

Effect of Reaction Parameters on Structural and Photoluminescence properties of Cerium doped PbWO₄ Nano Phosphor

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Abstract

In the present work, we synthesized undoped as well as Cerium doped PbWO₄ nanophosphor using a facile Low Temperature Hydrothermal method. PbCl₂ was used as a Lead source, Na₂WO₄ as a metallic cation and distilled water as solvent to synthesized PbWO₄. PbWO₄ was prepared at different reaction temperature and pH of reaction solution. Effect of different reaction conditions on structural and optical properties were studies by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Photoluminescence (PL). With increase in pH, size of PbWO₄ nanoparticles and length of the PbWO₄ increases and morphology changes from HNTs to nanorods. Among all the samples prepared at different temperatures, sample prepared at 200°C is single phase and highest crystalline in nature. Different pH promotes the formation of crystalline PbWO₄ powders at low synthesis temperature and optimum range is 3-11 pH

Keywords: Hydrothermal method, Lead Tungstate, Transmission Electron Microscopy, Photoluminescence

1. INTRODUCTION

Lead Tungstate PbWO4 (PWO) occurs in the nature as tetragonal stolzite with scheelite type structure (space group $I4_{1/a}$) and monoclinic raspite with wolframite type structure (space group $P2_{1/a}$). Raspite phase transforms irreversibly to the stolzite one at about 400°C [1]. The first information on the emission properties of PWO is dated as early as the late 1940s [2]. Compared to other well-known scintillators such as BaF₂, CeF₃ and CsI, PbWO₄ phosphor is most attractive for its high-energy physics application because of its high density (8.3 g cm-3), short decay time (less than 10 ns for a large light output), high irradiation damage resistance (107 rad for undoped and 10⁸ rad for La doped PbWO₄), small moliere radius, fast decay time, nonhygroscopicity and low production cost [3-5]. PbWO₄ shows interesting excitonic luminescence, Thermoluminesce and stimulated Raman Scattering behavior [6, 7]. Lead tungstate crystals are fast and dense scintillators found an application for high energy electromagnetic calorimeter of Compact Muon Solenoid (CMS)

detector at Large Hedron Collider (LHC) at Center of Europe for Research Nuclear (CERN).

2. EXPERIMENTAL

PbCl₂, Na₂WO₄·2H₂O and CeO₂ purchased from Alfa Aesar were all are A.R.(analytical reagent) grade purity and used without further purification. Distilled water was used to prepare all required solutions. Initially 30 ml solution of 0.01 M concentration of PbCl₂ was prepared by continuous stirring and 30 ml solution of 0.01 M concentration of Na₂WO₄ was added in it. 0.001 concentration Μ concentration of CeO₂ was added to prepare PbWO4:Ce. These three solutions were transferred to Teflon lined stainless steel autoclave of 90 ml capacity filled 80% with reaction media (i.e. distilled water) one by one in three separate experiments. HCl and NaOH was used to prepared solution with different pH. The autoclave was maintained at different temperature and then air cooled to room temperature. Obtained precipitates were washed several times with distilled water and lastly with absolute ethanol. Finally white powder was obtained after

drying in vacuum at 80°C for 2h.

3. CHARACTERIZATION

Powder X-ray diffraction (XRD) patterns were recorded with a Japan Rigaku D/max-RB diffractometer at a scanning rate of 3°/min using

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Cu K α radiation (λ = 0.15406 nm). Morphology of as-prepared samples were studied with JEOL JSM-6380LV scanning electron microscopy (FESEM). The microstructure and surface morphology of the microcrystalline powders were observed by transmission electron microscopy (TEM, Tecnai 20 G2 FEI made). The photoluminescence (PL) of these samples were investigated on a Shimadzu spectrofluorophotometer at room temperature with Xenon lamp as excitation source.

4. RESULTS AND DISCUSSIONS 4.1 X-ray diffraction (XRD)

To study the effect of reaction temperature on crystal structure and phase formation of PbWO₄, samples were synthesized at different temperatures: Room Temperature (RT), 100°C, 125°C, 150°C and 200°C. The XRD reflection spectra of undoped and PbWO4:Ce doped samples synthesized at different temperatures are shown in Figure 1 and Figure 2 respectively. All XRD reflection peaks are indexed to a tetragonal scheelite (stolzite) phase with space group $I4_{1/a}$ and monoclinic raspite phase with space group $P2_{1/a}[8]$. The identification of raspite phase peaks for all samples are marked with symbol (*). The formation of Tungstic acid H₂WO₄.nH₂O, other tungsten oxide hydrates WO3.nH2O and unwanted impurity of Na₂WO₄, Ce₂(WO₄)₃, PbO, and Pb(OH)₂ were not observed. XRD spectra of sample prepared at R.T.,100°C, 125°C and 150°C indicates the presence of secondary raspite phase while sample prepared at 200°C is free of secondary phase and contains pure stolzite phase.



Fig.1: XRD of PbWO₄ prepared at different Temperature

On doping with Cerium in PbWO₄, intensity of peaks representing raspite phase decreases, which means that doping of cerium also decrease the amount of raspite phase with increase in temperature.

XRD spectra of PbWO₄:Ce crystals prepared at 200°C temperature shows raspite free pure stolzite

phase. Among all the samples prepared at different temperatures, sample prepared at 200°C is highest crystalline in nature.

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*01	220 21	R.T.	220	-E	33
25	30 ;	35 40	45	50	55

Fig.2: XRD of PbWO₄:Ce prepared at different Temperature

In order to study the effects of pH of solvent on structural properties of PbWO4 was prepared with 3pH, 7pH and 11pH. During preparation of sample 7, pH of distilled water was set to 3 by adding Acetic acid (Glacial) (CH₃COOH) drop wise while pH of distilled water was increased up to 11 by adding Sodium Hydroxide (NaOH) for sample 9. In all this experiments temperature was kept at 125° C and synthesis time was kept for 10 h. Figure 3 shows the XRD pattern of PbWO₄ powders synthesized at 3, 7 and 11 pH. It can be seen that PbWO₄ synthesized at different pH of reaction solution is a single phase. All the reflection peaks can be completely indexed to a pure tetragonal stolzite phase of PbWO4 with space group I41/a. Highest crystallization observed for PbWO₄ prepared at 7pH and lowest crystallization observed for PbWO₄ prepared at 3pH. Samples prepared at 7pH and 11pH show better crystallization than the one made at 3pH.



Fig. 3: XRD of PbWO₄ prepared at different pH



4.2 Transmission Electron Microscopy (TEM)

Fig.4 TEM photogrphs of PbWO₄ prepared at (a) 100°C , (b)125°C with 7 pH, (e) 125°C with 11 pH and PbWO₄:Ce prepared at (a) 100°C , (b)200°C.

According to TEM, PbWO₄ obtained at 100 °C are mixture of microparticles (100nm) with stolzite phase and micro plates (few μ m) with raspite inclusions. Spherical nanoparticles (20-40 nm) and Hollow Nano Tubes (80-170 nm) of PbWO₄ having pure stolzite phase are obtained at 125 °C at 7pH.Upon rising pH to 11, nano particles were disappeared and bigger particles of irregular shape are formed as shown in Figure 4 (e). PbWO₄ nanorods are also produced at 11pH but their length increases from 80-170 nm to 2 μ m with 40 nm outer diameter. PbWO₄ nanorods produced at 11pH are not hollow like those formed at 7pH.

4.3 Photoluminescence

Figure 5.1-5.3 show Room temperature photoluminescence spectra of PbWO₄ phosphor prepared at different temperatures and pH excited with 254 nm wavelength. As expected both samples show broad blue-green emission in visible region. The PL spectra has "*spread-eagle-shape*" with a central peak surrounded by two broad shoulder peaks.

Emission spectrum reveals that it is composed of several sub-bands which are almost distributed throughout entire 350-550 nm region. As we can see from the PL spectra (Figure 5.1), PL intensity is least for the sample prepared at 100 °C which increases for the sample prepared at 125 °C. PL intensity is again decrease for the sample prepared at 200°C. It is well known that PL intensity has direct relation with crystallinity. The better crystallinity, the higher PL emission peak is. Morphologies and sizes also influence the luminescence properties of inorganic materials. Hence among all three samples (HNTs) of PbWO₄ prepared at 125 °C shows strong green luminescence due to its highest crystallinity while (microparticle + microplates) of PbWO₄ prepared at 100 °C shows weak luminescence due to poor crystallanity.



Fig.5.1: PL spectra of PbWO₄ prepared at different temperatures excited with 254nm.



Fig. 5.2: PL spectra of PbWO₄:Ce prepared at different temperatures excited with 254nm.



Fig. 5.3: PL emission of PbWO₄ synthesized at different pH excited with 254 nm.

PbWO₄ (Nanoparticles and HNTs) obtained at 7pH, display a strong emission peak cantered at about 485 nm at room temperature. However, the absolute luminescence intensity increased with increasing pH, over the range of 3-7 pH, implying that the Nanoparticles and HNTs had much improved luminescence intensity. Very weak PL intensity of the sample obtained for pH 3 due to poor crystallinity.

5. CONCLUSIONS

PbWO₄ and PbWO₄:Ce phosphor prepared with various morphologies using facile Low Temperature Hydrothermal method with self-designed Teflon Lined Stainless Steel Autoclave. Among all the samples prepared at different temperatures, sample prepared at 200°C is single phase and highest crystalline in nature. Different pH promotes the formation of crystalline PbWO₄ powders at low synthesis temperature and optimum range is 3-11 pH. With increase in pH, size of $PbWO_4$ nanoparticles and length of the $PbWO_4$ increases and morphology changes from HNTs to nanorods.

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