



Optical Properties of Cerium (IV) based compounds

Apsara A.P.¹ and Beena B.²

¹Department of Chemistry, FMN College, Kerala, INDIA

²Department of Chemistry, DB College Sasthamcotta, Kerala, INDIA

Available online at: www.isca.in, www.isca.me

Received 21st February 2014, revised 25th March 2014, accepted 15th April 2014

Abstract

Cerium(IV) based samples namely cerium phosphate (CP), cerium molybdate (CM) and cerium phosphomolybdate (CPM) in the present study were obtained as yellow solids. They show maximum absorption in the ultra-violet region. Ligand to metal double-charge transfer transitions, are responsible for the bright colours of the materials. The absorption edge around 250nm for the samples is an indication of the presence of band gap in the materials. The study reveals that the band gap of the materials can be tuned by incorporating different anions. The band gap energy of the synthesized samples obtained were in the range 1.2 – 3.5 eV.

Keywords: Cerium (IV), charge transfer transition, optical band gap.

Introduction

Rare earth ions absorb electromagnetic radiation in the near visible and near infra-red region. In rare earth ions electronic transitions are caused by incomplete 4f subshell¹. Charge transfer transitions are also observed in rare earth ions². The energy of charge transfer bands decreases as the ease of reduction of lanthanide ion increases. Cerium absorbs strongly below 400nm caused by charge transfer transitions. Band gap strongly influences the electrical and optical properties of a material³. Many beneficial properties of cerium and its compounds depend critically on their ultraviolet absorption characteristics⁴. On account of the several beneficial properties exhibited by cerium and its compounds due to their strong ultraviolet absorption capacity, it was thought of interest to analyze the ultraviolet-visible absorption spectra of the cerium based compounds covered in the present study namely- CP, CM, mixed material CPM.

Material and Methods

Preparation of samples: CP in the present study was prepared by adding an aqueous solution of disodium hydrogen phosphate to half its volume of ceric sulphate slowly, with continuous stirring at pH~2. Equimolar solutions of ammonium heptamolybdate and ceric sulphate were mixed in the volume ratio 1:2 at pH~2, for the preparation of CM. Aqueous solution of ammonium heptamolybdate (100ml) and disodium hydrogenphosphate (200 ml) were added to an aqueous solution of ceric sulphate (100 ml), slowly with continuous stirring at pH~2 for the preparation of CPM. In all the above cases, the gel obtained was kept overnight at room temperature in contact with the mother liquor for the growth of fine particles. The granular precipitate thus obtained in each case, was filtered, washed with demineralized water till free of chloride and sulphate ions and finally dried at 40^oC. All materials after drying were broken to desired particle size by grinding and sieving.

Instrumentation: The elemental analysis of the samples, were carried out with Thermo Electron IRIS Interpid II XSP Duo, ICP-AES Spectrometer. UV-Visible Perkin Elmer Spectrophotometer (Lamda-850) was used to obtain the optical absorption spectra of the samples. Data were collected in the absorbance mode in the wavelength range of 200 – 800nm.

Results and Discussion

CP was obtained as a pale yellow solid. CM was a hard bright orange solid while CPM was a bright yellow powder. Elemental analysis shows that the percentage of cerium in CP, CM and CPM are 38.36, 17.28 and 5.88 respectively.

Wide band gap materials appear bright yellow due to ligand to metal charge transfer transitions. Metal anions like vanadate, molybdate, tungstate are colourless⁵. However, when they are combined with a cation like Ce⁴⁺, in high oxidation state, the charge transfer may be shifted to the visible region. Therefore, the colour of CM and CPM may be solely attributed to the following charge transfer transitions: (O_{2p} → Ce_{6s}); (O_{2p} → Ce_{4f}); (O_{2p} → Mo_{3d}). The Ultra violet-Visible absorption spectra of the samples are presented in figure-1a.

All the samples show maximum absorption in the ultra-violet region which is a common characteristic of cerium(IV)⁴. The absorption edge around 250nm for the samples is an indication of the presence of band gap in the materials. The value of optical band gap is obtained by best-fit method by plotting (αhv)² versus hv, as per the Tauc relation⁶. The graphical representations for the samples is shown in figure-1b. The band gap energy obtained for the simple salts CP (1.211 eV) and CM (1.336 eV), were found to be close to the values reported for the semiconductors commonly used namely Si (1.1 eV) and CdTe (1.5 eV) respectively⁷.

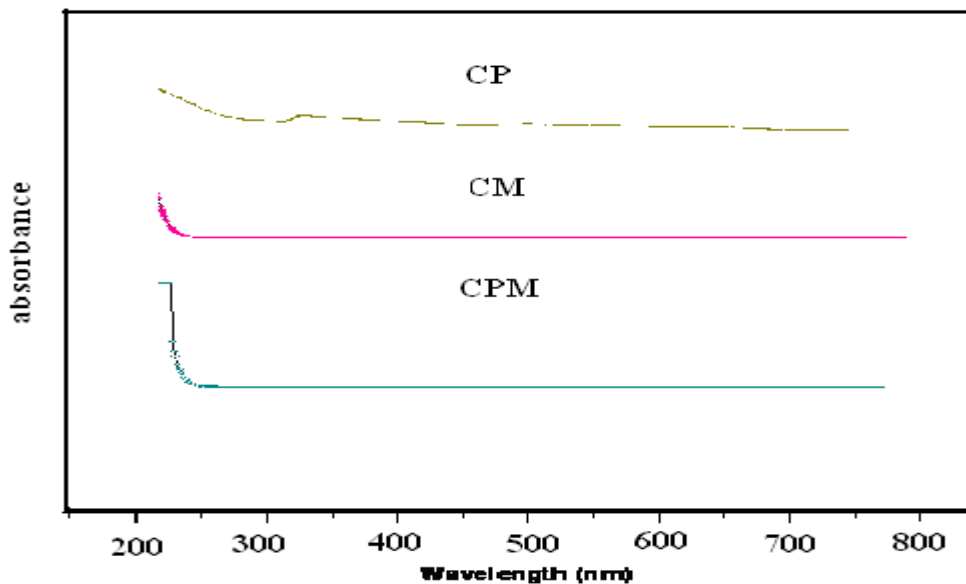


Figure-1a
UV-Visible spectrum of the samples

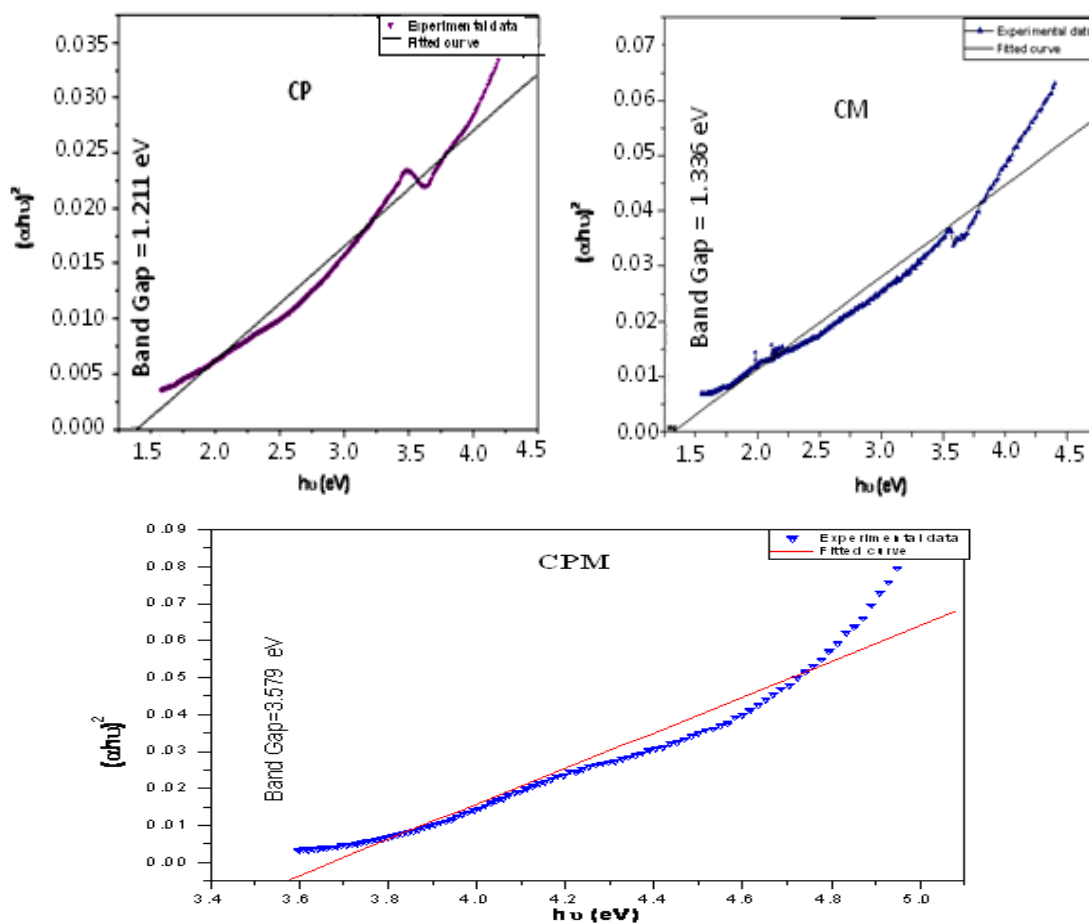


Figure-1b
Band gap of CP, CM and CPM as per Tauc relation

The optical band gap energy of CPM determined from absorption spectra is found to be 3.5 eV which is almost close to the band gap observed in the case of CeO₂ (~ 4 eV), a wide band gap semiconductor that has long been used for its catalytic capabilities⁸ wide band gap semiconductors are often utilized in optoelectronic and power devices. They are often utilized in applications where high temperature operation is important⁹. Thus CPM with wide band gap may find application in the above fields.

The bright colour and UV-absorption ability of the materials reveal their possible application as pigment and sunscreen¹⁰. Shinya et al. have reported that such inorganic pigments made of less toxic elements are usually inert and they are safe to be used¹¹. Toxic metals namely Cd, Cr, Pb and Co used in pigments can be replaced by less toxic cerium based materials^{12, 13}.

Conclusion

The materials in the present study show band gap ranging from 1.2 to 3.6 eV. Among the studied cerium based materials, the simple salts CP and CM possess a lower band gap energy in comparison to their mixed salt CPM. The study reveals that the band gap energy of the materials can be tuned by incorporating different anions. It is also observed that the increase in cerium content decreases the band gap energy of the materials.

References

1. Paul A., Mullholland M. and Zaman M.S., *J. Mater. Sci.*, **11**, 2082-2086 (1976)
2. Eiichiro Nakazawa and Fuminori Shiga, *Jpn. J. Appl. Phys.*, **42**, 1642-1647 (2003)
3. Ghoneim D., Marzouk K. H., EL-Sayed S. N., Mohsen N. A. and Mahmoud A.M.A., *Chalcogenide letters*, **7**, 307-316 (2010)
4. Naik S.J., Uma Subramanian, Tangsali R.B. and Salker A.V., *J. Phys. D : Appl. Phys.*, **44**, 115404 (2011)
5. Smith Jared Peters, Ph.D. Thesis, Humboldt-University, Berlin, Germany (2006)
6. Zallen R. and Moret M.P., *Solid State Commun.*, **137**, 154-157 (2006)
7. Madelung Otfried, *Semiconductors - Basic Data* (2nd Rev. Ed.), Springer-Verlag, (1996)
8. Jorgenson C.K. (Ed.), *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon, Oxford, (1972)
9. Kiyoshi Takahashi, Akihiko Yoshikawa and Adarsh Sandhu (Eds.), *Wide band gap semiconductors: Fundamental properties and modern photonic and electronic devices*, Springer, Berlin Heidelberg, New York, (2007)
10. Masui T., Tategaki H., Furukawa S. and Imanaka N., *Synthesis and characterization of new environmentally friendly pigments based on cerium phosphate*, *J. Ceram. Soc. Jpn.*, **112**, 646 (2004)
11. Shinya Furukawa, Toshiyuki Masui and Nobuhito Imanaka, **418**, 255-258 (2006)
12. Jean Noel Berte, *Cerium Pigments In: High Performance Pigments*, Mugh M. Smith (Ed.), Wiley-VCH Verlag GmbH and Co. KGaA, (2002)
13. Han Gao , Bing Qiao , Ting-Jie Wang *, Dezheng Wang , and Yong Jin, *Cerium Oxide Coating of Titanium Dioxide Pigment to Decrease Its Photocatalytic Activity*, *Ind. Eng. Chem. Res.*, **53(1)**, 189-197 (2014)