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Facile synthesis of lead iodide nanostructures by microwave irradiation technique and their structural, morphological, photoluminescence and dielectric studies

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ABSTRACT

Lead iodide (PbI_2) nanostructures have been synthesized by co-precipitation, hydrothermal and rapidly by microwave irradiation techniques. SEM analysis indicated the formation of well aligned nanocrystals and nanorods of average diameter between 100 nm and 400 nm. The powder X-ray diffraction and FT-Raman spectroscopic analysis confirms the formation of a 2H–PbI_2 polytypic predominantly. These studies also show that there is no extra phase due to impurity in the synthesized nanostructures. The optical energy band gap of nanostructures prepared by co-precipitation, hydrothermal and microwave irradiation techniques were found to be 2.283, 2.493, 2.542 eV and 2.331. 2.350, 2.375 eV calculated from UV–Vis absorption and diffuse reflectance data, respectively, which shows a clear blue shift in the wavelength due to confinement effect. Photoluminescence spectrum was recorded at different excitation wavelengths and shows clear blue shift in the emission peak which is due to the recombination of free excitons with band to band type transition and also may be due to confinement effect. Further the dielectric studies have been performed and a good enhancement in the dielectric constant has been observed due to small size of the fabricated nanostructures in comparison to bulk material.

1. Introduction

As per the current demands in modern world of advanced technologies, the materials with well-defined nanostructure morphology are one of the astonishing fields of scientific research and development owing to their broad applications in the field of fabrication of optoelectronic devices [1–7]. The materials with nanostructure have large surface to volume ratio which is remarkably soaring in link to bulk structure and provide exceptional quantum properties such as quantum confinement of materials in 0D (quantum dot), 1D (quantum wire) and 2D (quantum well) etc. The 1D nanostructured materials, such as nanocrystals, nanorods, nanotubes, nanowires, nanobelts, nanoribbons etc. have displayed the precise physical and co-precipitation properties due to nanometer size magnitude, which differs significantly from those of their bulk counterparts. The perfect choice for nanostructured materials is of wide band gap semiconductors [8–13]. As in optoelectronic applications, the only feasible choices for efficient green and blue light emitting diodes (LEDs) and lasers are wide-band gap materials. For traditional light emitting diodes (LED) which only offers yellow and red color and the missing color can be provides by green and blue LEDs. These LEDS offer gigantic prospects for energy-efficient solid-state lighting for future applications. For the next-generation of high-density DVD reader heads the blue laser diodes will be the toil stallion. The solid state light sources and detectors based on broad band gap semiconductor provides a large number of key applications like UV-light germicide sources for water sanitation applications and advanced solar-blind optical communication systems in the shorter wavelength regime. In recent time, the technologies developed with wide-band gap semiconductor have actively been sought as the next generation semiconductors owing to their inherent wide band gap, high electron saturation velocity, high thermal conductivity, and wide temperature operation range capabilities etc.

Lead iodide is a wide band gap semiconductor material hold

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layered structure with a hexagonal unit cell. It is a highly suitable in the development of active matrix flat panel imagers (AMFPIs) which can be used as detectors for X-ray digital radiography using direct conversion technique, mammography energy range detection [14–19] in which the X-ray photons are directly converting in to electronic charge. The other applications of titled material is in photoconductors, photo-detectors, photovoltaic, co-precipitation sensors, biological labeling and diagnostic, LEDs including photo electro co-precipitation solar cells, etc. applications [20]. There are several reports available in the literature on the synthesis and fabrication of nanostructures and thin films of PbI_2using different techniques and study their structural, vibrational, optical, dielectric and electrical properties and shows a great change in the properties [18,21–29]. Therefore in the current work the authors aim is to fabricate the nanostructures of PbI_2 with well-defined morphology using different techniques such as co-precipitation at room temperature, hydrothermal and microwave irradiation at low temperature (i.e. 140 °C). It is well know that the microwave technique delivers homogenous internal and volumetric heating at rapid rates [30,31] and found to be better than conventional heating. The fabricated nanostructures have been studied for different properties such as structural, vibrational, optical and dielectric properties and compared the obtained results with the existing literature. As a result we found that microwave irradiation technique is a better choice other techniques to fabricate the nanorods of the titled material.

2. Experimental

2.1. Synthesis of PbI_2 nanostructure

For the synthesis of PbI_2 nanostructures we have used all the reagents of analytical grade of high purity purchased from Alfa Aesar in the experiment. For the synthesis of PbI_2 we have taken 1 M lead acetate (39.987 g) and 50 ml of double distilled water, 50 ml CTAB and 50 ml of PVA in one beaker step by step and 2 M Sodium Iodide (37.795 g) was dissolved in 50 ml double distilled water in another beaker and both the solutions were homogeneously dissolved at room temperature using highly stable magnetic stirrer fixed at 500 rpm. After getting the transparent solution we have mixed them very slowly in one beaker and stirred continuously and clear yellow solution was obtained which is recognized as lead iodide (PbI2). Further the finally prepared solution was divided in three parts one as received and other two for hydrothermal and microwave irradiation process respectively. One portion of the resultant product was subsequently transformed in to a Teflon lined autoclave with a stainless steel shell for hydrothermal process and in Teflon vessel for microwave process. The temperature of the autoclave was maintained at 145 °C for 24 h and then cooled to room temperature naturally. ANTON PARR Microwave was used to irradiate the samples under fixed power at 800 W, the temperature of the microwave was programmed as rise in 15 min up to 145 °C and keep constant at the same temperature for 15 min then cooled in 30 min. The clear yellow products was obtained by all three techniques which were washed many times with double distilled water and filtered and dried in vacuum at 75 °C for5 h.The reaction mechanism involved in this experiment is described in Figure 1S (see supplementary data).

It is well known in the literature that the reaction media play a key role in the synthesis of nanostructure materials under hydrothermal conditions as well as in microwave process. We have used CTAB and PVA both as reaction media/surfactants in order to control the morphology of nanostructures and found that a compact and perfect structure of PbI_2 has been obtained in every process.

2.2. Characterization techniques

To perform the structural analysis of the synthesized nanostructures of PbI_2 we have recorded the powder X-ray diffraction (PXRD) patterns using a Shimadzu X-600 Japan powder X-ray diffractometer (PXRD) having CuK_α radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm) at the scan rate of 0.02°/m over the angular range of $5° \geq 2\theta \geq 90°$ at room temperature. Surface topography of the all the synthesized nanostructures were examined using scanning electron microscope (JSM 6360 LA, Japan) equipped with energy dispersive analytical X-ray unit (EDXS). Before subjecting to SEM analysis, the samples were sputter coated with 10 nm of platinum to eliminate charge build up. FT-Raman spectroscopic measurements were carried out to study the vibrational modes/functional groups of PbI_2 nanostructures. In this measurement the laser beam was made to incident normally on the surfaces of the specimens to record the spectrum and scattered intensity was collected at room temperature using THERMO SCIENTIFIC, DXR FT-RAMAN coupled with microscope using full range grating (3500–100 cm^{-1}). The used laser power was 0.2 mW (532 nm laser), at estimated resolution 5.1–8.3 cm^{-1} and the size of the aperture pinhole was kept 50 μm. The UV–Vis spectroscopic measurement was done at room temperature of all synthesized nanostructures of PbI_2 in methanol media on a JASCO V-570 UV–Vis–NIR spectrophotometer. Using the recorded data the various optical parameters were calculated. Using a Shimadzu UV–Vis.-NIR spectrophotometer (model UV-3600),the diffuse reflectance (DR) was recorded in the wide wavelength range by using an integrating sphere attachment. The photoluminescence (PL) spectra were recorded for all the prepared PbI_2 nanostructured samples at room temperature under the same conditions using a Lumina fluorescence spectrometer (Thermo Fisher Scientific) in the wavelength range of 280–480 nm. The spectral bandwidth is variable as 0.5, 1.0, 2.5, 5.0, 10, 20 nm for both excitation and emission monochromators and in the current work it was chosen 1 nm for emission monochromator. The dielectric measurements were carried out for all the prepared nanostructures of PbI_2 by making the pallets of similar thickness. The prepared samples were coated with 10 nm of platinum on both the sides using a sputter system before subjecting to measurement. The dielectric constant, loss and ac conductivity were studied in higher frequency range of 1 kHz–10 MHz at room temperature using a KEITHLEY 4200-SCS system.

3. Results and discussion

3.1. Structural analysis

The recorded powder X-ray diffraction (PXRD) patterns of the synthesized nanostructures of $PbI_2$are shown in Fig. 1. It is clear from the sharpness of the patterns that the synthesized nanostructures are highly crystalline in nature. The recorded PXRD data was used as input in POWDERX software and cell parameters were calculated and the single phase was confirmed. The refined cell values (Table 1) were found to be of Hexagonal phase of PbI_2 prepared by all methods which are in good agreement with the earlier reported value JCPDS-07-0235.The indexed XRD pattern shows that it is of a 2H-polytype of PbI_2 and also very minute deviation is observed from that. As clear from Fig. 1 that the presence of 111, 113 and 203 very low intensity reflections indicates a minute amount of 4H-polytype presence as well. No peak due to impurity such as PbOHI and $Pb(OH)_2$was observed which reveals the high purity of the synthesized nanostructures of the product.

The crystallite size of the fabricated PbI_2 nanorods was evaluated by using Scherer's formula; $D = \frac{0.9\lambda}{\beta \cos\theta}$ where, the average crystallite size, X-ray wavelength (1.54056 Å) and full width at half