

Nanophosphors: A Hot Topic in Material Science

Amandeep

Department of Physics,
D.A.V Centenary College, Faridabad

Abstract: Nano-crystalline semiconductors doped with optical active luminescence center create new opportunities for luminescence studies. Nano-crystalline phosphors have altogether different properties as compared to microcrystalline phosphors. Nano size semiconductors phosphors are used in radiation technology, sensor technology, laser and plasma physics as well as photochemistry and medical applications. These phosphors can also be used as information storage materials and coating materials of fluorescent screens and tubes which make them more efficient and stable. Nanophosphors can also be used in laser detection and alignment, plasma display panel, gene tagging and identification, drug delivery system etc. Laser induced photoluminescence study of these nanophosphors may explore the possibility of new phenomenon occurring in these phosphors at nano level. This paper reviews importance of nanophosphors, its characteristics and their application.

Keywords: nanophosphors, semiconductor, photoluminescence, importance, efficient.

I. INTRODUCTION

Luminescence is one of the most important method to reveal the energy structure and surface state of a semiconductor nanoparticle. When molecules are raised to an excited electronic state by illuminating them with the light of a definite frequency, they may revert to their initial state with the emission of discrete radiation of frequencies other than the frequency of the absorbed light. In 1989 Jayaraj et al [1] had studied the white electroluminescence in ZnS: Cu, Praseodymium, Cl phosphors. They observed that electroluminescence of ZnS: Cu, Pr, Cl gives white emission with spectral peaks at 470, 520, 570 and 640 nm. They also reported that relative intensities of spectral peaks were strongly dependent on the frequency of the excitation voltage. In 1992 McClean et al [2] had studied photoluminescence of MBE-grown films of ZnS and observed the intense blue emission at 460 nm from room temperature photoluminescence studies. They also reported that quenching of blue emission occurs when Mn is added to the ZnS films. In 1994 Bhargava et al [3] had studied optical properties of manganese doped nanocrystals of ZnS. They reported for the first time that nanocrystals of Mn-doped ZnS with sizes

varying from 3.5 to 7.5 nm prepared by a room temperature chemical process yielding an external photoluminescent quantum efficiency 18 % and a luminescent decay at least 5 orders of magnitude faster than the corresponding Mn^{2+} transition in bulk crystals. In 1996 Bhargava [4] had reviewed the properties and applications of nanocrystals doped with transition and rare-earth impurities. He observed high efficiency and ultra fast recombination time. In 1997 Chen et al [5] had studied the absorption and luminescence of the surface states in ZnS nanoparticles. They observed a broad absorption band around 500 nm in ZnS nanoparticle. They also reported that absorption becomes more intensive and blue shift take place as the particle size is decreased and glow peak of the semiconductor particles is not varied as much upon decreasing size. In 1998 Xu et al [6] had prepared ZnS nanoparticle by ultrasonic radiation method and studied by XRD, TEM, UV spectrophotometry and X-ray photoelectron spectroscopy. They observed that prepared ZnS nanoparticle were a zincblende structure from XRD study and was in spherical form with an average diameter of 40 nm from TEM observation. Their XPS results proved that binding energies of Zn 2p and S 2P were the same as those of bulk single-crystal, but the full width at half maxima of XRD peaks were

larger than those of bulk single-crystal. In 1999 Liu et al [7] had studied ZnS : Mn²⁺ nanocrystals embedded in Pyrex glass matrices. They observed from PL spectra that doped Mn can be classified as two types, occupying substitutional sites (Mn²⁺)_{sub} and interstitial sites (Mn²⁺)_{int}. They also observed increase in g factors and hyperfine structure constants with decreasing diameters of nanocrystals from EPR spectra. In 2000 Chen et al [8] had observed that the luminescence intensity of Mn²⁺ in ZnS: Mn nanoclusters formed in an ultrastable zeolite -Y was seven orders of magnitude stronger than that of other nanoparticles deposited out of solutions. In 2001 Chen et al [9] had observed strong up-conversion luminescence of Mn²⁺ in ZnS: Mn²⁺ bulk and nanoparticle. They reported that decay life-time of the up-conversion emission excited at 767 nm were shorter than the 300-nm excited luminescence life times, while in the bulk, the two decays were almost identical. In 2002 Su et al [10] had studied the temperature behaviour of orange and blue emissions in 10, 4.5, 3 nm ZnS: Mn nanoparticles. They found that with increase of temperature, the blue emission had a red shift and peak energy of orange emission was weakly dependent on temperature. In the same year Mohamed et al [11] had synthesized ZnS quantum dots in water and ethanol solutions coated with polystyrene and SiO₂ shells respectively. They found that the band edge emission was enhanced by nearly five times after PS coating and about thirteen times after SiO₂ shell coating. They also observed from PL properties of ZnS QDs coated with PS and SiO₂ Shells improvement of thermal stability. In 2003 Manzoor et al [12] had synthesized ZnS nanocrystals doped with Cu⁺ and halogen by wet-chemical precipitation method. They found the ZnS nanoparticle has zinc-blende structure from XRD study. They also investigated the effect of change in stoichiometry and doping with Cu⁺ and halogen on the photoluminescence properties of ZnS nanophosphors and reported that by controlling the defect chemistry and suitable doping, PL emission tunability over a wide wavelength range i.e. 434 to 514 nm, can be achieved in ZnS nanophosphors. In 2006 Murugan et al [13] had studied PL properties of nanocrystalline ZnS on nonporous silicon and observed that material was cubic in nature from XRD study and optical absorption edge of ZnS were blue shifted from the absorption edge of bulk ZnS from PL study. In the same year Jin et al [14] had studied two-photon absorption and non-linear refractive index properties of ZnS quantum dots and found that the two photon absorption coefficients initially increases and then decreases with increasing pulse irradiance. In 2007 Li et al [15] had synthesized hexagonal-shaped ZnS nanosheets with a zinc-blende structure via the solvothermal method. They also fabricated the ZnS nanorods with wurtzite structure and large ratio of length to diameter by simply changing the molar ratio of reactants. They found that phase transformation was easily induced and there was strong correlation between morphology and structure of ZnS nanocrystals by changing ratio of reactants.

II. CHARACTERISTICS

Exposing semiconductor material with ultraviolet light leads to absorption of the energy and results in one or more of the electrons of an atom to shift into a higher energy state, which here can be envisioned as moving to an orbit farther away from the nucleus. All such excited electronic states are unstable, and sooner or later the electron will lose its excess energy and fall back to its original orbit. This excess energy can be dissipated in several ways, the most common being simply to increase lattice vibrations of the material (non radiative transitions), but some materials also emit some of the energy as light called photoluminescence (radiative transitions). The fluorescence of many semiconductor compounds is not only due to the host material itself but to some chemical impurity or a defect in its crystal structure. The impurity added to the semiconductor compound in this way is said to be activator or dopant responsible for luminescence. A large change in the concentration of impurities results in different radiative emissions from these dopants. Temperature dependence of photoluminescence leads to detection of various impurity levels whose depth can be measured very accurately from photoluminescence decay curves. The decay curves can also be employed to study the distribution of the trapping levels introduced by the activators in the forbidden gap of the semi conducting material. For any material to fluoresce it must be capable of absorbing ultraviolet light. The presence of an activator may or may not help to introduce the impurity levels responsible for photoluminescence e.g. manganese is a potent activator but a poor absorber of ultraviolet light. For such materials an additional chemical impurity, which is capable of absorbing ultraviolet light and transmitting the added energy to the activator levels, is necessary for luminescence. Impurities that operate in this way in conjunction with an activator embedded in host semiconductor material are termed as co-activators. Co-activator also helps or facilitates the impurity to add its levels in band gap of host material very effectively. Some chemical impurities deter luminescence by promoting radiation less transitions causing a given substance to lose energy by processes that do not involve the emission of light. Typically the energy is dissipated as lattice vibrations. Among minerals the most notorious poisoners of fluorescence are iron, cobalt and nickel. For example, a ruby crystal containing 1% chromium will probably fluoresce bright deep red (chromium is the activator here), but if it also contains 1% iron (killer of luminescence) it probably will not fluoresce at all.

III. IMPORTANCE AND APPLICATION

Sustained glowing without further stimulus is known as phosphorescence and phosphor is a substance that exhibits this phenomenon. A very important application of the phosphors is as a coating material for cathode ray tubes used for computer and TV screens. The light that comes from these devices is emitted by tiny phosphor dots that are coated inside the screen, and are excited by a stream of electrons emitted by a cathode ray tube. Three colors of dots-blue, red, and green-are used in most computer monitors. In fluorescent tube ionization of gases generates UV light which further falls on the coated material (phosphor) and due to down conversion phenomena

visible emission takes place. Phosphors play a major role in applications such as display, diagnostic, sensing, and illumination technologies. For fast and efficient phosphor development, the emphasis is given to the materials having higher quantum yield, fast decay, higher stability and operating at low voltage. Wide ranges of the luminescent materials have been identified for various applications e.g. ZnO for green, ZnS: Cd for red, ZnS for blue colors etc. For low operating voltage applications, ZnS is used for green and blue, and yttrium oxide for red color (TV analog materials).

At Nano scale phosphors have altogether different properties as compared to the microcrystalline phosphors. The properties at nanoscale drastically change. These reasonable differences in properties arise from several phenomenon viz. quantum confinements of electrons and holes, surface effects, geometrical confinement etc. that may play vital roles depending on the investigated property. Luminescence spectra of nanophosphors can be easily tuned by controlling particle size. Due to confinement effects band gap of the phosphor material increase with decrease in particle size, so different colored emission can be observed from the same material by changing particle size. As band gap is tailored with size, so due to change in electronic structure partially spin forbidden transitions become spin allowed, which causes shortening of emission lifetime and increase in quantum yield. Therefore one can use these nanomaterials for various applications and already known bulk properties by a judicious control of size of the synthesized nanophosphors. Nanophosphors can be used for solid state lighting [16], various bio-imaging techniques [17-20], bio markers [21-22] or photodynamical therapies in cancer treatment [23-24]. Nanophosphors can be further used for the groundwork of homogeneous bulk optical ceramics which have already overcome single crystal scintillators in precise applications [25].

IV. CONCLUSION

Appropriate properties of nanophosphors make them future materials for consideration in various applications, including the bio-physics and medical fields. Therefore, quick future development of nanophosphors may be expected.

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