# Preparation and Optical Spectroscopy of BaFCl/$Eu^{2+}$: a Photoluminescent X-ray Storage Phosphor

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## Abstract

*Computed radiography, a digital X-ray imaging technique using photostimulable phosphor storage media is one of the primary candidates to replace the long-established screen-film radiography. It allows the combination of highly advanced photographic technology with digital computer techniques. X-ray storage phosphors such as BaFX/*$Eu^{2+}$ *(X= Cl, Br, and I) have been widely discussed in the field of the radiography and crystallography. In the present paper, a new method for the preparation of flake-like* $Eu^{2+}$ *doped BaFCl nano/submicrocrystal has been developed. A co-precipitation chemical reaction between* $BaCl_2$ *and* $NH_4F$ *aqueous solution in reverse micelles has been used at room temperature. Doping with* $Eu^{2+}$ *was carried out by adding* $EuCl_3$ *during preparation time. A fine powder consisting of 60 to 500 nm flake-like microcrystals has been obtained by a one-step chemical reaction without thermal treatment. The storage phosphor has been characterized by synchrotron X-ray powder diffraction, scanning electron microscope and optical methods. Photoluminescence (PL) measurements attest the europium impurification and oxygen contamination during preparation. We believe the prepared phosphors may have potential applications in imaging plates.*

## Introduction

Over the past few years, submicron- and nano-particle luminescent materials have attracted tremendous attention because of their narrow emission bandwidth, high emission quantum yield and inherent photostability [1-3]. Having low vibration energies, the nano/submicro rare earth ion doped fluorides phosphors will play outstanding roles in luminescent materials, solid-state lasers, lighting and displays devices, and bio-labels in the near future [4-7]. The BaFX (X = Cl, Br, I) compounds are ternary alkaline earth compounds that have the matlockite structure with the space group P4/nmm (No.129) [8], which are interesting for both fundamental research and various applications [9]. In addition, BaFX materials are one of the most efficient host into which rare ions can doped. The doped BaFX materials have many important technological applications. For instance, not only BaFCl:$Sm^{2+}$ can be used as a luminescence sensor in low pressure [10], but also can be made into pressure celebrants in diamond-anvil cells [11-12]. More important, europium doped BaFX can be wildly used as X-ray storage phosphors in the imaging plates (IPs) [13]. IPs are crucial component in computed radiography (CR), which is one of the primary candidates to replace the conventional screen-film radiography. Comparing to other imaging sensors, the imaging plates have many advantages, such as wider dynamic range, higher resolution, better quantum efficiency and reusable [14]. In most studies, the X-ray storage phosphors are prepared by conventional high temperature solid-state reaction. The as-obtained products are irregular, large in size and non-uniform, which result in that the currently X-ray storage phosphors suffer from some disadvantages, including limited signal-to-noise ratio, rapid erasure of the information and high cost [15]. Recently, Chen et al. discovered that the nanocrystalline phosphors had potential to overcome these problems because of their large specific surface areas, short luminescence lifetime and low Rayleigh scattering in polymer films [16]. Chen et al. had synthesized BaFBr:$Eu^{2+}$ particles in acid slutions with stabilizer poly (vinyl alcohol) under $N_2$ at 80 ℃ [16], and Riesen et al. had reported the synthesis of BaFCl:$Sm^{3+}$ nanocrystal by co-precipitation from $BaCl_2$ and $NH_4F.HF$ aqueous solutions [17]. However, these methods are rather complicated and involving toxic reactants, which limit the practical applications. Therefore, it is highly desirable to develop a facile one-step, benign and cost-efficient synthetic approach. Recently, reverse-micelle systems have been widely used to prepared nano/submicro particles at room temperature [18]. Accordingly, we present a general strategy for synthesing BaFCl:$Eu^{2+}$ nano/submicro particles via microemulsion process. In contrast to previous synthesis methods, this route is relatively simple, nontoxic and environmentally friendly. Moreover, the size of the products can be easily controlled by simply changing the reaction time. The phase structure, morphologies and photoluminescence properties are discussed in detail in this paper.

## Experiment Method

All of the chemical reagents were of analytical purity. The water used was distilled water. A typical procedure involved 1-octane (48.2 mmol) as oil phase, CTAB (5.5 mmol) as surfactant and n-butanol (21.6 mmol) as co-surfactant. Two microemulsions containing 2.0 mL 0.75 M $BaCl_2.2H_2O$ solution (A) and 2.0 mL of 0.6 M $NH_4F$ solution (B) were prepared and vigorously stirred for 10 minutes. Under continuous vigorous agitation, inverse micell B was added into inverse micell A slowly. The new microemulsion solution was stirred for some time at room temperature. The obtained white slurry was centrifuged and washed with ethanol and water for 5 times, and finally dried in a vacuum at 50 ℃ for 5 h. Different reaction time was varyed to investigate the morphological evolution of the BaFCl nanocrystals. The europium doped products were also synthesized by the same procedures as above, except for mixing a stoichiometric amount of $EuBr_2$ (2 mol %) powders into solutions A at the initial stage.

Powder X-ray diffraction (XRD) analysis was collected by using a X-ray diffractometer (Bruker) with Cu-$K\alpha$ radiation ($\lambda$ =

1.54056 Å). Morphologies of as-synthesized samples were characterized by a field emission scanning electron microscope (JEM 2100F). The chemical composition of the sample was identified by energy-dispersive X-ray spectroscope (EDS). Transmission electron microscopy (TEM), selected area electron diffraction (SAED) patterns and high resolution TEM images were recorded on a JEOL microscope (JEM 2100F). Infrared spectra of the sample were performed on a Fourier transform infrared (FT–IR) spectrometer (Varian 3100) by using the KBr pellet technique. Raman shift was carried out by using a Raman spectrometer (Via-Reflex). Photoluminescence excitation and emission spectra were recorded on the Cary Eclipse luminescence spectrometer (Varian). The luminescence decay curves were obtained from a Combined Fluorescence lifetime and Steady state Spectrometer (F900). All measurements were performed at room temperature.

## Results and discussion

### *Crystal Phase and Morphology analysis*

Figure 1 illustrates the XRD patterns of BaFCl:$Eu^{2+}$ particles prepared with different reaction times. All diffraction peaks can be indexed as a pure tetragonal phase of BaFCl with cell parameters of a = b = 4.4125 ± 0.0054 Å and c = 7.2697 ± 0.0032 Å (JCPDS card No. 24-0096). No other characteristic peaks were detected, implying the high purity of the prepared BaFCl.

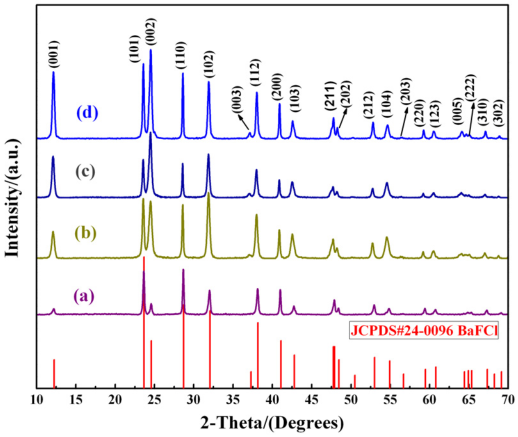

**Figure 1.** *Powder XRD patterns of BaFCl:$Eu^{2+}$ products prepared at the same microemulsion condition with different reaction times: (a) 10 min; (b) 30 min; (c) 1 h; (d) 3 h in comparison to the standard card (JCPDS Card No.24-0096).*

The peaks are weak and broad, which indicates the small size of the as-synthesized samples. It is found that the crystallization of BaFCl crystal can be controlled simply by varying the reaction time. From figure 1, when the reaction time prolong to 3 h, all peaks intensity of the products increase gradually, and demonstrating the crystallinity of products become better. Through a careful observation, we can easily discover that the diffraction peaks at about 12.25, 24.60 and 37.30º corresponding to planes of (001), (002) and (003) respectively changed significantly. The result implies that our BaFCl crystals preferred growth along <*hk0*> direction in the presence of surfactants that affect the final size and morphology of the products. Furthermore, according to the Debye-Scherrer equation from the half-width of the peaks (101), (002) and (110), the average crystalline sizes of the powders are estimated to be in the range of 10-30 nm.

Figure 2 shows the FE-SEM images of BaFCl:$Eu^{2+}$ nano/microcrystals. It is obvious that all the particles are roughly square flake, and tend to pile up and aggregate together. The average size of the particles for the sample A is in the range from 60 to 80 nm for length and 20-40 nm for the thickness (measured from standing thin plates), while that for the sample D is about 200-500 nm and 80-100 nm. It implies that increasing the reaction time leads the size of particles to increase, which confirms the XRD analysis. However, the particle sizes observed by SEM are larger than the crystalline sizes calculated from XRD patterns, which maybe caused by particle aggregation. And from the observation and analysis, the BaFCl:$Eu^{2+}$ particles with uniform flake-like morphology can self-assemble in the influence of surfactants. Consequently, the reverse micelles system, including the confinement of water pools and surfactants are crucial to the construction of the uniform flake-like two-dimensional structures.

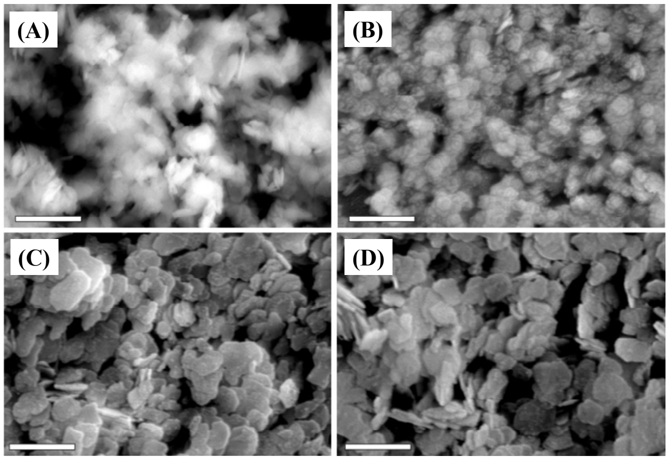

**Figure 2.** *FE-SEM images of the BaFCl:$Eu^{2+}$ samples synthesized at the same microemulsion condition with different times: (A) 10 min; (B) 30 min; (C) 1 h; (D) 3 h （scale bars correspond to 1μm）.*

The morphology and structures of the products are investigated by TEM. Figure 3A shows TEM images of BaFCl:$Eu^{2+}$ particles (30 min reaction time). The corresponding TEM image further demonstrates the sample is composed of roughly quadrangle geometrical shape. Furthermore, the TEM image shows that the surface consists of numerous tiny nanoparticles, which correspond well to the SEM observation. The energy-dispersive X-ray spectroscopy (EDS, figure 3B) confirms the product consists of only barium, fluoride, chloride and europium elements. Furthermore, the quantitative analysis result shows a Ba: F: Cl: Eu atomic ratio of 1: 0.94: 0.96: 0.016, which is almost in accord with stoichiometric of BaFCl:$Eu^{2+}$ sample. The signal attributed to the Au comes from the coater for SEM testing. Figure 3C depicts the SAED of recorded in the rectangular area of figure 3A. The regular diffraction spots of SAED image suggests that the products are single crystal nature, and can be well indexed as tetragonal phase. A HRTEM image (figure 3D) shows the lattice fringes. The interplanar spacing is about 0.310 and 0.712 nm denoted in the image, corresponding well to the (110) and (001) planes of tetragonal BaFCl single crystals respectively. The relevant fast Fourier transform (FFT) pattern (figure 3D) also displays the lattice clearly. The above results suggest that BaFCl:Eu$^{2+}$ with high crystallinity can be obtained.

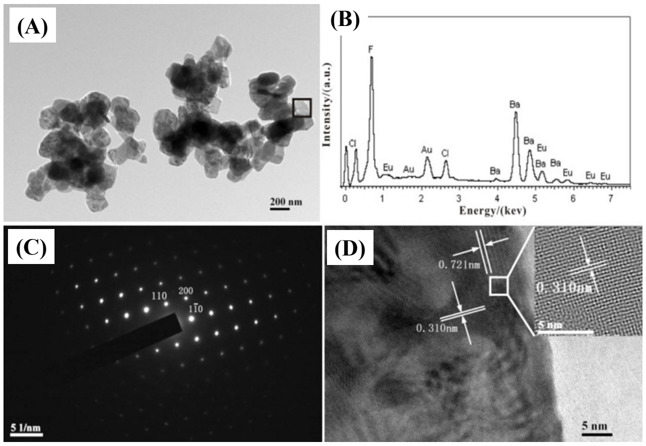

***Figure 3.*** *(A) TEM image, (B) EDS pattern, (C) SAED pattern, (D) HRTEM image of the sample (30 min reaction time, the inset shows high-magnification HRTEM image).*

FT-IR and Raman spectra were used to determine whether surfactant and other ions were removed from the products after washing, as shown in figure 4.

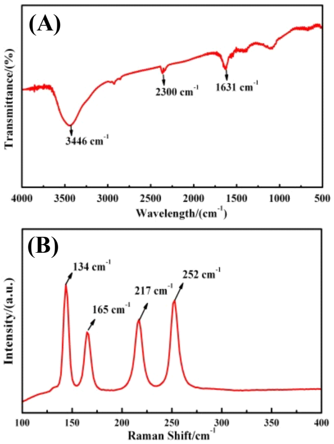

***Figure 4.*** *Fourier transforms infrared spectroscopy (A), laser Raman spectroscopy (B) of the synthesized sample.(30 min reaction time)*

In the FT-IR spectrum (figure 4A), three distinct IR peaks at about 3446, 1631 and 2300 cm$^{-1}$ can be assigned to stretching bands of water and carbon dioxide in the atmosphere [19]. Moreover, no typical C–H and C–O stretching vibration bands can be detected, indicating the complete removals of the CTAB molecules from the surface of the samples. We can safely conclude that trace or no organic species absorb on the surface of obtained particles after washing. Raman spectroscopy was further used to affirm the structural characterization of our synthesized crystals. In the Raman spectrum (figure 4B), four Raman modes are observed at 134, 165, 217 and 252 cm$^{-1}$. The peaks at about 134 and 252 cm$^{-1}$ arising from $E$g vibrations are assigned to Ba–Cl stretching. The band at 217 and 165 cm$^{-1}$ can be attributed to $B_{1g}$ and $A_{1g}$ symmetric vibrations modes. The results match well with the reported bulk tetragonal BaFCl [9]. No other impurities phonon modes are observed in the spectra. XRD, IR, EDS and Raman studies leave no doubt that our products are pure BaFCl:Eu$^{2+}$.

## *Photoluminescence properties*

Figure 5A presents the typical excitation and emission spectra of the BaFCl:Eu$^{2+}$ after annealing at 400 ℃ for 1 h under reduced atmosphere.

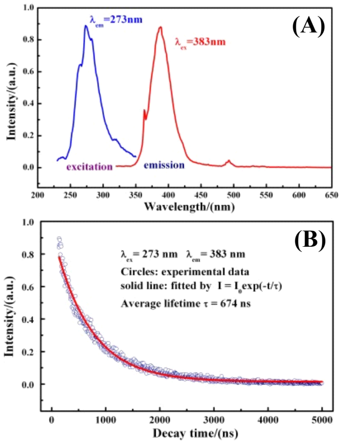

***Figure 5.*** *(A) Excitation and emission spectra, (B) decay curve of Eu$^{2+}$ luminescence of BaFCl:Eu$^{2+}$ nanocrystals (30 min reaction time) after sintering at 400 ℃ under reduced atmospheres.*

The excitation spectrum exhibits a broad excitation band in the range of 240–350 nm. The 263 nm excitation band may from O$^{2-}$– h centers in doped BaFCl crystals [20]. The band maxima centered at 273 nm can be assigned to the 4f$^7$ ($^8$S$_{7/2}$) → 4f$^6$5d$^1$ ($^2$t$_{2g}$) of Eu$^{2+}$ [21]. The peaks around 290 nm to 330 nm are attributed to spin–orbit multiplets 4f$^7$ ($^8$S$_{7/2}$) → 4f$^6$ ($^7$F$_J$, $J$ = 0-6) [22]. The emission spectrum shows a sharp band center at 387 nm and a small shoulder at 365 nm, and they are from the 4f$^6$5d$^1$ ($^2$t$_{2g}$) → 4f$^7$ ($^8$S$_{7/2}$) and 4f$^7$ ($^6$P$_{7/2}$) → 4f$^7$ ($^8$S$_{7/2}$) transition of Eu$^{2+}$ ion respectively. Noticeable, a weak band observed at longer wavelengths at about 490 nm can be due to the excited oxygen-vacancy centers transition to the ground state [13]. As is known, oxygen is easy to incorporate in the alkaline earth sub-lattice as O$^{2-}$ with a charge-compensating vacancy. The results are all good agreement with previous literatures [20, 21]. We also investigated the kinetic properties for the luminescence of the flake-like BaFCl:Eu$^{2+}$ (1.6 mol%) crystals by photoluminescence decay curve. The typical decay curve for the luminescence of Eu$^{2+}$ ions (monitored by 4f$^6$5d$^1$ → 4f$^7$), is shown in figure 5B. It can be observed that the decay curve can be well fitted into single-exponential function as $I = I_0 \exp(-t/\tau)$, in which $I_0$ is the initial emission intensity at t = 0 and $\tau$ is the 1/e lifetime of the emission center. The average lifetime for the $Eu^{2+}$ is determined to be 674 ns, which is shorter than that of the bulk about 800 ns [23]. Two reasonable explanations can be described as follows. On one hand, the increase of non-radiative transition rate caused by much more surface defects in flake-like nanocrystals. On the other hand, more electrons will be trapped on the exposed (001) faces; this promotes the recombination between electrons and defects.

## Conclusions

In conclusion, nano/micro flake-like BaFCl and $BaFCl:Eu^{2+}$ single crystals were successfully prepared by the simple reverse micelle microemulsion method at room temperature. Various spectroscopic techniques such as XRD, FT-IR, Raman, SEM, TEM, EDS, PL, and a dynamic process were used to characterize the phase, size, morphology, and luminescence properties of the products. The products have quasi-square flake-like morphology and a narrow size distribution. The preliminary results show that crystals may prefer the growth toward <*hk0*> direction under the influence of surfactants. Moreover, the size of the products can be simply modulated by varying reaction time. The prepared $BaFCl:Eu^{2+}$ does not exhibit any luminescence, while the samples show strong emission signal due to $4f^65d^1$ ($^2t_{2g}$) → $4f^7$ ($^8S_{7/2}$) transitions of $Eu^{2+}$ ion after annealing under reduced atmosphere. The decay curve of the phosphor can be well fitted into a single-exponential function with PL average lifetime about 674 ns, which is shorter than the bulk phosphors (about 800 ns). The BaFCl and $BaFCl:Eu^{2+}$ have potential applications as an X-ray storage phosphor used in computed radiography and other technology fields. Further work is under way to study the photostimulated and imaging properties of the $BaFCl:Eu^{2+}$ single crystals, as well as the possibility of synthesizing other rare ions doped matlockite structure compounds.

## References

[1] Yi,G.,Peng,Y.,et al.,"Strong Red-Emitting near-Infrared-to-Visible Upconversion Fluorescent Nanoparticles",Chem.Mater, 23, 2729 (2011).

[2] Yang, P.,Gai, S.,et al., "Uniform Hollow $Lu_2O_3$:Ln (Ln = $Eu^{3+}$, $Tb^{3+}$) Spheres: Facile Synthesis and Luminescent Properties", Inor.Chem, 50, 2182 (2011).

[3] Shi,F.,Wang,J.,et al.,"Facile synthesis of β-$NaLuF_4$:Yb/Tm hexagonal nanoplates with intense ultraviolet upconversion luminescence", Crystengcomm, 13, 3782 (2011).

[4] Zhang,C.M.,Li,C.X.,et al., "Facile and Controllable Synthesis of Monodisperse $CaF_2$ and $CaF_2:Ce^{3+}/Tb^{3+}$ Hollow Spheres as Efficient Luminescent Materials and Smart Drug Carriers", Chem-Eur J, 16, 5672 (2010).

[5] Ju, Q.,Luo, W., et al., "Poly (acrylic acid)-capped lanthanide-doped BaFCl nanocrystals: synthesis and optical properties", Nanoscale, 2, 1208 (2010).

[6] Wang, G. F.,Peng, Q., et al., "Upconversion Luminescence of Monodisperse $CaF_2:Yb^{3+}/Er^{3+}$ Nanocrystals", J. Am. Chem. Soc, 131, 14200 (2009).

[7] Li,C.X.,Quan,Z.W.,et al.,"Shape controllable synthesis and upconversion properties of $NaYbF_4/NaYbF_4:Er^{3+}$ and $YbF_3/YbF_3:Er^{3+}$ microstructures", J. Mate.Chem, 18, 1353 (2008).

[8] Beck,H.P., "Refinement of the Crystal-Structures of YbFCl, SmFCl, SrFCl, and BaFCl", ZACC Chemie, 451, 73 (1979).

[9] Hassan, F. E.,Akbarzadeh, H., et al., "Structural and electronic properties of matlockite MFX (M=Sr,Ba,Pb;X=Cl,Br, I) compounds", J. Phys. Chem. Sol, 65, 1871 (2004).

[10] Comodi, P.,Zanazzi, P. F., "Improved calibtration curve for the $Sm^{2+}$:BaFCl pressure sensor", J. Appl. Crystallogr, 26, 843 (1993).

[11] Shen, Y. R.,Holzapfel, W. B., "Effect of Pressure on Energy-Levels of $Sm^{2+}$ in BaFCl and SrFCl", Phys. Rev. B, 51, 15752 (1995).

[12] Shen, Y. R.,Gregorian, T., et al., "Progress in Pressure Measurements with Luminescence Sensors", High Pressure Research, 8, 73 (1991).

[13] Secu,M.,Matei,L.,et al.,"Preparation and optical properties of $BaFCl:Eu^{2+}$ X-ray storage phosphor", Optic. Mater,15,115 (2000).

[14] Amemiya,Y.,Miyahara, J.,"Imaging Plate Illuminates Many Fields", Nature, 336, 89 (1988).

[15] Liu,Z.Q.,Massil,T.,et al.,Spectral hole-burning properties of $Sm^{2+}$ ions generated by X-rays in $BaFCl:Sm^{3+}$ nanocrystals. In Proceedings of the Tenth International Meeting on Hole Burning, *2009*, 2010;3, 1539.

[16] Chen, W. S., Nanoparticle optical storage apparatus and methods of making and using same. (2006).

[17] Riesen, H.,Kaczmarek, W. A., "Efficient X-ray Generation of $Sm^{2+}$ in Nanocrystalline $BaFCl/Sm^{3+}$:a Photoluminescent X-ray Storage Phosphor", Inor. Chem, 46, 7235 (2007).

[18] Ganguli,A.K.,Ganguly,A., et al., "Microemulsion-based synthesis of nanocrystalline materials", Chem. Soc.Rev, 39, 474 (2010).

[19] Lian,H.Z.,Ye,Z.R.,et al., "Surprising arching sheet-like dendrites growing from $BaF_2$ nanocubes", Nanotechnology, 15, 1455 (2004).

[20] Meng,X.G.,Wang,Y.S.,et al., "Study on the hole-type traps in BaFCl : $Eu^{2+}$ phosphor", J. Lum, 122, 385 (2007).

[21] Chen, W.,Kristianpoller, N., et al., "X-Ray Storage Luminescence of $BaFCl:Eu^{2+}$ Single Crystals", J.Phys.Chem. B, 109, 11505 (2005).

[22] Kumar,V.R.,Narasimhulu,K.V.,et al., "EPR and optical investigations of $Eu^{2+}$ doped BaFCl phosphor", Phys.B-Conde.Mat,348,446 (2004).

[23] Spaeth,J.M.,"Recent developments in X-ray storage phosphor materials", Radiat Meas, 33, 527 (2001).

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