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S.No	TITLE OF THE PAPER	NAME OF THE AUTHOR	DEPT OF THE AUTHOR	JOURNAL NAME	ISSN NO	I.F
1	Improved classification accuracy for diagnosing early stage of Parkinson's disease using 3D SPECT images	Dr. S. Anita	ECE	Romanian journal of information science and technology	1453-8245	1.10
2	Synthesis and luminescence properties of Ca $Gd_2(MoO_4)_4$:Ln^{3+} (Ln = Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+}) phosphors	Dr. A. John peter	S&H (Physics)	Journal of Luminescence	0022-2313	3.599
3	Sol-gel synthesis and luminescence properties of $CaGd_2(MoO_4)_4$:Pr^{3+} phosphors with white LED applications	Dr. A. John peter	S&H (Physics)	Journal of Materials Science: Materials in Electronics	1573-482X	2.478
4	Synthesis and characterization of copper(II) dithiocarbamate complexes involving pyrrole and ferrocenyl moieties and their utility for sensing anions and preparation of copper sulfide and copper-iron sulfide nanoparticles	Dr. G. Gurumoorthy	S&H (Chemistry)	Applied Organometallic Chemistry	1099-0739	4.072
5	Synthesis and luminescence properties of $LiGd_3(MoO_4)_5$: Eu^{3+}, phosphors for white LED application	Dr. A. John peter	S&H (Physics)	Journal of Materials Science: Materials in Electronics	1573-482X	2.478
6	Three Dimensional Analysis of SPECT Images for Diagnosing Early Parkinson's Disease Using Radial Basis Function Kernel-Extreme Learning Machine	Dr. S. Anita	ECE	Current Medical Imaging Reviews	1573-4056	1.24
7	Synthesis and luminescent and Energy Transfer in Tb^{3+} and Eu^{3+} co-doped $Li_3Ba_2Gd_3(MoO_4)_8$ phosphors for W-LED's	Dr. A. John peter	S&H (Physics)	Journal of Material Science in Material Electronics	0957-4522	2.01
8	Hydrothermal synthesis, characterization and luminescence properties of $CaGd_2(MoO_4)_4$: Eu^{3+} ovoid like structures	Dr. A. John peter	S&H (Physics)	New journal of chemistry	1144-0546	3.591

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Improved classification accuracy for diagnosing early stage of parkinsons disease using 3D SPECT images

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Abstract. Early diagnosis of the neurodegenerative disorder called Parkinson's disease (PD) and that from the non-degenerative variant which is known as Scan Without Evidence of Dopaminergic Deficit (SWEDD) are essential for effective patient management in neuro disorders, as both have the same clinical characteristics. The present work intends to propose an efficient method for 3D Single-Photon Emission Computed Tomography (SPECT) images using the Alpha-stable distribution based intensity normalization techniques for discriminating early PD from Healthy Control (HC) or SWEDD. The 3D SPECT images of PD, HC or SWEDD are taken from the international Parkinson's Progression Markers Initiative (PPMI) database. The alpha-stable distribution technique is applied to normalize the intensity values outside the striatum. The shape and surface fitting features are extracted from the 3D SPECT images of the three groups and found to be a promising method in the diagnostic process. The Genetic Algorithm (GA) is employed to compute the optimum feature set based on its consistency. The computed optimum features of 3D SPECT images have brought about a remarkable performance in diagnosing the early stage of Parkinson's disease. The Radial Basis Function-Extreme learning machine (RBF- ELM) classifier confirms the best performance accuracy of 99.1%. The use of performance measures has ensured the validity of the experiments. The proposed method is advantageous to the neurologist in the early diagnostic process of Parkinson's disease.

Keywords: Early Parkinsons disease; Scan without Evidence of Dopaminergic Deficit; Alpha- stable distribution based intensity normalization; shape and surface fitting; RBF-ELM.

Synthesis and luminescence properties of $CaGd_2(MoO_4)_4$:Ln^{3+} (Ln= Eu^{3+}, Tb^{3+} , Dy^{3+} and Sm^{3+}) phosphors

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Abstract

The uniform monodisperse rectangular-like rare-earth-activated $CaGd_2(MoO_4)_4$:Ln^{3+} (Ln= Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+}) phosphors have been synthesized by conventional solid state reaction method. The prepared phosphors were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM) and photoluminescence (PL) spectroscopy measurements. The XRD and FTIR results showed a scheelite-type tetragonal structure for the prepared powder samples. FTIR spectra exhibited a high absorption band situated at around 846 cm^{-1}, which was ascribed to the Mo–O antisymmetric stretching vibrations into the $[MoO_4]^{2-}$ tetrahedron groups and the SEM image reveals particle size in the range of 120 – 160 nm. The excitation/emission spectra and life times were measured to characterize the luminescent properties of the phosphors. All properties show that $CaGd_2(MoO_4)_4$:Ln^{3+} (Ln= Eu^{3+}, Tb^{3+},Dy^{3+} and Sm^{3+}) compounds are a very appropriate red, green, yellow and orange-red emitting light–emitting phosphors promising for lighting applications.

Keywords: Solid state reaction, molybdate, photoluminescence, phosphors

1. Introduction

Because trivalent rare earth ions possess a profusion of energy levels and electron transfer are possible between 4f levels, its fluorescence wavelengths are possible from UV to IR range. Consequently, the overture of rare earth ions as luminescent center to matrices is well thought-out as an first-rate method for synthesizing better-quality luminescent material [1–3]. Very recently, $CaGd_2(MoO_4)_4$, a member of scheelite type ($CaMoO_4$) family, has been investigated

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Sol–gel synthesis and luminescence properties of $CaGd_2(MoO_4)_4:Pr^{3+}$ phosphors for white LED applications

Saravana Kumar Jaganathan[1,2,3] · Anthuvan John Peter[4]

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Abstract
A series of novel red emitting $CaGd_2(MoO_4)_4:xPr^{3+}$ (x = 0.005–0.045) micro phosphors were successfully prepared via a simple citrate assisted sol–gel method-ray powder diffraction, scanning electron microscope, photoluminescence spectra and decay life time measurement were utilized to study the properties of $CaGd_2(MoO_4)_4:xPr^{3+}$ phosphors well crystallized, fine and homogenous micro particles appeared at the heat treatment at 900 °C for 6 h. The results confirms that $CaGd_2(MoO_4)_4$ host has tetragonally distorted scheelite structure with space group $I4_{1/a}$. Under the excitation wavelength of 449 nm Pr^{3+} activated $CaGd_2(MoO_4)_4$ phosphor shows the red emission peaked at about 649 nm, which is attributed to $^3P_0$–$^3F_2$ transition of Pr^{3+} ions. The CIE co-ordinates of $CaGd_2(MoO_4)_4:0.035Pr^{3+}$ phosphor are x = 0.702 and y = 0.289, which are evidently close to the standard NSTC value. The luminescence properties of as prepared phosphors indicates that $CaGd_2(MoO_4)_4:xPr^{3+}$ phosphor may be a potential red emitting material for W-LED applications.

1 Introduction

In recent times, the design and synthesis of new materials for white light-emitting diodes (LEDs), as a next generation of solid state light source, continues to be a major focus of solid state chemists [1, 2] that has potential advantages of energy saving nature, high efficiency, long life time,pleasant color and high reliability [3]. At present, there are many methods involved in the fabrication of W-LED's. The most convenient approach is by combining red and green emitting phosphors on the surface of blue LED chip so called phosphor converted (pc) W-LED's. It is apparent that the luminescent behaviors of the coated phosphors strongly plays a vital role in the properties of this type of W-LED's. In comparison with the green phosphors, the red emitting phosphor exhibit lower luminescence efficiency, lower color rendering index and not as good as thermal stability [4]. Hence, it is essential to develop an efficient and stable red phosphor material to improve the performance of W-LED's. In recent times, Pr^{3+} remains an interesting luminescent ion due to good color saturation and luminous efficacy (LER) [5]. Pr^{3+} ions has an excitation band at 449 nm, due to the $^3H_4$–$^3P_2$, which matches well with emission of blue LEDs and has the emission due to the inherent transition of $^3P_0$–$^3F_2$ centered at the red light of about 646 nm [6, 7].

Guan et al. [8] and his co workers reported the concentration effect on the photoluminescence of the praseodymium Pr^{3+} ion for $BaGd_2(MoO_4)_4$ crystals. Concentration quenching were categorized into three broad ways. The first type (Type A) exhibit the maximum PL intensity at about 10 mol% with a non-zero intensity at high concentrations, which is observed for the $^3P_0$ emissions. The second and third types (Type B-1 and B-2) have the maximum at about 1 mol% with a finite residual intensity and nearly zero intensity at high concentrations, respectively, which are observed for the 621 nm emission and all the $^1D_2$ emissions. It is suggested that the energy migration mechanism is responsible for Type A, while the non-resonant cross-relaxation is responsible for Type B-1 and the resonant cross-relaxation for Type B-2. Recently, Durairajan et al. [9] investigated

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FULL PAPER

Synthesis and characterization of copper(II) dithiocarbamate complexes involving pyrrole and ferrocenyl moieties and their utility for sensing anions and preparation of copper sulfide and copper–iron sulfide nanoparticles

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Bis(*N*-(pyrrol-2-ylmethyl)-*N*-butyldithiocarbamato-*S*,*S*′)copper(II) (**1**), bis(*N*-(pyrrol-2-ylmethyl)-*N*-(2-phenylethyl)dithiocarbamato-*S*,*S*′)copper(II) (**2**), bis(*N*-methylferrocenyl-*N*-(2-phenylethyl)dithiocarbamato-*S*,*S*′)copper(II) (**3**) and bis(*N*-furfuryl-*N*-methylferrocenyldithiocarbamato-*S*,*S*′)copper(II) (**4**) were prepared and characterized using elemental analysis and infrared and UV–visible spectroscopies. X-ray diffraction (XRD) studies on **3** show that each copper centre adopts the square planar geometry by the coordination of four sulfur atoms of the metalloligand *N*-methylferrocenyl-*N*-(2-phenylethyl) dithiocarbamate. The Cu—S distances are symmetrical and are in the range 2.293–2.305 Å. The supramolecular architecture in complex **3** is sustained in the solid state by C—H···π, C—H···S, Fe···Fe and H···H interactions. Density functional theory calculations were carried out for **3**. Anion (F^-, Cl^-, Br^- and I^-) binding studies with complex **1** were performed using cyclic voltammetry. Copper sulfide, copper–iron sulfide-**1** and copper–iron sulfide-**2** nanoparticles were prepared from complexes **2**, **3** and **4**, respectively, and they were characterized using powder XRD, transmission electron microscopy (TEM) and energy-dispersive X-ray, UV–visible, photoluminescence and infrared spectroscopies. TEM images of copper–iron sulfide-**1** and copper–iron sulfide-**2** reveal that the particles are spherical and oval shaped, respectively. Photocatalytic activities of as-prepared nanoparticles were studied by decolourization of methylene blue and rhodamine-B under UV light. It was found that copper–iron sulfide degrades methylene blue and rhodamine-B much better than does copper sulfide.

KEYWORDS
anion sensing, copper sulfide, copper(II) dithiocarbamates, copper–iron sulfide, photodegradation

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Synthesis and luminescence properties of $LiGd_3(MoO_4)_5:Eu^{3+}$ phosphors for white LED applications

Saravana Kumar Jaganathan[1,2,3] · Anthuvan John Peter[4] · Venkatakrishnan Mahalingam[5] · Rajagopalan Krishnan[6]

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Abstract
Eu^{3+} activated $LiGd_3(MoO_4)_5$ phosphors were synthesized proficiently by simple sol gel method. Structural, morphological and luminescence characteristics of the phosphors were investigated in detail. The photo physical parameters and quantum efficiency values are studied by using Judd–Ofelt concepts. All the outcomes imply that $LiGd_3(MoO_4)_5:0.07Eu^{3+}$ phosphor may be a meritful candidate as red emitting component for white light emitting diodes applications.

1 Introduction

On the grounds of their superior advantages, as environmental friendliness, greater efficiencies, very less power consumption, high brightness and stability, white light emitting diodes (W-LEDs) have been considered as future generation of solid state lighting (SSL) sources for various applications such as mobile devices, vehicles, traffic signals and display devices. Many approaches to prepare the W-LEDs have been investigated [1–3]. Conventionally, by combining blue LED chip with yellow phosphor (cerium doped yttrium aluminium garnet) white light is generated, which exhibits low color rendering index (<65) due to deficiency of red emitting element in the emission color [4, 5]. Inspite of these drawbacks, in recent times near-ultraviolet (n-UV) LED chips blended with red ($Y_2O_2S:Eu^{3+}$) [6], green ($ZnS:Cu^+$, Al^{3+}) [7] and blue ($NaMgAl_{10}O_{17}:Eu^{3+}$) [8] phosphors based W-LEDs have gained major research focus. However, while having comparison with green and blue emitting phosphors, the commercial red emitting phosphors exhibit very less stability and luminescent efficiency. Hence enormous intentions have been steadfast to search for novel red phosphors that show good physio-chemical stability and efficiency to enhance the performance of near UV chip based W-LEDs. In recent times, europium (Eu^{3+}) activated molybdates having scheelite structure based phosphors have attracted much research interest as fluorescent material applications due to their high physio-chemical stability, high quantum efficiency and low preparation temperature [9]. Very recently, the molybdate $LiGd_3(MoO_4)_5:Eu^{3+}$ phosphor synthesized by solid state reaction route have been studied for uses in SSL devices [10]. $LiGd_3(MoO_4)_5$ was first investigated by Pandey and reported that $LiGd_3(MoO_4)_5$ exhibits a scheelite structure (space group $I4_{1/a}$) having the general formula $Li_{0.2}Gd_{0.6}\square_{0.2}MoO_4$ (□-vacancy) and isostructural to $CaWO_4$ (scheelite) [11, 12]. In the present work, Eu^{3+} activated $LiGd_3(MoO_4)_5$ phosphors were synthesized by sol gel method. The photoluminescence behavior and photophysical parameters of the as prepared phosphors were investigated in detail.

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RESEARCH ARTICLE

Three Dimensional Analysis of SPECT Images for Diagnosing Early Parkinson's Disease Using Radial Basis Function Kernel- Extreme Learning Machine

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Abstract: ***Background:*** Parkinson's Disease (PD) is caused by the deficiency of dopamine, the neurotransmitter that has an effect on specific uptake region of the substantia nigra. Identification of PD is quite tough at an early stage.

Methods: The present work proposes an expert system for three dimensional Single-Photon Emission Computed Tomography (SPECT) image to diagnose the early PD. The transaxial image slices are selected on the basis of their high specific uptake region. The processing techniques like preprocessing, segmentation and feature extraction are implemented to extract the quantification parameters like Intensity, correlation, entropy, skewness and kurtosis of the images. The Support Vector Machine (SVM) and Extreme Learning Machine (ELM) classifiers using Radial Basis Function kernel (RBF) are implemented and their results are compared in order to achieve better performance of the system. The performance of the system is evaluated in terms of sensitivity, specificity analysis, accuracy, ROC (receiver operating curve) and AUC (area under the curve).

Results: It is found that RBF-ELM provides high accuracy of 98.2% in diagnosing early PD. In addition, the similarity among the features is found out using K-means clustering algorithm to compute the threshold level for early PD. The computed threshold level is validated using Analysis of Variance (ANOVA).

Conclusion: The proposed system has a great potential to assist the clinicians in the early diagnosis process of PD.

Keywords: Early Parkinson's disease, three dimensional SPECT images, ELM, K means clustering.

1. INTRODUCTION

Parkinson's disease is said to be the second movement disorder, next to Alzheimer, which disturbs neurons in the human brain. This is caused by the neurons which fail to produce or produce less amount of dopamine- a chemical mediator (neurotransmitter) which is generated by the neurons in the human brain, which in turn leads to PD in the human mid brain [1-3]. The PD is characterized by the symptoms of impairment of movement with tremor, gait problem, slowness, stiffness, or balance problems and impairment of posture in an advanced stage. The diagnosis of PD is easy when the disease is in advanced stage. However, at an early stage, an accurate diagnosis is quite tough [4]. Hence, the early stage of PD demands the formulation of diagnostic techniques [5, 6].

Imaging of [123I] FP-CIT SPECT is the most sensitive imaging techniques for diagnosing PD at an early stage. The SPECT image locates the reduced number of specific uptake or Dopamine Transporters (DAT) in PD patients very clearly [7]. Thus, SPECT imaging technique is a valuable research tool in nuclear medicine. It also increases diagnostic accuracy for discriminating PD from Healthy Control (HC) [8, 9]. The SPECT image is obtained from the international database called Parkinson's Progression Markers Initiative (PPMI).

The GE healthcare report says that HC scan has bilateral, distinct specific uptake and two comma shaped focal regions that are symmetric; whereas PD scan has reduced specific uptake in both right and left striatum and has two circular or oval focal areas [10]. Hence, understanding the shape of the specific uptake assists neurologists to diagnose PD. In the earlier times, the visual inspection was carried out for assessing the shape of the SPECT images. The neurospecialists classify normal SPECT and abnormal SPECT image based on the appearance of the Region of Interest (ROI) and intensity of specific uptake region of both caudate and putamen in striatum. But, in the later period, the quantification of specific uptake is done through manually defined ROIs using stereotactic atlas. Moreover, visual analyses heavily depend on judgment and knowledge of the experts [11]. Hence, these may lead to unexpected threat to human

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Synthesis, luminescent properties and energy transfer in Tb^{3+} and Eu^{3+} co-doped $Li_3Ba_2Gd_3(MoO_4)_8$ phosphors for W-LED's

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Abstract For the first time, single phase monoclinic $Li_3Ba_2Gd_3(MoO_4)_8$: 0.08 Tb^{3+},yEu^{3+} (0, 0.005, 0.02, 0.04, 0.06, 0.08 and 0.10 mol) nano phosphors were prepared by the simple mechanochemically assisted direct solid state reaction method at room temperature. Their crystal structures, luminescence properties, energy transfer mechanism and life time were studied in detail. At the excitation wavelength of 378 nm, the emission spectra of $Li_3Ba_2Gd_3(MoO_4)_8$: 0.08 Tb^{3+},yEu^{3+} (0, 0.005, 0.02, 0.04, 0.06, 0.08 and 0.10 mol) phosphors exhibit the characteristic emissions of Tb^{3+} and Eu^{3+} ions at around 545, 594 and 615 nm due to energy transfer from Tb^{3+} ions to Eu^{3+} ions. It is confirmed from the results that electric dipole–dipole interaction phenomena is the main cause for having energy transfer from Tb^{3+} to Eu^{3+} ions in $Li_3Ba_2Gd_3(MoO_4)_8$ host. The CIE coordinates of the prepared nano phosphors illustrate that by changing the ratio of Eu^{3+} ions the white light emission can be realized from $Li_3Ba_2Gd_3(MoO_4)_8$ phosphor and it coexist very close to an ideal white chromaticity coordinates (0.33, 0.33). All properties show that $Li_3Ba_2Gd_3(MoO_4)_8$: 0.08 Tb^{3+}, 0.005 Eu^{3+} nano phosphor is a promising material for single-phase phosphor based white light emitting diodes.

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1 Introduction

Nowadays, the phosphor based white light-emitting diodes (WLEDs) are well thought-out as next age bracket of solid state lighting owing to their environmental friendliness, stability, extensive lifetimes, consistency, and low power consumption [1–5]. In broad-spectrum, there are a range of methods to pile up the white LEDs. A usual way is to mix up a blue emitting LED in the midst of a yellow-emitting phosphor, as $Y_3Al_5O_{12}$: Ce^{3+} [6]. In view of the fact that, this route is about easy, the device has been used for commercial purpose applications. On the other hand, the white light produced by this route has feeble CRI due to the color deficiency occurs in the red and green region of the spectrum. On the road to get the better of its shortcomings, the arrangement of near-ultraviolet (n-UV) LEDs emitting at 370–410 nm with a red Y_2O_2S: Eu^{3+}, green ZnS: Cu^+, Al^{3+}, and blue ZnS: Ag^+ phosphor combination has been demonstrated [7]. This type of white LED can pay for first-rate color homogeny and a sky-scraping color-rendering index. However, for the present tri color commercially available phosphor mixtures, the well-built re-absorption and nonuniformity of luminescence problems stay alive, this outcome en route for the failure of luminescence efficiency, properties, and tricolor emitting points. In recent times, it is demonstrated that judge against among phosphor mixtures, a single-phased white light emitting phosphor with UV/NUV chips has more advantages and prevail over the

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ARTICLE

Hydrothermal synthesis, characterization and luminescence properties of $CaGd_2(MoO_4)_4$: Eu^{3+} ovoid like structures

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Tetragonal phase $CaGd_2(MoO_4)_4$:Eu^{3+} with ovoid like hierarchical structures are prepared via employing ethylene diamine tetra acetic acid (EDTA) using hydrothermal route at 200°C for 24 h. X-ray diffraction patterns and Field emission scanning microscope images were used to characterize the crystal structure, phase, morphology and size of the nano samples. X-ray photo electron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (Edax) confirmed the presence elements in phosphor samples. The PL properties of the phosphors were studied thoroughly. The photophysical properties of the samples were examined by Judd-Ofelt theory. The CIE coordinates of the prepared phosphor samples illustrate that red light emission can be realized from $CaGd_2(MoO_4)_4$: Eu^{3+} phosphor and it coexist very close to NTSC standard values. All these results show that ovoid like $CaGd_2(MoO_4)_4$: Eu^{3+} micro/nano phosphor is a promising material for display applications.

1. Introduction

Superior-controlled synthesis of self-aggregated three-dimensional (3D) hierarchical micro/nanostructures with uniform size distribution and structure is at a standstill demanding, and it is of much concern to the research community. Extremely homogeneous self-assembled three-dimensional (3D) micro/nanostructures have created a center of attention worldwide because of their prospective applications in high-performance display device, opto-electronics, biological, waste water treatment and photo catalyst applications derived from their novel electronic and optical properties.[1-4] The most suitable and promising approach to fabricate self-aggregated 3D architectures is to make use of a solution phase route which is a simple way to organize and influence the physical and chemical properties of materials.[5] In this regard, various shapes of 3D micro- and nano-structures have been synthesized and investigated through a number of wet chemistry-based techniques, including hydrothermal,[6] solvothermal,[7,8] microwave synthesis,[9] the Pechini process,[10,11] co-precipitation,[12] molten salt synthesis,[13] template-assisted methods.[14] Among these techniques, the hydrothermal method is a promising alternative technique for the large- area production of 3D hierarchical micro/nanostructures under feasible environments.[15] Recently, Lin et al prepared mono-disperse flower-like $NaY(MoO_4)_2$ architectures by hydrothermal route using polyvinylpyrrolidone (PVP) as the surfactant.[16] Li et al reported $NaLa(MoO_4)_2$ spindle- and flower-like architectures using the hydrothermal method.[17] Dumbbell-like orthorhombic $Gd_2(MoO_4)_3$:Eu^{3+} nanostructures[18] almond-like $(Na_{0.5}La_{0.5})MoO_4$, and bipyramid- like $(Na_{0.5}Gd_{0.5})MoO_4$ micro/- and nanostructures have all been demonstrated.[19] Zhang et al. synthesized pancake- like $Fe_2(MoO_4)_3$ microstructures by a rapid microwave- assisted hydrothermal method.[20] Huang et al reported 3D bowknot-like $Y_2(WO_4)_3$:Ln^{3+} hierarchical microstructures that were synthesized by a hydrothermal method.[21] Xu et al. successfully synthesized tetragonal $NaEu(MoO_4)_2$ with self-assembled rugby-like microstructures using a hydrothermal route.[22] Self-assembled flower-like $NaCe(MoO_4)_2$ architectures have been synthesized using a hydrothermal approach.[23] Chrysanthemum-flower like $Gd_2O(CO_3)_2.H_2O$ structures have been prepared by a modified urea-based homogeneous precipitation via a template free hydrothermal synthesis.[24] Among many parameters in hydro thermal process, the mixing of surfactants and reaction time parameters are key tools in regulating the formation of nuclei, the growth rate and oriented aggregation mechanism. The particle–particle interaction by steric effects is minimized by selecting suitable surfactant or chelating agent to afford a spacious class of nanostructures in the midst of proper size and structure by adsorbing the metal cations into the center and forming a complex molecule thereby greatly mobilizing the metal cations.[25]

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