Detection of γ-Radiations using Lead Sulfide Nanostructures: Through Optical Properties

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Abstract— Homeland Security is the prime factor to weigh a nation's strength or its immune system to overlook all the threats from various terrorist groups. It's always better to have a prevention system than having a curing system. In order to prevent terrorism attacks and other civilized attacks in the home land, the security system must be the strongest one in all means. Apart from the other types of weapons used, the very dangerous weapon is the Nuclear weapon which can demolish the infrastructure of the nation along with its growth for upcoming years in greater impact. To avoid the nuclear weapon migration into the nation there are many technology such as Scanning process at airports, railway stations and harbors. They use metal detectors and CT scanners along with Scintillators to detect the nuclear weapon though the gamma radiation from the materials as U-235, also known as highly enriched uranium (HEU) and plutonium. This work concentrates on the detection of those gamma radiations in the atmosphere in minimum quantities even from 1KGy and below. The quantum dots of PbS are more efficiency in detecting the radiation from the materials or weapons. At present single crystal scintillators with sodium iodide being used worldwide for the Security Purposes. The Lead Sulfide Quantum Dots are prepared using the Hines and Scholes method of Hot Injection Technique, in Lead Oleate. The prepared PbS Quantum Dots are Examined Using Particle Size Analyzer, Dynamic Light Scattering Spectroscopy. Photoluminescence, FTIR Spectroscopy and the synthesized quantum dot was been found with a diameter of 4-6 nm. The Optical Properties of the PbS QDs are studied before and after irradiation of gamma radiation (with CO-60 as the Source of gamma Radiations) and using the difference the optical response of the lead sulfide are studied under gamma radiation**.**

Index Terms— CO-60 Gamma Source, Dynamic Light Scattering Spectroscopy, FT-IR, Gamma Radiation, Hines and Scholes Method, Lead Sulfide, Particle Size analyzer, Photoluminescence, Quantum dots, Scintillators.

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1 Introduction

THE inhabitants of the earth are persistently out in the open to all type of radiations that can be classified into two forms: charged radiation and uncharged radiation. It was realized early on that radiation increased rapidly with an elevation, suggesting that it had celestial origins. This hypothesis was confirmed by Robert Andrews Millikan, who gave the radiation the name of Cosmic Rays (CRs) [11]. The most vulnerable radiation of all types is gamma radiations which are very hazardous to the mankind and threatening starting from DNAs of the mankind. There are some reliable techniques to detect the gamma radiation, among them One type of Gamma Radiation Detector works with inorganic single crystal which is termed as scintillations using sodium iodide as the prime materials which absorbs the high energy radiation effectively and then converts it into comparable light pulses, that indicates the presence of gamma radiation and its dosages. In this mechanism the converted light pulse's from the gamma radiation dosage or energy are measured through the intensity of the light and compared to energies of known nuclides. Ever since one of the main challenges in home land security was detecting materials allied with prospective nuclear threats, effective filtering of the many genuine radioactive objects commonly found in retail and environment. For this reason detection should be more effective with higher accuracy. This can be achieved only by using Quantum dots of heavier elements such as Lead, YAG and etc, as an alternative of In-organic Single-Crystal Scintillation. Through which the reliability and efficiency can be improved. Researchers at GTRI (Georgia Tech Research Institute) are investigating for the replacement of crystals with heavier element nanoparticles or Quantum dots dispersed in polymer matrices [13]. "Scintillators designed with Quantum Dots or Nano particles may have more advantages over a single crystal Scintillations through better resolution"- said Brend Kahn, Associate Director of GTRI's Environmental Radiation Centre (ERC)[13]. By marking Brend Kahn's words on effective usage of Quantum Dots for gamma radiation detecting mechanism, which may lead to recompense comparing to the existing inorganic single crystal Sodium Iodide scintillations.

Quantum dot is a unit of substance which can be measured in Nanometers (10^{-9} sometimes closer to Angstrom), so small that the addition or removal of an

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electron can change the properties in any manner. The change can occur in Optical Parameter, Conductivity, Resistance or etc. The Quantum Dots can absorb and emit more energy as the size reduces to its maximum, i.e. the size of the particle determines the amount of energy required to eject the valance shell electron due to the force of attraction between the nucleus and valance electron. If the force of attraction is high then more amount of energy is required to eject that particular electron. If more energy is absorbed it can expel more energy to come back to the original state. If greater the energy, then frequency will be high implying the shorter wavelength. "Quantum Dots are promising because they can be tuned to certain wavelength by making them a specific size and suspending several different types of polymeric medium which allows for a broader wavelength range to be utilized"-said Principal Research Scientist Brent Karl Wagner, Georgia Institute of Technology. He also said, "In turn to obtain better performance and advanced stopping power, we need to deploy quantum dots made of heavier elements"[13]. Of course the nano-particles of the materials used in standard scintillator, like sodium iodide, can also have considerable advantages than the crystalline form of those materials, which can also play a major role in the efficiency of radiation detection process. As Literature status the researchers are currently developing and testing different types of quantum dots or nanoparticles including Lead sulfide and Cerium Doped-Yttrium Aluminum Garnet (YAG) isolated in polymeric medium, in order to hold quantum dots in its matrices. Quantum dots (QDs) are nanocrystals self-possessed of II-VI, III-V or IV-VI group elements, also known as zero-dimensional materials [1].

Due to their small direct band gap (0.41 eV) and larger exciton Bohr radius, PbS QD's are important semiconductor material. On analyzing various factors of all materials under heavier element category, the outcome obtained favors Lead sulfide (Quantum Dots) with many advantages in detecting Gamma Radiation. The Lead Sulfide Quantum Dots are prepared using Hines and Scholes Method of Hot Injection Technique. Normally this Method includes the injection of Bis (tri methyl silyl) Sulfide into the lead oleate solution at higher temperatures in an inert Atmosphere. But here in this work the Sodium Sulfide was been used instead of Bis (tri methyl silyl) Sulfide. The inert environment was taken as vacuum atmosphere as the setup shown in the Fig 2. The size of 4-6 nm was obtained as the product form this hot injection technique, with further improvements in the environment and increasing the temperature of injection will lead to further reduction of particle size implying to higher surface energy.

2 Materials And Methods

2.1 Material Study

The detection of higher energy radiation is a complicated in terms of identifying the suitable materials for the process. Because, the material deployed for the processes should withstand the higher energy in the case of gamma radiation detection. Also the materials should have an ability to expose the detected dosage in a form of optical, electrical (Conductivity) or through any other measurable terminologies. As explained above, through reliable literature surveys, it has been found that the heavier elements can perform well in this type of applications i.e. detection of high energy gamma radiations. Here Lead (II) sulfide was used in the purpose of gamma radiation detection through concentrating absorption energies. Likewise the absorbed high energy gamma radiations are calibrated through the optical properties of Lead Sulfide. It is been used in limited electronic devices. PbS, also recognized as galena, is the principal ore, and most significant compound of lead. The density of lead sulfide is 7.60 G/Cm3. The melting point of lead sulfide is around 1118oC (1391 K, 2044^{o}f) and boiling point is at 1281^{o}C (1554 K, 2338^{o}f) which shows it can withstand the high temperatures around 1281^{o}C. The molecular mass of this element is of 239.27, makes it as the heavier element and it has a refractive index of 3.91. At this juncture in this work, the optical property of the lead sulfide was alone taken into considered. There will be a variation in the optical property with respect to the particle size due to the surface energy.

2.2 Lead (II) Sulfide Quantum Dot

Quantum dots are with higher surface energy when compared to all other morphologies. Due to this factor the material will have an improvised property to absorb more energy and emit the equal amount to retain stability in the system. In accordance with this factor the Quantum dot morphology was been undertaken for this particular work of detecting gamma radiation. Quantum dots are Nano-crystals with a range of a hardly any nanometers, or numerous hundreds of atoms. At this size, quantum effects dictate, the electrons to be quantum confined with tapered energy levels, which is directly determined by the size of the particle. This means, quantum dots morphology can be worn to amend the band gap of the materials they are associated with "Due to their petite direct band gap (0.41eV) and superior exciton Bohr radius (18 nm), PbS QD's are imperative semiconductor material" [1].

2.3 Synthesis Of Lead Sulfide QD's

The synthesis process of lead sulfide Quantum Dots was carried out using hines and scholes method of Quantum dot preparation which is the Hot Injection technique. The chemicals used for this process was obtained from Laboratory reagent grade. The Lead(II) acetate trihydrate 99.999% (Anhydrous – Analytical Reagent grade)which is lead source for the preparation of PbS Quantum Dots. The sulfide Source was obtained from Sodium sulfide nonahydrate ≥ 99.99%. To obtain the nucleation process and to form lead oleate the Oleic acid ≥ 99% was used, followed by 1-Octadecene ≥ 95.0% (Analytical Reagent grade)and Toluene anhydrous 99.8%, Acetone, Ethanol for washing purpose and 1-Hexane as the medium of suspension for the Quantum dots. Also, some of the glass wares and apparatus required for the purpose of synthesis. They are Condenser - (1ft 3/4', Mouth size 26), Triple neck flask (Mouth size 26, 250 ml) and Separating funnel (250 ml). Finally, a syringe of 6 ml Capacity, to inject Sulfide source into hot lead oleate

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solution. Apart from these essential chemicals and equipments the vacuum pump is been used to create vacuum to form an inert atmosphere to achieve quality synthesis of Lead Sulfide Quantum Dots. Other equipment such as heating mantle with stirrer and temperature controller, Centrifuge with a maximum capacity of 5000 rpm with temperature controller facility were used in the process to obtain good quality and lofty quantitative synthesis of the

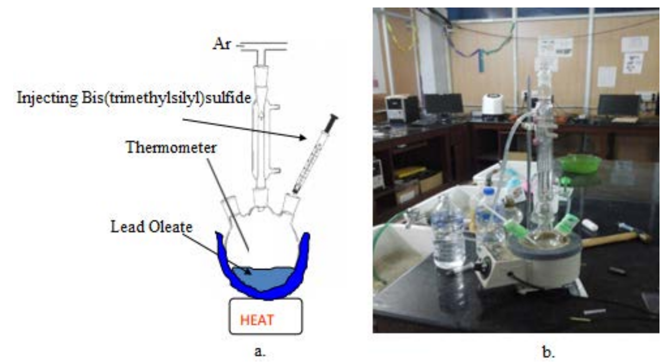

Fig 1-(a) Experimental Setup from Zach Lingley, Synthesis and Characterization of Lead Sulfide Quantum Dots, Nanostructure Materials and Devices Laboratory, October 31, 2008. October 3, 2008 and (b) Experimental Setup made at laboratory for synthesis of lead Sulfide Quantum Dots.

PbS Quantum dots. The setup was made with the reference of Zach Lingley, October 3, 2008 [14]. As shown in the Fig 1(a).

The setup was done as shown in the Fig 1(b) and 0.545gms of Lead(II) acetate trihydrate 99.999% was added to 10.0 ml of 1-Octadecene along with 1.80 ml of Oleic Acid in the Triple neck flask. Through the left limb of the three neck flask the air was drained out to create vacuum in the medium, in order to make the atmosphere more inert to the process to avoid, the byproducts and also to improve the qualitative factor of the synthesis process.

The solution was heated from minimum of 100oc to maximum of 180^{o}C. Meanwhile, the Sodium Sulfide solution was prepared by addition 0.765gms of Sodium Sulfide to 10 ml of distilled water with vigorous stirring. If the concentration of sulfide is increased, it can potentially amplify acquiesce of lead Sulfide Quantum dots. From the prepared 10.0 ml of Sodium Sulfide solution, 5.50 ml was injected to the 100^{o}C Lead Oleate with vigorous stirring for 2 to 5 minutes of duration.

Fig 2-Solution with lead sulfide Quantum dots and 1-Hexane in Separation funnel.

The whole system was unruffled for 2 minutes and 10 ml of Toluene was added to the triple neck flask and rinsed well to collect the entire synthesized product at one point. Then the solution was precipitated and isolated using acetone and ethanol correspondingly, followed by centrifugation at 5000rpm with the temperature of 35^{o}c for 10 minutes duration. Then the product was collected and 1-Hexane was added to the product and the whole solution was stored in the separation funnel as shown in the Fig 2. As seen in the same figure after 8 hours of duration the product will levitate in the 1-Hexane and those are collected and the previous process of adding acetone and ethanol was done. This process was repeated till the wastes were removed from the obtained product, in order to improve the qualitative factor of the process.

3 Results And Discussion

3.1 Centrifuge Particle Size Analysis Of Lead Sulfide Quantum Dots

The particle size was examined through centrifuge particle size analyzer and the obtained values were calibrated using histogram structure as shown in Fig 3. From the histogram obtained it's clear that the 64% of the solution contains the lead Sulfide particle of the diameter 4-6nm. And 28.16% of the particles in the solution are with a diameter of 6-8 nm and rest of the particles with the diameter around 39 nm to 99 nm. It was found that as the temperature increased with a well driven vacuum atmosphere the size of the particles can be considerably reduces to its maximum achievable diameters.

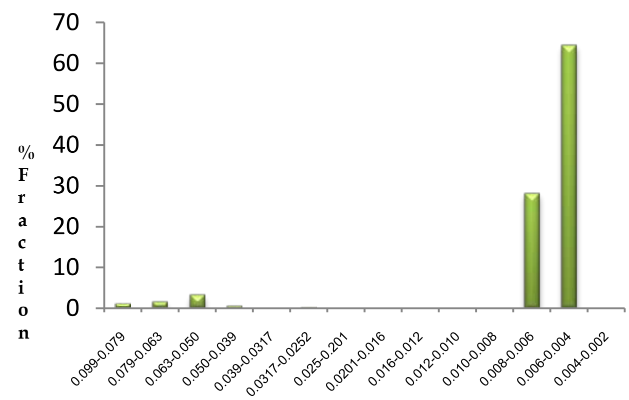

Fig 3- Histogram Generated for Lead Sulfide Quantum Dots.
Diameter Range (μm)

3.2 Dynamic Light Scattering Spectroscopy Study Of Lead Sulfide Quantum Dots

Dynamic Light Scattering Spectroscopy was used to find the used to determine the size distribution profile of small particles in suspension, through the optical properties of the materials. From the Figure3.2 there was a peak found at 4-

5nm diameter range with a cumulation percentage as 70% and the frequency percentage upto71%.

This indicates the dispersion of the material with particle size 4-5 nm is with more yield than other sizes. So hereby DLS proves the reduction of particle size up to 4nm that is the perfect quantum dot of lead sulfide which can be used for the application of gamma radiation detection using optical changes.

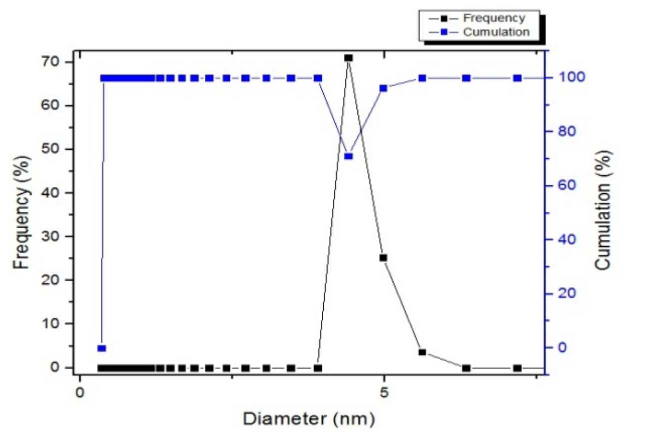

Fig 4-DLS Spectrum obtained for synthesized Lead Sulfide QD's

3.3 Photoluminesence Spectrum Study Of Lead Sulfide Quantum Dots

From the PL result obtained, the wavelength is computed as 280.7 nm and using this data the Band Gap of the product could be determined as well using the Eg value the size of

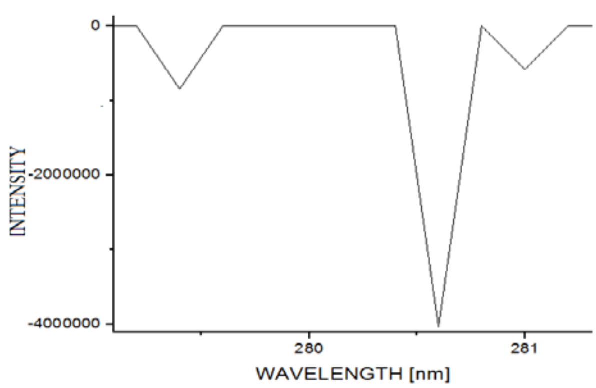

Fig 5- Photoluminescence Spectrum of Lead Sulfide Quantum Dots

the material can be calculated using Brus Equation. Band Gap Calculation is done below,

$Eg = 1240.8/\lambda$
$\lambda = 280.6x10^{-9}$
$Eg = 1240.8 / (280.6x10^{-9}) = 4.4$ eV.

Brus Equation - To determine the particle size is

$$\Delta E(r) = Egap + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Where Egap is Energy Band Gap, m_e^*, and m_h^* are unique for each nanocrystal composition. On substitution and calculation, we get,

r $=0.2139*10^{-10}$m $= 2.139*10^{-9}$m $=2.139$nm
Diameter (d) =2(r) = 2*2.139nm = 4.576nm

The particle size calculated using Brus equation coincides with the DLS result as well as CPS result showing 4.576 nm as diameter ranging within the limits prescribed in references to be declared as quantum dot.

3.3 FT-IR Spectroscopy Study On Non Irradiated (Γ-Ray) Lead Sulfide Quantum Dots

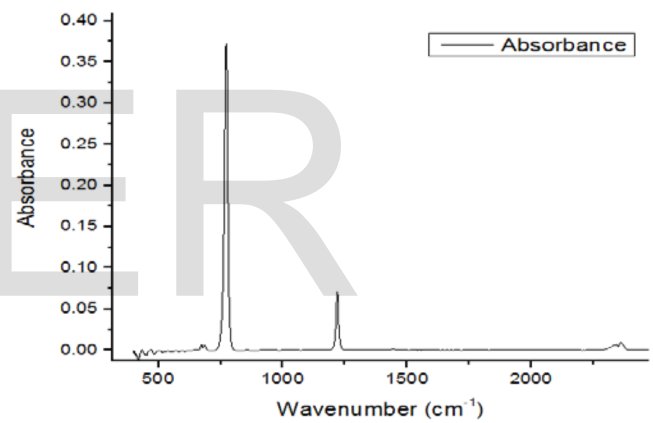

Fig 6 –FTIR Analysis Obtained

The FT-IR spectrum for non irradiated samples is shown below in the Fig 6

Since the analysis obtained by FTIR is confined between the range 500-1000 cm^{-1} hence it's been navigated using the software Infra Red file viewer and the below shown response is observed as given in Fig 8. As observed the peaks are at the following wave numbers such as 743.07cm^{-1} with an absorbance of 0.038. As known the lead sulfide QD's can be used as the IR detectors since its absorbance falls under the IR region. As defined absorbance between the range of 1µm to 200 µm. Fig 7 shows the spectrum of IR.

As reference of Fig 6 the peak at the wave number 743.07 cm^{-1} is considered and as such on conversion of cm^{-1} to nanometer to determine the wavelength of absorbance to identify the compound and also our project require the absorbance information hence its performed.

Calculating Nanometers from Wave number
$1/cm^{-1}x10^7$= Nanometers
On applying the values, x nm = 10,000,000 / x cm^{-1}

= 13457.59 nm = 13.475 µm.

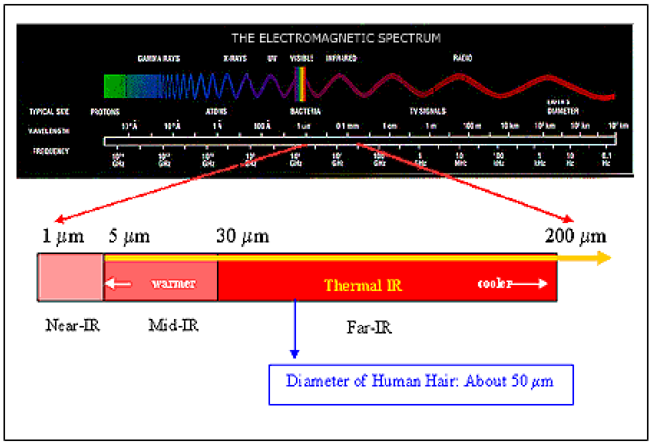

Fig 7- The Infra Red region in the Electromagnetic Spectrum

Hence on verifying the wavelength range from the Fig 7 it's been determined that the synthesized PbS QD's has an absorbance at the mid IR region.

3.4 Fourier Transform Infrared Spectroscopy Comparison Results

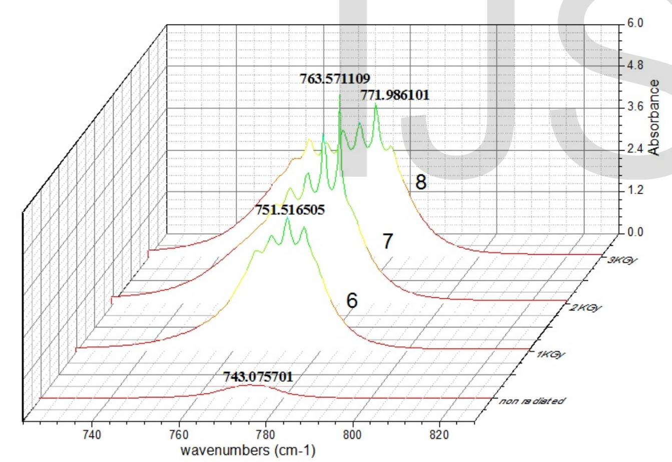

Fig 8 – FTIR Comparison.

As shown in the above figure the gamma interaction with the PbS quantum dot induce some changes in the absorption spectroscopy. Since found that the absorption is at MID IR region using the wavelength calculation.

The FTIR characterization is been done for both the non-irradiated and irradiated samples and plotted above to obtain the difference in the absorption due to gamma radiation. As suggested to do, the difference monitored are, while the maximum peak of the non irradiated sample of lead sulfide Quantum dots was at 743.076 cm^{-1} wave number implying to the wavelength of 13.475 µm (Mid IR Region), ultimately this particular sample of non irradiated PbS QDs consists of only one peak with more Absorbance. Likewise, the Irradiated Samples are also characterized using the FTIR and the results obtained are 751.516 cm^{-1}, 763.571cm^{-1}, 771.986 cm^{-1} as wave numbers of absorbance and 13.306(Mid IR Region), 13.096(Mid IR Region), 12.953(Mid IR Region) as wavelength of absorbance were a decrease in wavelength is experienced. Also the properties of getting an increment in number of peaks as 6, 7, 8 for the dosages as 1KGy, 2KGy, 3KGy respectively were also observed. Through this shift in peak and increments in number of peak with a change in wavelengths the detection of Gamma Rays or Radiations can be studied better than the scintillations of Single Crystal Sodium Iodide Scintillators. As a merit for the instrumentation all the variation in the wavelength takes place within the MID IR region which helps in installing a single range IR Source and Detector.

4 Conclusion

The Lead Sulfide Quantum dots were synthesized using Hines and Scholes method. They were characterized using the Centrifuged Particle Size Analyzer, Dynamic Light Scattering spectroscopy, Photoluminescence and found the particle diameter was 4 nm – 6 nm and it's with the wavelength of 280.6nm, on using the band gap calculation the band gap found to be as 4.4eV.Also by using Brus Equation it's been proved mathematically that the synthesized QD's is of the size 4.576 nm in Diameter. As said above earlier the size of the PbS QD's can be further be reduced by the following techniques, As temperature at which the sulfide source is injected is increased the size will be reduced as such here the sulfide source is injected at 100oc as it is increased up to 180oc with vigorous stirring the size of the QD's will be further constrained with increase in Yield comparatively. On the application part it's been proved that the PbS QD's have changes in the optical wave length as the dose rate of the Gamma radiation increase. Typically, it's found to be used as the sensor for the detection of gamma radiation effectively. As the further enhancement the material could be coated on the glass plate or dispersed in a polymer matrix to be used in an embedded device for the instrumentation process as an enhancement in Home Land defense.

References

[1] Abdelrazek Mousa (2011), *Synthesis and Characterization of PbS Quantum Dots* Submitted to the Department of Chemical Physics, Lund University, 2011 in Partial fulfillment of the Requirements for the Degree of Master of Science in Chemistry.

[2] Cafibr ANSI (1991). *Use of Germaniwn Spectrometers for the Measurement of Gamma · ray Emission* Rales of Rodionu ·elides, ANSIIN42.14-199l,IEEE. New York, NY, USA

[3] Comité 4 en 5 mei (2007), "*Nationaal Vrijheidsonderzoek 2007*,"(National Freedom Survey), http://www.4en5mei.nl/4en5mei/vrijheidsonderzoek /_rp_kolom2_2_elementId/1_110423

[4] Council of Europe, "Convention for the Protection of Individuals with regard to Automatic Processing of Personal Data of the Council of Europe of 1 January 1981,"www.conventions.coe.int/Treaty/en/Treaties/Html/1 08.htm

[5] Debenin, K. and Helmer, R. G. (1988). Ganuna and X-Ray Spectromerry with Semiconductor Defeclors, North-Holland, Amsterdam, The

Netherlands

[6] Francis AC and M Durante. 2006. Cancer risk from exposure to galactic cosmic rays. The Lancet Oncology 7 (5): 431-5

[7] Gu Y, Kuskovsky IL, Fung J, Robinson R, Herman IP, Neumark GF, Zhou X, Guo SP, Tamargo MC. Determination of size and composition of optically active CdZnSe/ZnBeSe quantum dots. Appl. Phys. Lett. 2003;83:3779–3781.

[8] Hazdra P, Voves J, Oswald J, Kuldova K, Hospodkova A, Hulicius E, Pangrac J. Optical Characterisation of MOVPE Grown Vertically Correlated InAs/GaAs Quantum Dots. Conference on European Nano Systems (ENS 2006); Paris, FRANCE. 14–15 December 2006; Paris, France: Elsevier Sci. Ltd.; 2006. pp. 1070–1074.

[9] Iwan Moreels,Karel (2005), Size-Dependent Optical Properties of Colloidal PbS Quantum Dots, Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S12, B-9000 Ghent, Belgium.

[10] J. H. Hubbel, "Photon Cross Sections, Attenuation Coefficients, and Energy Absorption Coefficients from 10 keV to 100 GeV;' National Bureau of Standads report NSRDS-NSB 29 (August 1969).

[11] Millikan RA. 1947. Cosmic Rays. The University of Chicago Press. 675 p

[12] Rameshwar T, Samal S, Lee S, Kim S, Cho J, Kim IS. Determination of the size of water-soluble nanoparticles and quantum dots by field-flow fractionation. J. Nanosci. Nanotechnol. 2006;6:2461–2467.

[13] Web source http://gtri.gatech.edu/casestudy/using-nanotechnology-detect-gamma-radiation

[14] Zach Lingley Siyuan Lu, Daniel Harris, and Prof. Anupam Madhukar(2008), Synthesis and Characterization of Lead Sulfide Quantum Dots ,Nanostructure Materials and Devices Laboratory,October 31, 2008.