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Synthesis of Nanoparticle Zinc Sulphide (ZnS) as Luminescence Pigment

Saptaria Rosa Amalia[1, a)], Yani Puspitarini[1, b)], Widya Nurul Jannah[1], Annisa Lidia Wati1[1], Tito Prastyo Rahman[2], Budi Astuti[1], and Agus Yulianto[1]

[1]*Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Semarang, Semarang, Indonesia.*
[2]*Research and Development Division of Nano Center Indonesia, Serpong, Indonesia.*
Corresponding author: [a)]saptariarosa@yahoo.co.id [b)]yani.puspitarini@gmail.com

ABSTRACT

Synthesis of zinc sulfide as luminescence pigment was obtained by precipitation method from zinc oxide and natrium sulfide materials. Zinc chloride as precipitate solution was prepared from leaching product between zinc oxide and HCl. Furthermore, natrium sulfide was added to obtain ZnS with various mass of 10, 20, 30, and 40 g. The precipitation product was heated at temperature 200°C for 2 hours and then it was calcined by direct firing technique. Visual characterization under UV lamp has gained the highest intensity of luminescence at sampel with varying mass of 10 g natrium sulfide. X-Ray diffraction anlysis indicates the best peak of ZnS phase at sampel with varying mass of 30 g natrium sulfide at diffraction angle 28,5°. The diffraction intensity rapidly decreases with decreasing of natrium sulfide mass. Synthesis of nanoparticle ZnS using this method was effective to produce luminescence material. In fact that the luminescence pigment are import material, so that this result are the excellent candidate for the luminescence pigment application such as a document security, money security, etc.

Keywords: *Luminescence Pigment, Precipitation Method, Zinc Sulfide*

INTRODUCTION

Fluorescence application which is related to luminescence are interesting to be observed. Recently many research have been done to obtain an optimal material for optical application that can generate a pure and clear emission [1]. Studies about luminescence material explained that oxide material with wide band-gap indicates a high quantum efficiency by its luminescence [2]. Luminescence pigment was used in many optical materials such as money security pigment [3]. This is what is developing nowadays to obtain a low cost luminescence material without import from other country.

Commonly, a luminescence on material cause of electron excitation occuring inside the material. Electron excitation involves two different energy level of orbital, which is one is higher than the other. Moment when electron excitation occur, the electron moves from a deeper orbital energy level to higher energy level. Electron movement process occurs by non-spontaneous reaction (needed driving force to force an electron excited, such as heating, burning or sunlight exposure).

Many of luminescence material has been developed, such as Eu, Cd, Sr, Y_2O_3 however it has a high cost [4]. For advance country like Indonesia it is prefer to evolves and optimize luminescence material such as zinc sulphide (ZnS). ZnS is a semiconductor material class II-IV in periodic system of element. It has width of band-gap up to 3.68 eV [5]. Based on

METHODS

The material used in this experiment are ZnO powder and Na_2S sheet local products. The solution of HCl 6M was used on leaching process. The aim of this process is to dissolve ZnO powder. Furthermore needed distilled water for washing process to remove impurities.

Synthesis of ZnS material from ZnO powder and Na_2S sheet by using precipitation method. Leaching process was required for extracting a soluble material from a solid using a solvent. Leaching ZnO was resulted by dissolving 100 grams of ZnO powder into a solution of 6M HCl with ratio of 1:5 the hot plate magnetic stirrer at temperature of 100 °C for 1 hour. The reaction process as follows:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O_{(gas)}$$

At temperature of 100 °C H_2O will evaporate, so that obtained final reaction of leaching as a solution of zinc chloride ($ZnCl_2$) with clear colorless.

Precipitation method was done by mixing 50 mL of zinc chloride solution with Na_2S by varying the mass of Na_2S 10, 20, 30, and 40 grams. Mixed solution was heated at temperature of 60 °C and stirred continously for 90 minutes. The chemical processes as follows :

$$ZnCl_2 + Na_2S \rightarrow ZnS + 2\ NaCl$$

The results of the reactions was produced a white viscous solution that has residual product in form of NaCl. By washing process, NaCl then eliminated using distilled water for many times until salt-free, because basically NaCl is a form of salt that will dissolve in water. Final product of this reaction is a white precipitate which is then curing within furnace at temperature of 200 °C for 2 hours to evaporate the residues and obtained a pure and dry powder.

Calcination is the process of heating to produce a new compound consisting of more than one composition. Calcination carried out by direct combustion technique. Sample was placed in a crucible then it was directly heated with liquid gas. This direct heating technique helps the reaction of ZnS occur quickly to prevent the reacting of Zn with ion of oxygen (O) that consequently will forming ZnO because Zn^{2+} is very reacted to oxygen.

Analysis technique used in this experiment are UV lamp and X-Ray Diffraction (XRD). UV lamp exposure resulted the identification of visual luminescence of the ZnS samples. UV lamp which is used has specification of KOSS powerful UV light detector (15 W). The XRD characterization was used to identify crystal structure, FWHM value and crystallite size. Powder X-ray diffraction patterns were recorded on a Rigaku MiniFlex 600 Diffractometer using Cu-Kα radiation (1,541874 A°). Samples were step scanned from 10° to 80° 2θ, at 0.020 increments.

RESULT AND DISCUSSION

UV-Lamp Characterization

The aim of UV lamp characterization was to know the effect of UV exposure, either is it glow or not. This is a visual proof of a material called luminescence material. According to Nurwati (2014) the exposure of UV on ZnS material will generate a luminescence in colour of green

Figure 1. Comparation of ZnS samples luminescence with variation of Na_2S mass of 10, 20, 30 and g (left to right).

for UV wavelength of 365 nm. Figure 1. shows the comparation of color in luminescence of ZnS samples under UV exposure.

Physically, there is difference colour of luminescence above (Figure 1). Highest intensity was gained at sample with variation of 10 grams Na_2S, with the colour of luminescence is green. The similar result was reported by Sun (2010) and Nurwati (2014) that optical characterization using photoluminescence spectrum and UV lamp on ZnS material indicates a green color emission.

Band-gap has very important role in the luminescence activity. ZnS is a semiconductor material with a wide band gap of 3.6 eV and has a UV absorption with wavelength range of 200 to 400 nm [4]. The relationship between the intensity of the fluorescence and absorbance of a particle due to excitation of a light source expressed by Lambert Beer law. The process of absorption that leads to fluorescence typically include an electron transition. Radiation absorbed by the compound was $h\upsilon_{ex}$; in this process that lasts no longer than 10^{-15} seconds, an electron is raised from the ground state to an excited state [6]. Molecule will absorb photon energy only if it has the right energy equal to the energy difference between two energy levels (ΔE) that is in accordance with the equation $\Delta E = h\upsilon$. The energy of the emitted electrons does not depend on the intensity of incoming light, but only on the energy or the frequency of individual photons ($h\upsilon$) [7]. It is the interaction between photons and the outer electrons. According to Abdullah [8] the mechanism of luminescence occurs when ZnS nanoparticle gain energy that can be an ultraviolet or collision by electrons. Excitation causes the electrons jump from the top of the valence band to the conduction band, that created the pairs of free electron-hole. Pair of free electrons and holes are not stable, so instantaneously forming bounded electron-hole pairs. Most eksiton were annihilated in which electrons jump back to the valence band, accompanied by the emission of ultraviolet luminescence. Most of exciton are shattered where the electrons jump to deep level state, which are

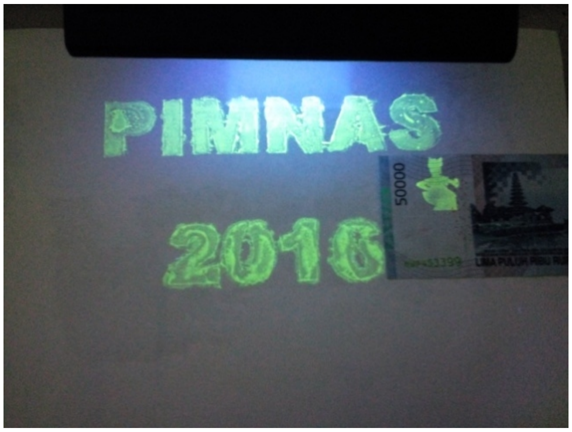

Figure 2. Comparation of applied ZnS sample of 10 g Na_2S mass variation with security pigment on money of IDR 50.000

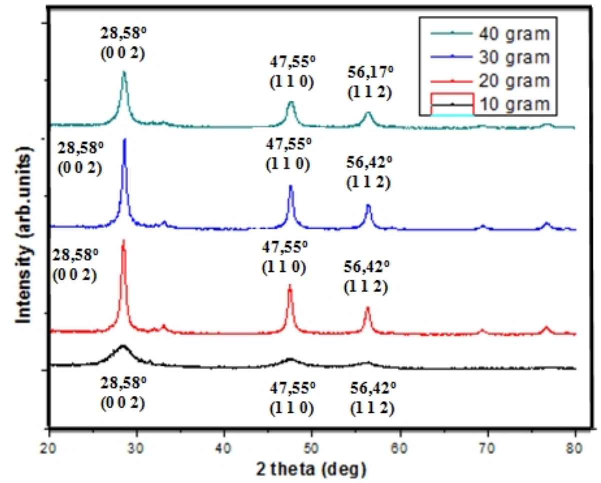

Figure 3. XRD pattern of zinc sulfide (ZnS) sample with Na2S mass variation.

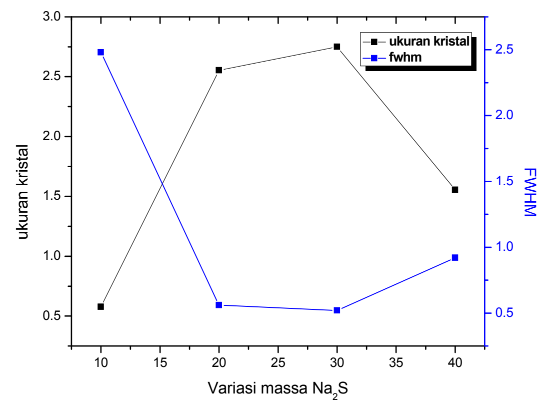

Figure 4. The effect of Na_2S mass addition towards crystal size and FWHM value.

located about 1 eV above the valence band and ended by the emission of visible luminescence.

The results of this experiment then applied and compared with industrially samples of luminescence material that can be found on a legal money of IDR 50.000 as a security pigment as shown in Figure 2. The result is both of the ZnS material sample with variation of Na2S mass of 10 g and the legal money of IDR 50.000 have the same colour of luminescence when exposure under UV lamp.

XRD Characterization

The structure of ZnS samples with variation of Na_2S 10, 20, 30, and 40 g have been characterized using XRD. The XRD pattern shown in Figure 3 revealed that ZnS sample has crystal form. Based on Figure 3, shows that all samples of ZnS has sharp peaks which is attributed to polycristalline structure.

The result of XRD characterization showed that all the samples has three peaks at $2\theta =$ 28,58; 47,55; and 56,42° which indicated to (002), (110), and (112) orientation of the ZnS crystal. Due to the orientation of the ZnS crystal, can be identified that all the ZnS samples has zinc blende crystal structure form with sphalerit phase structure (Aamodt 2011). Samples with the addition of Na_2S mass of 10 g appears that the diffraction peaks are less sharp than the sample for the addition of Na_2S masses of 20, 30 and 40 g. Based on characteristics of XRD indicated the sample with the addition of Na_2S mass 20 and 30 g has the highest intensity compared to the others. The high intensity is influenced by many areas of the reflector on the atomic arrangement of ZnS samples. More and more areas of the reflector, the interference of the diffracted waves will reinforce each other which causes increasing of the intensity [10].

Qualitatif analysis of crystal strustre not only specified by the intensity of the diffraction peak but also can be seen from the full width at half maximum (FWHM). The smaller FWHM value indicates the better quality of the crystals. The optimum crystal quality based on FWHM value was gained at ZnS sample with the addition of Na_2S mass of 30 g, it is $0{,}52^0$ for orientation (002). In addition, the other parameter to specified the quality of ZnS crystals from the XRD characterization are the diffraction angle, the distance between atoms, miller index (hkl), latice parameters, FWHM values and the crystallite size. ZnS crystal size can be calculated using Scherrer formula :

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Table 1. The calculation result of lattice parameter, FWHM, and crystal size

Na_2S mass (gram)	2θ (deg)	*hkl*	parameter kisi a (Å)	FWHM (deg)	*crystal size* (Å)
10	28,58^o	002	5,4093	2,48	0,5765
20	28,58^o	002	5,4093	0,56	2,5532
30	28,58^o	002	5,4093	0,52	2,7496
40	28,58^o	002	5,4093	0,92	1,5541

where D is the size of the crystals, λ is the wavelength sources used, β is the value of FWHM, and θ is the angle of diffraction. Based on the Equation 1 shows that the crystal size is inversely proportional to the value of FWHM. The relationship between the effect of Na_2S mass addition with the crystal size and FWHM values shown in Figure 4.

A good crystal is shown by the small FWHM value and big crystal size. This will cause the grain boundary of the formed ZnS crystal be smaller. Grain boundary is a surface or area which connected two grains of single crystal. The smaller the grain boundary, the denser the crystal arrangement. It causes the increasing of absorption power [11]. Furthermore due to the XRD data, lattice parameter also can be calculated. The value of the lattice parameter, FWHM and crytallite size were summarized on Table 1.

Based on Table 1, it shows that lattice parameter for all samples have the same value that indicates to all samples are have not occur a deformation form of crystal structures. Table 1 shows the smallest FWHM value belongs to ZnS sample with variation of Na_2S mass of 30 grams.

CONCLUSION

Synthesis of ZnS material based on ZnO powder and Na_2S has been done by precipitation method. UV lamp characterization resulted that ZnS sample with variation mass of Na_2S of 10 gram visually has similar color luminescence with security pigment on money of IDR 50.000 in green color. Furthermore, according XRD analysis confirmed that all samples are ZnS crystal with has zinc blende crystal structure form and sphalerit phase structure.

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