



# Composition and Fluorescence of Gadolinium (III) Acetylacetonate Derivatives by Solvothermal Method

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## Abstract

Gadolinium (III) acetylacetonate was treated by solvothermal method to produce gadolinium complexes with acetylacetonate and -OH groups. The composition, fluorescence, and magnetic properties of the products were studied in detail. The fluorescence showed the products possessed higher energy emission and excitation fluorescence compared to Gadolinium (III) acetylacetonate. Also the product produced at 160 °C possessed higher fluorescent intensity and responding ability toward external magnetic field. So the products were hydrophobic materials with magnetic and fluorescent properties.

## Keywords

Gadolinium (III) acetylacetonate derivatives, Solvothermal method, Luminescence

## Introduction

Generally, rare earth complexes have many potential applications in novel lighting devices, optical fibers and luminescent sensors benefiting from their long emission lifetime, narrow bandwidth and large Stokes shift in visible and near-infrared regions under Ultraviolet (UV) excitation [1-3]. The luminescence intensity of rare earth complexes related to the absorption efficiency of ligands, which is dependent on the ligand molecule with large  $\pi$ -conjugated system. Good solubility of substituted rare earth  $\beta$ -diketonate complexes in common organic solvents highly enhances their applications in the solution processable organic semiconductors and also provides more efficient approach to fabricate OLED devices by solution techniques [4,5]. So the fluorescence of some rare earth  $\beta$ -diketonate complexes were studied and modified to widen their application [6,7]. But preparation of multifunctional materials, such as materials with

fluorescence and magnetic properties, by simple method is the project of researchers [8,9].

Thermal decomposition of metal acetylacetonates has recently attracted much attention to fabricate thin films and nanoparticles of metals, metal alloys and metal oxides for microelectronic, catalytic and biomedical applications [10-13]. Colloidal cubic  $Gd_2O_3$  nanorings and nanoplates were selectively prepared from low-temperature (90 °C) hydrolysis of  $Gd-(AcAc)_3$  and subsequent in situ thermal dehydration of the hydrolyzed precursor-surfactant aggregates at 320 °C [14]. But seldom reports focus on the partial decomposed samples as which is preferred possessing solubility in organic solvent and changed fluorescence compared to rare earth acetylacetonate.

In the present work Gadolinium (III) acetylacetonate hydrate was treated by solvothermal method in absolute diphenyl ether which is a water lack system where the hydrolysis of acetylacetonate is limited. The products

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were preferred possessing solubility in organic solvent and changed fluorescence compared to rare earth acetylacetonate as well as magnetic properties. So different kinds of Gadolinium (III) acetylacetonate derivatives were produced. The composition, fluorescence and magnetic properties were studied in detail. Under appropriate preparation conditions, Gadolinium (III) acetylacetonate derivatives with higher fluorescent intensity and magnetic properties were produced.

## Experimental

### Materials

The raw material for synthesis of Gadolinium (III) acetylacetonate derivatives was gadolinium acetylacetonate trihydrate ( $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ , MW = 508.62 g/mol), which was purchased from Beijing HWRK Chemical Co., Ltd.. Diphenyl ether was applied by Sinopharm Chemical Reagent Beijing Co., Ltd. Other solvents were from Beijing Chemical factory.

### Preparation of Gadolinium (III) acetylacetonate derivatives

In a typical synthesis for the derivatives of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ , 1.5787 g (0.003 mol) of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  was dispersed into 10.5 mL of absolute diphenyl ether to form a solution under magnetic stirring, which was poured into 25 ml teflon-lined autoclave and heated at

different temperature for 2.0 h. After that the autoclave was cooled to room temperature, the as-obtained yellow suspension was mixed with an equal volume of acetone, and the formed precipitate was separated by centrifugation and washed with acetone. The final samples were assigned as Gd-S-T, where T indicated the formed temperature by solvothermal. Gd-S-160 was grounded and calcinated at 450 °C for 10 h in air to give Gd-C-160. Afterwards, Gd-C-160 was furnace-cooled to room temperature, and grounded again into powder for measurement.

### Characterization

Thermal Gravimetric Analysis (TGA) was measured on Perkin-Elmer TGA 7 with a heating rate of 20 °C/min ranging from 45 °C to 800 °C in air, on the same time a NETZSCH STA 449F3 Thermo Gravimetric Analyser was coupled, using a heated capillary at 190 °C, to a QMS 403 Mass Spectrometer (TGA-Ms) to identify the released gases during the thermal degradation of a material. The Fourier Transform Infrared Spectra (FTIR) of the solid samples was obtained with a Perkin Elmer Spectrum 100 FT-IR spectrometer. KBr pellet was used as background. The structure of the products was studied by powder X-ray diffraction (Rigaku D/max-rA) equipped with  $\text{Cu K}\alpha$  ( $\lambda = 0.1542$  nm) radiation at 40 kV and 30 mA. The surface morphology and the elemental distribution of the samples were probed with Scanning

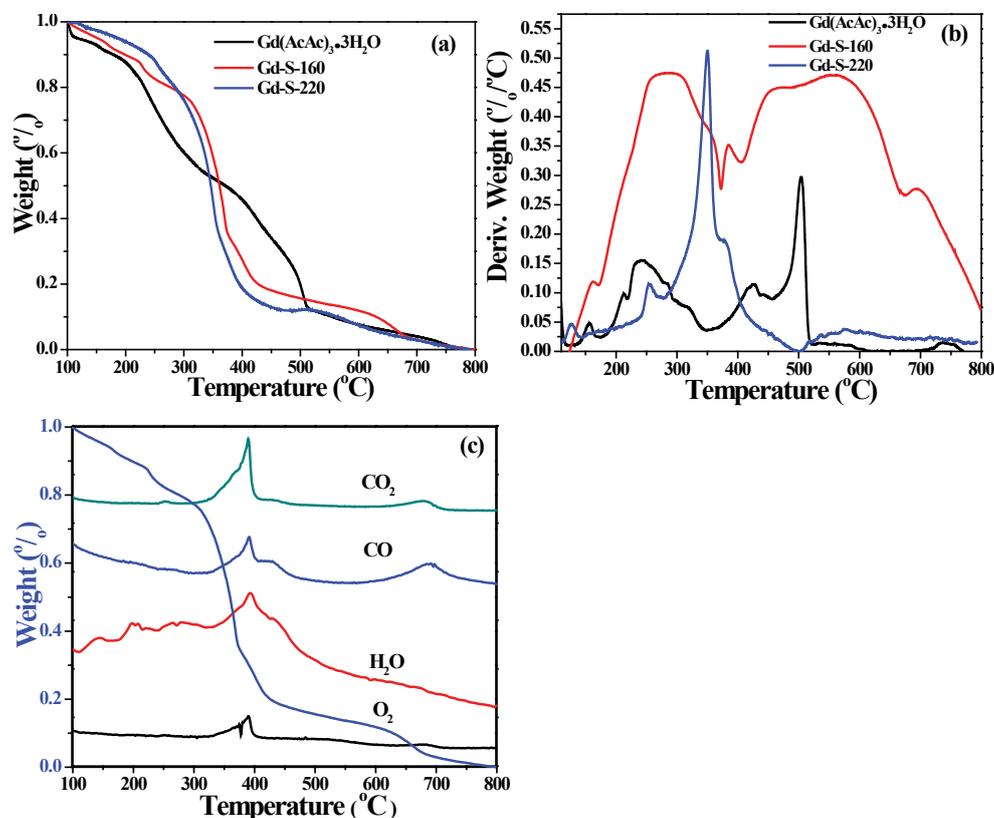


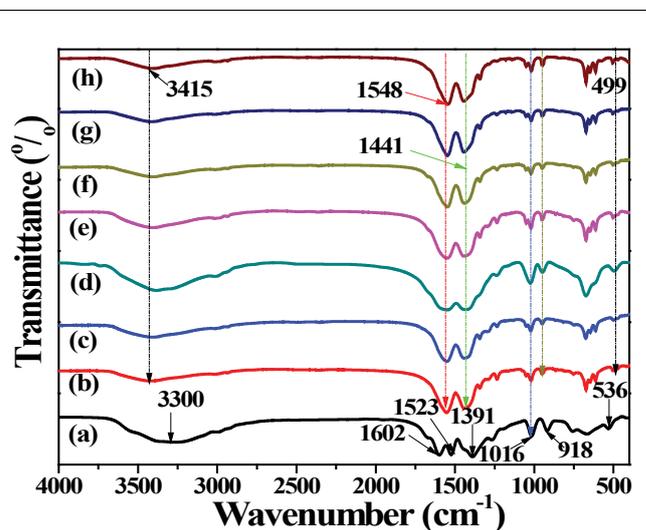
Figure 1: TGA (a) and DTA (b) curves of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ , Gd-S-160, and Gd-S-220, TGA-Ms of Gd-S-160 (c).

Electron Microscope (SEM, HITACHI S-4300) operated at an acceleration voltage of 5 kV. The zeta potential and size distribution of the hybrid particles were measured on Malvern Instruments Zetasizer Nano-ZS90. The Ultraviolet-Visible (UV-vis) spectra were measured with UV6100 double beam spectrophotometer. Room temperature excitation and emission spectra were characterized by F97 spectrofluorometer (Shanghai Lengguang Technology Co., China) with a 150 W Xe lamp as the excitation source. The temperature-dependent luminescence properties were measured on the fluorescence spectrophotometer (F-4600, HITACHI, Japan), which was equipped with a self-made heating attachment and a computer controlled electric furnace. The luminescence decay curve was obtained from a spectrofluorometer (HORIBA, JOBIN YVON FL3-21) with a 335 nm pulse laser radiation (nano-LED) as the excitation source, and the pulse width of the laser was 12 ns.

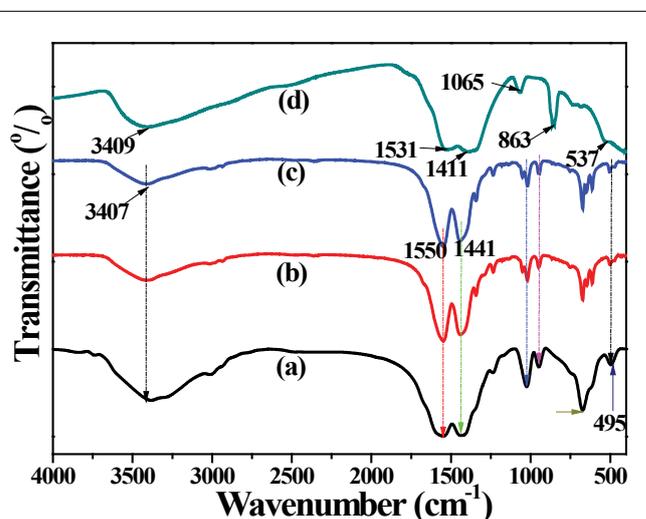
## Results and Discussion

To prepare derivatives of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  by solvothermal method, TGA together with Differential Thermal Analysis (DTA) were performed to determine the decomposition temperature of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ . As shown in Figure 1a, the weight losses for all the samples below 150 °C are assigned to the departure of adsorbed water and complexed water with gadolinium [15].  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  exhibits complicated decomposition behavior due to more ligands in it. It shows one little and two broad DTA peaks with shoulders between 190-350 °C and 350-500 °C (Figure 1b). So it is preferred,  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  derivatives may form around 200 °C where  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  decomposes partially.

Figure 2 shows the FT-IR spectra of the products prepared at around 200 °C. In the spectrum of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  (Figure 2a), the peak at 1602  $\text{cm}^{-1}$  is associated with the enol-keto tautomers of the  $\beta$ -diketone corresponding to the C = O stretching vibration of keto. The peak at 1523  $\text{cm}^{-1}$  is the C = C stretching vibration of enol. The peaks at 1391  $\text{cm}^{-1}$  and 1016  $\text{cm}^{-1}$  are the vibrations of  $-\text{CH}_3$  [15,16]. The wide band at about 3300  $\text{cm}^{-1}$  is the vibration of crystallized water of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ . The peak at 536  $\text{cm}^{-1}$  is the vibration of a Gd-O stretching absorption. While for the solvothermal samples (Figure 2b-2h), the still appearing peak at 1016  $\text{cm}^{-1}$  relating to the vibration of  $-\text{CH}_3$  confirms that some acetylacetonate groups are still in the final samples although the solvothermal temperature is up to 260 °C (Figure 2h). The peaks at 1548 and 1441  $\text{cm}^{-1}$  are the C = O and C = C stretching vibration of  $\beta$ -diketone which left shift due to the substitution of one or two acetylacetonate groups by OH in the solvothermal process [16]. The peak at 495  $\text{cm}^{-1}$  is the vibration of Gd-O-Gd. The broad peak at  $\sim 3415 \text{ cm}^{-1}$  is considered as structural hydroxyl groups



**Figure 2:** FT-IR spectra of a)  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ ; b) Gd-S-140; c) Gd-S-160; d) Gd-S-180; e) Gd-S-200; f) Gd-S-220; g) Gd-S-240 and h) Ga-S-260 prepared in 2 h.

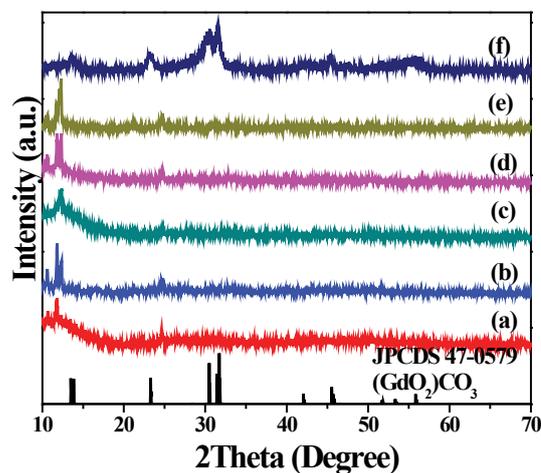


**Figure 3:** FT-IR spectra of Gd-S-160 prepared in a) 2; b) 4; c) 12 h and d) Gd-C-160.

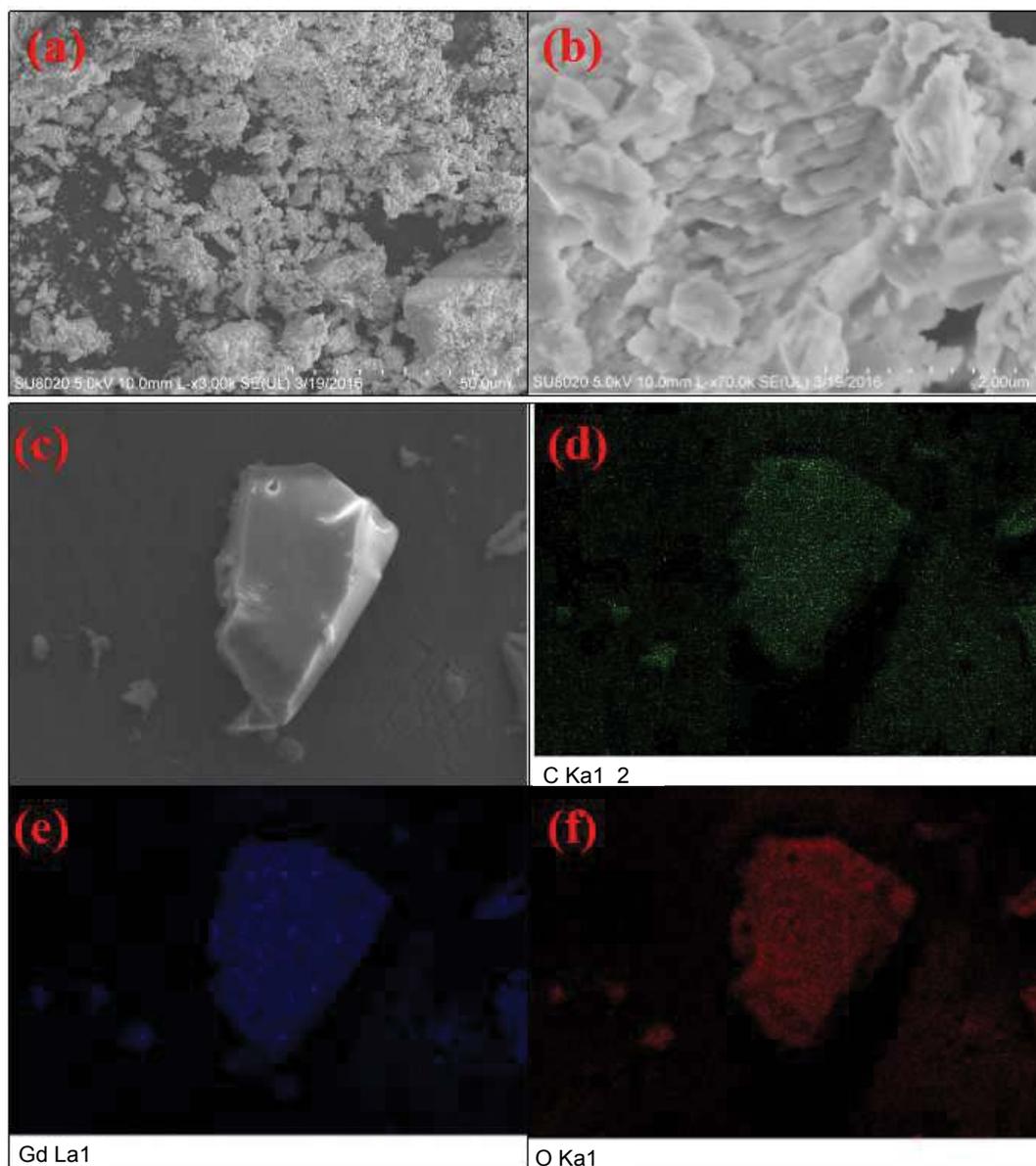
connecting Gd. As long then the reaction time from 2 h to 12 h, the FT-IR spectra of Gd-S-160 (Figure 3) have no obvious change indicating that acetylacetonate groups are stable in relative severe solvothermal process. In order to verify that acetylacetonate groups are still in the formed samples, Gd-S-160 is calcinated at 450 °C for 2 h to give Gd-C-160. Its FTIR spectrum (Figure 3e) shown the peaks at 1548  $\text{cm}^{-1}$  and 1441  $\text{cm}^{-1}$  disappear and bands at 1504  $\text{cm}^{-1}$ , 1398  $\text{cm}^{-1}$ , 1096 and 863  $\text{cm}^{-1}$  due to  $\nu_{\text{as}} \text{OC-O}$ ,  $\nu_{\text{s}} \text{C-O}$ ,  $\nu_{\text{as}} \text{CO}_3^{2-}$  appear, confirming the calcinated sample is  $\text{Gd}(\text{OH})\text{CO}_3^{2-}$  or  $(\text{GdO}_2)\text{CO}_3$  [17]. So it is referred that the solvothermal samples are  $\text{Gd}(\text{OH})_x(\text{AcAc})_{3-x}$  where  $x$  is between 0-3 and AcAc is the acetylacetonate group.

In order to clearly determine the composition of the prepared samples, TGA and DTA of Gd-S-160 and Gd-S-220 were measured (Figure 1). Gd-S-160 and Gd-S-220 all show one obvious degradation DTA peak be-

tween 250-400 °C which corresponds to ~44% and 32% weight loss, respectively. If considering the sample is  $\text{Gd}(\text{OH})(\text{AcAc})_2$  or  $\text{Gd}(\text{OH})_2(\text{AcAc})$ , its corresponding degradation weight loss would be 45% or 32%. That is the weight losses of Gd-S-160 and Gd-S-220 can well match that of  $\text{Gd}(\text{OH})(\text{AcAc})_2$  and  $\text{Gd}(\text{OH})_2(\text{AcAc})$ . So the formula of Gd-S-160 and Gd-S-220 are  $\text{Gd}(\text{OH})(\text{AcAc})_2$  and  $\text{Gd}(\text{OH})_2(\text{AcAc})$ , respectively. Meanwhile the degradation products of Gd-S-160 are measured by TGA-MS (Figure 1c). Between 300-400 °C, small molecules including  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  are produced confirming the organic groups are preserved in Gd-S-160. In the DTA curve of Gd-S-160 between 450-600 °C, one obvious broad band appear while no degradation occur showing a phase change takes place which may be indexed as the transition of Gd with 3 complex number to  $\text{Gd}_2\text{O}_3$ .



**Figure 4:** XRD patterns of a)  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ ; b) Gd-S-140; c) Gd-S-160; d) Gd-S-180; e) Gd-S-240 and h) Gd-S-260 prepared in 2 h, and f) Gd-C-160 prepared in 10 h.



**Figure 5:** SEM of Gd-S-160 (a,b,c) and the C (d), Gd (e), O (f) dispersion on the particles.

Figure 4 shows the XRD patterns of Gd-S-T and Gd-C-160. New peaks appear between 10-15° compared to  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  with the increase of reaction temperature and reaction time. This is due to the substitution of acetylacetonate by -OH with the hydrolysis. Similar phenomenon was reported by hydrolysis of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  in DMF [18]. The characteristic diffraction peaks of Gd-C-160 can well match that of  $(\text{GdO}_2)\text{CO}_3$  (JPCDS-47-0579). These results confirm that in diphenyl ether the trace water from structural water of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  can cause  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  to hydrolyze to form  $\text{Gd}(\text{AcAc})_x(\text{OH})_{3-x}$  where  $x$  is between 0 and 3.

The SEM and the element dispersions of the prepared Gd-S-160 are shown in Figure 5. In the magnified photograph (Figure 5b), it can be seen that Gd-S-160 is in rod shape with some irregular particles, the scanning photos show that C, Gd and O uniformly dispersed on the particle confirming the formation of  $\text{Gd}(\text{AcAc})_x(\text{OH})_{3-x}$ .

The particle sizes of Gd-S-160 and Gd-C-160 were measured by Z potential and shown in Figure 6. The particle size of most of Gd-S-160 is 200-400 nm with little part being about 800 nm. While about 40% of Gd-C-160 is in the particle size of 200-500 nm, about 50% in 700-1200 nm, and about 10% in 1300-1600 nm. These data show that under suitable solvothermal conditions, the prepared Gd-S-T not only contains organic groups but also has a relatively small particle size compared to the general solvothermal-calcination process. The interesting thing is that no matter Gd-S-T or its calcinated products show positive surface charges. The Z potential of Gd-S-160 and Gd-C-160 are 42.1 mV and 34.9 mV.

Figure 7 shows the UV-vis absorbance of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  and Gd-S-T. For  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$ , only one absorbant peak centered at 294 nm is observed which is attributed to the  $\pi-\pi^*$  transition of  $\beta$ -diketonate ligand [5]. Due to the forbidden electron transition between ligands and  $\text{Gd}^{3+}$  which has a stable electron arrangement, still only one peak is observed for Gd-S-140, but it shifts to 308 nm indicating the  $\pi-\pi^*$  transition of  $\beta$ -diketonate ligand becomes easier and the conjugation degree of Gd with acetylacetonate groups is weakened. For Gd-S-160 and Gd-S-200, two absorbant peaks appear. Except for the absorbance at 308 nm, a peak at 275 nm due to the  $\pi-\pi^*$  transition of  $\beta$ -diketonate due to the energy match of ligands after substitution of acetylacetonate by OH groups.

Generally speaking, rare earth organic complexes produce intense emission peaks in visible and near-infrared regions under ultraviolet (UV) excitation. For obtaining optimum emission spectra, the excitation wavelength for emission measurement is determined by excitation spectrum measurement. Figure 8a is the excitation fluorescence of Gd-S-T in the ultraviolet region under emission

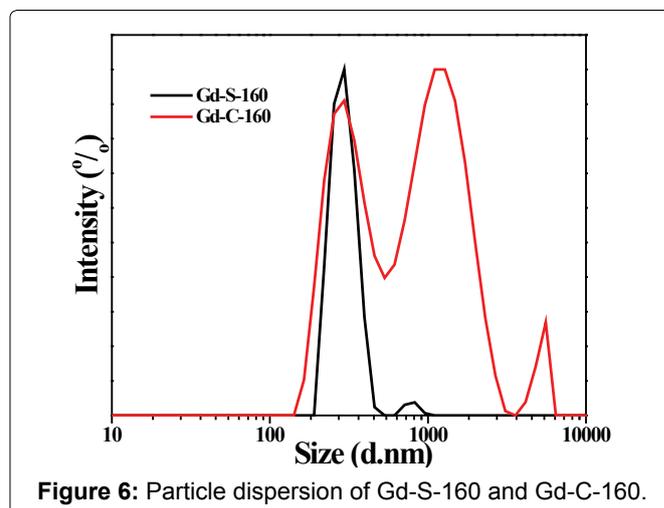


Figure 6: Particle dispersion of Gd-S-160 and Gd-C-160.

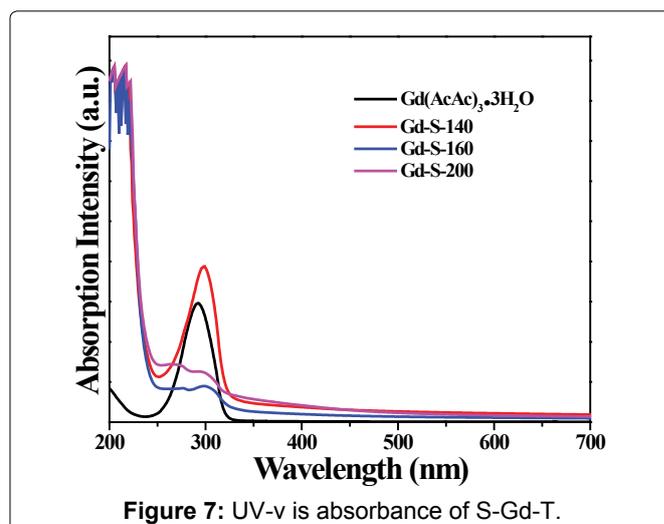
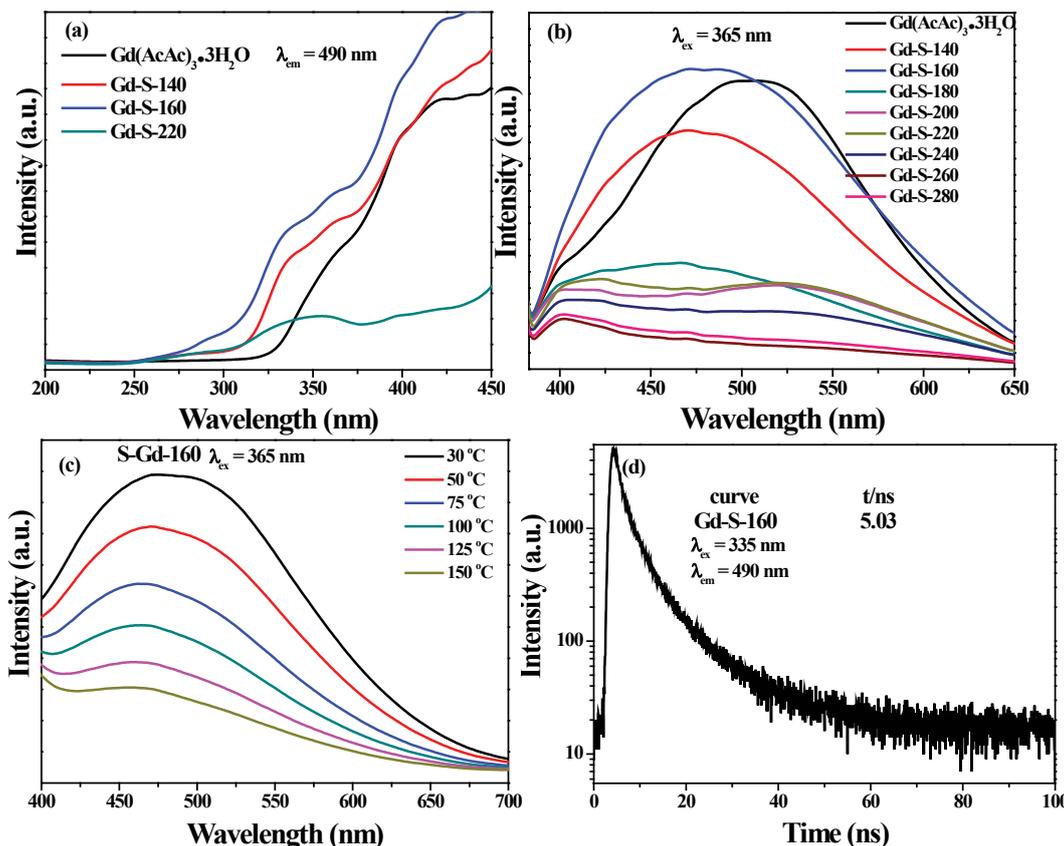
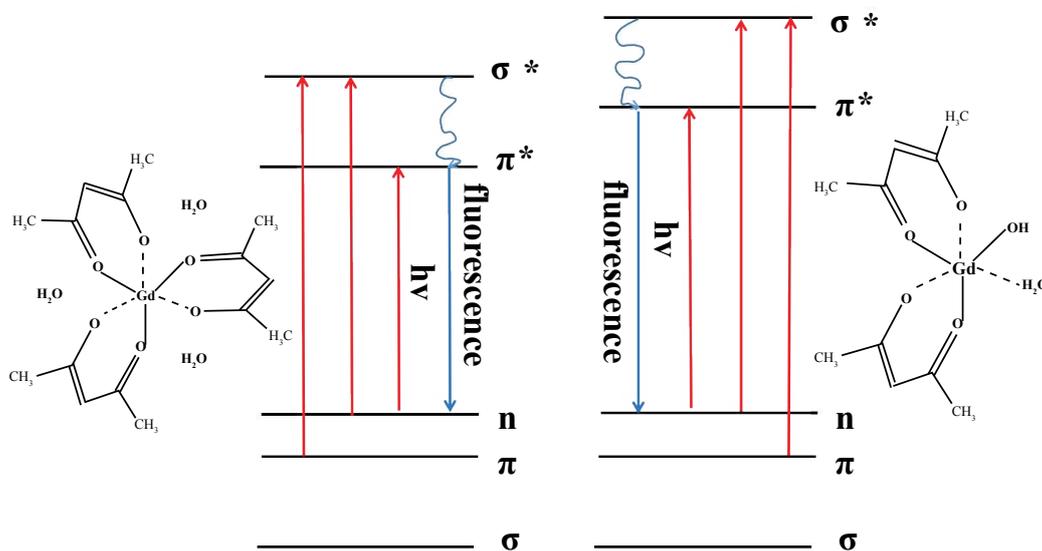


Figure 7: UV-vis absorbance of S-Gd-T.

of 490 nm.  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  shows two absorbance, one is between 320-370 nm, the other is between 370-450 nm attributed to  $\pi-\pi^*$  and  $n-\pi^*$  transitions of  $\beta$ -diketonate ligands [5]. While for Gd-S-140 and Gd-S-160, three peaks are observed which are at 310-350, 350-375 and 375-450 nm. As emission excited under UV irradiation is aimed in the present work, so emission fluorescence is excited by 365 nm and the spectra are shown in Figure 8b.  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  shows one strong emission peak at 520 nm. While the emission of Gd-S-140 and Gd-S-160 left shift indicating that high energy luminescence is produced. Although the acetylacetonate groups of  $\text{Gd}(\text{AcAc})_3 \cdot 3\text{H}_2\text{O}$  is more than Gd-S-160, but the emission peak of Gd-S-160 is the highest. Just as shown in Figure 9 [19], as the bond ability of -OH to electron is stronger than acetylacetonate group, substitution of some of the acetylacetonate group by -OH will result in weak interaction of  $\text{Gd}^{3+}$  with the left acetylacetonate groups of the prepared samples, and thus the controlling ability of acetylacetonate group to electron is increased. So the energy between the ground state and excited state in the prepared samples is higher which results in emission of fluorescence with shorter wavelength compared to Gd-acetylacetonate [7,20]. As



**Figure 8:** Excitation a) emission; b) fluorescence of Gd-S-T at room temperature and the temperature dependent fluorescence; c) and life time of; d) Gd-S-160.



**Figure 9:** Energy stage schematic of Gd(AcAc)<sub>3</sub>·3H<sub>2</sub>O and their products.

the temperature for preparation of Gd-S-T is higher than 200 °C, the emission of the products becomes weak as the amount of acetylacetonate groups decrease. Figure 8c shows the temperature dependence of Gd-S-160. Generally, the fluorescence of organic complex decreases with temperature. At higher temperature, the vibration of electron in acetylacetonate increases, so more energy is

consumed and the emission strength of the derivatives is decreased, which is confirmed by fluorescent life time measurement. The life time of Gd-S-160 is only 5.03 ns. Short lifetime indicates short time of electrons in existed state and more energy is consumed. With the increase of temperature up to 125 °C, the fluorescence of Gd-S-160 decreases sharply and left shifts due to the weakened

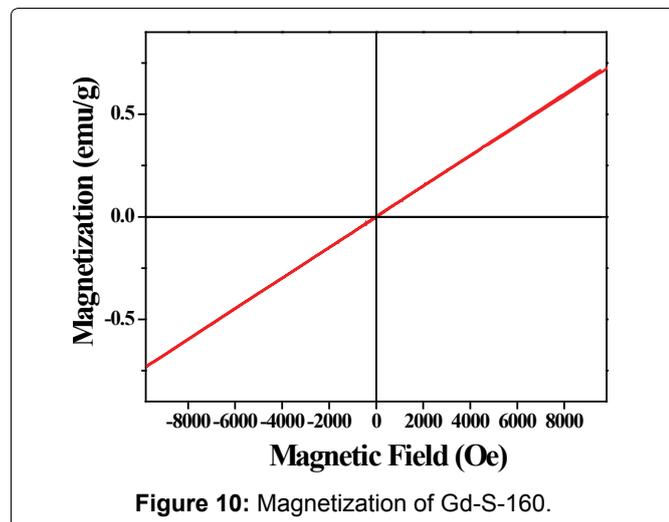


Figure 10: Magnetization of Gd-S-160.

interaction strength between acetylacetonate and Gd with temperature and the controlling ability of acetylacetonate to electrons is increased. Therefore the obtained samples are not temperature stable enough.

Figure 10 shows M-H curve of Gd-S-160 measured at 300 K. The magnetization of Gd-S-160 increases linearly with the testing magnetic strength increase. This phenomenon is due to the magnetizing current for  $M_s$  Measurement of Gd-S-160 is too high. In other words, Gd-S-160 is relatively easy magnetization. As the applied magnetic field is 8000 Oe, the magnetization of Gd-S-160 is 0.72797 emu/g confirming the produced samples can response to external magnetic field.

## Conclusions

Gadolinium (III) acetylacetonate was treated by solvothermal method to produce Gadolinium (III) acetylacetonate derivatives. The composition, fluorescence, and magnetic properties of the products are studied in detail. The fluorescence measurement showed the products possessed higher energy emission and excitation fluorescence compared to Gadolinium (III) acetylacetonate. Also the product produced at 160 °C possessed higher fluorescent intensity. Based on the fluorescent study the fluorescent emission mechanism is proposed. The magnetic measurement indicated the products were paramagnetic materials. So the products were hydrophobic materials with magnetic and fluorescent properties.

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