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EFFECT OF Pb²⁺ DOPING ON THE LUMINESCENCE PROPERTIES OF CoWO₄ NANO CERAMICS

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INTRODUCTION

CoWO₄ 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 CoWO₄ and none on Pb²⁺ doped CoWO₄. In this work we have prepared undoped and Pb²⁺ doped CoWO₄ 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 Pb²⁺ 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_xWO₄ [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(NO₃)₂.6H₂O, Pb(NO₃)₂ and Na₂WO₄ .2H₂O in aqueous medium without any surfactant, dried at 100⁰C and sintered at 600⁰C for 1Hr and were labeled according to increase in Pb²⁺ 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.

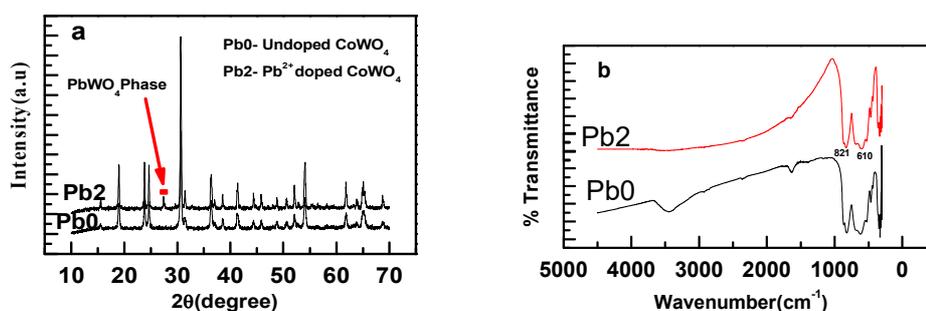


Fig. 1: (a) XRD Patterns and **(b)** FTIR spectra of undoped and Pb^{2+} doped CoWO_4

FTIR spectra given in Fig.1.(b) shows metal ion intense band appearing in the low frequency region of $400\text{-}1000\text{cm}^{-1}$ 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 $200\text{-}475\text{nm}$, 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 $4A_2 \rightarrow 4T_1(P)$ 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 $[WO_6]^{6-}$ 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).

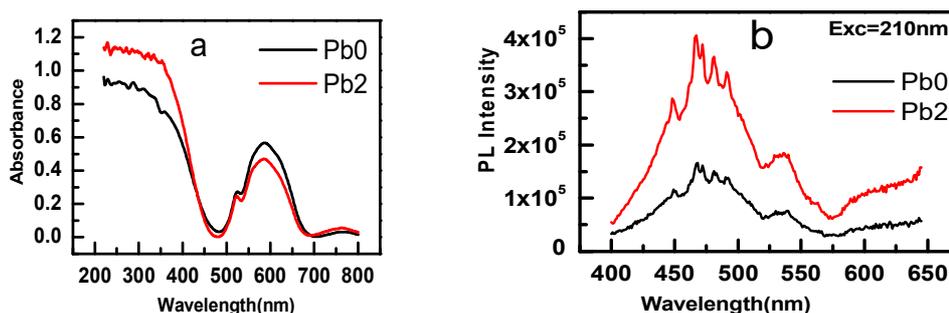


Fig. 3: (a) UV-Visible and (b) PL spectra of undoped and Pb doped $CoWO_4$

PRACTICAL SIGNIFIGANCE

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 Pb²⁺ 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 PbWO₄ and CoWO₄ phases enhancing its multifunctional property.

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REFERENCES

1. Zuwei Songa, Junfeng M, Huyuan Sunb, Yong Suna, Jingrui Fang.,et al., Low-temperature molten salt synthesis and characterization of CoWO₄ nano-particles, *Mater. Sci. and Eng. B*, 163, 62–65, 2009.
2. Zhi Kun Gao, QingWei Gao, Hai Sheng Liu, Bing Hui Yang, YingWang, et al., Three-dimensional molecular-based magnet of octacyanometalate-based tungstate(V)-cobalt(II) bimetallic assembly with T_c=26 K, *Inorganic Chem. Communications*, 43 ,131–134, 2014.
3. T. Gro , E. Tomaszewicz, Z. Kukuła, S. Pawlus, B. Sawicki, Dielectric permittivity of some novel copper/cobalt and rare-earth metal tungstates, *Mater. Sci. and Eng. B*, 184, 14–17, 2014.
4. Kandasamy Jothivenkatachalam, Saravanan Prabhu, Arjunan Nithya, Singaravelu Chandra Mohan, Kulandaivel Jeganathan, Solar, visible and UV light photocatalytic activity of CoWO₄ for the decolourization of methyl orange, *Desalination and Water Treatment*, 54, 11, 2014.
5. J. Juliet Josephine Joy, N. Victor Jaya, Structural, magnetic and optical behavior of pristine and Yb doped CoWO₄ nanostructure, *J .Mater Sci: Mater Electron*, 24, 1788–1795, 2013
6. G. Buvaneswari, Keerthi Valsalan, Structural and diffuse reflectance study of Ca_{1-x} Co_xMO₄ (M =W, Mo) *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 124, 514–518, 2014.
7. Uma Subramanian, S. J Naik, R.B.Tangsali, A.V.Salker, Upconversion luminescence of cerium doped CoWO₄ nanomaterials, *J.Luminescence* 134, 464–468, 2013
8. V. Pankratov, L. Grigorjeva, D. Millers, S. Chernov S, A. Voloshinovskii, Luminescence center excited state absorption in tungstates *J. Lumin.* 94, 427-432, 2001.