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RESEARCH PAPER

Preparation of Nanocomposite Scintillator of ZnS Doped with Ag, Cu and AgCu for Alpha Particle Detection

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ABSTRACT

ZnS nanoparticles (NPs) doped with Ag, Cu, and AgCu were synthesized using hydrothermal method in water solution. The NPS are characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy scanning (EDX), scanning electron microscopy (SEM) and dynamic light scattering (DLS). The produced NPs have approximately hexagonal structure and a cubic zinc blended structure. The size distribution of NPs has a medium around 10 nm. Optical properties of these NPs were investigated using photo luminescence (PL) spectra, that show the samples exhibit reasonable optical properties for scintillation applications. The produced NPs were mixed with methyl methacrylate and dimethylformamide to prepare a very thin layer of a nanocomposite that is uniformly coated on a substrate of Plexiglas. Response of the layers under alpha particles irradiation using a photomultiplier tube and a multichannel analyzer indicates that the doped ZnS NPs have reasonable scintillation response that capable them to be used in developing a low-cost and free-size structure of alpha particles detectors.

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INTRODUCTION

An important subject in radiation detectors research is the study of materials with better energy resolution, a fast response and a high quantum efficiency that can be fabricated in large volumes with a low cost. The search for scintillator materials with desired characteristics in the past years has typically focused on the discovery of new inorganic single crystalline materials. A different approach is described here, in which the known inorganic scintillators are synthesized as nanoparticles and incorporated into a matrix material to make a nonocomposite. However, one of the most important problems in this filed is lack of transparency of nanocomposites with high loading nanoparticles. This issue can be solved considerably by synthesizing particles with sufficiently small size. The expected optical attenuation length versus particle size calculated using T-matrix scattering code shows a significant increase when the size of NPs become less than 20nm [1].

Electronical and optical properties of nanometer scales particles show a great difference compare to bulk materials. The differences originate mainly from quantum confinement effect. This effect cause the “band” of energies to turn into discrete energy levels and also increases or widens up the band gap of a semiconductor [2]. So energy levels in nanocrystals make a transition from a continuous to a discrete form and the band gap shows a significant dependence to the size of particles [3]. Therefore, the optical properties of nanocrystals especially the emission

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and absorption wavelengths can be tuned by controlling the particle size [4].

ZnS nanocrystal is a non-toxic semiconductor with tunable optical and electronic properties which have wide application [5-8]. It is one of the important semiconductor among II-VI group which have two crystalline structures: a cubic structure with a band gape of 3.68 eV and a hexagonal structure with a band gap of 3.77 eV [9]. Recently, extensive efforts have been taken for the synthesis of various ZnS morphologies such as nanoparticles [10], nanorods [11], nanobelts [12], [13], nanotubes [14], nanosheets [15], well aligned tetrapods [4], nanowires bundles [16] and hollow spheres [17-20].

Due to high surface to volume ratio of one dimensional nanomaterial, which has shown better performance in the development of devices, more attention is paid to the synthesis of these nanoparticles. Different methods have been used for the synthesis of ZnS nanomaterial. Aamong these methods, the hydrothermal method is a preferable method due to its simplicity, cost effectiveness, high yield, catalyst-free growth, environmental friendliness, less hazardous and capability of morphology controlling [21-22].

The ZnS nanopowder phosphor doped with different impurities can be produced using a proper synthesizing method and then a very thin layer uniformly coated with the nanophosphor can prepared to be used as a detector for alpha particles. The added dopant to the crystal is called activator. The activator is one of the main factors determining the phosphor emission wavelength in scintillators.

The produced nanocomposites are expected to have a large optical attenuation length since the produced nanocomposites contain particles with sizes 10~20nm. Therefore, these scintillator material is expected to have improved properties with respect to the one of the bulk scintillators. Improvements include enhanced light output, cost reduction and possibility of embedding them in a free-size structures.

MATERIALS AND METHOD

Undoped and doped ZnS were synthesis in water with hydrothermal method [23] using the materials listed in the Table 1. All materials used in this study were of AR grade with 99% purity used without further purification. The precursors were Zinc acetate dehydrate and thiourea and also Copper nitrate and Silver nitrate for synthesis ZnS:Cu, ZnS: Ag and ZnS:AgCu.

For example the Cu-doped ZnS were produced using zinc acetate, copper nitrate and thiourea as raw materials in the following steps. 50 ml (0.25M) aqueous solutions of zinc acetate was prepared. In order to add 0.2 moll% of Cu activator, .030 ml (0.0008 M) of $Cu(NO_3)_2$ aqueous solution was mixed with zinc acetate solution under stirring. Then 50 ml (0.25M) aqueous solution of thiourea was slowly added drop by drop to previous mixture (over a period of about 15min), under vigorous stirring at 15 min and continuously stirred for 30 min. In order to prevent the rapid growth of the Nps, during the synthesis process the solution is irradiated with an ultrasonic wave with a frequency of 20 KHz [24-29]. The resulting transparent solution was transferred to a 500 ml Teflon-lined autoclave and heated at 423K for 15 hours under auto-generous pressure. After being cooled to room temperature, the solid-state products were collected by high speed centrifuging at 2500 rpm and washed several times with deionized water and ethanol. Then it dried in the oven for 2 hours at 90° C to obtain the Cu-doped ZnS. Nanopowder of ZnS:Cu with different activator concentration and also other dopant were prepared using similar procedure mentioned for Cu-doped ZnS. Activator percentages of 0.05, 0.1, 0.2, and 0.5 mol% were chosen to find optimum concentration.

Table 1. list of materials used in synthesis

Material	Chemical formula	Company
Zinc acetate	$C_4H_{10}O_6Zn.2H_2O$	Merck.
Thiourea	CSN_2H_4	Merck
Silver nitrate	$AgNO_3$	Merck
Copper nitrate	$Cu(NO_3)_2$	Merck
Ethanol	CH_3CH_2OH	Merck
Deionized water	H_2O	---
Dimethylformamide	C_3H_7NO	---

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of Ag, Cu and AgCu-doped ZnS nanocrystals prepared by hydrothermal method. The peaks are well matched with standard PDF card for cubic and hexagonal ZnS (JCPDS NO. 05-0566).

It is clear that the peaks are relatively broad, indicating that the nanoparticles have small size. The nanocrystal size was estimated according to the Debye-Scherrer equation [30]

$$D = \frac{09\lambda}{\beta cos\,\theta} \quad (1)$$

where D is the average diameter of the nanoparticles, λ is the wavelength of Cu-K_α (0.1543 nm) radiation, β (in radians) is the full width at half maximum (FWHM), and θ is the Bragg angle. The average estimated size for samples are 11.26nm, 11.35nm for undoped and doped ZnS with 0.5% of Ag as impurities, respectively.

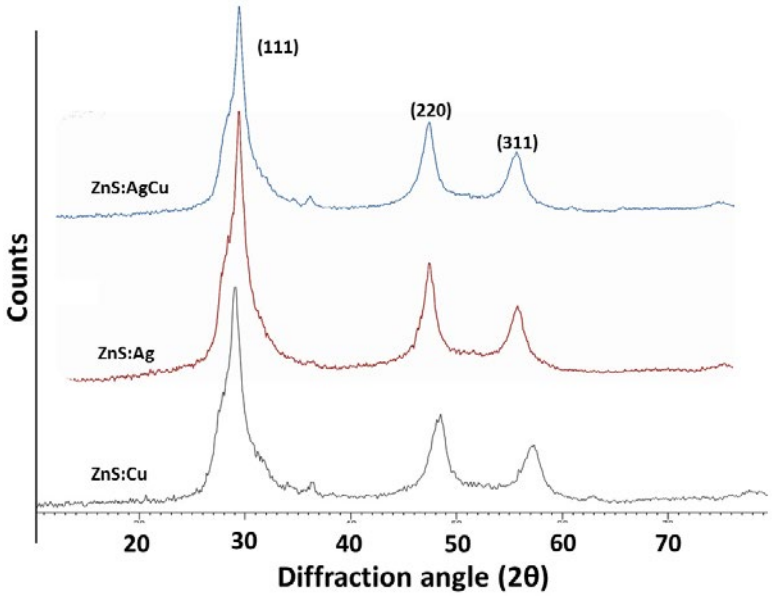

Fig. 1. The XRD patterns of Ag, Cu and AgCu-doped ZnS nanocrystals.

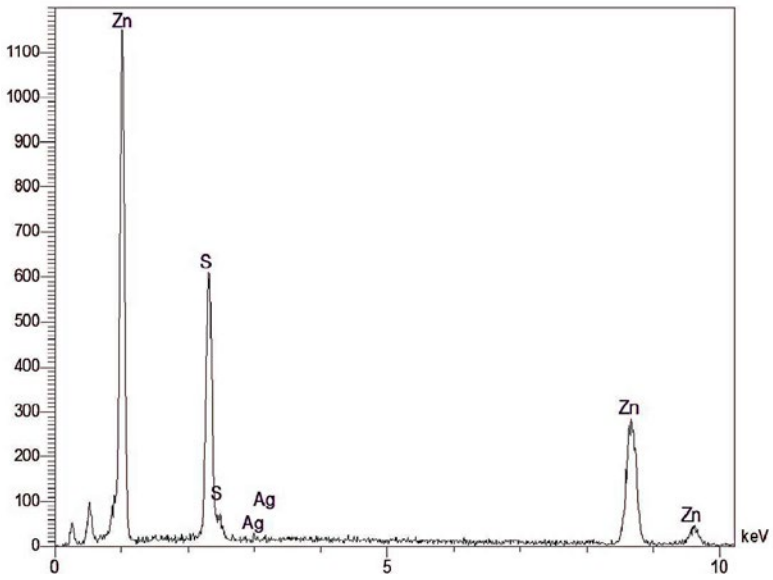

Fig. 2. The EDX spectrum of Ag-doped ZnS.

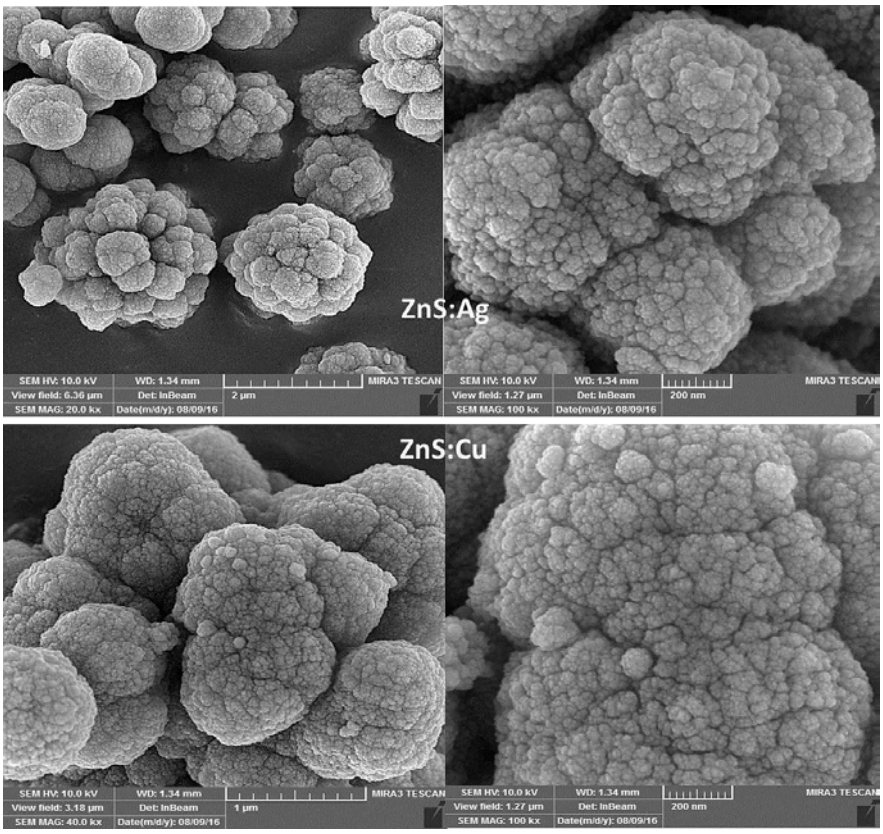

Fig. 3. The SEM image of produced ZnS:Ag and ZnS:Cu by hydrothermal method.

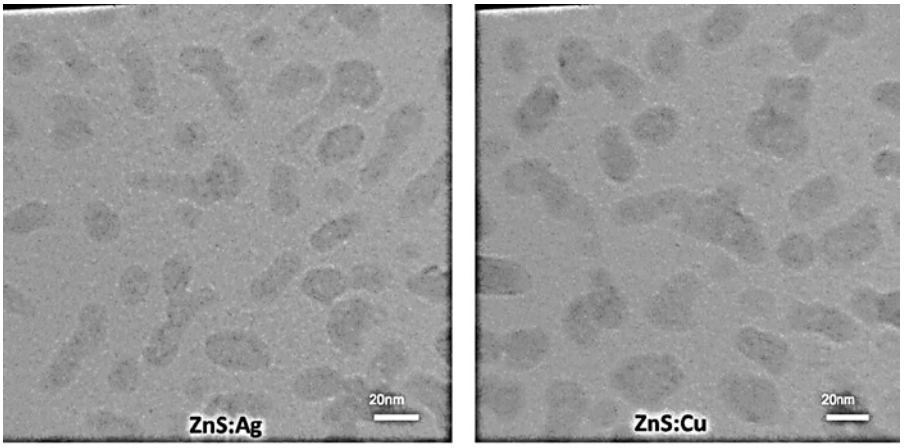

Fig. 4. The TEM image of produced ZnS:Ag and ZnS:Cu by hydrothermal method.

The performed synthesis without ultrasonic wave irradiation resulted in nanoparticles with much bigger sizes. Also it turned out that average size of nanoparticles increases as the doping percentage of Ag ions increases.

The composition of produced ZnS NPs with Ag, Cu and AgCu dopant was analyzed using EDX spectroscopy. Fig. 2 represents the EDX spectrum of Ag-doped ZnS.

The SEM image of manufactured nanoparticles is shown in Fig. 3. According to this figure, it can be observed that made nanoparticles have relatively homogeneous structure.

Transmission electron microscopy (TEM) is

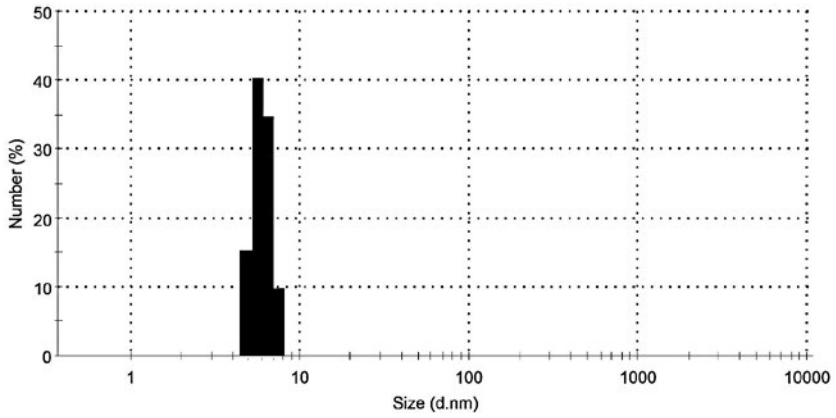

Fig. 5. Size distribution of prepared ZnS:Ag NPs obtained by DLS technique.

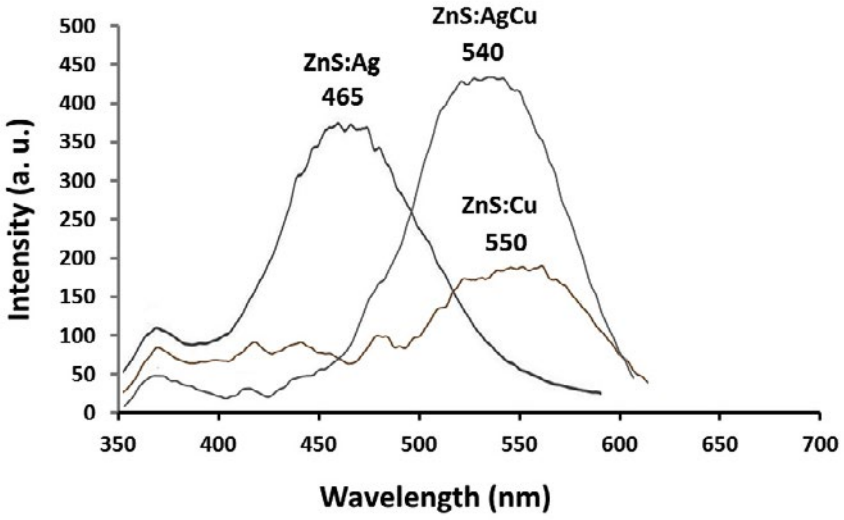

Fig. 6. The PL spectra of ZnS with Ag, Cu and AgCu impurities.

used to directly obtain the image of produced nanoparticles. Fig. 4 depicts the TEM images of ZnS:Ag and ZnS:Cu NPs which confirm the obtained sizes from XRD analysis.

The size distribution of prepared ZnS:Ag NPs obtained by DLS technique is shown in Fig. 5. Results show a sharp distribution of particle size around ~10 nm. The SEM, TEM and DLS analysis confirm that applied procedure was successful to produce NPs with sizes 10~ 20nm which is crucial for scintillation application of NPs.

Room temperature photoluminescence (PL) spectra of ZnS with Ag, Cu and AgCu as impurities are shown in Fig. 6. The measurements were performed at an excitation wavelength of 325 nm. When ZnS was doped with Ag, Cu or AgCu the PL emission spectrum shows a peak at about 465 nm, 550 nm and 540 nm, respectively. The emission wavelengths are compatible with commercial Photomultiplier tubes (PMTs).

The XRD study confirms that the resultant particles are ZnS nanoparticles having cubic and hexagonal structure. EDX spectra confirmed the presence of Ag is incorporated at the ZnS sites and samples are free from other impurities. Indeed XRD, DLS and DLS are three different physical methods for measuring the size of nanparticles. Beside the difference between principle of these methods, we notice that the nanoparticle diameter obtained by XRD, DLS and XRD are consistent with each other.

To study the scintillation results of produced samples, they were mixed with methyl

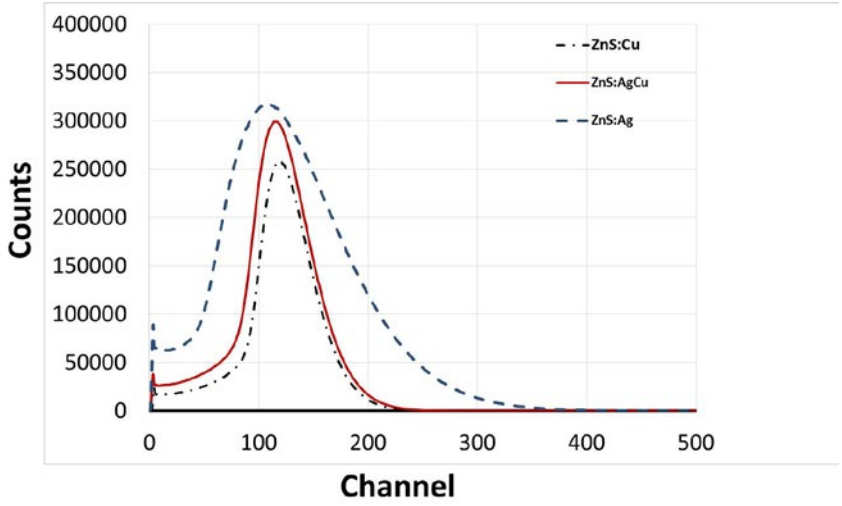

Fig. 7. The pulse height spectra of ZnS with Ag, Cu and AgCu impurities.

methacrylate and dimethylformamide to prepare a very thin layer of a nanocomposite that is uniformly coated on a substrate of Plexiglas. The thin layer of nanocomposite was coupled with a PMT and irradiated with alpha particles emitted from ^{241}Am source. The output signals of PMT were studied using a pre-amplifier, amplifier and finally a multichannel analyzer. We used Hamamatsu R6095 head on photomultiplier tube which has spectral sensitivity of 300-650 nm and wavelength of maximum sensitivity at 420 nm. Fig. 7 shows the pulse height spectrum of three produced nanocomposites. The optimum concentration of impurity of samples was 0.1 mol % that obtained by study of pulse height spectrum of samples as a function of concentration of impurity.

CONCLUSIONS

Synthesizing of Ag, Cu and AgCu-doped ZnS using hydrothermal in presence of ultrasonic wave method is reported in this work. The XRD, EDX, SEM and DLS analysis methods were used to determine the structure and morphology of produced NPs. The produced NPs have approximately hexagonal structure with average size around 10~20 nm and have a cubic zinc blended structure. The optical properties of these nanoparticles were investigated using PL spectra, which show that the samples exhibited reasonable optical properties with a maximum emission peak at wavelength of 465nm, 550nm and 540 nm for ZnS:Ag, ZnS:Cu and ZnS:AgCu NPs, respectively. The nanopowder phosphor were used to prepare a very thin layer uniformly coated with the nanophosphor. The response of the samples under alpha particles irradiation using a photomultiplier tube and a multichannel analyzer indicates that the doped ZnS NPs have reasonable scintillation response that capable them to be used in developing a low cost and possibility of embedding them in free-size structures detectors as well as further fundamental studies of nanoscale optical applications.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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