Opto-Structural (XRD) Characterization of Locally Synthesized Barium Sulfate ($BaSO_4$) Nanoparticles from an Aqueous Solution of Barium Chloride ($BaCl_2$) and Sulfuric Acid (H_2SO_4)

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***Abstract*—** The study investigated the optical and XRD structural properties of locally synthesized Barium sulphate $BaSO_2$ nanoparticles from an aqueous solution of barium chloride ($BaCl_2$) and sulfuric acid (H_2SO_4) at a constant PH value of 4.5. The Optical and structural properties of any nanoparticles play a crucial role in substantiating the suitability of such materials in device applications. Nano-crystalline materials with excellent optical quality can find applications in optoelectronics, and in other light dependent devices. In this study the synthetic barium sulphate ($BaSO_4$) was prepared by mixing a solution of 0.5 M $BaCl_2$ with diluted 30 ml of 0.5 M H_2SO_4 at a maintained PH value of 4.5. The optical and structural properties of the locally prepared $BaSO_4$ were characterized using UV-visible 1650 PC Shimadzu Ultraviolet spectrophotometer and GPC X-ray diffractometer respectively. The optical results reveal that the nanoparticle of $BaSO_4$ is an indirect wide band gap with a value of 4.0 eV. The nanoparticle showed a high transparency in the visible region, and a well-defined characteristic in the UV regions; this however, indicates that the material can find potential applications in UV detecting devices. The XRD results revealed that $BaSO_4$ nanoparticles are crystalline and exhibit the orthorhombic crystal structure. The details of the study are discussed.

***Keywords*—** $BaSO_4$, Band gap energy, Optical properties, XRD.

I. INTRODUCTION

Optical and structural properties of inorganic nano powders play a vital role in determining the suitability of such materials in various device applications. Well crystalline nano powders with excellent optical quality can find potential applications in optoelectronic devices like LED, solar cells and other light dependent devices[1]. Barite ($BaSO_4$) is one of the most important inorganic fillers used in the plastics, rubber and paint industries and also in pharmaceutical formulations. Barium sulphate is white or colourless, chemically inert and insoluble in water with high density; the insolubility of barite in water makes it a non-toxic compound [2]. Barite is desirable for several applications on the account of its high specific gravity, opaqueness to X-rays, inertness and whiteness. Barium sulphate has been estimated to significantly improve radio-opacity and mechanical strength of calcium phosphate cements for kryphoplasty applications [3]. Barium sulphate has been employed as a thermo-luminescent phosphor to enhance the performance of CTV screens, scintillaotrs, x-ray storage and screens intensifying phosphors and as laser material [4]. It is a potential material for many industrial applications like sugar refining, and a white pigment for textile, paper and paint [5]. However, about 80% of the world barite production is consumed in the oil and gas industry as a component of oil well drilling fluid, in such a way, it serves to increase the density of drilling muds which then allows rocks to move freely and thereby preventing boreholes from blocking [6]. Additionally, $BaSO_4$ nanoparticles have also been utilized in other areas such as in electronics, glass, car filters, and ceramics and in radio-imaging analysis [5]. Barite particles have been applied as a model system to test different theories of crystal growth. The production of nanoparticles based X-rays contrast agent has made significant contributions in the field of diagnostic and molecular imaging of which barite has become a promising candidate [3].

Currently, studies are intensely focused on the preparation of barium sulphate in a cost effective way. Many studies have reported various techniques of synthesizing barite nanoparticles; Barium sulphate particles have synthesized by monolayer and micro-emulsion [2], micro channel reactors [7]. It has also been found in oceanic water column in association with decaying organic matter and biogenic debris [8]. The accumulation rate of marine barite in oxic pelagic sediment has been used to reconstruct changes in ocean export production [9]. Barite nanoparticles have been synthesized from sea water [10]. In the sea water column, barite crystals are most abundant at depth of 500-1500 meters [11]. However, the occurrence of barite particles in under saturated water has been attributed to organisms [12]. Additionally, bacterially induced barite precipitation was reported extensively [13] while the terrestrial precipitation of barite nanoparticles was reported [14].

Barite nanoparticles have been prepared by the reversed micelles and micro-emulsion method [15]. The synthesis of barite has been reported through suitable organic templates [16]. Amongst all these preparation methods, direct precipitation technique is the most cherished due to its low cost, less instrumentations, and doping possibility [17]. For the control of the size and morphology of barium sulphate, amino-carboxylate additives, phosphonate/phosphate inhibitors [18], PMMA, double-hydrophilic block copolymers, and water-in-oilmicro-emulsion systems were employed.

Scientific information on the structure and optical properties especially the optical band gap energy of barium sulphate is useful in identifying areas of potential applications in device applications. However, this information on the optical band gap energy has been extensively documented which has invariably affected the possibility of integrating barium sulphate in recent technology.

To advance the suitability of barium sulpahte in today's technology, there is need to harvest the optical band gap energy and examine the structure barium sulpahate in its intrinsic form. In this study, we investigated the structure and optical band gap energy of locally synthesized Barium sulphate ($BaSO_4$) from an aqueous solution of barium chloride ($BaCl_2$) and sulphuric acid at a PH value of 4.5. To the best of our knowledge, the optical properties such as the band gap of $BaSO_4$ nano powders have not been extensively studied.

We have been able to demonstrate that Barium sulphate can be prepared locally with less sophistication of instrument. We have also shown from our optical results that $BaSO_4$ is an indirect wide band gap with a value of 4.0 eV. Our results have revealed that these $BaSO_4$ nanoparticles can find applications in radiation dosimetry as well as for detecting very small exposure of low energy UV rays.

II. EXPERIMENTAL PRECEDURE

A. Chemicals

The raw materials used in this study were Barium chloride and sulfuric acid. Deionized water served as solvent in the reaction. These chemicals were used as received without any further purification.

B. Preparation Steps

The Barium sulphate ($BaSO_4$) nano-powders were prepared from an aqueous solution containing 20 ml of 0.5 M $BaCl_2.2H_2O$ (85. 55% purity) and 10 ml of 0.5 H_2SO_4 (98.25% purity). The Barium Chloride solution was prepared separately first by thoroughly dissolving 20 ml of 0.5 M barium chloride salt in 20 ml of deionized water to obtain a homogenous solution of barium chloride. 10ml of 0.5 M H2SO4 was diluted in deionized water. 10 ml of 0.5 M H_2SO_4 diluted solution was added drop wise with equal amount of $BaCl_2$ solution; the mixture was stirred magnetically at room temperature for 20 min for homogeneity. The PH value of the mixture was maintained at 4.5 by adding more of the sulfuric acid. As the stirring continued, a white precipitate was formed; the mixture was centrifuged each time to form the precipitate in the glass beaker. The top liquid was incanted to quicken filtration; funnels and filter papers were used to separate the precipitate from the clear solution. The synthesized Barite precipitates were washed repeatedly in deionized water and allowed to dry in dust free environment at open air for 6 h. and kept for further processing. The experimental reaction is shown in equation 1.

$$BaCl_2\,(aq) + H_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2HCl\,(aq) \quad \ldots\ldots.1.0$$

C. Characterization

The prepared $BaSO_4$ nanoparticles were further characterized for structural and optical properties. The structural properties and average crystallite size of the synthesized Barium sulphate nanoparticles were studied at room temperature using GPC X-ray diffractometer, with a source of Cu Kα (λ = 1.5405 Å) at speed of 2.5º per min. The diffraction patterns were recorded over the 2-theta values in the region 5º – 70º. The average crystallite size was calculated using Debye Scherer formula as shown in equation (2.0)

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.0$$

Where λ is wavelength of X-ray radiation used, β is the Full width at half Maximum (FWHM), and 2θ is the highest diffraction angle. The optical measurements were analyzed by UV-vis 1650 PC Shimadzu ultraviolet spectrophotometer.

III. RESULTS AND DISCUSSION

The XRD patterns of the locally synthesized barium sulphate powders are shown in Fg.1. The samples exhibited the typical orthorhombic structure of $BaSO_4$.

The crystal peaks of the barium sulfate particles perfectly marked with those of the JCPDS (NO 72-1390) data of the crystalline barium sulfate nano powders. The XRD pattern was indexed with reference to the unit cell of the barite structure (a = 8.909 Å, b = 5.467 Å, c = 7.188 Å.); space group (Pnma). From the XRD patterns, the highest peaks are observed at 2θ 20.15°, 23.99°, 25.50°, 26°, 27.05°, 28.95°, 31.7°, 32.92°, and 42.75° corresponding to the following miler indices (011), (002), (101), (210), (102), (211), (301), (020) and (312) respectively. These results suitably alignes with the report [2] and [17,18]. Only $BaSO_4$ peaks were observed in the XRD spectra.

This indicated that the locally prepared barium sulphate had high purity and it is well crystalline. Fig. 2 shows the optical transmission spectrum of the locally prepared synthesized barium sulfate nanoparticles prepared in aqueous solution of barium chloride and sulfuric acid. The absorption and transmission spectra were recorded at the wavelength range (200-800) nm by using 1650 PC Shimadzu spectrophotometer. Optical transmittance increases with increase in wavelength and was approximately 85% at wavelength of 400 nm. This indicates that the material is transparent in the visible region and can find various applications in short wavelength optoelectronic devices such as light emitting diodes, and laser diodes. The barium sulfate nanoparticles also showed a strong characteristic in the ultraviolet region. This reveals that the $BaSO_4$ compounds can find suitable applications in radiation dosimetry as well as for detecting very small exposure of low energy x-rays [9]. The optical energy gap (Eg) of the $BaSO_4$ nanoparticles has been estimated from the absorption coefficient data as a function of photon energy. In accordance with the generally accepted indirect transition model for amorphous materials as proposed by Tauc.

$$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad ....3.0$$

Where A is a constant related to the properties of the valence and conduction bands, $h\upsilon$ is the photon energy, E_g is the optical band gap energy, r = 2 or 3 for indirect allowed and indirect forbidden transition, from the linear Tauc plots of $(\alpha h\upsilon)^{1/2}$ against $h\upsilon$ for the $BaSO_4$ nanoparticles as shown in Figure (3).

The optical energy gap has been estimated from the intercepts of extrapolation of zero with the photon energy axis where $(\alpha h\upsilon)^{1/2}$ tends to zero. From the results, the optical band gap energy is 4.0 eV. These results indicate that the $BaSO_4$ is a wide band gap material.

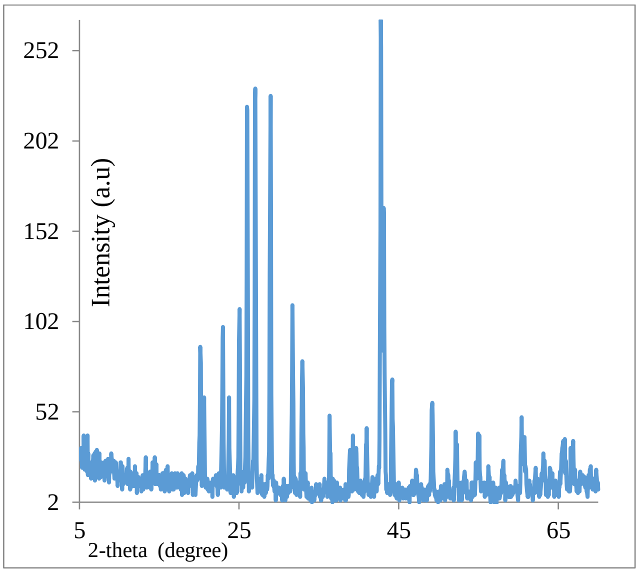

Fig.1: - X-ray patterns of $BaSO_4$ nanoparticles locally prepared from aqueous solution of $BaCl_2$ and H_2SO_4

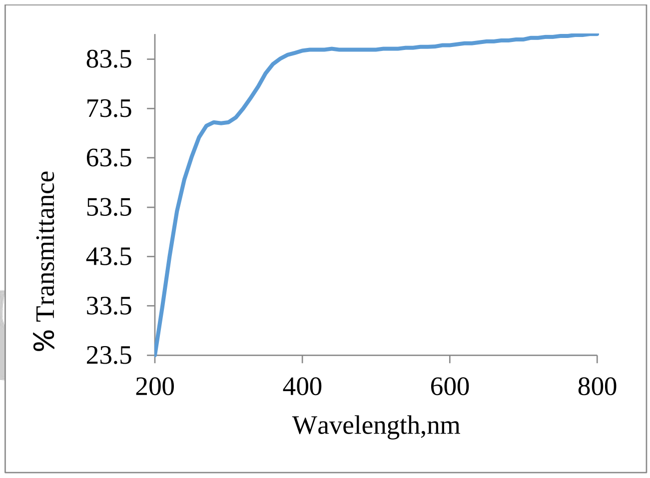

Fig.2: - %Transmittance versus Wavelength plot for the locally prepared $BaSO_4$

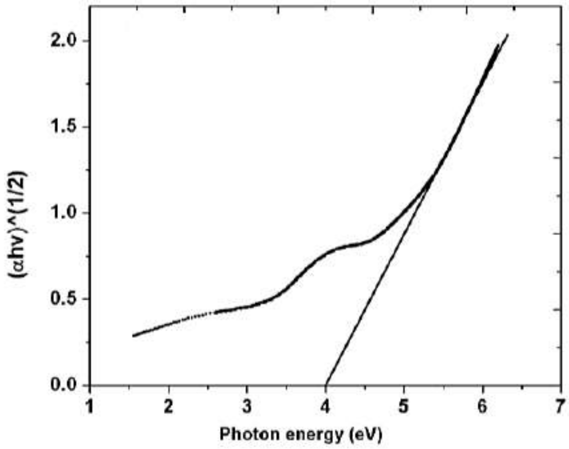

Fig.3: - A plot of $(\alpha h\upsilon)^{1/2}$ versus hv (Photon energy) representation to determine the band-gap energy of $BaSO_4$, assuming indirect optical transition

IV. CONCLUSION

We conclude that:

- The $BaSO_4$ nanoparticles revealed many crystal peaks that suitably matched with those of JCDS (No 72-1390) data, and exhibited the orthorhombic phase structure.
- The $BaSO_4$ nanoparticles are transparent in the visible region, and its transmittance increases with increasing wavelength. It transmittance reaches a maximum value of 85.4% at wavelength of 400 nm.
- The nanoparticles also showed a strong characteristic in the UV region indicating a potential application in UV photo-detection.
- The $BaSO_4$ nanoparticle exhibited an indirect transition with wide band gap value of 4.0 eV.

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