



Temperature Dependent Photoluminescence Properties of Nanocrystalline BaFCl:Sm³⁺ X-ray Storage Phosphor

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The temperature dependence of photoluminescence properties of the Sm³⁺ ⁴G_{5/2}-⁶H_{7/2} and the Sm²⁺ ⁵D₀-⁷F₀ transitions in nanocrystalline BaFCl were investigated upon X-irradiation and photobleaching. Upon X-irradiation, two types of Sm³⁺ sites with different local coordination environments are created below 80 K. For the Sm²⁺ ions, photoluminescence occurs from five inequivalent sites below 120 K whereas two sites are detected at 293 K.

1. Introduction

Considerable attention has been paid to the spectroscopic properties of samarium ion activated alkaline-earth fluorohalides *MeFX* (*Me* = Ca, Sr and Ba; *X* = Cl, Br and I) since the first observation of photon-gated spectral hole-burning in BaFCl:Sm²⁺ by Winnacker *et al.* [1]. We have recently reported that nanocrystalline BaFCl:Sm³⁺, as prepared by wet chemistry, is an efficient photoluminescent storage phosphor for ionizing radiation [2]. Upon X-irradiation, the Sm³⁺ ions in the BaFCl host are reduced to the +2 oxidation state which can be efficiently read out by measuring the narrow *f-f* luminescence lines via excitation into the parity-allowed 4f⁶→4f⁵5d transitions in the blue-violet region of the spectrum that are very intense. The phosphor has a range of potential applications such as in medical X-ray imaging and personal radiation monitoring (dosimetry).

2. Experimental

A.C.S. reagent grade chemicals were used without further purification. The nanocrystalline BaFCl:Sm³⁺ was prepared by a co-precipitation method [3]. The X-irradiation of the sample was realised by exposure in a powder X-ray diffractometer (40 kV, 25 mA, Cu K_α) and the radiation dose was cross-calibrated against a dental X-ray unit (Belmont Searcher Model DX-068).

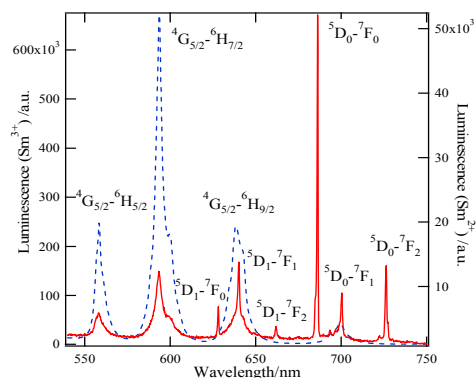
To measure the photoluminescence spectra, the sample was mounted on the cold finger of a closed-cycle refrigerator (Janis/Sumitomo SHI-4.5) and excited by the light of a focused 405 nm blue-violet laser diode. The emission light was collimated and then focused onto the entry slit of a Spex 1404 monochromator (1200 grooves/mm holographic grating) using 75 mm and 200 mm lenses. The light was modulated with a chopper and detected by a photomultiplier (Hamamatsu R928). The signal was processed by a current-to-voltage preamplifier (Femto DLPCA-200) and a lock-in amplifier (Stanford Research System SR910 DSP) before being collected on a PC.

3. Results

Fig. 1 shows the photoluminescence spectra of nanocrystalline BaFCl:Sm³⁺ at 293 K before and after X-irradiation [4]. As follows from Fig. 1, before X-irradiation, the photoluminescence spectrum of the sample consists of four broad emission lines at 559, 594, 639, 701 nm corresponding to the ⁴G_{5/2}-⁶H_J (*J* = 5/2, 7/2, 9/2, 11/2) transitions of Sm³⁺ ions. After X-irradiation, in addition to the broad Sm³⁺ emission lines, narrow and characteristic Sm²⁺ luminescence lines at 629, 640, 663, 687, 702 and 727 nm due to the ⁵D₁-⁷F_{0,1,2} and



Fig. 1. Photoluminescence spectra of nanocrystalline BaFCl:Sm³⁺ at 293 K before (blue dashed lines) and after (red solid lines) irradiation with 50 mGy surface dose of X-rays. The initial and final electronic terms for the Sm³⁺ and Sm²⁺-based transitions are indicated. The spectra before and after X-irradiation were excited at 401 nm and 415 nm, respectively.



⁵D₀₋₇F_{0,1,2} transitions are observed. From Fig. 1 it follows that upon X-irradiation, the Sm³⁺ ions can be reduced efficiently to Sm²⁺ ions in nanocrystalline BaFCl:Sm³⁺.

To gain a better understanding of the storage mechanism of the nanocrystalline BaFCl:Sm³⁺ X-ray storage phosphor, we have further investigated the photoluminescence properties of the ⁴G_{5/2-6}H_{7/2} transition of Sm³⁺ ions and the ⁵D₀₋₇F₀ transition of X-ray generated Sm²⁺ ions in the temperature range of 2 to 293 K upon X-irradiation and subsequent photobleaching. The results are illustrated in Fig. 2 and Fig. 3.

Fig. 2 shows the photoluminescence spectra of the ⁴G_{5/2-6}H_{7/2} transition of Sm³⁺ ions in nanocrystalline BaFCl:Sm³⁺ from 2 to 293 K before and after X-irradiation, and after subsequent photobleaching. As shown in Fig. 2(a), before X-irradiation, the temperature dependence of the photoluminescence spectra can be divided into two temperature ranges,

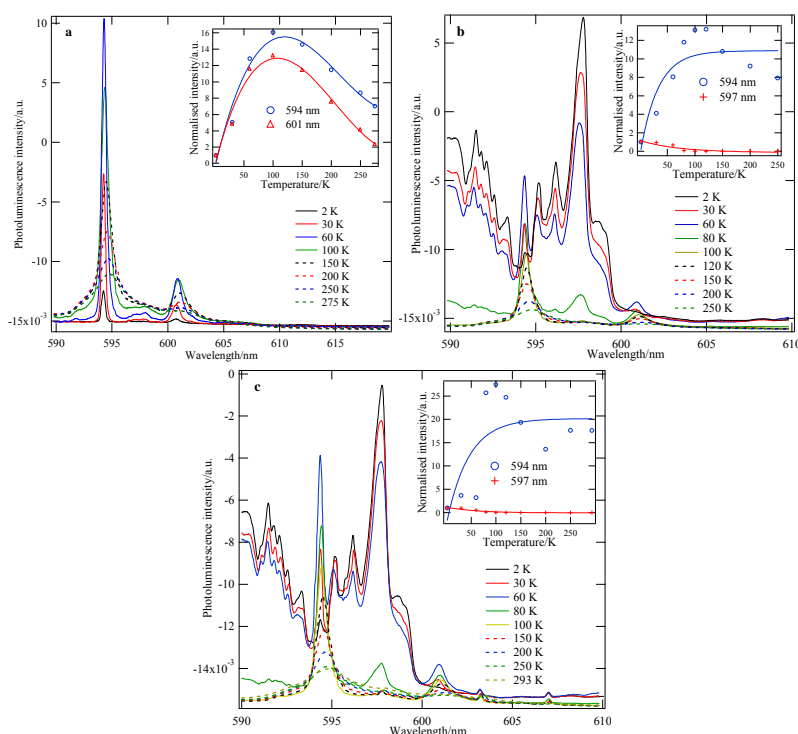


Fig. 2. Temperature dependent photoluminescence spectra of the ⁴G_{5/2-6}H_{7/2} transition of Sm³⁺ ions in nanocrystalline BaFCl:Sm³⁺ (a) before X-irradiation, (b) after X-irradiation and (c) after photobleaching. The luminescence was excited by 0.14 W·cm⁻² of a 405 nm blue-violet laser diode. The sample was irradiated with 150 Gy of X-rays (40 kV, 25 mA, Cu K α) and subsequently photobleached by 1 x 10⁴ J·cm⁻² of 405 nm blue-violet laser diode light. The insets show the photoluminescence intensities at selected wavelengths as a function of temperature.



below 100 K and above 100 K. Below 100 K, the spectra consist of mainly two emission lines at 594 and 601 nm, with increasing photoluminescence intensities from 2 to 100 K. In contrast, above 100 K, the two emission lines become broader and red-shifted by 0.4 nm. The integrated photoluminescence intensities of the two peaks decrease with increasing temperature from 100 to 293 K.

Upon X-irradiation, significantly different photoluminescence spectra of the Sm^{3+} ${}^4\text{G}_{5/2}$ - ${}^6\text{H}_{7/2}$ transition are observed, as is shown in Fig. 2(b). In the temperature range of 2 to 80 K, except for the luminescence lines at 594 and 601 nm, an additional group of emission lines, e.g. at 595, 596 and 597 nm originating from the ${}^4\text{G}_{5/2}$ - ${}^6\text{H}_{7/2}$ transition of Sm^{3+} ions are detected. Here we define the two groups of emission lines, i.e. the lines at 594 and 601 nm which are similar as those observed before X-irradiation and the lines at 595, 596, and 597 nm as group I and group II, respectively. As shown in Fig. 2(b), the highest emission line below 80 K is at 597 nm which is 3 nm red-shifted in comparison with those observed before X-irradiation (at 594 nm). With increasing temperature from 2 to 80 K, the integrated photoluminescence intensities of the group II emission lines decreases whereas those of the group I emission lines increases, leading to the highest emission line at 80 K observed at 594 nm. With the temperature increased above 80 K, the group I emission lines at 594 and 601 nm return to dominate the photoluminescence spectra of the ${}^4\text{G}_{5/2}$ - ${}^6\text{H}_{7/2}$ transition of Sm^{3+} ions. The different temperature dependence of the two groups of Sm^{3+} emission lines indicates the presence of two Sm^{3+} sites with different local structures in the BaFCl host after X-irradiation. This is further confirmed by the similar temperature dependence of the photoluminescence spectra of the Sm^{3+} ${}^4\text{G}_{5/2}$ - ${}^6\text{H}_{7/2}$ transition after photobleaching, which is shown in Fig. 2(c). Furthermore, a detailed examination of the photoluminescence spectra before and after photobleaching shows that upon photobleaching, the photoluminescence intensities of emission lines from group I increase whereas those of the emission lines from group II decrease for all temperatures, implying that the two groups of lines correspond to two Sm^{3+} centres with different local surroundings.

The significant change in the photoluminescence spectra of Sm^{3+} ${}^4\text{G}_{5/2}$ - ${}^6\text{H}_{7/2}$ transition upon X-irradiation and photobleaching must be due to some changes in the local coordination environment of Sm^{3+} ions. In BaFCl: Sm^{3+} , the Sm^{3+} ions enter the host lattice by replacing Ba^{2+} ions. Due to the requirement of charge compensation, the presence of various defects such as F or Cl vacancies and oxygen defects around the Sm^{3+} ions as well as multiple sites of Sm^{3+} ions can be expected. Upon X-irradiation, free electron-hole pairs are created. Some of the created electrons are trapped at certain Sm^{3+} ions (denoted as type I Sm^{3+} ions), leading to the formation of Sm^{2+} ions [4]. The holes, e.g. V_{K} centres (holes shared between two adjacent halide ions), may be trapped at the charge-compensating defects of different Sm^{3+} ions (denoted as type II Sm^{3+} ions), causing the change of the Sm^{3+} local surroundings. The two different types of Sm^{3+} centres, i.e. type I and type II, play the different roles of creating Sm^{2+} ions and capturing holes upon X-irradiation, respectively, and account for the photoluminescence observed at 594 and 601 nm (group I) and 595, 596 and 597 nm (group II), respectively. Furthermore, from Fig. 2(b) it follows that the defect-related coordination environment of type II Sm^{3+} ions created by X-irradiation is only stable at temperatures up to 80 K. It is likely that at temperatures above 80 K, the defects (or the holes trapped at charge-compensating defects) around the type II Sm^{3+} ions start to diffuse away and become mobile in the host lattice. Similar temperature dependent behaviour was also reported in the investigation of the storage mechanism of photostimulable BaFBr: Eu^{2+} X-ray storage phosphor by optically detected electron paramagnetic resonance (ODEPR) [5]. It was found that upon X-irradiation of BaFBr: Eu^{2+} , $V_{\text{K}}(\text{Br}_2^-)$ centres are formed below 120 K. Upon



warming up to 120 K, the $V_k(\text{Br}_2^-)$ centres start to move around and recombine with O_F^{2-} centres, forming O_F^- centres.

In addition to the spectroscopy of the Sm^{3+} ions, the temperature dependence of photoluminescence spectra of the $^5\text{D}_0$ - $^7\text{F}_0$ transition of Sm^{2+} ions in nanocrystalline $\text{BaFCl}:\text{Sm}^{3+}$ after X-irradiation and photobleaching was also investigated. As shown in Fig. 3(a), after X-irradiation, five narrow emission lines at 685, 686, 687, 688 and 689 nm are detected originating from the $^5\text{D}_0$ - $^7\text{F}_0$ transition of Sm^{2+} ions at 2 K. Since the $^5\text{D}_0$ and $^7\text{F}_0$ are non-degenerate energy levels and each emission line associated with this transition must correspond to a different Sm^{2+} centre, it follows that five different Sm^{2+} crystallographic sites are generated in nanocrystalline $\text{BaFCl}:\text{Sm}^{3+}$ upon X-irradiation. With increasing temperature from 2 to 293 K, the five emission lines broaden and shift to shorter wavelength. Also, the integrated photoluminescence intensity at 688 nm increases from 2 to 293 K. The blue shift and broadening of photoluminescence lines of the $^5\text{D}_0$ - $^7\text{F}_0$ transition of Sm^{2+} ions in BaFCl with increasing temperature has also been demonstrated by Vink *et al.* [6]. This behaviour can be rationalised based on the phonon-induced dephasing processes which are negligible at low temperature and become more pronounced at higher temperatures.

After the sample is photobleached, only two emission lines at 688 and 689 nm due to the $^5\text{D}_0$ - $^7\text{F}_0$ transition of Sm^{2+} ions are detected over the entire temperature range, with increasing photoluminescence intensity at 688 nm from 2 to 293 K, as shown in Fig. 3(b). It has been shown that the photobleaching of Sm^{2+} ions is due to the photoionization process of Sm^{2+} to Sm^{3+} ions [4]. From Fig. 3(b) it follows that the photoionization of Sm^{2+} to Sm^{3+} ions is strongly associated with the local structure of Sm^{2+} ions.

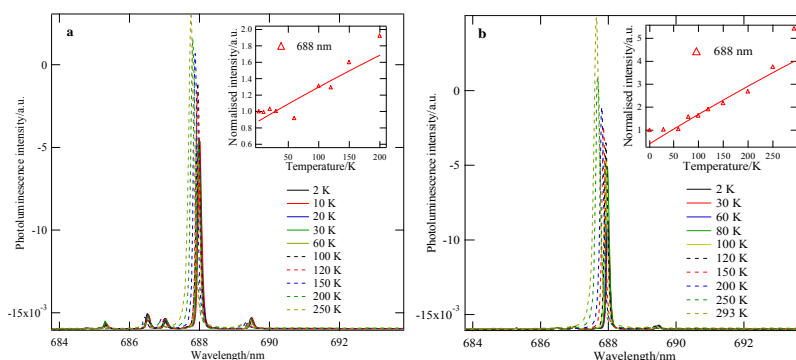


Fig. 3. Temperature dependent photoluminescence spectra of the $^5\text{D}_0$ - $^7\text{F}_0$ transition of Sm^{2+} ions in nanocrystalline $\text{BaFCl}:\text{Sm}^{3+}$ (a) after X-irradiation and (b) after photobleaching. The luminescence was excited by $0.14 \text{ W}\cdot\text{cm}^{-2}$ of a 405 nm blue-violet laser diode. The sample was irradiated with 150 Gy of X-rays (40 kV, 25 mA, Cu $K\alpha$) and subsequently photobleached by $1 \times 10^4 \text{ J}\cdot\text{cm}^{-2}$ of 405 nm blue-violet laser diode light. The insets show the photoluminescence intensities at selected wavelengths as a function of temperature.

Acknowledgments

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