CHAPTER - 1

General Introduction

1.1 Background- Tungstate

Metal tungstates have attracted considerable attention for present and prospective applications in photoluminescence, optical fibers, medical science, scintillators, photocatalyst and humidity sensors [1-7]. Tungstate crystals can be divided in two groups: Scheelite ($CaWO_4$, $BaWO_4$ and $PbWO_4$) and Wolframite ($MgWO_4$, $ZnWO_4$ and $CdWO_4$). $BaWO_4$ shows very weak luminescence at liquid helium temperature which vanishes at room temperature. $MgWO_4$ is used as photoluminophor already for a long time [1]. $ZnWO_4$ and $CdWO_4$ are perspective materials in the field of computer tomography [2]. $CaWO_4$ is an effective luminophor which is used for more than hundred years for medical purpose and in luminescent lamps but it has slow luminescence decay (about 100ns) which restricts its use in optical devices based on low time resolution. Out of all tungstates, $CdWO_4$ became a subject of renewed interest about few years ago when its favorable characteristics as scintillation detector was reported. Recently, M. You et al. (2014) demonstrated that $CdWO_4$: Eu^{3+} is promising red light phosphor blue based white LEDs.

Cadmium tungstate ($CdWO_4$ or CWO), the cadmium salt of tungstic acid, is a dense, chemically inert solid which is used as a scintillation crystal to detect gamma rays. Cadmium tungstate ($CdWO_4$) have been also investigated for many applications, such as, oil well logging, industrial processing control and inspection, dosimetry, nuclear weapons and waste monitoring [8-12]. Cadmium tungstate ($CdWO_4$) with a monoclinic wolframite structure belongs to one of the families of metal tungstates.

1.2 Objectives and Scope

The aim of the work is to study the effect of different dopants, temperature and pH of reaction media on the structural and optical properties of $CdWO_4$ phosphor.

In order to achieve this aim, following objectives have been set.

- To design and develop stainless steel autoclave with teflon vessel to synthesize pure $CdWO_4$ phosphor with different dopants and by varying the reaction conditions.
- To grow pure $CdWO_4$ phosphor with different dopants of different size and shape by low temperature and low cost hydrothermal method.
- To grow pure $CdWO_4$ phosphor with different dopants and pH to observe its effect on its optical properties.
- To characterize prepared samples using X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR) for structural studies.
- To characterize prepared samples using Thermoluminescence (TL) and Photoluminescence (PL) for optical studies.

1.3 Cadmium Tungstate ($CdWO_4$)

$CdWO_4$ is a highly functional material due to its low radiation damage, low afterglow, high average refractive index, high density, and high X-ray absorption coefficient [13]. $CdWO_4$ is toxic if inhaled or swallowed. Its crystal is transparent, colorless, with slight yellow tint. It is odorless. It has also potential to use as an advanced medical X-ray detector in computerized tomography [14] that has attracted interest of many researchers. It emits light when it is hit by gamma rays and x-rays, making it useful as a detector for ionizing radiation. Scintillation wavelength emits an intense peak at 480 nm (with emission range between 380-660 nm) and efficiency of 13000 photons/MeV. Its CAS number is 7790-85-4. It has relatively a high light yield. The properties of $CdWO_4$ are mentioned in table given in table 1.1

Crystal structure	Wolframite
Density [g/cm^3]	7.9
Melting point [K]	1598
Thermal expansion coefficient [C^{-1}]	10.2 x 10^{-6}
Cleavage plane	<010>
Hardness (mho)	4 - 4.5
Hygroscopic	No
Wavelength of emission max [nm]	475-480
Lower wavelength cutoff [nm]	325-330
Refractive index @ emission max.	2.2 - 2.3
Primary decay time [ns]	14000
Light yield [photons/keVγ]	12 – 15
Photoelectron yield [% of NaI(Tl)] (for γ-rays)	30-50
Afterglow (% after 3 ms)	<0.1

Table 1.1 General properties of Cadmium tungstate [http://www.crystals.saint-gobain.com/$CdWO_4$_scintillator.aspx].

1.4 Literature Review

Cadmium tungstate was used as a replacement of calcium tungstate in some fluoroscopes since 1940's [15-16]. Very high purity allows using this scintillator as a detector of rare nuclear processes (double beta decay, other rare alpha and beta decays) in low-background applications [17]. The first indication of the natural alpha activity of tungsten had been found in 2003 with CWO detectors [18]. Due to different types of light emission for different types of ionizing particles, the alpha-beta discrimination technique has been developed for CWO scintillators [19].

Initially the photoluminescence properties of cadmium tungstate were done by Kröger in 1948. He observed a sharp blue-green emission peak near 480 nm (2.58 eV) at temperature 300K. This inherent "blue" emission was attributed to allow transitions within the tungstate molecular unit WO_4^{2-} (Lammers 1981). The optical absorption edge of cadmium tungstate is located near 325 nm (3.8 eV) at room temperature and it shifts to lower wavelength (i.e., higher energy) when the temperature decreases. Also, pure single crystals were studied by high transparency in the scintillation outburst region from 450-700 nm (Nedelko 1996).The intrinsic blue photoluminescence originating from the tungstate group can be explained as follows: when the crystal is excited with above band gap energy, electron-hole pairs are created. The electrons are attracted only by W^{6+} ions because they are the most highly ionized and the holes will be attracted by O^{2-} ions. When electrons and holes recombine, the blue luminescence will occur. $CdWO_4$ have exhibited the same emission spectra under the same conditions and only the tungstate octahedra groups contribute to the intrinsic luminescence and that the cations Cd^{2+} have negligible contribution to this emission. Tungstate complexes are examples where transition metal ions have an empty *d* shell. Such complexes are known to luminesce in more than one type of coordination (e.g. coordination of 4 or 6) and are usually characterized by a broad band emission with a large shift (10,000-20,000 cm^{-1}) from the absorption [20]. This is often referred to as the "Stokes" shift. The excited state is considered to be a charge-transfer state, i.e., electronic charge has transferred from the oxygen ligands to the central metal ion. The real amount of charge transfer is usually small, but a considerable amount of electronic reorganization occurs. The value of the local ion displacement is large, the Stokes shift is large, and the spectral bands are broad in this case (Blasse 1994).

A second emission band in $CdWO_4$ was observed near 570 nm at liquid helium temperature for excitation wavelengths longer than 320 nm (Lammers 1981). He was suggested that this yellow emission to a transition within a tungstate group which lacks one oxygen ion. Second article of this emission band in doped $CdWO_4$ have been reported in a comparative study of photo excitation, luminescence, and 6 time resolved luminescence of $ZnWO_4$ and $CdWO_4$ done by Ovechkin *et al.* in 1987, the yellow emission observed is attributed to the same intrinsic defect.

1.5 Crystal Structure

$CdWO_4$ crystallizes in the wolframite-type structure like $ZnWO_4$, $NiWO_4$, or $MgWO_4$, as opposed to the scheelite structure of $CaWO_4$, and it has a monoclinic symmetry (C_{2h}^4) with unit cell dimensions of a = 5.029 Å, b = 5.859 Å, and c = 5.074 Å, and $\beta = 91.47°$. The unit cell consists of two formula units, that there are two equivalent Cd atoms occupying sites of symmetry C_2, two equivalent W atoms occupying sites of symmetry C_2, and three inequivalent sets of oxygen atoms [20]. The tungsten and cadmium atoms are located within highly distorted octahedron of oxygen atoms (see Fig.1.1). Two oxygens of each octahedron are shared by adjacent octahedra resulting in a chain-type structure. The chains of octahedra are in a zigzag array. There are four shorter (1.80 and 1.87 Å) W - O bonds and two longer and thus much weaker bonds (2.22 Å), as revealed by the prominent <010> cleavage plane which intersects them. These octahedra show some similarities with the tetrahedral oxo-complexes of scheelite (Douglas 1980, Burshtein 1988).

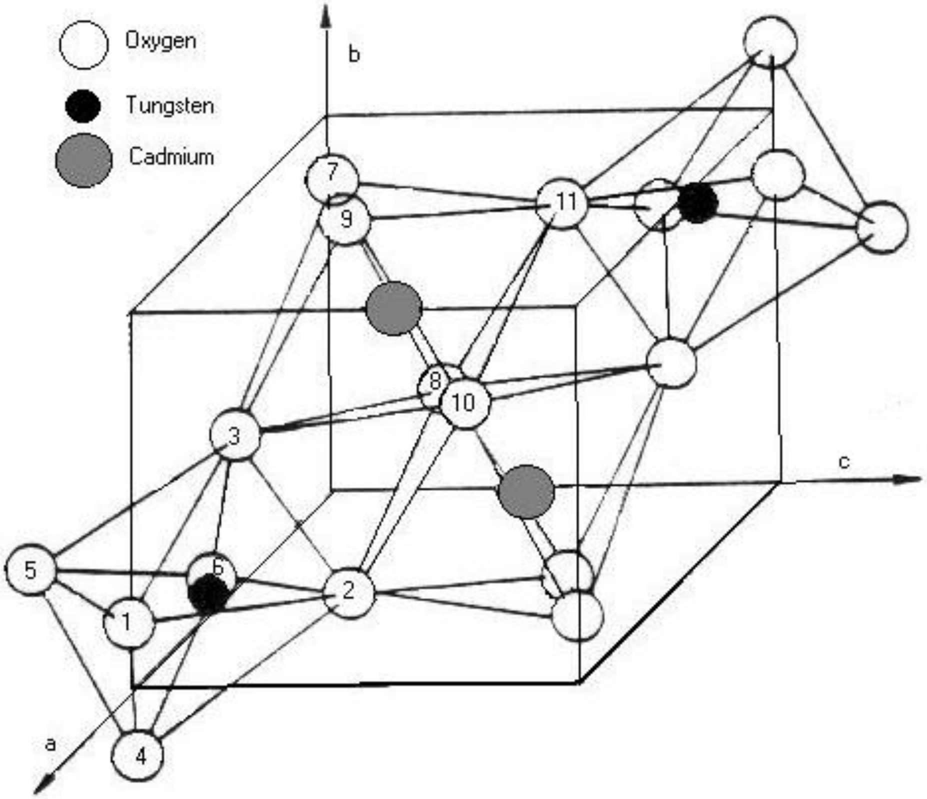

Figure 1.1 Crystal Structure of $CdWO_4$ (from Morell *et al.*). In this reference, the unique axis is considered to be ***c***. The number of formula units per unit cell is 2.

1.6 Different Synthesis methods

Synthesis methods for nanoparticles are usually grouped into two types: ‘top-down’ and ‘bottom-up’. The first encompasses division of a heavy solid into smaller portions. Nanoparticles are synthesized by breaking down bulk materials gradually into smaller sizes. Examples are ball milling (mechanical milling), mechanochemical processing (mechanical activation), mechanochemical processing (mechanical activation) (self-propagating high-temperature synthesis), solid-state synthesis etc.

The second, ‘bottom-up’, method of nanoparticles are built up atom by atom or molecule by molecule. This approach is more popular in the synthesis of nanoparticles. In this section some synthesis methods of later category will only be focused for semiconductor nanoparticles. Examples are chemical (reactive) precipitation or co-precipitation, hydrothermal synthesis (thermal hydrolysis), plasma arcing, forced hydrolysis, molecular beam epitaxy(MBE), solvothermal synthesis, chemical vapour deposition, supercritical hydrothermal processing or supercritical fluid processing, sol-gel synthesis, microwave heating synthesis, synthesis in micro emulsions or reverse micelles and sono-chemical synthesis.

Although these strategies are widespread demonstrated effective methods to fabricate $CdWO_4$ nanostructures with various morphologies, large scale application of these methods have been limited due to some shortcomings, such as some methods need expensive templates or surfactants, and others needing complicated process, or even tedious procedures.

To synthesize $CdWO_4$ nanoparticles we have used hydrothermal method. Hydrothermal synthesis of these materials by the synthetic route is a simple and cost effective method. It provides a high yield of phosphors with easy scale up, and is emerging as a viable alternative approach for the synthesis of inorganic materials with appropriate choice of experimental parameters, such as temperature, time, pH, mineralizer and surfactant. It offers several advantages over other synthesis process, such as mild experimental conditions, high purity, and good particle size distribution of product. It can be used to synthesize a product pure product with homogeneity, crystal symmetry and metastable compounds with unique properties with narrow particle size distributions. It is a single-step process which produces dense sintered powders having sub-micron to nanoparticles with a narrow size distribution.

1.7 Electronic Structure of $CdWO_4$

From literature review, according to, T.yan et.al., the conduction band (CB) is dominated by O2p,W5d, and Cd5s orbitals, while the valence band is mainly composed of the O2p and W5d orbitals for monoclinic $CdWO_4$. The energy level diagram of $CdWO_4$ are explained in fig 1.2The width of CB ranges from 2.91 to 8.77 eV. The band-gap energy theoretically calculated for the monoclinic is 2.91 eV, which is much smaller than those experimentally determined. The differences in band-gap energies may be originated from the discontinuity in the exchange-correlation potential. The different electronic state distribution width in CB is probably caused by the difference in their crystal fields around W atoms (tetrahedra vs octahedra). It is known that the crystal field can greatly influence the orbital distribution of the central atom [21]. In this sense, the monoclinic is consisted of WO_6 octahedra. Due to the fact that the WO_6 crystal field is much stronger than WO_4, the former would result in a greater splitting of the W5d orbitals and give rise to a wider W5d electronic state distribution.

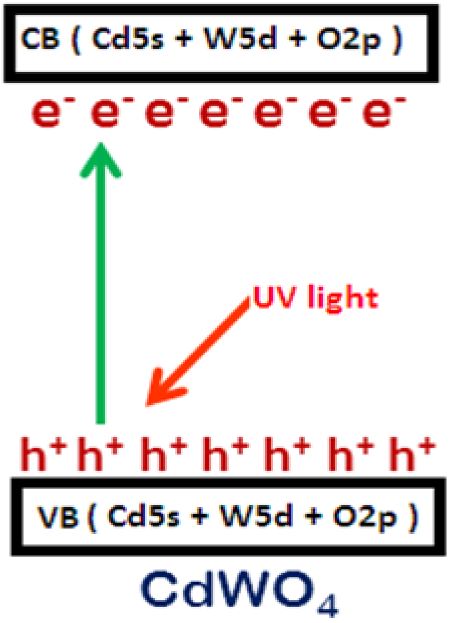

Figure 1.2 The energy level diagram of $CdWO_4$.

The Cd_{5s} state has appreciable contributions throughout the valence band and conduction band, respectively. When the $CdWO_4$ is excited within fundamental absorption band, charge transfer occurs by two types of electronic transitions.1) From O^{2-} to W^{6+} , 2) From O^{2-} to Cd^{2+}

1.8 Self Trapped Exciton (STE)

An exciton is an excited quasi particle in a solid, which is formed by a Coulomb-bound electron-hole pair [22]. The free exciton luminescence had never occurred. A self trapped exciton is usually providing rich spectrum in many crystals and glasses. In short, excitons are energy transporting quasi particles, which do not providing photo conductivity [23]. In $CdWO_4$, PL spectra exhibits violet - green emission band peaking in blue region with a band edge UV emission. An electron from oxygen 2p goes into one of the empty tungsten 5d orbital (the bottom of W_5d) in the WO_4^{2-} group by absorbing ultraviolet irradiation in $CdWO_4$. In the excited state of the WO_4^{2-}group, the hole (on the oxygen) and the electron (on the tungsten) remain together as an exciton because of their solid interactions. This type of exciton which is produced in $CdWO_4$ is called Frenkel exciton where, the radius of such exciton is very small. The exciton binding energy was estimated about 0.1 eV. The lowest exciton transition is connected to an electronic excitation from the mixed $Cd(5s)\rightarrow O(2p)$ ground states to the mixed $Cd\ (5s)\rightarrow W(5d)$ excited states. The Cd contributions to the top of the valence band and the bottom of the conduction band are small so that the exciton transition is very weak. Such exciton is a molecular-type exciton of the WO_6^{6-} anion complex with covalent bonding within the oxo-complex. The emission bands were attributed to the $^1A_1\rightarrow\ ^3T_1$ transition within the WO_6^{6-} complex [24]. This is mainly due to the charge-transfer transitions between the O_{2p} orbital and the empty d orbital of the centralW^{6+} of WO_6 octahedra or to the self-trapped exciton at a

WO_6^{6-} oxyanion complex [25, 26]. The band edge UV emission may be due to recombination of free excitons through exciton-exciton collision process or the radiative recombination of excitons bound to neutral donor [27, 28].

1.9 Nature of impurity - Dopant

In order to use $CdWO_4$ crystal as scintillation detector its radiation hardness should have higher value. The radiation damage in $CdWO_4$ crystals is caused by host structural defects called color centers e.g. Oxygen vacancies (*Vo*) and Cadmium vacancies (*Vcd*). Such vacancies are produced due to high synthesis temperature during crystal growth which introduces local charge imbalance, as to improve radiation hardness by decreasing concentration of these vacancies, hence low temperature hydrothermal method is preferable. To balance charge these vacancies act as charge traps centers. *Vo* and *Vcd* act as electron and hole traps respectively.

It is found that the luminescence characteristics of $CdWO_4$ can be tuned by doping different active cations(Co^{2+}, Bi^{3+}, Mn^{2+}, Cr^{3+}, etc.), accordingly with their ionic electro- negativities. Doping with trivalent rare earth ion is another approach which minimizes the charge imbalance produced by vacancies. In 1997, Kobayashi et al. reported that La^{3+} doping into lead tungstate could improve both the radiation hardness and the transmittance in the short-wavelength region. Since then, doping with different impurity ions, especially rare-earth ions (RE^{3+}), has become the focus of studies to ameliorate its scintillating characteristics. In trivalent ions 5d, 6s, and some 4f electrons are removed and so RE^{3+} ions act with transitions between electronic energy sublevels of the $4f^n$ electronic configuration. Divalent lanthanide ions having one more f electron compare to trivalent ions. They exhibit f → d inter-configurational optical transitions. This facet assigns to quite different optical properties between divalent and trivalent ions.

In fact, the $4f^n$ electrons are the valence electrons which are responsible for the optical transitions.

References

1. Z. Shan, Y. Wang, H. Ding and F. Huang, J. Mol. Cat. A: Chemical 302, 54-58, 2009.
2. S. J. Chen, J. H. Zhou, X. T. Chen, J. Li, L. H. Li, J. M. Hong, Z. L. Xue, X .Z. You, Chem. Phys. Lett. 375, 185, 2003.
3. S. Kwan, F. Kim, J. Akana, Chem. Commun. 447, 2001.
4. B. Liu, S. H. Yu, F. Zhang, L. J. Li, Q. Zhang, L. Ren, K. Jiang, J. Phys. Chem. B 108, 2788, 2004.
5. X. L. Hu, Y. Zhu, J. Langmuir 20, 1521, 2004.
6. C. L. Melcher, Nucl. Inst. Meth. Phys. Res. A 537, 6-14, 2005.
7. G. Zhang, S. Yang, Z. Li, L. Zhang, W. Zhou, H. Zhang, H. Shen and Y. Wang, Applied Surface Science, 257, 302-305, 2010.
8. C. L. Melcher, R. A. Manentem, J. S. Schweitzer, IEEE Trans. Nucl. Sci. 36, 1188, 1989.
9. C. L. Melcher, private communications 75, 1994.
10. D. Brown, R. H. Olsher, Y. Eisen, J. F. Odriguez, Nucl. Instrum. Methods Phys. Res. A 373, 139, 1996.
11. C. M. Bartle, R. C. Haight, Nucl. Instrum. Methods Phys. Res. A 422, 54, 1999.
12. V. Ryzhikov, L. Nagornaya, V. Volkov, V. Chernikov, O. Zelenskaya, Nucl. Instrum. Methods Phys. Res. A 486, 156, 2002.
13. H. Lotem, Z. Burshtein, Opt. Lett.12, 1987.
14. Greskovich, C. D. Cusano, D. Hoffman, D. Riedner, R. J. Am. Ceram. Soc. Bull. 71, 1120, 1992.

15. Patterson Hand-Held Fluoroscope, Oak Ridge Associated Universities, 1999. Retrieved 2008-04-26.
16. Kroeger, F. A., Some Aspects of the Luminescence of Solids, Elsevier, 1948.
17. Bardelli L. et al.,Nucl. Instrum. and Methods in Phys. Research A 569 (3): 743–753 ,2006.
18. Danevich F. A. et al., Phys. Rev, 67(1), 2003.
19. Fazzini T. et al. (1998). Nucl. Instrum. and Methods in Phys. Research A 410 (2): 213–219 ,1998.
20. M. M. Chirila, M.Sc. Thesis, Department of Physics, West Virginia University, 2000
21. M. Oshikiri, M. Boero, J. H. Ye, Z. G. Zou, G. Kido, J. Chem. Phys. 117, 7313–7318, 2002.
22. http://blog.disorderedmatter.eu/2008/04/15/polaron-polaron-pair-exciton-exciplex/
23. A. N. Trukhin, Electrochemical society proceedings volume 98-25,365,1998
24. K. Polak, M. Niki, K. Nitsch, M. Kobayashi, M. Ishii, Y. Usuki and J. Jarolimerk, J. Lumin.,781, 1997.
25. O.V. Rzhevskaya, D.A. Spasskiı, V.N. Kolobanov, V.V. Mikhaılin, L.L. Nagornaya, I.A. Tupitsina, B.I. Zadneprovskiı, Opt. Spectrosc., 104, 2008.
26. Y.A. Hizhnyi, S.G. Nedilko and T.N. Nikolaenko, Nucl. Instrum. Methods Phys. Res. A, 537, 2005.
27. Y. C. Kong, D. P. Yu, B. Zhang, W. Fang and S. Q. Feng, Appl. Phys. Lett.,78, 2001.
28. R. Chen, G.Z. Xing, J. Gao, Z. Zhang, T. Wu and H.D. Sun. Appl. Phy Lett. 95, 2009.