Study on the optical band gap and photoluminescence of PbMoO₄ nano powder synthesized by an auto igniting combustion technique.

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Abstract. Nano crystalline PbMoO₄ was synthesized through an auto-ignited combustion technique. The X-ray diffraction studies of PbMoO₄ nanoparticles reveals that the as-prepared powder itself is single phase and possess tetragonal structure. The average particle size of the as-prepared powder calculated using scherrer formula is 28nm. Fourier transform Infrared spectrum shows that the as prepared powder itself is phase pure with no formation of secondary phase. The optical band gap determined from UV-Visible absorption spectra is 3.20eV. Photoluminescence spectra of the samples shows blue emission.

1. Introduction
Synthesis of advanced ceramics materials as nanocrystals is one of the major fields in materials processing technology. The importance of nanomaterials is that its properties can be tuned by controlling the particle size. Molybdates with scheelite structure have received much attention owing to their remarkable characteristic properties in the field of optical devices. In the scheelite structure \([\text{MoO}_4]^{2-}\) group adopts a tetrahedral co-ordination in space group \(I\bar{4}1/a\) and the cation is bonded to eight oxygen atoms forming an octahedron. Lead molybdate (PbMoO₄) is a well-known scheelite class of compound with various applications in numerous fields [1,2].

In this paper we report the synthesis of nanocrystalline phase pure PbMoO₄ through an auto ignited combustion technique for the first time. The structural characterization, optical band gap study and photo luminescent emission behavior are also presented.

2. Experimental
Nano crystalline PbMoO₄ was synthesized through a modified combustion technique using MoO₃ and Pb(NO₃)₂ as starting material. The precursor solution was prepared by dissolving stoichiometric amount of Pb(NO₃)₂ in double distilled water and MoO₃ in ammonia solution. Citric acid was added to the solution as complexing agent. Oxidant to fuel ratio of the system was adjusted by adding ConHNO₃ and ammonium hydroxide. The precursor solution of pH ~7.0 was heated on a hot plate in a ventilated fume hood. The solution boils and dehydrates accompanied by foam. On persistent heating the foam ignites by itself giving nano powders of PbMoO₄.

Structure of the as-prepared powder was examined by powder X-ray diffraction (XRD) technique using a Bruker D-8 X-ray Diffractometer with Nickel filtered Cu Kα radiation. The infrared (IR) spectra of the samples were recorded in the range 400–4000 cm⁻¹ on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FTIR) Spectrometer using the KBr pellet method. The absorption spectra of the powder were measured using a Jasco U.V-Visible spectrophotometer. The photoluminescence spectra of the samples were measured using Flurolog®-3 Spectrofluorimeter.

3. Results and discussions
The X-Ray diffraction pattern of as-prepared nano crystalline PbMoO₄ shown in figure 1. All the peaks are indexed for a perfect tetragonal structure with lattice parameters \(a=b=5.38\) and \(c=12.075\text{Å}\). The calculated lattice parameter values are well agreeing with the standard one reported in the JCPDS file no:44-1486. The average particle size calculated by Scherrer formula is 28nm. The as prepared...
powder itself is phase pure which implies that the phase formation was completed during the combustion process itself without the need of any calcination. Thus modified combustion technique in which citric acid is used as complexing agent and ammonia as fuel is a single step process unlike other conventional synthesis techniques such as solid state method in which high temperature calcinations is required for exact phase formation.

Figure 1. XRD pattern of nano PbMoO$_4$

Figure 2. FT-IR spectrum of PbMoO$_4$

The phase purity of the as-prepared nano powder was studied using FT-IR spectra shown as figure 2. PbMoO$_4$ have tetrahedral symmetry (T$_d$) and hence the $F_2(v_3,v_4)$ modes are infrared active. In the FT-IR spectra the respective bands at 3424 and 1670 cm$^{-1}$ can be ascribed to O–H stretching vibration and H–O–H bending vibration of physically absorbed water on the sample surface. A strong absorption peak at 406 cm$^{-1}$ can be assigned to $F_2(v_4)$ vibration mode which represents the bending vibration of Mo–O. The antisymmetric stretching vibration $F_2(v_3)$ originating from the Mo–O in MoO$_4^{2-}$ tetrahedron is corresponds to broad intense peak at 815 cm$^{-1}$. Besides this strong bands, two other very weak bands can also be seen in the region 765 cm$^{-1}$ and 811 cm$^{-1}$, attributed to Mo–O anti symmetric stretching vibrations. This occurred due to the fact that the combustion takes place at a relatively higher temperature, resulted in highly ordered crystal structure and well defined bands relating to Mo–O bonds. Thus vibrational analysis corroborates the XRD results.

The optical properties of nano crystalline PbMoO$_4$ were studied using UV-Visible spectra. Figure 3 shows the UV-Visible absorption spectrum. The sample absorbs heavily in the UV region and moderately in the visible region. Such materials found application in the field of UV filters and sensors. The optical band gap determined from the Tauc’s plot given as figure 4 is 3.2 eV which is exactly matching with the reported values [3]. The band gap value suggest that PbMoO4 is a semiconductor. The absorption edge of the samples prepared by the combustion technique is blue-shifted compared to that of the sample prepared by the solid-state route which can be attributed to the nano nature of the sample.
An intense blue PL emission at room temperature was observed when excited at 380nm and is shown in figure 4. Generally MoO₄ tetrahedron unit is regarded as the reason for luminescent activity in scheelite compounds. PbMoO₄ is reported to show green and blue luminescence depending on structural distortions, particle size, morphology, processing temperature etc [4-6]. The PL spectra of PbMoO₄ shown in figure 4 has intense blue emission. Sczancoski et al [4] reported that the blue PL emissions are due to structural distortion in [MoO₄] and [PbO₄] clusters in the lattice. As our sample has no structural distortions the emission spectrum of the metal molybdates might be ascribed to the charge-transfer transitions within the [MoO₄] clusters. The blue PL emission of PbMoO₄ is assigned to 1T₂ to 1A₁ electronic transitions within the [MoO₄] tetrahedron groups.

4. Conclusions
Nano crystalline semiconducting PbMoO₄ was synthesized through a modified combustion process. The X-ray diffraction studies have shown that the nano powder was single phase and possess tetragonal structure with a lattice constant a=5.540 and c=12.795Å. The average particle size calculated from FWHM is 28nm. The FT-IR study also corroborates the XRD results. The average of band gap determined from the UV–Vis spectrum is 3.20 eV. The nano crystalline PbMoO₄ is found to be a photo luminescent material with strong blue emission due to MoO₄ clusters.

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