synthesis of Zn nanoparticles by inert-gas evaporation with induction heating. These particles were made to react with sodium sulfide aqueous solution under ultrasonic radiation at 50 °C. XRD analysis showed highly crystalline phase of β -ZnS and TEM confirmed spherical particles with narrow size distribution averaging 40 nm.

Heat Assisted Chemical Reaction Strategy

Wang and Hong⁴⁶ reported in 2000 a new preparation procedure for nanosized zinc sulfide particles by solid-state method at low temperature. Zinc acetate and thioacetamide were milled separately, mixed and further milled for thorough and uniform dispersion of the components in the mass. Formation of nanocrystalline zinc sulfide with size of 3.2 nm at 100 °C is confirmed.

H. Chander

TEM and PL studies establish nanocrystalline nature of the sample.

Konrd et al⁴⁷ in 2001 synthesized nanocrystalline cubic yttria and Ebstein et al⁴⁸ in 2002 reported fluorescence quantum yield of CdSe/ZnS core/shell nanophosphors synthesized by them. The particles were made by following the route of high temperature pyrolysis of organometallic precursors in coordinating solvents. Alternatively some samples were prepared with trioctylphosphine oxide (TOPO) and hexadecyl amine capping.

Chemical Reaction

Dijken et al⁴⁹ in 2001 prepared colloidal solutions of nanocrystalline ZnO particles and studied quantum efficiency with particle size. NaOH solution is added slowly to zinc acetate solution. Both the solutions are in 2-propanol and pre-cooled to 0°C. Colloidal suspension of ZnO particle of 0.7 nm radius is generated. Particle size grows with time due to aging. Growth up to 3 nm was recorded and analyzed.

Chemical Precipitation from Homogeneous Solution

Yang et al⁵⁰ in 2001 synthesized ZnS nanocrystals co-activated with Cu and rare-earth metals like Ce, Y, Nd, Er, Tb. Doped zinc sulfide nanoparticles were made by precipitation from homogeneous solution. Zinc acetate solution with dopants in form of chloride salt and solution of thioacetamide were separately heated to 80 °C and mixed, pH of the solution raised to 2.0 and reaction time of 30 min was given. Reaction was arrested by cooling the solution to less than 10 °C. PL spectra for all combinations was measured and analyzed. Spectra with rare-earth impurities showed practically no change in emission peak from that of pure ZnS. However intensity enhancement by factor of 5-6 was observed. In case of double doping with Cu and rare-earth peak PL emission was around 540-550 nm with 15 times increase in intensity for Tb³⁺, Cu²⁺ sample compared to samples of pure ZnS.

Lee et al⁵¹ in 2002 prepared ZnS nanoclusters thin films by solution growth technique; Lee et al⁵² studied in 2004 effect of synthesis temperature on particle size/shape of ZnS:Cu nanocrystals. PL spectra was measured at different synthesis temperature and it was found that Cu is transformed to CuO at synthesis temperatures >90 °C.

Preparation within Matrix/Templet

Chen et al⁵² in 2001 reported detailed synthesis and studies on nanosized ZnS:Mn with size variation and in cavities of ultra stable zeolite-Y. The nanosized ZnS:Mn was prepared by slow simultaneous addition of aqueous solutions of Na₂S and zinc nitrate with manganese nitrate to a container with DI water. The mass was kept stirred, nitrogen atmosphere maintained and heated to 80 °C for 24 hrs. ZnS:Mn nanophosphors of size ~4.5 and ~ 3.5 nm were also prepared in methacrylic acid/ethanol and methacrylic acid/citric acid ethanol solution respectively. ZnS:Mn

nanoparticles were placed in zeolite matrix by mixing 100 mg of the phosphor of ~10 nm size and 2 g of zeolite powder and pressing to form pellets which were heated at 900 °C in vacuum (10⁻⁵ torr) for two days. Cryo EFTEM was performed on samples to confirm actual doping of samples. ESR spectra were recorded for the samples in order to determine the valence and distribution of Mn²⁺ ions in nanoparticles. PL spectra of the samples gave emission peaks at 591, 588, 581 and 570 for the particles of 10, 4.5, 3.5 nm and the clusters in zeolites.

Nandakumar et al⁵³ in 2002 synthesized CdS quantum dots in polymer matrix Nafion following ion exchange reaction.

Strategy of Reaction via Microemulsion

Pingbo et al⁵⁴ prepared nanocrystalline ZnS:Mn using surfactant DBS – dodecyl benzene sulfonic acid sodium salt. Chemical precipitation method has been used employing aqueous solutions of Zn(NO₃)₂, MnCl₂ and Na₂S. Different amount of Na₂S was taken to create Zn²⁺ vacancies. They studied PL properties with varying Mn concentration and also compared the luminescence with and without surface modification. In this work, fluorescence lifetime have also been analyzed for different emission wavelengths and observed that nanosecond decay is due to zinc vacancies and millisecond decay is attributed to Mn. Photo aging was also studied for these samples.

Cao et al⁵⁵ reported in 2002 preparation of core-shell ZnS:Mn/ZnS nanoparticles and studied enhancement of luminescence. A microemulsion of aqueous solution of Zn and Mn acetates with 0.04 M AOT heptane solution was prepared. Yang and Holloway⁵⁶ in 2003 synthesized CdS:Mn/ZnS core/shell quantum dots and found substantially enhanced PL to CdS:Mn quantum dots prepared by other techniques say organic capping. Basic technique was based on reverse micelle method. Mn doped CdS core nanocrystals were formed by mixing (Cd²⁺ + Mn²⁺) and S²⁻ containing micellar solutions rapidly for 10-15 min. Then Zn²⁺ containing micellar solution was added at a slow rate into the core forming micelle. PLE and PL spectra of n-dodecanethiol capped CdS:Mn and ZnS capped CdS:Mn have been compared. Both spectra are peaked for ZnS capped CdS:Mn. Thus it has been concluded that surface passivation in case of ZnS capping is more effective than n-dodecanethiol capping.

Electrochemical Processing Strategy

Natter and Hempelmann⁵⁸ in 2003 developed process for tailor-made nanomaterials using electrochemical methods. The crystallite size of the nanoparticles can be controlled by variation of physical and chemical parameters. Pulsed electrodeposition and DC-plating procedures have been employed for preparation of catalyst films. Large quantities of nanostructured metal oxides were reportedly prepared with electrodeposition under oxidizing conditions that is based on the reduction of metal ions generated from the anodic dissolution of a sacrificial anode with subsequent oxidation of the formed metal crystals. Using the

H. Chander

technique, many metal oxides and mixed oxides such as ZnO, Mn₃O₄, CuO, In₂O₃, In₂O₃/SnO₂ and others have been prepared at a rate of 1 kg per day. Preparation of nanophosphors in bulk amounts should be possible with the process after some modifications.

Autocombustion Strategy

Anh et al⁵⁹ in 2003 reported preparation, optical properties and application potential of two nanophosphors, Y₂O₃ and SiO₂-TiO₂/ZrO₂ doped with various rare earths. Particle size ranged from 4.4 to 72 nm. PL spectrum of yttrium oxide samples doped with different proportions of Eu/Tb has been recorded and ratio of 8:2 had best luminescence yield.

Nanosized spherical particles of doped yttrium oxysulfide were synthesised by Pires et al⁶⁰ in 2004 and studied for up-conversion luminescence.

Harish et al⁶¹ reported in 2004 synthesis of nanophosphor crystals of long persisting SrAl₂O₄:Eu²⁺, Dy³⁺ by modified combustion technique. In this technique, reaction components were placed in a partially closed ceramic /quartz tube and heated from 400-600°C. Low-density mass of the nanophosphor less than 50 nm in size was obtained. The samples obtained by combustion method were compared with bulk samples made by solid-state reaction technique. Higher excitation energy and lower decay times are attributed to quantum confinement of dopants because of nanostructure formed in the samples.

Huang and Yan⁶² reported in 2004 synthesis of Gd₂SiO₅:Tb nanophosphor using polymer precursors. PL spectrum of the nanophosphor prepared was recorded and is found to have characteristic green emission of terbium. This indicates that nanophosphor of Gd₂SiO₅:Tb is successfully synthesized using sol-gel technique.

Conclusions

It is observed that field of nano luminescent materials are immensely resonant and dynamic. Many processes such as chemical precipitation with and without capping agents, sol-gel, sol-gel with heating, microemulsion, solid state heating, chemical vapour synthesis, hydrothermal synthesis, chemical synthesis within matrix, molecular beam epitaxy, electrochemical route, autocombustion, chemical precipitation from homogeneous solution have been developed for synthesis of nanophosphors. Commercial viability of the technique may be low due to costly capping agents and processing difficulties of finished nanophosphors for display devices. The processes of sol-gel, sol-gel with heating, microemulsion, chemical vapour synthesis, molecular beam epitaxy and autocombustion are not likely to be economically and environmentally friendly as these are chemical and energy intensive. Chemical precipitation with capping using inorganic compounds, chemical precipitation from homogeneous solution, synthesis within a matrix, electrolysis based process, hydrothermal synthesis are the techniques that are likely to be technologically acceptable. Early success of ZnS:Mn nanophosphor prepared by

Bhargava et al with increased efficiency and spectrum shift has been the inspiration for the large quantum of work in the field.

References

1. Bhargava R N; Gallagher D; Hong X; Nurmikko A; *Phys. Rev. Lett.*, 1994, 72, 416.
2. Jain R K and Lind R C; *J. Opt. Soc. Am.*, 1983, 73, 47; Ekimov A I; Efros A L; Omushchenko A A; *Solid State Comm.*, 1985, 56, 920.
3. Henglein A; *Chem. Rev.* 1989, 89, 1861.
4. Rosetti R; Nakahara S; Brus L E; *J. Chem. Phys.*, 1983, 79, 1086.
5. Khosravi A A; Kundu M; Kuruvilla B A; Shekhawat G S; Gupta R P; Sharma A K; Vyas P D; Kulkarni S K; *Appl. Phys. Lett.*, 1995, 67 (17), 2506.
6. Khosravi A A; Kundu M; Kuruvilla B A; Shekhawat G S; Gupta R P; Sharma A K; Vyas P D; Kulkarni S K; *Appl. Phys. Lett.*, 1995, 67 (17), 2506.
7. Yu I; Isobe T; Senna M; *J. Phys. Chem. Solids*, 1996, 57(4), 373.
8. Bhargava R N; *J. Lumin.*, 1996, 70, 85.
9. Zhou H S; Honma I; Haus J W; Sasabe H; Komiyama H; *J. Lumin.*, 1996, 70, 21.
10. Yang H; Wang Z; Song L; Zhao M; Chen Y; Dou K; Yu J; Wang L; *Mater. Chem. and Phys.*, 1997, 47, 249.
11. Kundu M; Khosravi A A; Kulkarni K K; Singh P; *J. Mater. Sci.*, 1997, 32, 245.
12. Vogel W; Urban J; Kundu M; Kulkarni S K; *Langmuir*, 1997, 13, 827
13. Senna M; Igarashi T; Konishi M; Isobe T; *Fourth Intl. Display Workshop*, Nogoya, Japan, Nov. 19-21, 1997, 613.
14. Xu S J; Chua S J; Liu B; Gan L M; Chew C H; Xu G Q; *Appl. Phys. Letts.*, 1998, 73(4), 478.
15. Bol A A; Meijerink A; *Phys. Rev. B*, 1998, 54 (24), R15 997.
16. Kezuka T; Konishi M; Isobe T; Senna M; *J. Lumin.*, 2000, 87-98, 418.
17. Nanda J; Sarma D D; *J. Appl. Phys.*, 2001, 90 (5), 2504.
18. Konishi M; Isobe T; Senna M; *J. Lumin.*, 2001, 93, 1.
19. Igarashi T; Ihara M; Kusunoki T; Ohno K; Isobe T; Senna M; *J Nanoparticle Research*, 2001, 3, 51.
20. Kulkarni S K; Winkler U; Deshmukh N; Borse P H; Fink R; Umbach E; *Appl. Surf. Sci.*; 2001, 169-170, 438.

H. Chander

21. Qu S C; Zhou W H; Liu F Q; Chen N F; Wang Z G; Pan H Y; Yu D P; *Appl. Phys. Lett.*, 2002, 80 (19), 3605.
22. Manzoor K; Vadera S R; Kumar N; Kutty T R N; *Mater. Chem. and Phys.*, 2003, 82, 718.
23. Chory C B; Buchold D; Schmitt M; Kiefer W; Heske C; Kumpf C; Fuchs O; Weinhardt L; Stahl A; Umbach E; Lentze M; Geurts J; Müller G; *Chem. Phys. Letts*, 2003, 379, 443.
24. He C; Guan Y; Yao L; Cai W; Li X; Yao Z; *Mater.Res.Bull.*, 2003, 38, 973.
25. Zhang S C and Li X G; *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2003, 226, 35.
26. Lee S; Song D; Kim D; Lee J; Kim S; Park I Y; Choi Y D; *Mater.Lett.*, 2003, 58, 342.
27. Manzoor K; Vadera S R; Kumar N; Kutty T R N; *Solid State Comm.*, 2004, 129, 469.
28. Lee J; Lee S; Cho S; Kim S; Park I Y; Choi Y D; *Mater. Chem. and Phys.*, 2002, 77, 254.
29. Karar N; Harish Chander; Shivaprasad S M; *Appl. Phys. Letts.*, 2004, 85, 5058.
30. Stanic V; Etsell T H; Pierre A C; Mikula R J; *Mater. Lett.*, 1997, 31, 35.
31. Park C H; Park S J; Yu B U; Bae H S; Kim C H; Pyun C H; Yan H G; *J Mat. Sci. Letts.*, 2000, 19, 335.
32. Yu Z Q; Chang D; Li C; Zhang N; Feng Y Y; Dai Y Y; *Mater. Res. Society*, 2001,16 (7), 1890.
33. Ishizaka T; Nozaki R; Kurokawa Y; *J. Phys. Chem. Solids*, 2002, 63, 613.
34. Lu C H and Jagannathan J; *Appl. Phys. Lett.*, 2002, 80 (19), 3608.
35. Yang P; Lü M K; Xu D; Yuan D R; Song C F; Liu Q; Chen D H; *Mater. Sci. & Engg.*, 2002, B 96, 33.
36. Pan Y; Su Q; Xu H; Chen T; Ge W; Yang C; Wu M; *J. Solid State Chem.*, 2003, 174, 69.
37. Wang J; Song H; Sun B; Ren X; Chen B; Xu W; *Chem. Phys. Letts*, 2003, 379, 507.
38. Gu F; Wang S F; Lu M K; Qi Y X; Zhou G J; Xu D; Yuan D R; *J. Cryst. Growth*, 2003, 255, 357.
39. Morita M; Rau D; Kajiyama S; Sakurai T; Baba M; Iwamura M; *J. Mater. Sci.-Poland*, 2004, 22(1), 5.
40. Yan B and Zhou L; *J. Alloy and Compounds*, 2004, 374, 238.
41. Haranath D; Nitesh Bhalla; Harish Chander; Rashmi; Kar M; Ram Kishore; *J Appl. Phy*, 2004, 96, 6700.
42. Xu S J; Chua S J; Liu B; Gan L M; Chew C H; Xu G Q; *Appl. Phys. Letts.*, 1998, 73(4), 478.
43. Haase M; Riwozki K; Meyssamy H; Kornowski A; *J. Alloy and Comp.*, 2000, 303,191.
44. Qiao Z P; Xie Gang; Tao J; Nie Z Y; Lin Y Z; Chen X M; *J.Solid State Chem.*, 2002, 166, 49.
45. Xu J; Ji W; *J. Mater. Sci. Lett.*, 1999, 18, 115.
46. Wang L P; Hong G Y; *Mater. Res. Bull.*, 2000, 35, 695.
47. Konrad A; Herr U; Tidecks R; Kummer F; Samwer; *J. Appl. Phys.*, 2001, 90 (7), 3516.
48. Ebenstein Y; Mokari T; Banin U; *Appl. Phys. Lett.*, 2002, 80 (21), 4033.
49. Dijken A V; Makkinje J; Meijerink A; *J. Lumin.*, 2001, 92, 323.
50. Yang P; Lü M; Xü D; Zhou G; *J. Lumin.*, 2001, 93, 101
51. Lee J; Lee S; Cho S; Kim S; Park I Y; Choi Y D; *Mater. Chem. and Phys.*, 2002, 77, 254.
52. Lee S; Song D; Kim D; Lee J; Kim S; Park I Y; Choi Y D; *Mater.Lett.*, 2003, 58, 342.
53. Chen W; Sammynaiken R; Huang Y; Malm J O; Wallenberg R; Bovin J O; Zwiller V; Kotov N A; *J. Appl. Phys.*, 2001, 89 (2), 1120.
54. Nandakumar P; Vijayan C; Murti Y V G S; *J. Appl. Phys.*, 2002, 91 (3), 1509.
55. Pingbo X; Weiping Z; Min Y; Weiwei Z; Liren L; Shangda X; *J. Colloid and Surf. Sci.*, 2000, 229, 534.
56. Cao L; Zhang J; Ren S; Huang S; *Appl. Phys. Lett.* 2002, 80 (23), 4300.
57. Yang H and Holloway P H; *Appl. Phys. Lett.*, 2003, 82 (12), 2002.
58. Natter H and Hempelmann R; *Electrochimica Acta*, 2003, 49, 51.
59. Anh T K; Minh L Q; Vu N; Huong T T; Huong N T; Barthou C; Strek W; *J. Lumin.*, 2003, 102-103, 391.
60. Pires A M; Serra O A; Davolos M R; *J. Alloy and Compounds*, 2004, 374,181.
61. Harish Chander; Haranath D; Shanker V; Sharma P; *J. Cryst.Growth*, 2004, 271, 307.
62. Huang H and Yan B; *Inorganic Chemistry Communications*, 2004, 7, 595.
63. Harish Chander, *Materials Science and Engineering*, R49, 2005. 113.