Effect of CTAB Concentration and pH Value of the Reaction Solution on the Properties of Hydrothermally Synthesized GdVO4: Eu3+ Phosphor (Postprint)

Authors: Yan Yinglin, Wang Juan, Wang Liangliang, LU Zhengxin, Ren Bing, Xu Yunhua

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Abstract

Using gadolinium oxide, europium oxide, and ammonium metavanadate as raw materials and CTAB as the surfactant, a series of GdVO4:Eu3+ phosphors ranging from microscale to nanoscale were prepared via hydrothermal synthesis by varying the amount of surfactant CTAB added and the pH value. The phase, morphology, and luminescent properties of the samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and photoluminescence spectroscopy (PL), and the effects of surfactant CTAB concentration and pH value of the reaction solution on the morphology and properties of GdVO4:Eu3+ phosphors were investigated. The results indicate that the pH value of the reaction solution significantly affects the grain size of the samples: micron-sized crystal particles were obtained at pH=1, platelet products with edge lengths of approximately 200 nm were obtained at pH=4, small platelets with dimensions of 10-20 nm were obtained at pH=7, and hydroxide impurities appeared under alkaline conditions at pH=10. Different amounts of surfactant added significantly altered the crystal growth direction and agglomeration mode, thereby changing the final morphology of the samples. The luminescent properties of the samples varied significantly with grain size and crystallinity, with the GdVO4:Eu3+ tetragonal platelets with good crystallinity and hundred-nanometer edge lengths exhibiting optimal luminescent performance.

Full Text

Preamble

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Influence of CTAB Concentration and Reaction Solution pH on the Properties of Hydrothermally Synthesized $GdVO_4$:Eu^{3+} Phosphors

YAN Yinglin[1], WANG Juan[2], WANG Liangliang[2], LU Zhengxin[1], REN Bing[1], XU Yunhua[1]

[1] School of Materials and Mineral Resources, Xi' an University of Architecture and Technology, Xi' an 710055, China
[2] School of Materials Science and Engineering, Xi' an University of Technology, Xi' an 710048, China

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Corresponding author: YAN Yinglin, Tel: 13468830584, E-mail: yyl3550@xaut.edu.cn

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Abstract

Luminescent phosphors $GdVO_4$:Eu^{3+} were prepared in solutions with different pH values by hydrothermal synthesis using Gd_2O_3, NH_4VO_3, and Eu_2O_3 as precursors, and cetyltrimethylammonium bromide (CTAB) as surfactant. The synthesized products were characterized in terms of morphology, structure, and luminescent performance by means of XRD, SEM, TEM, and PL. The results show that in an acidic solution with pH=1, the size of synthesized $GdVO_4$:Eu^{3+} crystal grains is on the micron scale; in a solution with pH=4, their size shrinks to the nanoscale; well-dispersed nano-flakes of about 50 nm are obtained in solution with pH=7; additionally, in solution with pH=10, a certain amount of impurity $Gd(OH)_3$ was detected by XRD in the synthesized $GdVO_4$:Eu^{3+} crystal grains. On the other hand, the surfactant obviously affected the final morphology of the synthesized $GdVO_4$:Eu^{3+} crystal grains by altering the crystal growth direction and aggregation pattern, which correspondingly affected the luminescent properties that are influenced by grain size and crystallinity. It was found that square $GdVO_4$:Eu^{3+} nanocrystals with good crystallinity exhibited optimal emission performance. However, it should be noted that the aggregation effect may weaken the luminescent property of the products.

KEY WORDS: inorganic non-metallic materials, rare earth luminescent materials, hydrothermal synthesis, $GdVO_4$, pH values, surfactant

1. Introduction

As a novel inorganic luminescent material, rare earth ion-doped rare earth vanadates possess abundant f-f transition energy levels, diverse emission colors, high quantum efficiency, and excellent thermal and chemical stability [1-5]. In the vanadate system, europium-doped gadolinium vanadate red phosphors have attracted widespread attention [6-9] due to their outstanding performance and potential applications in various flat panel display screens [10]. Rare earth ion-doped gadolinium vanadate materials also exhibit scintillation crystal characteristics [11], making them suitable for computed tomography applications. Compared with rare earth-doped yttrium vanadate materials, gadolinium vanadate materials demonstrate superior thermal properties and higher luminescence intensity at elevated temperatures [12].

In recent years, research has focused on the preparation of gadolinium vanadate materials with special morphologies, particularly nanoscale gadolinium vanadate. Inspired by natural mineral formation processes, researchers have employed hydrothermal methods to prepare various crystalline materials. The use of organic surfactants to control crystal nucleation and growth and to induce self-assembly into novel morphologies has been especially noteworthy [13-16]. Fan et al. [17] prepared tetragonal zircon-type $LaVO_4$ nanocrystals via a hydrothermal method using sodium dodecylbenzenesulfonate (SDS), cyclohexane, and n-hexane in solution. Cetyltrimethylammonium bromide (CTAB) is a widely used cationic surfactant [18, 19] that can assist in the hydrothermal preparation of YVO_4:Eu^{3+} nanoluminescent materials [18]. Valentin Rădiţoiu et al. [19] prepared α-FeOOH crystals with regular morphologies using CTAB. In this work, we prepared $GdVO_4$:Eu^{3+} phosphors via CTAB-assisted hydrothermal synthesis and investigated the influence mechanisms of reaction solution pH and CTAB concentration on $GdVO_4$:Eu^{3+} crystal growth, as well as the effect of crystal morphology on luminescent properties.

2. Experimental

2.1 Materials and Synthesis

The experimental materials included high-purity gadolinium oxide (Gd_2O_3, 4N, 99.99%), europium oxide (Eu_2O_3, 4N, 99.99%), ammonium metavanadate ($NH_4VO_3 \cdot 6H_2O$, analytical grade, 99%), concentrated nitric acid (HNO_3, analytical grade AR), sodium hydroxide (NaOH, analytical grade AR, 99.7%), ethanol (CH_3CH_2OH, analytical grade AR), cetyltrimethylammonium bromide (CTAB, analytical grade AR, 99%), and double-distilled water.

Standard samples were prepared as follows: Appropriate amounts of Gd_2O_3 and Eu_2O_3 were placed in a beaker, mixed with distilled water, heated in a water

bath, and stirred until clear upon dropwise addition of concentrated nitric acid solution to prepare $Gd(NO_3)_3$ solution (0.25 mol/L) and $Eu(NO_3)_3$ solution (0.125 mol/L). A quantity of $NH_4VO_3 \cdot 6H_2O$ (2.5 mmol) was placed in a 50 mL beaker, heated in a water bath after adding 10 mL distilled water, then mixed with 9.5 mL of the prepared $Gd(NO_3)_3$ solution and 1 mL of the $Eu(NO_3)_3$ solution (corresponding to 5% Eu^{3+} doping concentration). NaOH solution (1 mol/L) was added dropwise to adjust the pH to specific values, followed by the addition of a certain amount of surfactant CTAB. After stirring for 30 minutes, the mixture was transferred to a polytetrafluoroethylene-lined autoclave, sealed, and reacted at 180°C for 24 hours. The product was cooled to room temperature, centrifuged, washed 2-3 times with ethanol and distilled water, and dried at 80°C to obtain $GdVO_4$:Eu^{3+} phosphors.

Two experimental series were conducted: Series one investigated the effect of pH on crystal morphology by adding 0.4555 g (1.25 mmol) of CTAB and adjusting pH values to 1, 4, 7, and 10. Series two examined the effect of surfactant concentration on sample crystal morphology by maintaining pH=1 and varying the amount of CTAB added (0 mmol and 2.5 mmol).

2.2 Characterization

Phase analysis of samples was performed using a D/Max2550 X-ray diffractometer (XRD) with Cu Kα radiation source (λ=0.15406 nm) at 40 kV and 50 mA. Morphology was examined using a Quanta 200 scanning electron microscope (accelerating voltage 15 kV) and a JEM-2100F transmission electron microscope (accelerating voltage 300 kV). Excitation and emission spectra were measured using an FLS920 spectrometer with calibration. All tests were conducted at room temperature.

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3. Results and Discussion

3.1 Effect of Reaction Solution pH on $GdVO_4$:Eu^{3+} Crystal Phase and Morphology

In hydrothermal synthesis, pH is a crucial reaction parameter that significantly influences the purity, phase, and morphology of target products. Therefore, we first investigated the effect of solution pH in the reaction system by preparing samples at pH values of 1, 4, 7, and 10.

3.1.1 X-ray Diffraction (XRD) Analysis Figure 1 [Figure 1: see original paper] presents the XRD patterns of $GdVO_4$:Eu^{3+} phosphor crystals synthesized at 180°C for 24 hours with 1.25 mmol CTAB at different pH values. All diffraction peaks are clearly distinguishable. Comparison with standard PDF card #17-0260 reveals that pure $GdVO_4$ phase was obtained at pH=1, 4, and 7, while some impurity peaks appear in the XRD pattern at pH=10. The diffrac-

tion peak intensity gradually decreases and peak width broadens, indicating changes in sample size and crystallinity. At pH=10, analysis using Jade software and comparison with standard PDF card #38-1042 identified the second phase as $Gd(OH)_3$.

The XRD patterns demonstrate that at pH=1, the diffraction peaks are high and sharp, indicating large phosphor crystal particles with good crystallinity. When pH increases to 4, diffraction peak intensity decreases and width broadens, suggesting refined crystal size but still high crystallinity. At pH=7, diffraction peak intensity reaches its minimum while width reaches its maximum, predicting further reduction in crystal size and severe degradation of crystallinity. At pH=10, the diffraction peaks show continued decline in crystallinity and increased peak width, indicating still small crystal size but with $Gd(OH)_3$ impurity formation due to increased OH^- concentration.

3.1.2 Scanning Electron Microscopy (SEM) Analysis Figure 2 [Figure 2: see original paper] shows SEM images of $GdVO_4$:Eu^{3+} crystals synthesized hydrothermally at different pH values. Figure 2a reveals the morphology at pH=1, showing large complex granular crystals approximately 10 m in size. Figure 2b, a high-magnification SEM image of Figure 2a, clearly shows $GdVO_4$:Eu^{3+} crystal particles with square outlines formed by layered stacking, with some angular protrusions on the surface caused by stacked square crystal growth. SEM images of $GdVO_4$:Eu^{3+} powder at pH=4 are blurred because the crystal particles are too small for clear observation. The situation is similar at pH=7. Figure 2c presents the SEM image at pH=10, clearly showing two distinct morphologies: fine small grains and one-dimensional needle-like crystals. Combined analysis with the corresponding XRD pattern (Figure 1d) indicates these needle-like crystals are $Gd(OH)_3$.

3.1.3 Transmission Electron Microscopy (TEM) Analysis Figure 3 [Figure 3: see original paper] shows TEM images of $GdVO_4$:Eu^{3+} crystals synthesized hydrothermally at pH=4 and 7. Figure 3a displays the TEM image at pH=4, where the main feature is a square-shaped micron-scale crystal particle with a square base approximately 400 nm in side length and about 200 nm in thickness. Some small particle clusters are also visible, with sizes less than 100 nm as determined by comparison with the scale bar. Figure 3b shows the corresponding selected area electron diffraction (SAED) pattern, revealing a single-crystal pattern. Due to large deviation between the electron beam direction and a crystal orientation [uvw], reciprocal points on higher-order reciprocal planes intersect with the reflection sphere, forming higher-order Laue zone diffraction patterns. Spots on the $±$1st (or possibly $±$2nd) order show identical symmetry to zero-order spots, with main spots appearing on this higher-order pattern and other spots caused by small particles attached to the single crystal. Faint diffraction lines in the pattern are Kikuchi lines, also indicating few crystal defects, though these are weak due to the large crystal size.

Figure 3c presents the TEM image at pH=7, showing numerous nanoscale thin crystal flakes that mostly aggregate into clusters. These small flakes are only 10-20 nm in size with unclear outlines and varied shapes, indicating poor crystallinity. Electron beam diffraction at the nanocrystalline cluster region produces the pattern shown in Figure 3d, which consists of multiple concentric diffraction rings of varying brightness with several bright diffraction spots, indicating a polycrystalline state consistent with the crystal morphology analysis.

3.1.4 Influence of Reaction Solution pH on $GdVO_4$:Eu^{3+} Crystal Morphology At pH=1, sample particles exhibit layered stacked octahedral morphology with grain sizes in the 10-20 m range. At pH=4, tetragonal particles approximately 400 nm × 400 nm × 200 nm coexist with small grains around 50 nm. At pH=7, samples consist entirely of uniform nanoscale flakes 10-20 nm in size. Thus, sample particle size decreases sharply with increasing pH, accompanied by declining crystallinity. This occurs because solution pH affects the existence form of vanadate groups in solution, thereby influencing the reaction process. At pH=1, vanadate exists primarily as $V_3O_9{}^{3-}$, while $VO_4{}^{3-}$ dominates at pH>7 [24]. The reaction mechanism also shifts from homogeneous precipitation producing $GdVO_4$ at pH<7 to formation of $Gd(OH)_3$ nuclei that subsequently transform to $GdVO_4$ at pH>7 [25]. Additionally, OH^- adsorption on crystal surfaces [26] hinders crystal growth.

3.2 Effect of CTAB on $GdVO_4$:Eu^{3+} Crystal Phase and Morphology

Based on the above findings, pH=1 yields the most complete $GdVO_4$:Eu^{3+} crystal growth with relatively large grain size. Therefore, pH=1 was selected as the fixed reaction condition to investigate the effect of varying CTAB molar amounts on $GdVO_4$:Eu^{3+} crystal growth and final morphology.

3.2.1 X-ray Diffraction (XRD) Analysis Figure 4 [Figure 4: see original paper] shows XRD patterns of $GdVO_4$:Eu^{3+} phosphor crystals synthesized at 180°C for 24 hours at pH=1 with different CTAB amounts. All three samples show clear diffraction peaks that match standard PDF card #17-0260, indicating pure $GdVO_4$ phase. However, diffraction peak intensity increases progressively, reflecting changes in sample size and crystallinity. Comparison reveals that as CTAB addition increases, diffraction peak intensity gradually improves while peak width remains essentially unchanged, indicating enhanced crystallinity with minimal change in grain size.

3.2.2 Scanning Electron Microscopy (SEM) Analysis Figure 5 [Figure 5: see original paper] presents SEM images of $GdVO_4$:Eu^{3+} crystals synthesized under identical conditions with different CTAB amounts. Sample morphology changes significantly with increasing CTAB addition. Without CTAB, particles exhibit mostly octahedral cushion-shaped grains (Figure 5a). With 1.25 mmol CTAB, samples maintain octahedral morphology but show pronounced overlapping stacked growth, presenting a layered square flake stacked morphology

(Figure 5b). When CTAB addition is doubled (2.5 mmol), crystal morphology changes dramatically to quasi-spherical features, with small octahedral particles aggregated among large spherical particles (Figure 5c).

3.2.3 Influence of CTAB on $GdVO_4$:Eu^{3+} Crystal Growth Process Analysis of these experimental results confirms that CTAB addition indeed influences crystal growth processes and alters final microstructure morphology. Without CTAB influence, $GdVO_4$:Eu^{3+} crystals naturally grow as octahedral particles (Figure 5a). With equimolar CTAB addition (1.25 mmol), layered dislocations occur at the waist of octahedra during growth, continuing toward octahedral morphology with increased layer number and rotation of each layer, forming an interesting morphology resembling multiple square flake crystals stacked together (Figure 5b). When CTAB addition is doubled, surfactant concentration exceeds its critical micelle concentration, causing surfactant to exist as micelles in solution. The presence of numerous micelles restricts free growth of $GdVO_4$:Eu^{3+} crystals, resulting in smaller octahedral particles that adhere to micelle surfaces and aggregate, ultimately forming spherical morphologies. Since micelles evaporate after high-temperature treatment, some spherical products exhibit hollow features (Figure 5c). Figure 6 [Figure 6: see original paper] schematically illustrates the effect of CTAB addition on $GdVO_4$:Eu^{3+} crystal growth.

3.3 Photoluminescence Properties

3.3.1 Excitation Spectra of $GdVO_4$:Eu^{3+} Phosphors Figure 7a [Figure 7: see original paper] shows excitation spectra of $GdVO_4$:Eu^{3+} phosphors synthesized hydrothermally at different pH values, monitoring the excitation peak corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition at 618 nm at room temperature. The excitation spectrum displays a broad band from 250 nm to 340 nm arising from $VO_4{}^{3-}$ charge transfer (CT) transitions. According to literature [4, 19], typical Eu^{3+} f-f transition peaks were not detected, indicating their intensity is too weak for instrumental detection limits. The $VO_4{}^{3-}$ CT excitation band lies in the UV region, enabling efficient application in UV LED chips for bright red emission. Comparison of excitation intensities reveals that layered octahedral grains obtained at pH=1 show moderate intensity, square flake crystals at pH=4 exhibit the highest intensity, while nanoflake crystals at pH=7 show a sudden intensity drop. This occurs because micron-sized particles have low surface luminescent center concentration, whereas reducing size to the hundred-nanometer scale yields more regular crystal structure with higher surface luminescent center concentration and excitation activity. Further size reduction results in low crystallinity nanoflake crystals with excessive grain boundaries causing boundary quenching.

Figure 7b [Figure 7: see original paper] presents excitation spectra of $GdVO_4$:Eu^{3+} phosphors synthesized with different CTAB amounts, also monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 618 nm. Results show that excitation

peak intensity gradually increases with surfactant addition, accompanied by significant blue shift of the maximum position. This arises because increased surfactant reduces particle size and decreases crystal structure symmetry, both beneficial for increasing specific surface area and improving excitation efficiency. Additionally, surfactant induces lattice distortion that progressively increases —from regular octahedral to layered square flake stacked morphology, then to spherical and fine particle morphology. These distortions cause reduced grain size, increased specific surface area, and increased crystal defects, resulting in blue shift of the excitation maximum [1, 20].

3.3.2 Emission Spectra of $GdVO_4$:Eu^{3+} Phosphors Figure 8 [Figure 8: see original paper] shows emission spectra of $GdVO_4$:Eu^{3+} phosphors synthesized at different pH values under 314 nm UV excitation at room temperature, revealing four distinct emission peaks at 594 nm, 608 nm, 615 nm, and 618 nm. According to literature [26], the 615 nm and 618 nm peaks belong to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition of Eu^{3+} ions with relatively high intensity, with 618 nm being the strongest. The 594 nm emission corresponds to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition. The $^5D_0 \rightarrow {}^7F_2$ transition is highly sensitive to the chemical environment and symmetry around luminescent centers, while the $^5D_0 \rightarrow {}^7F_1$ transition is insensitive, allowing determination of Eu^{3+} site symmetry in the crystal. The observed higher intensity of the $^5D_0 \rightarrow {}^7F_2$ transition compared to $^5D_0 \rightarrow {}^7F_1$ indicates that doped Eu^{3+} ions occupy primarily non-inversion center Gd^{3+} sites, and the phosphor should emit mainly red light under 314 nm UV irradiation.

Comparison of emission spectra for different pH values (Figure 8a) shows similar trends to excitation spectra: layered octahedral morphology at pH=1 exhibits moderate intensity, hundred-nanometer square flake crystals at pH=4 show the highest intensity among all samples, while nanocrystalline clusters at pH=7 display very weak emission, even lower than large particles at pH=1. This confirms that grain size significantly influences luminescence performance.

Comparison of emission spectra for different CTAB amounts (Figure 8b) indicates that 1.25 mmol CTAB yields the highest intensity, followed by the sample without CTAB, while 2.5 mmol CTAB produces weaker emission. This correlates with Figure 7b because the emission spectra used a fixed excitation wavelength of 314 nm.

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4. Conclusion

CTAB-assisted hydrothermal synthesis can produce $GdVO_4$:Eu^{3+} phosphors. Reaction solution pH significantly affects nucleation rate in solution, thereby determining final grain size. By adding different CTAB concentrations, various morphologies can be prepared at pH=1. CTAB surfactant addition alters crystal growth modes and self-assembly patterns. $GdVO_4$:Eu^{3+} phosphors exhibit

primarily the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, with doped Eu^{3+} ions occupying mainly non-inversion center Gd^{3+} sites, emitting red light under 314 nm UV irradiation. Sample morphology significantly affects luminescence performance, with regular morphology and high crystallinity yielding superior luminescent properties.

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Note: Figure translations are in progress. See original paper for figures.