ABSTRACT

The controlled synthesis of inorganic nano- and microcrystals with specific size, shape and structure is of fundamental significance in modern material science and engineering because it could determine not only the relevant optical, electronic and magnetic properties of the material but also the performances of those material-based devices for applications. Recently, many efforts have been made to synthesize tungstate crystals with controlled morphologies because of their excellent luminescent properties and promising applications. Out of all tungastate, $PbWO_4$ is the most attractive for high-energy physics applications because of its high density (8.3 g/cm^3), short decay time (less than 10 ns for the most part of light output), high-irradiation damage resistance (10^7 rad for undoped and 10^8 rad for La-doped $PbWO_4$), small moliere radius, fast decay time, non-hygroscopicity. $PbWO_4$ become a subject of renewed interest about 15 years ago when its favourable characteristics as scintillation detector was reported. Though $PbWO_4$ has low light yield (100 time smaller than $CaWO_4$), it has very short decay time (ns) makes it strongest candidate for scintillation detector.

In the present work, we have reported a facile, an economical and green chemical route to synthesis $PbWO_4$. We have prepared undoped as well as Cerium doped $PbWO_4$ phosphor with various morphologies using Low Temperature Hydrothermal method. We have divided our experiment in to two parts. In the first part of our experiment undoped as well as Cerium doped $PbWO_4$ crystals were synthesized with different Lead sources (Lead Acetate, Lead Nitrate and Lead Chloride), Na_2WO_4 as a metallic cation and distilled water as solvent. In the second part of our experiment $PbCl_2$ was kept constant as a Lead source and undoped as well

as Cerium doped $PbWO_4$ crystals were produced by varying reaction temperatures and pH of solution.

We have designed a Teflon lined stainless steel autoclave having 90ml capacity used to synthesize all $PbWO_4$ samples. Powder X-ray diffraction (XRD) was performed to identified crystal structure and phase produced. Calculation of lattice parameters, unit cell volume and average crystallite size were performed for all $PbWO_4$ samples using PowderX program. Structural studies of $PbWO_4$ and $PbWO_4$: Ce sample reveals that all prepared samples are polycrystalline in nature and contains two phases of $PbWO_4$: stolzite and raspite. All X-ray diffraction peaks were indexed to a tetragonal stolzite phase with space group $I4_1/a$ and monoclinic raspite phase with space group $P2_1/a$. At low temperature raspite phase is produced predominantly and with increase in temperature it transforms irreversibly into stolzite phase.

Cerium doping at different temperatures does not change the crystal structure of $PbWO_4$ or induce a new phase. Cerium also acts as catalyst and helps raspite phase to convert into stolzite phase when Lead Chloride was used as Lead source. Cerium doping reduce the crystallite size in the case of $Pb(CH_3COO)_2$ or $Pb(NO_3)_2$ while it is increased in the case of $PbCl_2$ as a Lead source. Cerium increases the average crystallite size for more than 50% at all the temperatures. Lead Chloride proved to be better Lead source to produce high crystalline $PbWO_4$ crystals over Lead Nitrate and Lead Acetate.

In order to study morphology, samples were characterized with Field Effect Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). SEM and TEM images reveal that prepared samples have micrometer to nanometer in size and with different morphology such as single or multi branched dendrite (1-2 μm), bypiramidal octahedral microcrystals (1.5μm), one dimensional

nanobelts 5μm x1μm, nanoplates few μm, Spherical Hollow Nanoparticles (HNPs) (20-40 nm), Hollow Nano Tubes (HNTs) (12.37 nm x 80-170 nm) and nanorods (40nm x 2μm).

The photoluminescence (PL) of the samples was investigated using Spectrofluorophotometer at room temperature with 254 nm, 300 nm and 625 nm excitation wavelengths. Effect of different reaction parameters on PL emission was investigated. The shape of PL spectra of $PbWO_4$ synthesised using $PbCl_2$ 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. PL emission spectra of $PbWO_4$ consists two components, a fast blue component around 450 nm which is an intrinsic feature of scheelite phase and a slow green one around 480– 520 nm which is an intrinsic feature of raspite phase. The emission spectra in blue range are occurring due to radiative transition of $[WO_4^{2-}]$ complex. The cerium-doped samples show weaker luminescence intensity than that of undoped samples. The reduction in PL intensity is due to the nonradiative *5d–4f* transition of the excited Ce^{3+}. The green emission of undoped crystals was ascribed to the WO_3 oxygen-deficient complex anion in scheelite phase. The decomposition of PL spectra into individual Gaussian components results four Gaussians to achieve a good agreement with the experimental data. The presence of four Gaussian components indicates the excited states of emission center are relaxed and degenerated under the influence by some type of perturbation. We proposed that the Gaussian peak I (367 nm), the Gaussian peak II (392 nm) and the Gaussian peak III (452 nm) may correspond to the radiative transitions from $^3A_1 \rightarrow {}^1A_1$, $^3A_2 \cong {}^3E \rightarrow {}^1A_1$ and $^3A_2 \rightarrow {}^1A_1$, respectively. Hence blue emission occurs from the lower lying triplet state split by Jahn-Teller interaction.

Cerium doped $PbWO_4$ prepared at 200°C is enhance the green luminescence and give some contributions to the "slow" decay components which may be negative to the scintillating properties not preferable to use for scintillation detector purpose. PL intensity has direct relation with crystallinity. The better crystallinity, the higher PL emission peak is. PL spectra of nano-sized $PbWO_4$ crystallites are strongly relied on their particle size and crystallinity. The PL intensity of blue emission peak is highest for sample prepared at 7pH (HNTs), it is intermediate for sample prepared at 11pH (Nanorods) and lowest for sample prepared at 3pH which indicates that $PbWO_4$ HNTs have more regular lattice structure and uniform morphology compared to Nanorods. Sample prepared at 3pH has lowest regular lattice structure. We have proposed possible applications of $PbWO_4$ nano phosphor as Green Emitting Lamp Phosphor, HNTs as Nano Fluidic devices in medical diaganosis.