EFFECT OF Pb$^{2+}$ DOPING ON THE LUMINESCENCE PROPERTIES OF CoWO$_4$ NANO CERAMICS

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INTRODUCTION

CoWO$_4$ has attracted great attention due to its luminescence [1], magnetic [2], dielectric [3], and catalytic properties [4]. According to our knowledge only limited investigations are reported on the optical properties of trivalent doped CoWO$_4$ and none on Pb$^{2+}$ doped CoWO$_4$. In this work we have prepared undoped and Pb$^{2+}$ doped CoWO$_4$ nano powder samples by co-precipitation method, characterized them and studied the optical properties. The particle size, band gap energy and the PL intensity were found to be controlled by the Pb$^{2+}$ concentration. The enhanced PL emission intensity and easy preparation makes these systems potential candidates for application as multifunctional materials.

EXPERIMENTAL

Sample Preparation and Characterization

Co$_{1-x}$Pb$_x$WO$_4$ [where x is varied between 0.00 and 0.06] nano powder samples were prepared at room temperature by co-precipitation method by using Analytical grade Co(NO$_3$)$_2$.6H$_2$O, Pb(NO$_3$)$_2$ and Na$_2$WO$_4$.2H$_2$O in aqueous medium without any surfactant, dried at 100°C and sintered at 600°C for 1Hr and were labeled according to increase in Pb$^{2+}$ concentration as Pb0, Pb1, Pb2, Pb3, Pb4 and Pb5. The samples were characterized by XRD, SEM, EDS, TEM, FTIR instruments. Optical absorbance were recorded with UV-Vis spectrometer and photoluminescence (PL) by spectrofluorometer.

RESULTS AND DISCUSSION

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The XRD patterns of undoped and Pb$^{2+}$ doped CoWO$_4$ samples are shown in Fig. 1.(a) All the Pb$^{2+}$ doped samples showed secondary phase formation of PbWO$_4$ which coincide with reported data of scheelite type tetragonal structure with space group 141/a [JCPDS: 08-0476]. The XRD pattern of undoped sample Pb0 shows pure single phase formation having wolframite monoclinic structure and space group P2/c matching with JCPDS: 072-0479. The average crystalline size of samples were calculated using Scherrer and Williamson-Hall methods and were found to be between 22 to 37nm by Sherrer method. Particle size did not vary linearly with increase in Pb$^{2+}$ concentration. Higher particle sizes were observed for Pb2 and Pb3 samples compared to others. SEM pictures also showed maximum agglomerations for the same samples.

FTIR spectra given in Fig.1.(b) shows metal ion intense band appearing in the low frequency region of 400-1000cm$^{-1}$ which belongs to the characteristic deformation modes Co-O, W-O, and W-O-W bridges. IR spectra below 500 cm$^{-1}$ could have been due to the deformation modes of W–O bonds in WO$_6$ octahedra or the deformation of W–O–W bridges. The bands positioned at 821 and 610 cm$^{-1}$ were associated to the O–W–O vibration mode and the W–O bond stretching, respectively [5, 4].

The UV-Vis absorption spectra of samples Pb0 and Pb2 are shown in Fig. 3(a). Similar spectra were observed for all the samples exhibiting broad absorption in the range of 200-475nm, a small shoulder around 525 nm and a broad peak around 586 nm. The absorption intensity of the band between 200 nm and 475 nm is almost double than that of the band peaked around 586 nm. Intensities of the former are higher for Pb$^{2+}$ doped samples as compared to the undoped one which arise due to O→W ligand to metal
charge transfers [6]. The peak absorption observed around 586nm is due to the d–d transitions from 4A2 → 4T1(P) levels of the Co$^{2+}$ ions and were found to be less intense for Pb2 and Pb3 samples compared to others [7]. Band gap energies calculated from these spectra were found to be least for Pb2 and Pb3 samples.

Room temperature photoluminescence (PL) spectra of Pb0 and Pb2 samples with 210nm excitation are shown in Fig.3(b). The spectra exhibit broad bluish – green emissions centered at 467nm and shoulder around 536nm are intrinsic luminescence caused by the annihilation of self-trapped exciton, which forms excited $[\text{WO}_6]^{6-}$ complex that can be either excited in the absorption band or in the recombination process [8]. The Pb$^{2+}$ doping changed the emission intensities but did not alter the structure of spectrum for all the samples. The PL intensities are maximum for Pb2 and Pb3 samples (approximately 2.5 times more than that of undoped sample).

![Fig. 3: (a) UV-Visible and (b) PL spectra of undoped and Pb doped CoWO$_4$](image)

**PRACTICAL SIGNIFICANCE**

These samples can be used for scintillating, photocatalytic and magneto-optic applications.

**CONCLUSION**

Undoped and Pb$^{2+}$ doped CoWO$_4$ nanosamples were successfully prepared by simple co-precipitation method without using surfactant in an aqueous medium and characterized.
Particle size, band gap energy and the PL intensity were found to be controlled by Pb$^{2+}$ concentration. The middle doped samples Pb2 and Pb3 were giving maximum PL emission intensity which is attributed to the increased particle size and contributions from PbWO$_4$ and CoWO$_4$ phases enhancing its multifunctional property.

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