CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of metal tungstates and metal molybdate

a) Solid state method

Z.H. Ju et al. (2010) presented a novel emissive phosphor $SrWO_4$:Sm^{3+} for white light-emitting diodes were synthesized by solid-state reaction method, a series of phosphors $Sr_{1-x}Sm_xWO_4$ (x = 0.02–0.06). The fluorescent intensities of the phosphors excited by 364, 377 and 346 nm reach a maximum at x = 4 mol%. The quantum yield of the phosphor $Sr_{0.96}Sm_{0.04}WO_4$ is about 70.65% under excitation of 377 nm. In addition, the phosphor shows a small thermal quenching, at 190 ^{o}C, the fluorescent intensity still maintains about 100% of that measured at the temperature of 20 ^{o}C. Given good overall luminescent performances, this phosphor is a potential candidate as orange-emitting component for white LED [17].

Z. Ju et al. (2011) presented a series of red-emitting phosphors $Sr_{x-1}WO_4$: (x = 0.02–0.10) and $Sr_{0.84}WO_4$: $Eu^{3+}_{x0.08}$, $Eu^{3+}_{x0.08}$ (M = Li, Na, K) were prepared by solid state method. For phosphors $Sr_{0.84}WO_4$: $Eu^{3+}_{x0.08}$, (x = 0.02–0.10), the fluorescent intensity of the phosphors excited by 394 and 465 nm reach a maximum at x = 0.08. The bright red emission locate at about 615 nm originating from the electric dipole transition $^5D_o \rightarrow {}^7F_2$ excited by the light of 394 and 465 nm. Enhanced emission intensities are observed in the phosphors co-doped with efficient charge compensators. $Sr_{0.84}WO_4$: $Eu^{3+}_{x0.08}$, $Eu^{3+}_{x0.08}$, $Li^{+}_{0.08}$ has the best charge compensation effect. The results of fitting the experimental data of fluorescent decay curves revealed that Eu^{3+} - doped SrWO$_4$ phosphor in terms of a single exponential decay model. The fluorescent lifetimes of the phosphor are short enough for applications in white LEDs. In addition, the phosphors show small thermal quenching. Given good overall luminescent performances, this phosphor is a potential candidate as red-emitting component for white LED [18].

M. Zhang et al. (2011) investigated, xMgWO$_4$–(1-x) Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ composite ceramics have been synthesized by the solid-state reaction route. The introduction of MgWO$_4$ resulted in a change in lattice constant of the perovskite phase and making for grain growth of the composite ceramics. With increasing MgWO$_4$, tunability of the samples decreased, due to the increase in the amount of non-ferroelectric phases. However, their dielectric permittivities were effectively reduced and microwave properties were improved, owing to the increase in the amount of microwave material BaWO$_4$ and MgTiO$_3$. The Ba$_{0.5}$Sr$_{0.5}$TiO$_3$–MgWO$_4$ composite ceramics break through contradictory in satisfying simultaneously low loss tangent and higher tunability versus lower permittivity. Specifically, the sample with 35 wt% MgWO$_4$ has a tunability of ~16.8% (at 60 kV/cm), microwave dielectric permittivity of 65 and Q value of 309 (at~4.403 GHz), making it a suitable material for electrically tunable microwave devices [74].

L.Y. Zhou et al. (2009) synthesized Eu^{3+} doped MgMoO$_4$ phosphors were prepared by solid-state reaction. Compared with the Y$_4$O$_2$S:0.05Eu^{3+} phosphor, the obtained MgMoO$_{0.80}$MgMoO$_4$: Eu$^{3+}_{0.20}$ phosphor shows a stronger excitation band around 400 nm and enhanced red emissions due to Eu^{3+} f–f transitions under 394 nm light excitation. The CIE chromaticity coordinates (x = 0.651, y = 0.348) of the phosphor are close to standard of NTSC. As the calcination temperature rises from 700 ^{o}C to 900 ^{o}C, the emission intensity increases due to the improvement of crystallinity, and the size distribution of the phosphors increases significantly and the average diameter of the particles is about 1.8 mm, which is fit to fabricate the solid-lighting devices. All the results indicated that this red phosphor is a suitable candidate for the fabrication of near UV InGaN-based LEDs [75].

b) Simple wet chemical method

E.K. Ryu et al. (2008) looked at the Morphology-controlled synthesis of $SrWO_4$ crystals. Various shapes of $SrWO_4$ crystals were synthesized using a simple precipitation method. The molar ratio of $[WO_4^{2-}]$ to $[Sr^{2+}]$ played an important role in the formation of various morphologies of $SrWO_4$ crystals. The mechanism of the morphology evolution of the $SrWO_4$ crystals from rods, through peanut-like and dumbbell morphologies, to notched spheres was explained by fractal growth at both ends of each rod. Kayak-like $SrWO_4$ single crystals can also be prepared using a micro emulsion method [76].

X. Wang et al. (2005) investigated $BaWO_4$ powders with different morphologies. $BaWO_4$ were successfully prepared via a simple soft solution processing based on precipitation technique at room temperature without using any template. On changing reaction conditions, including reaction temperature, pH of the starting solution and additive agents, some interesting morphologies such as double-taper-like, scissors-like, fasciculus-like, flower-like, shuttle-like, obtuse-taper-like and spherical shape were obtained [77].

Y. Sun et al. (2011) synthesized $SrMoO_4$ and $CaMoO_4$, and $SrMoO_4$ by a simple electrochemical process. The photoluminescence (PL) of $SrMoO_4$ can be greatly improved by incorporating Ca^{2+} into its matrix to form solid solutions, and their emission bands slightly red-shift from 500 nm to 509 nm due to the local structure relaxation. Doping Ca^{2+} would inhibit the growth of $SrMoO_4$ solid solution crystallites to result in smaller size crystallization. The smaller the particle sizes of the solid solutions, the higher their PL intensity [78].

G. Xing et al. (2011) controlled morphologies $SrMoO_4$ have been successfully prepared via a simple precipitation method. The molar ratio of reactants and reaction concentration were found to play important roles in the including spindle-rod, peanut, dumbbell and notched sphere have been successfully synthesized via a simple precipitation method by varying the molar ratio of $[MoO_4^{2-}]/[Sr^{2+}]$, which was found to have great effect on the formation of various morphologies of $SrMoO_4$ crystals under the condition of lower reactant concentration, while has little effect under relatively higher concentration. The as-synthesized $SrMoO_4$ samples exhibited different photoluminescence properties, which are dependent on their different morphologies [79].

c) Sonochemical method

T. Thongtem et al. (2008) presented characterization of $MeWO_4$ (Me = Ba, Sr and Ca) nanocrystallines prepared by sonochemical method. They are in the ranges of 7.5–75, 1–35 and 2–24 nm for $BaWO_4$, $SrWO_4$ and $CaWO_4$, respectively. Their atoms are uniformly arranged in lattice array. Their emission peaks at 384–416 nm. They are blue-shift relative to the corresponding bulks [80].

L.D. Feng et al. (2010) synthesized $SrWO_4$ nanobelts by the sonochemical method. Experiment results indicated that simply controlling the concentration of Na_2EDTA and high-intensity ultrasonic irradiation, different morphologies of $SrWO_4$ could be obtained. The emission peaks of $SrWO_4$ prepared in Na_2EDTA are red-shift, the morphologies of $SrWO_4$ play important roles in their emission properties The PL spectra reveal that $SrWO_4$ nanobelts gained the strongest emission intensity [16].

d) Hydrothermal/solvothermal method

J. Liao et al. (2011) presented the hydrothermal preparation and luminescence property of $MWO_4:Sm^{3+}$ (M = Ca, Sr, Ba) red phosphors. The Sm^{3+} activated MWO_4 (M = Ca, Sr and Ba) red phosphors by the mild hydrothermal method. The SEM photograph demonstrated that the crystalline particles are nearly monodisperse and spherical shape. The emission spectra show the strong reddish orange emission of $MWO_4:Sm^{3+}$ under near ultraviolet excitation (404 nm). The strongest line (404 nm) in excitation spectra of these phosphors matches with the out-put wavelength of UV InGaN-based light-emitting diodes (LEDs) chip. Therefore, the high emission intensity and the easy preparation of these systems make them potential candidates for LED application [81].

J. Liao et al. (2011) reported the hydrothermal synthesis and photoluminescence of $SrWO_4:Tb^{3+}$ novel green phosphor. The spherical $SrWO_4:Tb^{3+}$ phosphors with different Tb^{3+} concentration can be prepared by a mild hydrothermal method at 180 ^{o}C for 12 h. The excitation spectra show the strong energy transfer from WO_4^{2-} group of the host material to the Tb^{3+} ions. The optimum concentration for Tb^{3+} was determined to be about 12 at. % of Tb^{3+} ions in $SrWO_4:Tb^{3+}$ phosphors. Furthermore, the reaction temperature for $SrWO_4:Tb^{3+}$ phosphors is much lower than that for $LaPO_4$:Ce,Tb. Therefore, this material seems to be promising for application in fluorescent lamps [82].

D. Chen et al. (2003) reported the low-temperature synthesis of metal tungstate, MWO_4 (M= Ca, Sr, Ba, Cd, Zn, Pb) nanocrystallites. By reaction between metal chloride and sodium tungstate in ethylene glycol by hydrothermal method at 180 ^{o}C for 10 h, the product powders consist of nanosize particles. Photoluminescence measurement reveals that the as-obtained $CaWO_4$, $CdWO_4$, and $PbWO_4$ show excitonic peaks at about 430, 500 and 500 nm, respectively [83].

L. Sun et al. (2007) synthesized $SrWO_4$ by a simple cationic microemulsion system under solvothermal conditions. With careful control of the fundamental experimental parameters including the *w* value and the concentration of reactants, the morphologies of spheres, peanuts, and rods have been efficiently obtained, respectively. But they also found that the reaction temperature and time had little influence on the shape and size of the $SrWO_4$ products. The possible formation mechanism of these unique morphologies has also been proposed based on surfactant self-assembly under different experimental conditions. The as-synthesized $SrWO_4$ samples with different morphologies exhibited different photoluminescence properties. These interesting properties of $SrWO_4$ nanostructures have many potential applications [84].

e) Microwave-assisted synthesis method

T. Thongtem et al. (2008) presented the preparation and characterization of nanocrystalline $SrWO_4$ using cyclic microwave radiation. The advantages of microwave radiation are rapid, simple and efficient process used for producing nanocrystalline $SrWO_4$ in ethylene glycol at different microwave powers, prolonged times and pH values. All of the crystalline products are pure phase with scheelite structure and $I4_1/a$ space group. They compose of nano-sized particles and lattice planes in systematic array. The W–O stretching vibration in WO_4^{2-} tetrahedrons was detected at 781–912 cm^{-1}. Their emission peaks are due to the $^1T_2 \rightarrow {}^1A_1$ transition in WO_4^{2-} tetrahedrons at 420–428 nm (2.901–2.956 eV) [85].

J.T. Kloprogge et al. (2004) reported a variety of metal tungstates have been synthesized in a microwave-assisted oven at 100 and 150 ° C and corresponding autogenous water vapour pressure within a time frame from 30 min to 2 h. The crystals formed are of submicrometer size and show equidimensional and needle-like crystals. Increasing the synthesis time and temperature results in the disappearance of the needles and the growth of the equidimensional crystals. The Raman spectra are consistent with those reported for the natural equivalents of these tungstates. The lead tungstate $\nu_1(A_g)$ mode is observed at 904 cm^{-1}, while the $\nu_2(A_g)$ vibration is observed as a strong band at 326 cm^{-1} accompanied by a weak $\nu_2(B_g)$ at 356 cm^{-1}. The $\nu_3(B_g)$ vibration is located around 741 cm^{-1}, whereas the $\nu_3(E_g)$ is found at 751 cm^{-1}. Finally, the $\nu_4(B_g)$ vibration is completely overlapping with the $\nu_2(A_g)$ vibration. The band around 271 cm^{-1} may be the equivalent of the infrared active $\nu_4(Au)$ activated due to strain in the crystal. The two bands at 190 and 177 cm^{-1} are ascribed to the ν(Pb–O) and as a translational mode of the WO_4 group in stolzite [86].

f) Microwave-hydrothermal method

J.C. Sczancoski et al. (2009) synthesized growth process and photoluminescence properties of $SrWO_4$ powders. $SrWO_4$ powders were synthesized by the co-precipitation method and processed at 140 °C for different times in a microwave-hydrothermal system. XRD patterns revealed that these powders crystallize in a scheelite-type tetragonal structure with space group I41/$_a$. The small deviations in the lattice parameter values were associated with the effect of microwave radiation. MR and FTIR spectra showed characteristic modes of these powders. XRD patterns and MR spectra indicated that independent of the processing time in a microwave-hydrothermal system, $SrWO_4$ powders are ordered at long and short- range. FEG-SEM micrographs showed that the processing time is an important factor in the growth mechanism of $SrWO_4$ powders. These micrographs also indicated that the PEG is a surfactant that favors the growth of $SrWO_4$ micro-octahedrons along the [001] direction. A possible growth mechanism for the formation of $SrWO_4$ micro-octahedrons was proposed. UV–vis absorption spectra showed different optical band gap values, which were associated with the presence of intermediary energy levels within the band gap. PL behavior was explained through distortions on the $[WO_4]^{2-}$ tetrahedron groups by the microwave radiation [87].

g) Electrospinning method

Z. Hou et al. (2009) synthesized $CaWO_4$ and $CaWO_4$:Tb^{3+} by electrospinning technique in conjunction with sol-gel process. After annealing the precursors at high temperature at 700 ^{o}C, the as-prepared samples are well crystallized with the scheelite structure of $CaWO_4$. These $CaWO_4$ and $CaWO_4$:Tb^{3+} samples with wire and tube morphologies compose of nanoparticles with the diameters around 70 nm, 120 nm and 150 nm, respectively. Due to an efficient energy transfer from the group to Tb^{3+} ions, Tb^{3+} ions show its characteristic strong emissions in the $CaWO_4$:Tb^{3+} 1D nanomaterials upon excitation into the group at 249 nm. Under low-voltage electron beam excitation, $CaWO_4$ and $CaWO_4$:Tb^{3+} phosphors show blue (416 nm) and green

(545 nm) emission, nanotube samples have a higher CL intensity than the nanowire samples due to lower defect concentration in the former [88].

h) Co-precipitation method

T. Thongtem et al. (2010) synthesized alkaline earth metal molybdates and tungstates (M= Ca and Sr) nanoparticles were successfully synthesized by the co precipitation process. It is a simple method, low energy consumption and friendly to the environment. XRD and SAED patterns show that all products are body-centered tetragonal scheelite structure. Their vibrations were studied by Raman and FTIR spectroscopy, of which the results are in accordance with the XRD and SAED analyses. TEM revealed the morphologies of the products which show the nanosized particles with narrow normal distributions. The direct allowed energy gaps of $CaMoO_4$, $SrMoO_4$, $CaWO_4$ and $SrWO_4$, determined using Wood and Tauc method, are 5.07, 3.72, 5.40, and 4.47 eV, respectively [89].

J.C. Sczancoski et al. (2008) synthesized $SrMoO_4$ by the co-precipitation method and processed in a domestic microwave-hydrothermal. XRD patterns and FT-Raman analyses revealed that obtained powders after microwave-hydrothermal processing are free of secondary phases and exhibit a single tetragonal structure. Ultraviolet–visible absorption spectroscopy revealed a characteristic optical band gap of 3.98 eV, which is associated with the difference of energy between the valence band and conduction band. Intense PL at room temperature was verified at 540 nm (green emission) under the excitation of 488 nm, which can be associated with the transitions in the tetrahedral $[MoO_4]^{2-}$ group or surface defects [27].

i) Spray pyrolysis method

Z. Lou et al. (2002) synthesized thin films of $CaWO_4$ and $SrWO_4$ prepared on glass by spray pyrolysis exhibited identical blue and blue-green emissions at 447 and 487 nm. The growth of crystalline films with the scheelite structure required either substrate or annealing temperature greater than 300 ^oC. The PL emission intensity increased with increased annealing temperature, and the highest luminance and efficiency were obtained for the $CaWO_4$ film by rapid thermal annealing at 900 ^oC. The luminance and efficiency for $CaWO_4$ film were 150 cd/m^2 and 0.7 lm/W, respectively, at 5 kV and 57 μA/cm^2. Changing oxygen vacancy concentration of the films by annealing in argon and oxygen or by doping with Ag^+ and La^{3+} did not greatly affect the blue-green emission intensity, indicating that the blue-green emission, like the blue one, came from transitions within the WO_4^{2-} groups [90].