Hydrothermal Synthesis and Luminescence Properties of Monodisperse Spherical CaF_2 and $\text{CaF}_2:\text{Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Ce/Tb}$) Microcrystals

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Abstract: Spherical CaF_2 and $\text{CaF}_2:\text{Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Ce/Tb}$) with tunable particle size (about 2.5 μm) have been synthesized by one-step facile and effective hydrothermal method. The spherical structure was highly uniform and well-dispersed. It was found that reaction time, pH value, and reaction temperature have important effects on the controlled synthesis of spherical CaF_2 . The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), photo-luminescence (PL) and luminescence decay curve. Under UV excitation, the $\text{CaF}_2:\text{Eu}^{3+}$ showed the red emission ($^5\text{D}_0 \rightarrow ^7\text{F}_{J=0,1,2,3}$) and the $\text{CaF}_2:\text{Tb}^{3+}$ presented the green emission ($^5\text{D}_4 \rightarrow ^7\text{F}_{J=6,5,4,3}$), respectively. Furthermore, $\text{Ce}^{3+}/\text{Tb}^{3+}$ co-doped CaF_2 showed efficient energy transfer from Ce^{3+} to Tb^{3+} , which presented strong green photo-luminescence of Tb^{3+} . Due to excellent luminescent properties, the obtained samples can be used in many fields, such as light display systems, optoelectronic devices and biological imaging.

Keywords: CaF_2 , Hydrothermal Synthesis, $\text{Ce} \rightarrow \text{Tb}$ Energy Transfer, Spherical, Luminescence Properties

1. Introduction

Considerable interest has been focused on the synthesis of lanthanide-doped luminescent nano/micro-particles because of their versatile features. Compared with conventional luminescent materials, such as organic fluorescent dyes and semiconductor quantum dots, rare earth (RE) ions-doped materials have sharp absorption, longer luminescence (PL) lifetimes, low toxicity and low photo-bleaching [1]. Especially, the bright luminescence, smaller size and bio-safety are important demands for fluorescent probe in the application of active bio-imaging [2].

It is very important to coordinate the physic-chemical properties of the RE^{3+} -doped luminescent nano/micro-particles and discover their potential bio-applications in various fields. To the best of our knowledge, all kinds of chemical synthetic approaches such as thermal decomposition, high-temperature co-precipitation, hydrothermal synthesis, sol-gel procedure, cation exchange

and ionic liquid-based synthesis have been proposed to synthesize high-quality RE^{3+} -doped luminescent nano/micro-particles with tunable crystalline phases, shapes and sizes [3]. Thermal decomposition is usually using organ-metallic compounds as precursors, in a high boiling point organic solvent, and decomposing under a certain temperature. Furthermore, the high-temperature co-precipitation method is another cracking synthetic method to prepare highly-uniform RE^{3+} -doped luminescent nano/micro-particles, which has advantages in mild reaction conditions, low cost for the required equipment, and short reaction time compared with the thermal decomposition method [4]. The hydrothermal synthesis is different from thermal decomposition and co-precipitation methods, because it is generally performing a special reaction vessel, called autoclave, which is used to provide a high-pressure and sealed environment for the synthesis of solid products. It is turned out to be that this approach enables the synthesis of highly crystalline nano/micro-materials under relatively mild

conditions, when in contrast to other methods [3]. As we all know, Li and co-workers had explored a perfect example of hydrothermal synthesis, in which they proposed a general strategy to prepare mono-disperse NPs based on a liquid–solid–solution (LSS) phase transfer and separation mechanism coming from the interfaces of the liquid, solid and solution [5].

Fluorides, with their high chemical stability and low phonon energies, are acknowledged as being good hosts of luminescent dopants, especially the rare earths, which have received widespread applications in optical communication, display devices, and solid-state lasers [6, 7]. It is noting that alkaline earth metal fluorides are dielectric among various fluorides, which have applications in microelectronic and opto-electronic devices, including wide-gap insulating over-layers, gate dielectrics, insulators, buffer layer and so on [8]. CaF_2 , as a very significant fluoride, has been used as a fantastic host for phosphors because of its charming up/down-conversion luminescent properties [9]. To the best of our knowledge, the edge of the fundamental absorption band in CaF_2 rest with the vacuum UV at 12 eV. The remarkable structure of CaF_2 have been reported that Ca^{2+} ions located in the nodes of a face-centered lattice, yet F^- ones lie at the centers of the octants [10]. As is known to all, a cationic replacement needs an anion as supplement in RE-doped CaF_2 nanocrystals, and as a result, we can find some interesting luminescence properties [11]. What's more, CaF_2 has a large amount of excellent properties, such as low refractive index, wide band gap ($E_g = 12.1$ eV) and optically transparent in a wide range of wavelength from mid-infrared to vacuum ultraviolet [13, 14]. As a result, with the development of inorganic nano/micro-scale fluorides materials, CaF_2 is going to play an essential role in UV lithography, UV-transparent optical lenses, glass surface modification, bio-mimetic materials processing for bone/tooth building and biological fluorescent labels [12, 14, 15].

The incorporation of dopants into pure host lattices provides a variety of fantastic properties to achieve the goals which we think impossible compared with the un-doped counterparts [16–24]. With respect to the excellent properties and promising application in promoting phase transformation and tuning luminescence properties, the Ln^{3+} -doping has been considered to be a simple and effective method to modify the shape and size [25–32]. Furthermore, as a promising route, doping has an advantage in decorating the local environment with the lanthanide ions in the host lattices, improving luminescence efficiency [33]. Ln^{3+} doped luminescent UC/DC nano/micro-crystal of CaF_2 have been widely investigated over the past few years [34–37]. Lin's group has reported that in the presence of oleic acid, CaF_2 nanocrystals (NCs) were synthesized via a solvothermal process [38]. The following year, they also prepared mono-disperse CaF_2 and $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$ hollow spheres by a facile and controllable synthesis, simultaneously, studying efficient luminescent properties of hollow spheres and their smart applications in drug delivery [39]. Soon after, three-dimensional flower-like CaF_2 and $\text{CaF}_2:\text{Ln}^{3+}$ nano-structures have been successfully prepared by a facile hydrothermal method [40]. Li's group has

reported that sub-10 nm mono-dispersed $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$ nanocrystals were prepared according to liquid-solid-solution (LSS) strategy [11]. Very recently, the UC luminescence properties of CaF_2 have become a research hot spot. However, the DC luminescence properties of CaF_2 have received comparatively little attention. Herein, we demonstrate one-step synthesis of mono-disperse spherical CaF_2 via a facile hydrothermal method. Furthermore, the DC emission properties of samples have been systemically discussed.

2. Experimental Section

2.1. Preparation of Samples

All of the chemicals used in this paper were of analytical grade and used without further purification. Rare earths oxides were absolutely dissolved in dilute HNO_3 solution, and then the rest of HNO_3 was removed by heating, stirring and evaporation, finally, we received an aqueous solution of the corresponding $\text{RE}(\text{NO}_3)_3$ [41]. For the synthesis of CaF_2 , in a typical synthesis, 2mmol of $\text{Ca}(\text{Ac})_2$ and 10mmol $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2\cdot\text{H}_2\text{O}$ (Na_2EDTA , ethylenediamine tetraacetic acid disodium salt) were dissolved in 40mL distilled water at room temperature by magnetic stirring for 20 min to form clear solution. Then 4mmol of NaBF_4 was added to the complex solution. Subsequently, the solution was transferred to a 50mL Teflon-lined autoclave, and heated at 160°C for a given time. After cooling to room temperature, the final products were by means of centrifugation, washed with distilled water, ethanol for several times and dried at 60°C in air. The synthetic procedures for Eu^{3+} or Tb^{3+} single doped and $\text{Ce}^{3+}/\text{Tb}^{3+}$ co-doped CaF_2 were the same as that used to prepare CaF_2 , except that stoichiometric amounts of $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ or $\text{Ce}(\text{NO}_3)_3$ were added to complex solution.

2.2. Characterization

The crystal structure was determined using a D8 Focus diffractometer (Bruker) with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15405$ nm). The morphology of the samples was inspected using a scanning electron microscope (SEM, S-4800, Hitachi). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) micrographs and selected area electron diffraction (SAED) were obtained from a FEI Tecnai G2S-Twin transmission electron microscope with a field emission gun operating at 200 kV. The photo-luminescence (PL) measurements were performed on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

3. Results and Discussion

3.1. Crystal Structures and Morphologies of Samples

Synthetic samples via a facile hydrothermal method have many factors to control, such as reaction time, pH value, reaction temperature and so on. In our work, the effects of reaction temperature, time, and pH value will be investigated.

We first study phase and morphology of the final products of doping with different RE ion, as is shown in Fig. 1, apparently, all diffraction peaks can be indexed to pure cubic CaF_2 phase (JCPDS card No. 35-0816), and no impurity phase can be detected. It reveals that we have successfully prepared $\text{CaF}_2:\text{Ln}^{3+}$ (Eu^{3+} , Tb^{3+} , $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Tm}^{3+}$, $\text{Yb}^{3+}/\text{Ho}^{3+}$, $\text{Ce}^{3+}/\text{Tb}^{3+}$) crystal.

Figure 1. XRD patterns of the as-prepared crystallites at 160°C for 1h with $\text{pH}=4$: (a) $\text{CaF}_2:\text{Eu}^{3+}$, (b) $\text{CaF}_2:\text{Tb}^{3+}$, (c) $\text{CaF}_2:\text{Yb}^{3+}/\text{Er}^{3+}$, (d) $\text{CaF}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$, (e) $\text{CaF}_2:\text{Yb}^{3+}/\text{Ho}^{3+}$, (f) $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$.

Figure 2. SEM (a, b, c), TEM (d, e), and HRTEM (f) images of $\text{CaF}_2:5\% \text{Eu}^{3+}$ (160°C , $\text{PH}=4$, 1h). (inset shows the SAED pattern)

The low-magnification SEM image (Figure. 2a) shows that the prepared products are uniform and mono-disperse spheres. Detailed structural information on the spheres of the $\text{CaF}_2:5\% \text{Eu}^{3+}$ sample can be received by the

high-magnification SEM images (Figure 2b, c). The mean diameter of the sphere is about $2.5 \mu\text{m}$. The TEM images (Fig. 2d, 2e) of the as-prepared $\text{CaF}_2:5\% \text{Eu}^{3+}$ demonstrates a well-dispersed and uniform spherical micro-spheres, which are almost similar to the SEM images. Furthermore, the lattice fringes in the HRTEM image (Fig. 2f) are obvious, indicating the high-crystallinity of the product. The fringe distances (d spacing) in micro-spheres synthesized are 0.315 nm on the basis of (111) planes. The SAED patterns shown in inset can be indexed as pure cubic CaF_2 phase according to their (111), (200), (220) and (311) reflections, which are consistent with XRD data.

3.2. Effect of Reaction Time

We first study the effect of reaction time on morphology of the final products at the reaction temperature of 160°C . The SEM images of the $\text{CaF}_2:5\% \text{Eu}^{3+}$ samples prepared with different reaction time are displayed in Fig. 3. It is fantastic to find that the products present similar spherical morphologies with increasing the reaction time. In a very short reaction time (20 min), $\text{CaF}_2:5\% \text{Eu}^{3+}$ has become a sphere with an average diameter of $1.5 \mu\text{m}$ (Fig. 3a). In contrast to reaction time of 20 min, it remains spherical and clear structure which has a mean diameter of $2 \mu\text{m}$ when reacting 30 min (Fig. 3b). When the reaction time increases to 40 min, we are surprised to see that the products are composed of big sphere with a average diameter of $2.5 \mu\text{m}$ and small sphere of $0.8 \mu\text{m}$ (Fig. 3c). The uniform and mono-disperse spherical structures with $2.5 \mu\text{m}$ in diameter are observed in Fig. 3d. Further when prolonging reaction time to 90 or 120 min, the morphologies keep perfect spheres, whose diameter are also about $2.5 \mu\text{m}$ (Fig. 3e, f), being similar to 60 min (Fig. 2d). Therefore, we choose 60 min as the best reaction time.

Figure 3. EM images for $\text{CaF}_2:5\% \text{Eu}^{3+}$ samples prepared at 160°C with $\text{pH}=4$ for different reaction time: 20 min (a), 30 min (b), 40 min (c), 60 min (d), 90 min (e) and 120 min (f).

3.3. Effect of Reaction Temperature

We also study the effect of different reaction temperature on morphology of final samples. Figure 4 shows the corresponding SEM images of the synthesized crystals at different temperature. Apparently, Fig. 4a performs a perfect spherical structure with an average diameter of 2.5 μm . However, non-uniform spherical structures are found in Fig. 4b.

Figure 4. SEM images for $\text{CaF}_2:5\% \text{Eu}^{3+}$ samples prepared at (a) 160°C, (b) 180°C. Both of the samples were treated at different reaction temperature for 1 h, keeping $\text{pH}=4$.

3.4. Effect of pH Value

Figure 5 shows the SEM patterns of the as-prepared samples synthesized with different PH value as well as XRD data of $\text{CaF}_2:5\% \text{Eu}^{3+}$. As is shown, cubic $\text{CaF}_2:5\% \text{Eu}^{3+}$ (JCPDS No.35-0816 card) is formed, when $\text{PH}=4$ (Fig. 5d). When pH is below 4, such as 2, 3, impurity phase can be detected. While pH is above 4, all of the diffraction peaks of the XRD pattern can be indexed as pure cubic phase. Moreover, we also investigate the SEM patterns of the samples formed with different pH. Fig. 5a shows well-dispersed and highly-uniform spherical microsphere, when the pH value is 4. However, when pH value is 5 (Fig. 5b) and 6 (Fig. 5c), both of them indicate non-uniform morphologies and structures. Obviously, some micro-spheres with small sizes are observed in Fig. 5b and Fig. 5c.

Figure 5. SEM patterns with different pH value. pH: (a) 4, (b) 5, (c) 6. XRD patterns of the $\text{CaF}_2:5\% \text{Eu}^{3+}$ at 160°C, for 1h.

3.5. Photo-Luminescence Properties

As we all know, cubic CaF_2 is a better host lattice for the DC or UC luminescence of a variety of active rare ions. As a result, we mainly focus on the DC luminescence of Eu^{3+} , Tb^{3+} , $\text{Ce}^{3+}/\text{Tb}^{3+}$ in the as-prepared CaF_2 micro-spheres.

3.5.1. $\text{CaF}_2:\text{Eu}^{3+}$

Fig. 6 shows PL excitation and emission spectra of the $\text{CaF}_2:6\% \text{Eu}^{3+}$ sample at room temperature. We can find that excitation spectrum consists of the characteristic excitation lines of Eu^{3+} which has $4f^6$ configuration from 200 to 550 nm, and shows no difference in contrast to the excitation spectra of Eu^{3+} , which is doped in other fluoride materials [42-44]. Generally speaking, the main excitation lines are recognized as transitions, which are from the ground state 7F_0 to a variety of excited states: 5H_6 (320 nm), 5D_4 (370 nm), 5G_2 (380 nm), 5L_6 (393 nm) (strongest), 5D_3 (415 nm), 5D_2 (464 nm), 5D_1 (528, 537 nm). Furthermore, there are also weak peaks at 251, 268, 298 nm, which have little effect on the excitation of Eu^{3+} [45].

Figure 6. PL excitation ($\lambda_{\text{em}}=594 \text{ nm}$) and emission ($\lambda_{\text{ex}}=393 \text{ nm}$) spectra for the as-prepared $\text{CaF}_2:6\% \text{Eu}^{3+}$ micro-spheres.

In view of the strongest $^7F_0 \rightarrow ^5L_6$ transition of Eu^{3+} at 393 nm, the emission spectrum shows the most of emission lines of Eu^{3+} . $^5D_{0-3} \rightarrow ^7F_J$ is observed, such as: $^5D_1 \rightarrow ^7F_2$ at 554 nm; $^5D_0 \rightarrow ^7F_1$ at 582 and 590 nm; $^5D_0 \rightarrow ^7F_2$ at 620 nm and so on. Apparently, both $^5D_0 \rightarrow ^7F_1$ at 582 and 590 nm and $^5D_0 \rightarrow ^7F_2$ at 620 nm are the major emission spectrum.

3.5.2. $\text{CaF}_2:\text{Tb}^{3+}$

Fig. 7 shows PL excitation and emission spectra of the 6mol % Tb^{3+} -doped CaF_2 . It is found that the excitation peaks can be designated as the transitions from the ground state 7F_0 to other excited states: 215 nm (5I_6), 259 nm (5H_6), respectively. Taking 215 nm as excitation wavelength, which is the strongest excitation wavelength, we received the emission spectrum of the sample. It performs four obvious peaks centered at 494, 544, 591, and 625 nm, growing out of the transitions from the 5D_4 excited-state to the 7F_J ($J=6, 5, 4, 3$) ground states of the Tb^{3+} ion. Obviously, the most main

transitions is centered at 544 nm ($^5D_4 \rightarrow ^7F_5$), which emerges strong green emission.

Figure 7. PL excitation ($\lambda_{em}=544$ nm) and emission ($\lambda_{ex}=215$ nm) spectra for the as-prepared $\text{CaF}_2:6\% \text{Tb}^{3+}$ micro-spheres.

3.5.3. $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$

As is shown in Figure 8a, under examination at 544 nm which corresponds to $^5D_4 \rightarrow ^7F_5$ emission of Tb^{3+} , $\text{Ce}^{3+}/\text{Tb}^{3+}$ co-doped CaF_2 micro-spheres performed a broad and strong peaks derived from the allowed $4f \rightarrow 5d$ transitions of Ce^{3+} and some weak peaks coming out of parity-forbidden $4f \rightarrow 4f$ transitions of Tb^{3+} ions. The weak peaks below 275 nm originates from the $\text{Tb}^{3+} 4f^8$ transitions, containing the peaks at 215 nm ($^7F_6 \rightarrow ^5I_6$), 259 nm ($^7F_6 \rightarrow ^5H_6$). With increasing Ce^{3+} content (below 1%), the intensity of the bands at 260 nm, 259 nm and 303 nm increased gradually, and the peak at 215 nm is dominant. However, when the Ce^{3+} content increases to 1% or beyond 1%, the peak at 303 nm is dominant.

To the best of our knowledge, Ce^{3+} is a great sensitizer for the luminescence of Tb^{3+} in many host materials. As a result, co-doping Ce^{3+} into host lattices is an excellent strategy to improve the luminescence of Tb^{3+} . In our work, Ce^{3+} and Tb^{3+} ions were concurrently doped into CaF_2 matrix. As a result, the existence of the Ce^{3+} absorption broad band (Figure 8a) and the excitation band of Ce^{3+} and Tb^{3+} emission transitions (Figure 8c), verified the appearance of the energy transfer from Ce^{3+} to Tb^{3+} . As demonstrated in Figure 8b, highly efficient green emission of Tb^{3+} ions was observed because of $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer in the $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$ system.

Figure 8b shows the emission spectra of $\text{CaF}_2:y\text{Ce}^{3+}/6\%\text{Tb}^{3+}$ ($0.01\% \leq y \leq 6\%$) products with different Ce^{3+} -doping concentrations. Under excitation at 303 nm, each emission spectrum is composed of a broad peak coming from Ce^{3+} ions and some intense peaks at 494 nm, 544 nm, 584 nm and 625 nm on account of the $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4$, and 3) transitions of Tb^{3+} ions, respectively. The strongest peak is at 544 nm which is in the green emission peak from $^5D_4 \rightarrow ^7F_5$ transition. With increasing Ce^{3+} concentration (y value), the emission intensity of Tb^{3+} ions increases gradually. When adding up to a maximum value at $y = 1\%$, however, the

emission intensity of Tb^{3+} ions decreases with further increasing y value. The emission intensity of Ce^{3+} ions is very weak in comparison with Tb^{3+} ions.

Figure 8. (a) Excitation spectra of $\text{CaF}_2:y\text{Ce}^{3+}/6\%\text{Tb}^{3+}$ ($0.01\% \leq y \leq 6\%$) monitored at 544 nm. (b) Emission spectra of $\text{CaF}_2:y\text{Ce}^{3+}/6\%\text{Tb}^{3+}$ ($0.01\% \leq y \leq 6\%$) micro-spheres under 303 nm excitation. (c) $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer of $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$.

4. Conclusion

In summary, highly uniform and well-dispersed $\text{CaF}_2:\text{Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Ce/Tb}$) microsphere with DC luminescence were successfully synthesized by a one-step facile and effective hydrothermal method. The effects of reaction temperature, time, and pH value on the structures, morphologies, and sizes of samples have been investigated. It is found that a preferred reaction temperature of 160°C , controlling $\text{pH} = 4$ and reacting for 60 min are the optimum conditions which make us receive uniform and mono-disperse spherical structures with $2.5\ \mu\text{m}$ in diameter. With regard to DC luminescence, under UV excitation, the as-prepared $\text{CaF}_2:6\%\text{Eu}^{3+}$ products perform the red light, whereas the $\text{CaF}_2:6\%\text{Tb}^{3+}$ sample shows a intense green emission. Furthermore, compared with the $\text{CaF}_2:6\%\text{Tb}^{3+}$ sample, highly efficient green emission of Tb^{3+} ions was detected in $\text{CaF}_2:\text{Ce}^{3+}/\text{Tb}^{3+}$ sample because of $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer. It turns out that the received CaF_2 materials are great host lattice for the DC luminescence of Eu^{3+} , Tb^{3+} and $\text{Ce}^{3+}/\text{Tb}^{3+}$. On account of their charming luminescence properties, these phosphors are expected to have more promising applications.

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