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A review on the progress of ZnSe as inorganic scintillator

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ABSTRACT

Modern scintillator detectors act as an efficient tool for detection and measurement of ionizing radiations. ZnSe based materials have been found to be a promising candidate for scintillation applications. These scintillators show much-needed scintillation efficiency along with advantages such as high thermal and radiation stability, less-toxicity, non-hygroscopicity, emissions in the visible range and small decay time etc. Further, in quantum confinement regime, they show improvement in luminescent properties and size dependent emissions. In this review article, the attempt has been made to trace the progress of ZnSe based materials towards highly efficient quantum dot scintillators. Here, the fundamental process of scintillation has been explained. Factors such as doping, annealing, heavy ion irradiation which affects the scintillation response of ZnSe based scintillators have also been discussed. Method of synthesis plays a key role in optimization of quantum dot properties. Hence, it has been tried to trace the development in methods of synthesis of quantum dots. With optimized synthesis, we can extend applications of these highly efficient quantum dot scintillators for various scientific and industrial applications.

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1. Introduction

Scintillators are luminescent materials which absorb ionizing radiation efficiently and convert the energy of absorbed radiation into light. The emitted radiation can be detected by photomultiplier tube or photodiode. Most commonly known ionizing radiation are alpha, beta, gamma, X-rays and neutron rays. Ionizing radiation can be charged (alpha, beta radiations) and uncharged (neutrons, X-rays, gamma-rays). Charged radiation undergoes coulombic interaction with electrons of the medium through which they pass and cause direct ionization. However, uncharged radiation have an indirect ionizing effect i. e. these radiations first transfer their energy via electromagnetic or nuclear interactions to produce charged particles which then results in ionization of the medium [1,2]. Although ionizing radiation such as cosmic rays, naturally occurring radioactive materials have been present in nature, human beings have no specific sense to respond to these radiations. The presence of these radiations can be detected by various tools [1]. Efforts for detection of radiations started with the phenomenon of thermoluminescence which was first introduced in the 17th century. Thermoluminescence is a physical phenomenon in which some inorganic scintillation materials absorb radiation energy at a given temperature and then release it in a form of light at elevated temperatures. However thermoluminescent dosimeter was introduced very late in 1948 [1,3,4]. Further, the doors of the completely new field of science were opened by W.C. Roentgen (1895) and by H. Becquerel (1896), with the discovery of X-rays and radioactivity, respectively. During his experiments, Roentgen observed that air conducts electricity when traversed by the X-rays [5]. This effect was later used as an operating principle for various kinds of detectors. After Becquerel's discovery of radioactivity with uranium compounds [6], scientists started searching for further elements with radiation-emitting properties [7]. In July 1898, Madame Skłodowska Curie together with her husband discovered the radioactive element polonium and radium. She also realized that the ionization effect produced by radiations would be well suited for their detection [7]. With the advancements in science and technology, the relatively low cost, high sensitivity and easy to handle gold -leaf electroscope came into practice as a preferred measuring instrument for work with the radioactive material [1]. This electroscope and some very early detection methods such as a fluorescent screen, a photographic plate or a galvanometer were found to have one common limitation that these could respond to "bulk" radiations but they were insensitive to single rays. Considering the disadvantages of photographic plates for detection of ionizing radiations, other detection methods have been investigated. The very first instrument which could detect individual ionizing ray was the spintharoscope, invented by Crooks in 1903 [1,7]. The device used a ZnS screen and observed scintillations with the naked eye using a microscope. Even though this technique was tedious but it led to the number of important discoveries. In 1944 Curran and Baker replaced this naked eye measurement with the newly developed photomultiplier tube. Here was the birth of a modern scintillation detector [8]. With the development of experimental physics, it became clear that scintillating materials are ideal for detection of elementary particles and measurement of their parameters [9]. With the tremendous development in research in particular to scintillating materials, several scintillating media such as various organic and inorganic crystalline media [9–13], fluids

[9,14–17], gases [9,18,19] and polymeric compounds [9,20] came into practice. In 1948 organic scintillator such as thallium-activated sodium iodide crystal was discovered [9,21]. With progress in this field after NaI: Tl, few more scintillating materials such as CsI:Tl, CsI, CsI:Na etc. were found which were widely used thereafter.

The most widely applied scintillators include the inorganic alkyl halide crystal, organic based liquids, and plastics. Inorganic scintillator materials show best light output and linearity but limit its performance due to slow response time. Organic scintillators are generally faster but with lesser light yield. Hence, selection of scintillator type depends upon the application. For gamma-ray spectroscopy, high atomic number materials which have high density are the favourable choice, whereas for beta spectroscopy and for fast neutron detection organic scintillators are preferred [22]. This review article summarizes the progress and development of inorganic scintillating material ZnSe. Factors affecting the physical and optical properties of ZnSe such as doping, annealing, heavy ion irradiation, methods of synthesis etc. have been discussed. Current developments in nanotechnology and materials science have created the great possibility for ZnSe to be used as a scintillator.

2. Fundamentals of scintillation

Physical phenomenon of scintillation

Scintillators are luminescent materials that have a function to absorb ionizing radiation and to emit light of wavelength in or around visible spectrum region. Luminescent materials when exposed to certain forms of energy (e.g., light, heat, radiation etc.), reemission occurs immediately after absorption (within 10⁻⁸s). This process is usually called fluorescence. However, it is possible that reemission is delayed because the excited state is metastable, then the process is called phosphorescence or afterglow. This delay time between absorption and reemission may last from a few microseconds to hours depending on the type of material. One may get confused in between scintillation and luminescence. Luminescence is basically radiative relaxation of an active ion of the material after the direct excitation between its fundamental state and excited energy level by an electrostatic discharge or a pulse of light. However, in case of scintillation, there is basically energy loss of ionizing radiations through matter [9]. To understand this we must know the scintillation mechanism.

The physical phenomenon in scintillators can be explained in three basic steps (Fig.1)

- 1 Conversion of incident photon energy into a large number of electron-hole pairs.
- 2 Transfer of electron-hole pair energy to luminescent ion involved.
- 3 Emission process in which luminescent ion undergoes a radiative transition from excited state to ground state.

The first step involves the interaction of high energy photon with the lattice of scintillator material through photoelectric effect and Compton scattering. The multiplication of electrons and holes occurs by radiative decay in the form of secondary X-rays, non-radiative decay by Auger process, and inelastic electron/electron scattering. Electron hole-pairs thus created are thermalized with the production of phonons. This produces low kinetic energy electrons at the bottom of a conduction band and holes at the top

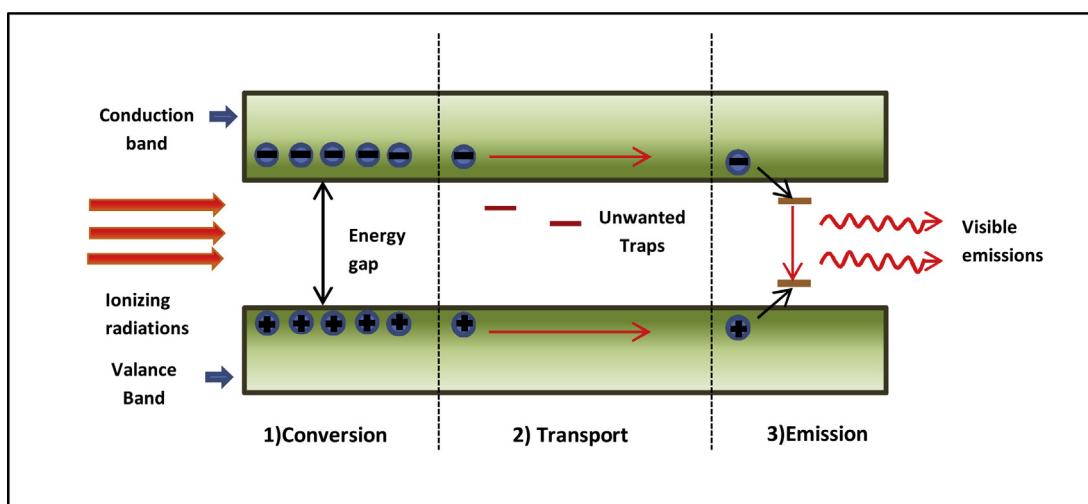


Fig. 1. Physical phenomenon of scintillation [6].

of valence band when electron energies become less than ionization threshold. This first step process ends in less than 1 psec. In a transfer process electrons and holes (eventually created excitons) migrate through the material. This is because the site of absorption of incoming radiations and final emission usually do not match. Hence energy has to migrate towards luminescence centre before radiative recombinations. During this process, there can be energy loss of charge carriers by trapping in lattice defects and also through non-radiative transitions. However, losses are strongly dependent on manufacturing technology and, hence can be minimized. The final stage is luminescence which consists of trapping of an electron and hole at the luminescence centre and their radiative recombination [9,23–25].

The efficiency of the scintillator is given by the equation:

$$\eta = \Upsilon S Q, \quad (1)$$

where, Υ is the efficiency of the conversion process, S is the efficiency transfer processes, Q is the quantum efficiency of the luminescent centre [23].

Physics behind the scintillations is discussed by G. Bizarre [24] in terms of quantum efficiency Q , efficiency of energy transfer S and absorption and multiplication stage which can provide pathways to assist in scintillator discovery. In general, if the material is irradiated with gamma -rays or other radiations, the number of scintillation photons (N_{ph}) emitted is given by:

$$N_{ph} = \frac{E}{\beta E_{gap}} S Q \quad (2).$$

Here, E = The energy absorbed by the scintillator,

E_{gap} is the band-gap energy between the valence band and conduction band

and β is the parameter which indicates the average energy required to produce one thermalized electron-hole pair, given by, $E_{e-h} = \beta E_{gap}$ and $\beta \approx 2-3$ [25].

The transfer efficiency S of the electron-hole pair to the luminescent centre is least predictable out of three stages of scintillation process. It depends very much on defects present in the scintillator, other than luminescent centres, that may capture electrons or holes or both. These defects can arise from the interaction itself, from crystal growing, or due to impurities [26–28].

Basic terms

Light yield

It is amount of light quanta emitted by a scintillator per unit energy deposited by ionizing radiation in the medium.

Decay time

It is a time after which the amplitude of scintillation light has decreased by a factor e .

Afterglow

It is an amplitude of the luminescent signal, excited by ionizing radiation and measured after a fixed time.

Radioluminescence

This is the wavelength distribution of scintillation light when it is excited by ionizing radiations [9].

Properties of good scintillating material

- 1 The material should be able to convert the kinetic energy of incident charged particles into visible radiations with high scintillation efficiency.
- 2 The light yield should be proportional to deposited energy covering a wide range of radiations, i.e. it should give a linear response.
- 3 The material should be transparent to its own visible emissions.
- 4 The decay time of luminescent pulse generated should be small for fast response recording.
- 5 The material should be homogeneous and of a good optical quality.
- 6 Refractive index of material should be comparable to that of glass to ensure efficient coupling with the photomultiplier tube or other light sensors [22,29].

Efficiency and light yield of inorganic scintillators

The ability to convert ionizing radiations into a visible light determines the efficiency of a scintillator. P.A. Rodnyi [30] has explained this efficiency and derived a generalized equation for maximum light output which is related to energy gap. The efficiency ' η ' may be represented by equation:

$$\eta = \frac{\langle h\nu_r \rangle N_{ph}}{E_\gamma}. \quad (3)$$

N_{ph} in this case is number of photons emitted after interaction with ionizing radiations of energy E_γ :and $\langle h\nu_r \rangle$ is the mean energy of emitted photons. It is given by equation:

$$\langle h\nu_r \rangle = \int_{\nu_{min}}^{\nu_{max}} \frac{h\nu_r J(\nu_r) d\nu_r}{\int_{\nu_{min}}^{\nu_{max}} J(\nu_r) d\nu_r}. \quad (4)$$

Where, $J(\nu_r)$ is the intensity of scintillator emission at a frequency of ν_r

ν_{min} and ν_{max} are the minimum and maximum frequencies of the emission spectrum respectively.

The efficiency η is the physical characteristic of a scintillator and its knowledge is important for efficient working of detector. However, for scintillation counting relative light output or scintillation yield L_R is more significant than η . L_R is defined as number of emitted photons per unit of absorbed energy (usually 1 MeV):

$$\text{Hence, } L_R = \frac{N_{ph}}{E_\gamma}. \quad (5)$$

Assuming $\langle h\nu_r \rangle$ is the approximately equal to the energy of the maximum of the emission spectrum $h\nu_m$, the light output of scintillator is given by:

$$L_R = \frac{N_{ph}}{E_\gamma} \approx \frac{\eta}{h\nu_m}. \quad (6)$$

Considering α as average number of photons produced by every e-h pair, the light output can be written as:

$$L_R = \frac{\alpha N_{eh}}{E_\gamma} \approx \frac{\alpha}{\beta E_g}, \quad (7)$$

Where, $\alpha = (N_{ph} / N_{eh}) \leq 1$.

The quantity α depends on transfer efficiency of e-h pair energy to luminescent centres and the quantum efficiency of the final luminescent process. β is numerical coefficient which is nearly in the range of 1.5–2 for ionic crystals. Finally, the expression for the energy efficiency of inorganic scintillator becomes:

$$\eta = \frac{\alpha h\nu_m}{\beta E_g}. \quad (8)$$

Hence the scintillation efficiency can be predicted by ratio $\frac{h\nu_m}{E_g}$.

Further, maximum light output of ionic crystals is approximated by the following equation [30]:

$$L_{max} = \frac{0.5}{E_g} \times 10^6 \frac{\text{photons}}{\text{MeV}}. \quad (9)$$

3. ZnSe as a scintillator

In this review paper, the attempt has been made to explore investigations done on inorganic scintillating material ZnSe. ZnSe has a wide band gap of 2.7 eV at room temperature. Development of ZnSe based scintillators has provided much-needed scintillation efficiency for high-speed light imaging applications by overcoming limitations of conventional scintillators [9]. ZnSe is $A^{II}-B^{VI}$ type of compound semiconductor which is a combination of group II metal and group VI cation. Group II metals generally include Zn, Cd, Hg and that of VI are S, Se or Te. The broad range of band gaps (from 0.15 for HgTe to 4.4 eV for MgS), high effective atomic number Z and the possibility of their synthesis by MBE and MOCVD have attracted scientists to study these compounds. These compound semiconductors have physical properties like piezoelectricity, photo-electricity, luminescence and scintillations. Results of $A^{II}-B^{VI}$ compound semiconductors for radiation detection have shown that these materials contain a combination of acceptable physical properties like light-output, decay time, radiation stability etc. and operational properties like non-hygroscopicity,

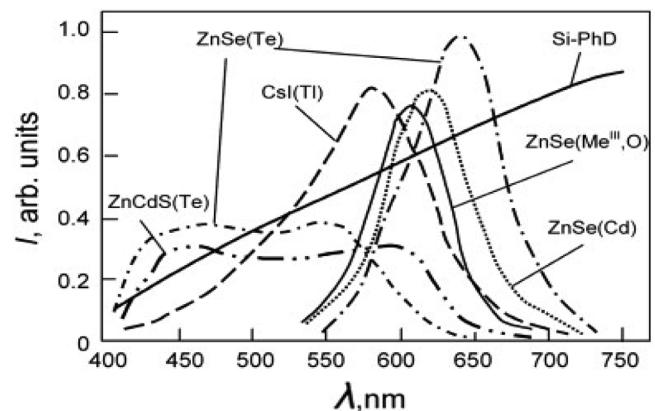


Fig. 2. Radio-luminescence spectrum of All-BVI scintillators and photosensitivity of Si-PD. Used with permission from ref. [94], Copyright-2013 Elsevier B.V.

mechanical strength, no cleavages etc. Hence in comparison to conventional scintillators, they were found more suitable for detection of low-energy gamma-radiation, alpha- and beta-particles. They can also work as efficient scintillators under high temperatures (up to 120 °C) and powerful (up to 10⁸ rad) dose loads [90]. But their single crystals were not found suitable for scintillation application because they have low transmittance and recrystallization. It is advanced single crystal growth technique which has made it possible to use single crystals as radiation sensors. Compound semiconductors, in general, have the number of distinct advantages over their elemental counterparts, as they have a wide range of stopping power, as well. A material with largest stopping power enables thinner detectors to be produced which can tolerate a high dose of radiations. For space research it induces mass and cost benefits while designing a spacecraft, maintaining the desired spectral response characteristics [91].

ZnSe based scintillators have an additional advantage as its response wavelength matches well with silicon photodiode spectral sensitivity. The region of maximum spectral sensitivity of Si-PIN-PD and ZnSe crystal radio luminescence shows of about 80% overlap [92,93]. X-ray luminescence spectra of $A^{II}-B^{VI}$ semiconductor scintillators and photosensitivity of Si-PD are given in Fig. 2 [94]. From the figure, it is evident that ZnSe based scintillators are suitable to be used with silicon photodiode. ZnSe based scintillators are highly efficient for detection of alpha, beta particles, low energy gamma-rays, X-rays with high radiation stability. These scintillators also have a better light output and fast decay time [90,92,93]. The response time of photodiode is of the order of 10⁻⁵ s which is same as that of scintillation flash duration of ZnSe doped scintillator [95]. Some widely used conventional semiconductors like NaI (Tl), CsI (Tl), are found to have various disadvantages such as low radiation stability and a high afterglow. Apart from these, as these scintillators are hygroscopic, they create difficulties under high humidity conditions. Now in case of oxides such as CdWO₄ (CWO), PbWO₄ (PWO), Bi₄Ge₃O₁₂ (BGO), Gd₂SiO₅ (GSO), inherent low conversion efficiency is observed. So to overcome these problems, $A^{II}-B^{VI}$ compounds with isovalent dopants are found to be suitable candidates [96,97].

Factors affecting scintillation response

Effect of doping on ZnSe based scintillators

It is possible to achieve highly efficient $A^{II}-B^{VI}$ scintillators with predictable emission spectra if they are doped with suitable dopants. In these materials, isovalent dopants substantially differ in ion radii and electronegativities. The radiation parameters of doped scintillators are predominantly prescribed by crystal lattice point imperfection created due to doping [96,98]. ZnSe acti-

Table 1

Properties of Common Inorganic Scintillators.

	Wavelength of Max. Emission λ_{max} , nm	Refractive Index	Decay Time (μs)	Light yield in photon/MeV	References
Alkyl Halides					
Nal (Tl)	415	1.85	0.23	38000	[31]
Nal (Tl)	410	1.85	0.23	41000	[32,33,34,35,36,37,38]
CsI(Tl)	540	1.8	0.68, 3.34	65000	[31,39,40,41]
CsI(Tl)	565,420	1.8	0.8 -> 6	66000	[32,36,37,42,43,44,45]
CsI(Na)	420	1.84	0.46, 4.18	39,000	[31,46]
CsI(Na)	420	1.80	0.63	40000	[36,37,47,48]
Li(Eu)	470	1.96	1.4	11000	[31]
Slow Inorganics					
BGO	480	2.15	0.3	8200	[31]
BGO	480	2.15	0.3	9000	[32,34,36,37,49,50,51,52]
CdWO ₄	470	2.3	1.1, 14.5	15000	[31,53,54,55]
CdWO ₅	500	2.2	3 / 17	28000	[32,36,37,38,56,57]
ZnS(Ag)(Polycrystalline)	450	2.36	0.2	-	[31]
CaF ₂ (Eu)	435	1.47	0.9	24000	[31]
Unactivated Fast Inorganics					
BaF ₂ (fast component)	220	-	0.0006	1400	[31,58,59]
BaF ₂ (slow component)	310	1.56	0.63	9500	[31,58,59]
BaF ₂ (fast component)	220	1.5	0.8	1500	[32,60,61]
BaF ₂ (slow component)	310	1.5	0.6	11000	[32,60,61]
CsI(fast component)	305		0.002, 0.02	2000	[31,62,63,64]
CsI(slow component)	450	1.8	multiple, upto several μs	varies	[31,63,64]
CsI(fast component)	320	1.95	1	200	[32,65,66]
CsI(slow component)	450	1.95	0.006/0.028	2000	[32,65,66]
CeF ₃	3,10,340	1.68	0.005, 0.027	4400	[31,67,68,69]
Cerium Activated Fast Inorganics					
GSO	440	1.85	0.056, 0.4	9000	[31,70,71,72]
GSO	440	1.85	0.6	8000	[32,36,73,74,75,76]
YAP	370	1.95	0.027	18000	[31,77,78]
YAP	350	1.93	0.030	21000	[32,79,80]
YAG	550	1.82	0.088, 0.302	17000	[31,77,81]
LSO	420	1.82	0.047	25000	[31,82,83]
LuAP	365	1.94	0.017	17000	[31,84,85,86]
Glass scintillators					
Ce activated Li glass	400	1.59	0.05-0.1	3500	[31,87]
Ce activated Li glass	400	1.56	0.075	4000, 6000	[32,88,89]

vated with different dopants was first time reported by Ryzhikov *et al.* [95,99]. Further, his group continued their investigations on zinc chalcogenide crystals doped with suitable dopants such as Te, Al etc. During the studies, it was found that Te doped ZnSe shows enhancement in formation of defects in Zn sublattices and favours the augmentation of vacancies. Addition of Te as an isovalent dopant stimulates the formation of a stable association of vacancies in Zn lattice with Te atoms (i.e. $V_{\text{Zn}} + \text{Te}_{\text{Se}}$) and mobile interstitial zinc. This association makes main elements of radiative recombination centres and they are responsible for principle working band of ZnSe:Te. In this way, isovalent dopants were found stimulating the formation of a stable association of inherent point imperfection with dopants [96,100–102] (Table 1).

Further, studies revealed that Te not only hardens the mixed crystal ZnSe: Te but also decreases the density of dislocations both in bulk crystals and epilayers [103–105]. Oxygen doped ZnSe have also shown a considerable advantage for radiation detection in the 20–200 keV range as compared with conventional scintillator CsI(Tl) [97]. P. Vitta *et al.* compared the photo luminescent properties of isoelectronically doped ZnSe(Te), ZnSe(O) and ZnSe(O, Al). Their investigations have shown that there is increased luminescent intensity in case of doped crystal by a factor of 40 over undoped ZnSe. Also, a blue shift of 10–20 nm in emission wavelength was reported. Doping of ZnSe with oxygen and aluminium was found to be favourable over doping of tellurium to achieve a higher light output. The best results in case of co-doping of ZnSe with O and Al is due to the fact that aluminium impurity augments incorporation of oxygen into ZnSe crystal. The higher density of the defects centres formed due to this is responsible for efficient emissions [106]. In recent years the mechanism of the influence of the rare-earth doping on the afterglow has also been studied

on doped ZnSe samples by introducing CeO₂, Sm₂O₃ or Sm₂S₃etc. These studies have shown a considerable decrease in afterglow level. However, with such additional dopings few studies reported decrease in light yield, as well. Hence the trade off between afterglow and light yield has to be taken into account for purposeful fabrication of scintillator [107]. The clearer picture of comparison of ZnSe doped compounds and conventional scintillating materials have been given in Table 2. The overall study with ZnSe doped compound semiconductor has shown that they have high values of thermal and radiation stability. Also, as they have good light output, they can be considered as a suitable candidate for identifying decay products of various radioactive materials under extreme conditions [92,93]. Their luminescence kinetics, physico-chemical and electrical parameters extend their applicable not only in X-ray introscopy systems, but also in other branches of radiative control and nuclear investigations. ZnSe(Te) crystals, based on their scintillation and amplitude kinetic characteristics are found to be most suitable to be used with a silicon photodiode coupled with a photomultiplier tube. Hence, ZnSe has effectively filled the gap in “scintillator-photodiode” detector series for modern radiation detector [97].

Effect of annealing and heavy ion irradiation on ZnSe based samples

The fabrication of ZnSe scintillators to enhance their performances includes not only doping [110] but various kinds of heat treatments that lead to the reconstruction of the ensemble of intrinsic point defects. This reconstruction not only changes the properties of starting material but also affects the characteristics of the impurity atoms. Annealing can change solubility, position

Table 2

Comparison of ZnSe doped scintillators with conventional scintillators.

	Scintillator	Radiations	Operating Temp. ° K	Max. λ_{max} , nm	Absorption coefficient α , cm^{-1}	Decay Time τ , μs	S, photon/MeV	Thermal and radiation stability	Ref.
ZnSe doped Scintillators	ZnSe(Te)	α , β and γ radiations	300–450	600–640	0.05–0.15	2–20/ 30–80	7×10^4	High	[92,93]
	ZnSe(Te)	X-rays	300	630–640	0.05–0.15	30–150	7.5×10^4	High	[96,108]
	ZnSe(O)	α , β and γ radiations	300	600	0.05	2.0–8	5×10^4	High	[92]
	ZnSe(Cd)	α , β and γ radiations	300	620	0.1–0.15	5–20	4×10^4	High	[92]
	ZnSe(Cd,Te)	α , β and γ radiations	300	635	0.1–0.15	40–100	6×10^4	High	[92]
	ZnSe(O,Al)	α , β and γ radiations	300	605	0.1–0.15	3–15	5×10^4	High	[92]
	ZnSe(Te,O)	α , β and γ radiations	–	610	0.1–0.3	5–7	–	High	[95]
	ZnSe(Me ^{III} , O)	X-rays	300	590–610	0.1–0.2	0.5–10	up to 5×10^4	High	[96]
	ZnSe(Cd,Hg)	X-rays	300	615–625	0.1–0.3	5–20	up to 4×10^4	High	[96]
	ZnSe(Al)	X-rays	300	610	0.05–0.15	1–3	8×10^4	High	[108]
Conventional Scintillators	ZnSe(Te,O)	X-rays	–	620–640	–	5–3	–	–	[109]
	CsI (Tl)	α , β and γ radiations	350–400	550	>0.05	0.63–1	–	High	[93]
	CWO	α , β and γ radiations	–	490	0.02–0.05	5–9	–	High	[95]
	CsI (Tl)	α , β and γ radiations	–	570	0.05	1	–	High	[95]
	CsI (Tl)	X-rays	300	550	<0.05	1	5.5×10^4	High	[96]
	CWO	X-rays	300	490	<0.05	10–15	1.3×10^4	High	[96]
	CsI(Tl)	X-rays	–	580	–	0.8–1.2	–	–	[109]

and charge state of impurity atoms. Hence due to heat treatment, the change in emission spectra of ZnSe based scintillators can be seen [111]. It has been observed that isoelectronic doping combined with annealing gives better results for the formation of stable defect complexes acting as efficient emission centres. This can be utilized in ZnSe:Te single crystals employed in scintillation detectors. Luminescence of ZnSe:Te scintillators (1.95–2.1 eV) is found to be increased by annealing in Zn-rich environment [100]. Also, the annealing of ZnSe based films in Zn-vapour-rich ambient increases the density of the complex defects which in turn increases defect-related emissions. Minimum afterglow is desirable for ideal scintillator and annealing was found suitable to achieve this. It has been found that the afterglow level reduces by several orders of magnitude by annealing [107,112]. The annealing also affects crystal structure parameters. Although doping and annealing in Zn do not change the cubic crystal structure of ZnSe but affects lattice constant. The overall study indicates that annealing is a suitable method to improve the structural and scintillation properties of ZnSe based scintillators [111,112].

Luminescent properties of quantum dots were also found improved by annealing. Post-growth thermal treatment of CdSe/ZnSe quantum dot heterostructures have shown up to a 100 meV blue shift of band position and of 2–3 times increase in luminescence intensity. [113]. Similar results have been reported by various research groups who studied the effect of annealing on luminescent properties of quantum wells [114–117]. E. M. Dianov *et al.* investigated the effect of thermal annealing on the luminescence properties of ZnCdSe/ZnSe quantum well structures. The annealed sample shows the characteristic decrease in the intensity of the exciton luminescence and an increase in the intensity of the luminescence of the deep levels. Annealing was found to result in narrowing of the exciton luminescence line nearly at 400 °C and a displacement of the maximum toward longer wavelengths [114]. D. Tonries *et al.* studies also revealed that the wavelength of optically active quantum wells can be tuned by thermal treatment without destroying the optical quality of the grown structures [117]. Hence, whether the material is a bulk material or it lies in quantum confinement regime, annealing seems to be an effective method to improve scintillation performance.

Effect of heavy ion irradiation

Heavy ion irradiation has been found affecting structural, electrical and optical properties of materials and results have been reported by various groups [118–122]. Ion beams with sufficiently

high energy of about MeV to GeV range are used to create changes in crystalline material such as moving pre-existing defects and create new defects (e.g. point defects, columnar defects etc.). A.A. Khurram *et al.* [118] studied effect irradiation of heavy ion beams of carbon, phosphorus and copper on ZnSe thin films. In this study due to heavy ion irradiation, the increase in grain size and decrease in lattice strain has been observed i.e. the improvement in structural properties of ZnSe thin film is seen. This study concludes that heavy ion beams can be used effectively to control structural as well as electrical properties of semi-conductor material. The behaviour of new ZnSe(Te, O) scintillators has also been investigated by V.D. Ryzhikov *et al.* [119] under irradiation of gamma-rays, electrons, protons and neutrons. The light output and transparency in the visible range is found to be decreased due to gamma-rays and electron irradiation. The neutron irradiation has shown an increase in light output by 20–150%. However sharp degradation of scintillation properties of ZnSe(Te,O) crystals is observed due to proton irradiation. From these studies, it is clear that selection of energy and type of ion can play a key role in producing scintillating materials with desired properties.

Towards ZnSe quantum dots scintillators

Basics of quantum dots

Nano-composite materials based on semiconductor quantum dots have great potential for radiation detection via scintillation. These materials can emerge as a new class of efficient scintillators that can operate at room temperature. Changes in optical and electronic properties of materials can be seen in quantum confinement regime. Quantum confinement effect in nano-world arises due to the influence of ultra-small length scale on the energy band structure [123,124]. The length scale corresponding to quantum confinement regime is 1–25 nm for typical semiconductor groups of IV, III–V and II–VI. In this regime, particle size becomes comparable to electronic wave function and electrons start experiencing pressure due to geometrical constraints. As electrons feel the presence of particle boundaries, they respond to it by adjusting their energy. This phenomenon is known as the quantum-size effect [123]. Size dependence of energy levels starts when particle dimensions are near to or below bulk semiconductor Bohr exciton radius. Bohr exciton radius for a particle is given by, $r_B = \epsilon (m/m^*)a_0$, where ϵ is the dielectric constant of the material, m^* is the mass of the particle, m is the rest mass of the electron, and a_0 is the Bohr radius of the hydrogen atom [123,125,126]. Illustration of quantum confinement

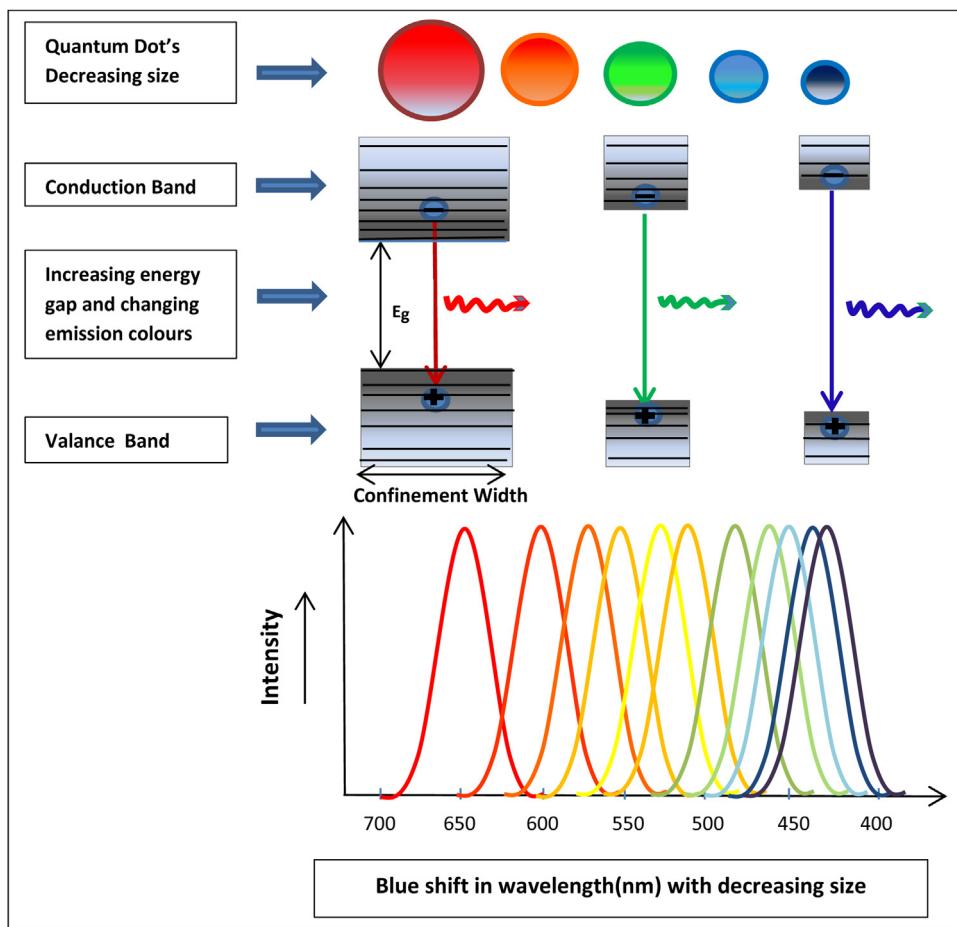


Fig. 3. Illustration of quantum confinement effect [125].

effect has been given in Fig. 3. It shows decreasing confinement width with decreasing size of the particle and corresponding blue shift in emission wavelength due increased energy gap.

Based on the confinement direction, a quantum confined structures have been classified into three categories as a quantum well (1D confinement), quantum wire (2D confinement) and quantum dots or nanocrystals (3D confinement). Quantum dot is hence a zero-dimensional semiconductor crystal which is also called as an artificial atom. The reason behind this is that its quantum and electronic properties are closely related to size and shape of the individual crystal [127]. With the decrease in the size of quantum dot, energy gap between valence band and conduction band increases and hence a blue shift in emission wavelength can be observed [128]. In the era of nanotechnology, material synthesis can be controlled at molecular levels and, hence it becomes possible to control size dependent key optical parameters such as emission wavelength and quantum efficiency [129]. This ability to tune the material emissions with the help of modern synthesis methods have attracted scientists towards quantum dots in both academic and industrial research.

Several researchers studied quantum dots and found them suitable for various applications such as infrared photo-detector [130], lasers [131], particle detectors [132], solar cells [133] etc. Brus gave the first theoretical calculation for semiconductor nanoparticles (e.g., CdS, CdSe) based on “effective mass approximation” (EMA). The Brus equation is thereafter used to describe the emission energy of quantum dot semiconductor nanocrystals in terms of the band gap energy E_{gap} , Planck's constant h , the radius of the quantum dot r , as well as the effective masses of excited electron(m_e^*) and

hole(m_h^*) [134]. E.O. Chukwuocha *et al.* investigated the effect of quantum confinement using the Brus equation in case of CdSe, ZnS and GaAs quantum dots [135]. The size-dependent properties predicted by the particle-in-a-box model were very well confirmed for these three different semiconductors. Results also have shown that the ground state confinement energy is inversely proportional to the size.

Efforts towards QD synthesis and property optimization

With an interest in the three-dimensional quantum confinement of exciton, III-V quantum dot structures have been extensively studied for various applications. However, excitonic properties were found to be enhanced in II-VI semiconductors because of the higher exciton binding energies and they were mainly studied in the form of micro particles embedded in insulator matrices [136,137]. The luminescent properties of quantum dots strongly depend on the method of synthesis. The continuous evolution in methods of synthesis can be seen with an extensive study on this topic. To achieve electronic access of quantum dots they were preferably grown on semiconductor surfaces. The radiative recombination efficiency of quantum dots was found to be superior over quantum wells [138].

Several groups studied relatively narrower band-gap CdSe and CdTe semiconductor quantum dots. These materials have luminescence from the red to green region. However, less stability is reported for self-organized CdSe and ZnSe dots on semiconductor surfaces by I. Suemune *et al.* [139]. Studies have also been reported on self-organized ZnSe dots which have a wider band gap and

luminescence in the blue region. Size dispersion and luminescence properties of ZnSe quantum dots synthesized by metalorganic vapour phase epitaxy were investigated by T. Tawara *et al.* [140]. Effect on PL properties of ZnSe quantum dots was found to be in good agreement with calculated quantum size effect estimated by AFM size measurements. The synthesized quantum dots were found to have a zinc-blende crystalline structure and a diameter of about 11 nm. Further, the author observed that the quantum dot size can be varied by changing growth time. Blue-shift was clearly observed for smaller average quantum dot size as an effect of quantum confinement.

M.A. Hines *et al.* [141] firstly reported an organometallic route to produce highly luminescent (quantum yield = 20–50 %) ZnSe nanocrystals with improved crystallinity. During investigations on CdSe quantum dots, few limitations were found by researchers such as low quantum yield and broad emissions spectra. To overcome these limitations, ZnSe was introduced as an efficient alternative to CdSe. However, synthesis of ZnSe by sol-gel method did not give favourable results. ZnSe, when prepared by sol-gel method, have shown problems such as no luminescence for arrest precipitation technique, no optical spectra for quantum dots prepared by super-saturated glass solution and also large size distribution etc. Later the organometallic route of synthesis was found to be successful for production of good optical quality ZnSe quantum dot scintillators which can replace CdSe based scintillators.

Studies have reported the synthesis of high-quality quantum dots by organometallic and aqueous approach having emissions in visible or near infrared ranges, such as CdTe, CdSe, some alloys nanocrystals etc. [142]. During this type of synthesis, the nanocrystals were grown from organometallic precursors nucleated and slowly grown in hot alkylamine co-ordinating solvent which gave relatively monodisperse colloidal nanocrystals. ZnSe was prepared with organometallic diethylzinc in a trioctylphosphine oxide (TOPO)-hexadecylamine (HAD) mixture. However, it was found that key chemicals used in the organometallic route are toxic, expensive, pyrophoric, and even explosive at high temperatures. Considering these disadvantages Peng *et al.* and group [143] tried to design optimized green-chemical synthetic approach for CdSe nanocrystals. The highest photoluminescence quantum efficiency of CdSe nanocrystals was up to 20–30%. Results reported by this group provided a starting point to establish a precursor/solvent/ligand database for designing optimized green-chemical synthetic approaches to get high quality nanocrystals in broad size range. In this method of synthesis, not only the control over phase of nanocrystals crystal was possible but also a size range was broader than that of the original organometallic method. Peng *et al.* and group further continued their efforts and developed a one-pot synthesis of high-quality quantum rods and dots of CdTe, CdSe, and CdS using a CdO as greener cadmium precursor [144]. These efforts can be considered as a major step toward a green-chemistry approach for synthesizing high-quality semiconductor nanocrystals. The reaction conditions were mild and simple. This made a large-scale synthesis possible without using a glove box.

Use of water as a solvent for nanocrystal synthesis attracted considerable research interest as it is cheap, non-toxic, non-flammable and readily available solvent. Murasea *et al.* [145] developed a water based alternative method for synthesis of blue light emitting ZnSe nanocrystals (2–3 nm) using thiol-based stabilizers. Thioglycerol not only stabilized ZnSe colloidal solution but also led to defect emission. So it was suggested that the surfactant should be minimum, i.e. just required to avoid agglomeration of particles. In this method, optimized results can be achieved by adjusting reflux time and concentration of surfactant. The water-based method has been found favourable over organometallic method because of advantages such as low toxicity, good reproducibility and good water solubility etc.

The time taken by the aqueous method for synthesis of quantum dots is about 1–2 days. To minimize the time of reaction and overcome limitations of water-based methods, rapid synthesis method like microwave synthesis was investigated. Nanocrystal synthesis by microwave irradiation was first introduced by Kotov group [146]. Conventional heat transfer sources such as oil bath or temperature bath are comparatively slow and inefficient methods for transferring heat into the system. Microwave irradiation is comparatively fast and can avoid creation of temperature gradient in the system by uniform heating the sample. A significant quantum yield of about 17% has been reported by H. Qian *et al.* [146] for ZnSe(S) quantum dots which were synthesized by microwave irradiation. In this study, results of characterization indicated that improvement of luminescence is attributed to the sulphur ions released from stabilizer and forming a ZnSe(S) alloy shell on the surface of the ZnSe nanocrystals. M.F. Budykaa *et al.* [147] reported the synthesis of CdS quantum dots by microwave synthesis method. This study tried to study the effect of coordinating ligand benzylmercaptan (BM) on spectral-luminescent properties of CdS quantum dots. Synthesized quantum dots were of about 2.4 nm in diameter. Further, the author suggested BM: CdS optimized the molar ratio of 1:5, to achieve monodisperse quantum dots.

Amongst various synthetic pathways, organometallic/inorganic hybrid thermolysis routes are found to be most successful once. In these synthesis routes capping agent plays a key role. It can actually be considered as a stabilising agent, providing colloidal stability, stopping uncontrolled growth and agglomeration. The ligands are responsible for controlling the growth rate, particle morphology, reaction pathways and particle size distribution. Basically electronic structure of these passivating ligands affects the electronic and optical profile of nanoparticles. Basic ligands such as Tri-n-octylphosphine oxide (TOPO), Trioctylphosphine (TOP), Amines, Thiols, Carboxylic acids etc. are normally used for quantum dot synthesis. In-depth discussion of ligand properties is done by M. Green [148] in the recent article. Effect of ligand and oxidation over quantum dots is elaborated by T.M. Inurbave *et al.* [149]. However, the role of ligands in quantum dot applications and exchange transfer in hybrid CdSe-OPV composite nanostructures is explained by N.J. Hammer *et al.* [150]. These studies can be found useful in optimization of engineered nanoparticles for photodetectors and photovoltaic devices.

With continuous improvement in semiconductor nanocrystals synthesis, they can now be synthesized in a wide range of sizes, shapes, crystal structure and compositions. Furthermore, nanocrystal heterostructures such as core/shell nanoparticles, dot-in-rod structures or core/crown nanoplatelets etc. have been introduced to open up new possibilities to tune the optical properties of these semiconductor nanoparticles. Core-shell nanoparticles are structures with inner-core and an outer shell made up of different components. These structures can show unique properties depending upon the combination of core and shell material, geometry and design [151,152]. An inorganic material with a wider band gap can be used to passivate a core material. This leads to a reduction of surface-related defects with improvement in quantum yield [153,154]. ZnSe and ZnS with wide band gap have become ideal choice for core/shell type of semiconductor nanocrystals and also can be the attractive host for doped nanocrystals to improve upon the properties of semiconductor core nanocrystals with a relatively narrow band gap. H.V. Demir *et al.* [155] have introduced a novel CdSe/ZnS core-shell scintillator for detection of UV radiation. This scintillator has demonstrated the enhancement in UV detection up to 800% with respect to the host polymer.

Formation of monodisperse zinc chalcogenide nanocrystals in the quantum confinement size regime has always been challenging for traditional organometallic routes, the alternative routes, or the single precursor routes. Considering the importance of studies over

these materials, the greener chemical approach was put up by L.S. Li *et al.* [156]. They achieved desired output especially for ZnSe, by the introduction of two new concepts of “activation of precursors” and “identical injection/growth temperatures”. The first concept of activation of precursor allows applying generic compounds (such as zinc carboxylates salts) for ZnSe nanocrystal’s growth. However, the second concept tries to find a delicate balance between nucleation and growth. The growth is found to be dependent on various factors such as monomer and ligand ratio, ligand concentration, and reaction temperatures. Further, the generic oxygen-containing ligands (such as fatty acids) with a controlled concentration in non-coordinating solvents were found to be reasonable ligands for the formation of ZnSe and ZnS nanocrystals.

With advancement in scintillating materials, highly emissive doped quantum dots (d-dots) were introduced for applications requiring high power, a high concentration of emitters. The greener approach of synthesis for doped quantum dots has been developed by Pradhan and Peng [157]. Synthesis of Mn: ZnSe d-dots with the emission range of 470–590 nm has been achieved by this method. Resulting d-dots were found to have a quantum yield as high as ~50%. This method allows controlling the formation of quantum dots at high temperatures (240–300 °C). The variable parameters in this method are a concentration of the inhibitors, and free fatty acid, also the concentration of the activation reagents. PL properties were also tunable in the large optical window, from 565 to 610 nm. Studies have shown that d-dots such as Mn: ZnSe, Cu: ZnSe are more preferable as compared to ZnSe quantum dots as they overcome self-quenching problems of undoped quantum dots. However, d-dots can potentially retain all advantages of quantum dots. Hence, they became a new class of practical emissive materials.

Various approaches such as the traditional organometallic route, hydro/ solvothermal method, newly developed nucleation doping have been reported for Mn-doped ZnSe nanocrystals [158–162]. However, these methods use toxic and expensive starting material, such as trioctylphosphine (TOP) and tributylphosphine (TBP). Hence, environment-friendly chemical method was developed by Lanlan Chen [163]. This method is greener, cheaper and phosphine free synthesis. They used environmentally friendly N, N-dimethyl-oleoyl amide as the solvent for Se, which eliminates the need for air-sensitive, toxic and expensive chemical TOP. Also uses natural surfactant oleic acid (OA) to dissolve zinc acetate and form zinc oleate solution in the non-coordinating solvent. Interestingly flower shaped nanocrystals were formed by ZnSe QDs. In this method, the particle size can be easily tuned by simply altering the amount of ligand or precursors by elevating the injection temperature to 310 °C and keeping this temperature for growth. ZnSe quantum dots formed flower-shaped nanocrystals via van der Waals force of surfactant molecules and still keeping preserving their own crystalline properties. One more new water-based approach of ligand-selective synthesis was demonstrated by Z. Deng *et al.* [164] for the synthesis of ZnSe and Zn_xCd_{1-x}Se quantum dots. The developed quantum yield was as high as 40% and PL peaks tunable over the range of 350–490 nm. Optical properties of quantum dots could be tuned by 3-mercaptopropionic acid (MPA), thioglycolic acid (TGA), and L-glutathione (GSH) ligands. But a method to separate QDs from reaction constituents is to be developed. Then the synthesized quantum dots can be utilized for various applications like biological labels and biosensors, light-emitting diodes, lasers, and electronic devices etc.

From the studies on synthesis of nano-composite materials, it is seen that organometallic approach is most successful for nanoparticle synthesis. However, the comparatively newly developed hydrothermal and aqueous synthesis is favourable to be used in terms of lower cost, lower toxicity and greener processing. But it is seen that quantum dots prepared by aqueous methods may need additional post-synthesis treatment for further improvement in

the quality of quantum dots. This adds complexity and cost which makes aqueous synthesis less desirable for large-scale production. The microwave synthesis has enabled the production of good optical quantum dots in both organic and aqueous media. This method features simple operation and potential for large-scale production [165].

4. Quantum dot as a scintillator

To the best of our knowledge very less work is seen over quantum dots as scintillators and still, there is a scope for identification and optimization of various materials which can emerge as an efficient quantum dot scintillator. Use of quantum dots for alpha and gamma-ray detection has been investigated by S.E. Létant and T.-F. Wang [127,129,166]. Standard gamma-ray detection technologies relies on cooled germanium detectors [127,167–170] and scintillating crystals (e.g., sodium iodide) [146]. The main problem associated with the former is that it needs cooling assembly for its stable working and that of later is its poor energy resolution and the limited choice of photon transducers (photomultipliers) [127]. Room temperature detector like cadmium-zinc-telluride is favourable for high energy applications, but the size of the crystals that can be grown is limited to a few centimetres in each direction [171]. Use of nanocomposite materials can be considered as one of the solutions to these problems and can emerge as a new class of scintillators that can efficiently work at room temperature [127].

Quantum dot material emissions are in the visible range and, hence they are more suitable as compared to conventional scintillators. The conventional scintillating materials have output wavelengths in UV and blue regions (NaI = 460 nm) in which a photomultiplier tube has a quantum efficiency below 25%. However, use of quantum dots as a scintillator allows fine-tuning of the output wavelength in the visible range with increased quantum efficiency up to 70% [127]. The visible band gap of quantum dots also ensures both efficient photon counting (because of better coupling with photomultipliers), and high photon output (smaller individual photon energy results in more photons produced) at room temperature [127,129].

S.E. Létant *et al.* [166] studied porous glass doped with quantum dots under alpha irradiation. This study demonstrates the ability of quantum dots to convert alpha radiation into visible photons. However, the energy resolution of the system was found to be poor and it needs a large volume of material for charged particle detection. Hence, for future applications, increased dot density and optimized surface treatments were suggested by the author for improved light output and efficient photon collection. Further, the effect of gamma radiations over nanoporous glass-quantum dot composite material was also studied by S.E. Létant *et al.* [166]. The material has shown adequate photon output at low gamma ray energy. The author still suggests the use of densely packed high atomic number semiconductor quantum dots (e.g., PbS) embedded in polymer matrices for detection of gamma rays. This can give better results with high detection efficiency and large gamma ray stopping power. Few more studies can be found for gamma-ray detection using quantum dots based materials. R.Z. Stodilka *et al.* [172] investigated CdSe/ ZnS quantum dot ensemble for gamma-ray irradiation. CdSe/ ZnS quantum dots were found to have a dynamic range of at least three orders of magnitude for γ -ray detection and also shown excellent agreement with experimental data by fitting the spectra using a three-component Gaussian model. Their three control samples exhibited consistent unchanged fluorescent spectra during experimental time scale. Fluorescent spectra shown by these quantum dots very well supported the concept of using quantum dots as novel dosimeters. All these scientific efforts [127,129,166,172] have contributed towards the development of

new quantum dot scintillating materials for detection of ionizing radiations.

Applications of ZnSe based scintillators

The broad possibilities of purposeful variation of photoelectric, luminescent, and electric properties have created continuous scientific interest for practical application of $A^{II}-B^{VI}$ type of compounds. These compounds show low transparency and poor reproducibility which limits their use in radiation instruments. However, achievement in process of growing crystals have shown possibility of using these scintillators in systems of radiation and non-destructive control [90,173,97,174]. ZnSe based scintillators have been tested for diverse applications such as medical-tomography, industrial-non-destructive testing, security and specialist applications in high energy, nuclear, space and medical physics etc. Study of these materials have shown some important advantages over other materials for detection of low-energy gamma-radiation, alpha- and beta-particles, as well as detectors operating under high (up to 120 °C) temperatures and powerful (up to 10^8 rad) dose loads [109]. In case of ZnSe(Te,O), the combination of semiconductor properties and characteristics of a highly efficient scintillator makes it possible to create scinti-electronic detectors of X-ray radiation. But at higher energies' use of ZnSe(Te,O) is limited by bad transparency and also the high value of refractive index ($n=2.4$) which leads to significant light losses. To overcome this problem combined X-ray detectors based of semiconductor-scintillator ZnSe (Te,O) were suggested [95]. Detectors of charged particles and ultraviolet radiation based on the Schottky barrier structure of "metal-nZnSe(Te)" have also been developed [95].

ZnSe(Te) have also been found useful for advanced medical application of computer X-ray tomography. Computer X-ray tomography is a powerful tool for early recognition of various diseases, especially those requiring surgery. The detector pairs of ZnSe/CsI and ZnSe/CdWO were found to be useful in dual-energy receiving-detecting circuits which allows for distinction between muscular and bone tissues. As ZnSe(Te) have low transparency and a lower atomic number compared to CsI(Tl), it is more suitable in the range of low and moderate values of X-ray radiation energy, i.e., up to 160–200 keV. This is working range of the installations intended for computer tomography. Hence, ZnSe(Te) crystals can be used in low energy detectors in computer X-ray tomography [175]. Further the dual-energy and multi-energy radiography have also been found as promising methods for detection of explosives using X-ray inspection equipment. Hence, scintillator-photodiode type detectors based on ZnSe crystals are applicable in homeland security for distinction between explosives and safe organic. In medical equipments these detectors help distinguish between soft and bone tissues [176].

ZnSe crystals were tested for their use in scintillating bolometers which operate at very low temperatures for their use in double beta decay experiment. The excellent low temperature luminescence of ZnSe indicated that ZnSe is among the best suited materials for this application. Further studies are needed on ZnSe samples prepared in different growth conditions for deep understanding of the scintillation process in ZnSe material at low temperature [177].

Scintillator-photodetector systems are used for registration of X-rays. In such systems scintillator should completely repeat the shape of a photodetector to avoid distortion of information about the object. Flexible scintillation panels are most successful solution of this problem. These flexible scintillation panels can fit maximally tightly to the surface of photodetector of any type. As reported by V. Littichevskyi et al. [178] the ZnSe(Te) based scintillation panels have shown high quantum yield and luminescence homogeneity. Methodology of production of these panels was developed based on fine dispersed power of ZnSe(Te) particles

for obtaining high scintillation parameters with stable and steady scintillations.

The performance of ZnSe(Te) material was evaluated for fibre optic dosimetric detector [179]. Fibre optic dosimetry is used for in-vivo, real time dosimetry and also in radio therapy treatments. This method relies on using a small scintillator coupled to one end of a long optical fiber. The scintillator in this case is placed at a point where dose rate is to be determined and the light detector at the other end of an optical fibre. A good reproducibility of the radioluminescence response with a percent standard deviation lesser than 0.5% was obtained by M. Ramirez et al. [179]. Although further research is required in order to determine the feasibility of using this material as a fibre optic dosimetric detector, results presented in this work demonstrate prospects for further research of ZnSe(Te)-based fiberoptic probes.

Recent efforts are more focussed on quantum dot scintillators to develop more efficient detectors [127,129,166,172] for various applications. It is seen from literature that applicability of quantum dots for practical applications still needs extensive and focussed efforts.

5. Conclusions

Development of experimental physics promoted the use of scintillating materials for detection of radiations. The excitation effect caused by ionizing radiations creates light pulses in scintillating materials and this works as the principle of scintillation detectors. With research on scintillating materials, several organic and inorganic scintillating materials were discovered. This article is a comprehensive review of inorganic scintillating material ZnSe and its progress towards more efficient quantum dot scintillators. Development of ZnSe based scintillators have provided much needed scintillation efficiency for high speed light imaging applications by overcoming limitations of conventional scintillators. ZnSe based scintillators have also been found to be the most suitable candidate to be used with silicon photodiode coupled with a photomultiplier tube. Though most of the scintillation research was found focussed on CdSe based compound semiconductor, highly toxic component cadmium is their major disadvantage. Hence, non-toxic ZnSe gave the best suitable replacement for Cadmium based scintillators.

In further studies, the performance of these scintillating materials is found being affected by factors such as doping, annealing, heavy ion irradiation etc. ZnSe doped with isovalent dopants (e.g., Tl, O, Al) has shown improvement in performance over undoped scintillators. They show high values of thermal and radiation stability, increased luminescence intensity, the blue shift in emission wavelength and reduction in afterglow etc. Hence, these factors support the idea of using ZnSe compound semiconductors with a suitable dopant for scintillation applications. Further, various kind of heat treatments was also found enhancing the performance of ZnSe based scintillators. Also, its structural, electrical and optical properties were found to be altered by heavy ion irradiation. Hence, it is clear that isoelectronic doping combined with annealing and irradiation of material by a suitable ion is an effective method for improvement of scintillation properties of the material.

With further progress in research on scintillating materials, nano-composite materials based on semiconductor quantum dots have shown great potential for radiation detection via scintillation. These scintillators were found to be more suitable as compared to conventional scintillating materials because of advantages such as emission in the visible region, tunable band gap, high photon output, efficient photon counting, high quantum efficiency, effective working at room temperature etc. However, the major challenge lies in the synthesis of quantum dots as it requires a combination of skill and extensive experimentation to obtain high optical qual-

ity particles having well-defined size and shape. Several groups tried to synthesize ZnSe quantum dots with optimized properties by various methods such as organometallic method, water-based methods, microwave synthesis etc. High-quality quantum dots have also been achieved by several green synthesis routes. Here, the attempt has been made to trace the progress in synthesis of ZnSe quantum dots.

ZnSe quantum dot scintillators have been found to be one of the most promising candidates for detection of a wide range of radiations. However, to the best of our knowledge, very less literature is available based on synthesis and property optimization of ZnSe quantum dot scintillators. Hence, still there is much scope to work on quantum dot synthesis and extending its applications in various fields.

Authors statement

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