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Facile one pot synthesis of novel Hg^{2+} doped PbI_2 nanostructures for optoelectronic and radiation shielding applications

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ABSTRACT

Facile one pot synthesis of pure and Hg^{2+} (= 0.101 nm) doped PbI_2 (Pb^{2+} = 0.133 nm) single crystalline nanoplates (NPs), nanosheets (NSs) and nanorods (NRs) were achieved through chemical route at room temperature. The single phase and high quality of the synthesized NPs, NSs and NRs was proved by X-ray diffraction and FT-Raman spectroscopic analyses. The lattice constants, crystallite size, lattice strain, dislocation density were calculated. The crystallite size was calculated to be in the range of 16–22 nm. The Hg doping in PbI_2 was approved by energy dispersive X-ray spectroscopy (EDXS) and its homogeneous distribution was confirmed by scanning electron microscopy (SEM) mapping. The morphology of pure and doped synthesized nanostructures was observed to be single crystalline NPs, NSs and NRs of nanoscale thicknesses. The optical band gap was calculated from Tauc's plot and found to be in the range of 3.27–3.20 eV. The value of dielectric constant was improved from 20 to 25 and also ac electrical conductivity due to Hg^{2+} doping. The radiation parameters such as linear absorption coefficient, half value layer, tenth value layer and mean free path were calculated and a remarkable enhancement was observed due to Hg^{2+} doping. These parameters confirm that the nanostructures are highly sensitive to ^{214}Am 59.5KeV γ-ray. The facilely synthesized nanostructures of PbI_2 with enhanced properties due to Hg^{2+} doping makes them more suitable for nanoelectronics and room temperature radiation detector applications.

1. Introduction

Nanostructured materials like: nanocrystals, nanorods, nanoribbons, nanoplates, single crystal nanosheets, nanotubes, nanowires, are the back bone of the current modern technology and have wide-range of applications in fabricating nanoscale devices with advanced optical, electrical, magnetic and radiation properties [1–14]. The nanostructured materials can also be embedded in polymer matrix to make user friendly devices [15,16]. Lead iodide (PbI_2) also known as plumbous iodide is one of the most important key p-type semiconductor and highly applied as a precursor material for the fabrication of highly efficient solar cells, detection of high-energy photon for γ and X-rays at room temperature, owing to its wide band gap value (i.e. 2.27 eV) in bulk crystal [17], which ensures of low noise operation [6,17–22]. It is well known the band gap of PbI_2 (in pure as well as with suitable dopant) at nanoscale is considerably increased which makes it more appropriate for radiation detection applications [6,23,24]. Recently few reports on synthesis of pure and Zn, Gd, Cs, Nd doped PbI_2 nanostructure using different methods with unique applied properties are available [5,11,13,25–33].

To date, there is no/least report on the synthesis of mercury (Hg)-doped PbI_2 nanostructures and it is known that by selective element doping in semiconducting materials, they offers a very effective approach to fine-tune the structural, optical, dielectric, electrical, magnetic, radiation etc. properties, which are vital for real use [13,34,35]. The covalence radius of Hg (0.149 nm) is similar to that of Pb (0.147 nm), and the ionic radii for Hg^{2+} and Pb^{2+} are 1.01 and 1.33 Å, respectively, hence it is expected that Hg can be easily incorporate in PbI_2 matrix either at substitutional or interstitial position and so the Hg doped PbI_2 can be achieved easily. Therefore, here we are motivated to synthesize the pure and Hg doped PbI_2 nanostructures using a cost effective chemical route at room temperature. The synthesized nanostructures were subjected to scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction, FT-Raman, UV–Vis–NIR, Impedance spectroscopy and radiation measurements to study the morphological, elemental mapping, structural, vibrational, optical, dielectric, electrical and radiation activity properties and discussed in this work.

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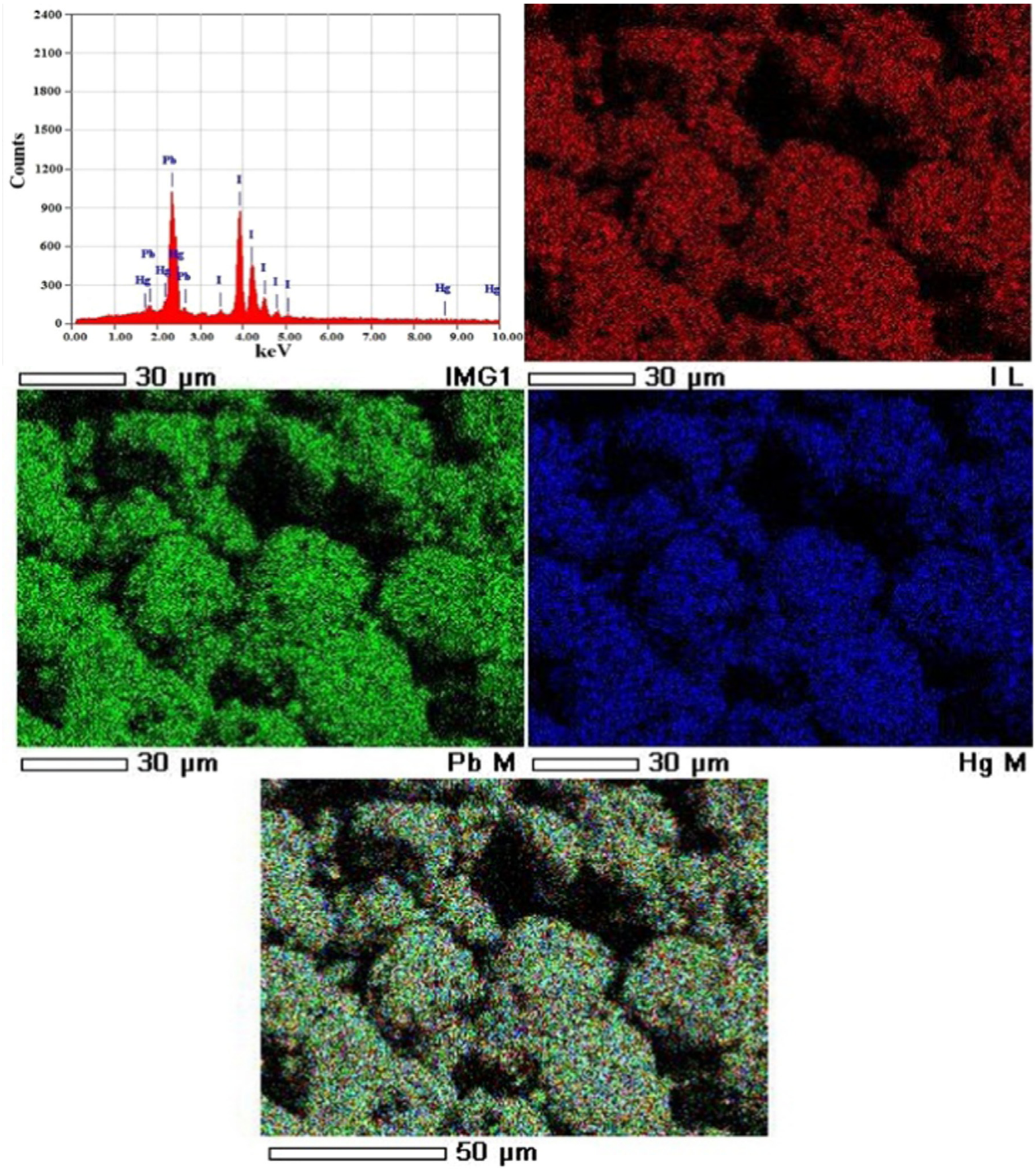

Fig. 1. EDX and SEM mapping images of 2.5% Hg doped PbI_2 nanostructures.

2. Experimental details

2.1. Synthesis

For the synthesis of pure and different concentration of Hg (i.e. 0.5, 1 and 5 wt%) doped PbI_2 a simple chemical route has been used at room temperature. The whole process is as follows: Lead acetate (Pb $(C_2H_3O_2)_2$), CTAB, acetic acid (CH_3COOH), sodium iodide (NaI) and Mercury chloride [$HgCl_2$] for Hg^{2+} doping were obtained from Alfa Aesar and Sigma Aldrich.

To achieve the one pot synthesis of aimed product a cost effective and facile chemical route has been applied at room temperature by taking 0.5 M lead acetate (18.967 g) in one 500 ml volume cylinder and dissolved in 50 ml diionized water by stirring at the rate of 700 rpm and a clear solution was achieved within 10 min of stirring and then 50 ml CTAB (10 g/1000 ml) solution was added to it which acts as surfactant [36–40] and continuous stirring was maintained. Within few minutes the solution becomes slightly milky, then 30 ml of acetic acid was added to have again a clear solution. Similar process was done to prepare the other three solutions. In the later 3 cylinders three different concentrations i.e. 0.5 wt%, 1.0 wt%, 5.0 wt% of $HgCl_2$ [M.W. 271.52 g/mol] were added for Hg doping in titled product. At the end, the prepared 0.5 M Sodium Iodide (14.988 g) solutions in 50 ml deionized water were dropwise added in all four cylinders and continuous stirring was maintained. Within few second the solutions becomes dark yellow which confirms the synthesis of PbI_2. Finally, we have washed the synthesized products using deionized water many times and dried at 80 °C inside an oven.