

X-ray excited optical luminescence of CaF_2 : A candidate for UV water treatment

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Abstract

Secondary optical processes are becoming more and more important in health and environmental applications. Ultraviolet produced from secondary emission or scintillation can damage DNA by direct photoexcitation or by the creation of reactive oxygen species. X-ray Excited Optical Luminescence (XEOL) and Time Resolved XEOL (TRXEOL) results for the fast emitter, $\text{CaF}_2\text{:ZnO}$, that have been treated by heating in air and in vacuum, show that the scintillation from the Self Trapped Exciton (STE) emission of CaF_2 at 282 nm is dominated by a slow process (>100 ns). A faster but weaker 10 ns component is also present. The ZnO and CaF_2 show independent emission. The ZnO bandgap emission at 390 nm has dominant lifetimes of less than 1 ns.

1. Introduction

Use of optical processes in health and environment is well established. Deep ultraviolet light is known to directly destroy DNA and cells to the extent that it is used in environment technology to purify and clean water [1,2]. Nanomaterials such as CaF_2 and ZnO are good UV emitters but before they are used in any applications, the scintillations characteristics need to be investigated for intensity, frequency and persistence of luminescence. The persistence has implications for the stability and efficiency of the particles and the type of high energy radiation that can be used i.e. pulsed versus continuous wave excitation. The optical emission of both ZnO and CaF_2 are well investigated but not fully understood. The main emission from CaF_2 (282 nm) is from a self- trapped exciton whereas the ZnO emission at 380 nm is a bandgap emission [3-6].

For environmental application, such as clean water technology, it is important to disperse the emitters so that they are as close as possible to the target molecule or microbes so that the emitted UV photons will not be attenuated by the matrix (water). In addition to an increase in effectiveness, the entire process becomes very energy efficient to the extent that it could compete with UV lamps used in water treatment.

An understanding of the scintillation process would enable optimization of the nano emitters. A dual particle [CaF_2 : ZnO] that independently emits in two UV ranges would increase the range of activity.



2. Experimental

2.1 Synthesis : Zn(acac) powder was dissolved in 70% ethanol and was ultrasonicated and refluxed. Sodium hydroxide (1.5 equivalent) kept at 0°C was added and the mixture refluxed for 45 minutes. The white precipitate was filtered and washed with acetone then with DI water and left to dry in air for 2 days[7]. The CaF₂:ZnO mixture was synthesized from a solution of ZnO, CaCl₂ and NH₄F in ethanol and then washed with DI and dried in air for 2 days. Samples were subjected to several treatments by heating in a vacuum oven or by heating in air. The mixture was then characterized with XRD to determine the sizes of particles and percentage composition. Pure CaF₂ particles were carefully precipitated from an ethanol solution containing CaCl₂ and NH₄F.

2.2 X-ray Absorption : X-ray Absorption Spectroscopy measurements were conducted at the Ca L_{3,2} edge, the F K edge, Zn L_{3,2} edge and at the O K edge for powder samples. The powders were embedded in conductive carbon tape and excited with a beam size of 25 µm x 25 µm at the SGM beamline at the Canadian Light Source. Absorption was measured by both total electron yield (TEY) and fluorescence yield (FLY). The FLY is relatively weak and has the same features as the TEY.

2.2.1 XEOL and TRXEOL : XEOL measurements were made by exciting at several wavelengths below and above the absorption edge of all the constituent elements. UV-Vis photons were collected by using an Ocean Optics QE65000 spectrometer which was connected by fibre optic and a collimating lens to the sample chamber. Several excitation energies that yielded high intensity of a characteristic emission were used and the monochromator was set at the appropriate emission (282 nm and 532 nm for CaF₂, and 390 nm and 510 nm for ZnO). Lifetimes were fitted by using a multi-exponential function [8]. In most cases the best fit was obtained with two exponential. However, in some cases three exponentials were required for a proper fit.

3. Results and discussion

XANES measurements shown in figure 1a-1d indicate that the materials were relatively pure. Within the level of detection and as expected, a small amount of calcium oxide was formed at the CaF₂:ZnO interface. A sample that is heated in air would have more surface oxide and evidence for the oxide of calcium is shown in figures 1a and 1c (labelled a,b,c,d) by the broadening of the Ca L_{3,2} edge of the ZnO:CaF₂ heated in air. XANES of the Zn L_{3,2} edge and the O K edges of the mixed samples were relatively weak compared to pure ZnO, but overall the results indicated that ZnO remains in the pure nanocrystallite form. The small change observed at the O K edge is consistent with some surface reaction to form an oxide of calcium.

XEOL data are shown in figures 2a-2c. Figure 2a shows spectra obtained by scanning over the edges (shown by arrows in figures 1a and 1c) of Ca and F in CaF₂. Scanning across the Ca L_{3,2} edge (330-360 eV) resulted in a primary STE emission band at 282 nm. Also, an extremely weak band at 532 nm suggests that the CaF₂ nano crystals have few additional defects. Excitation of CaF₂ below and above the fluorine edge (670-710 eV) results in higher XEOL intensity compared to the Ca L_{3,2} edge. The stoichiometry of CaF₂ suggests that more photons will be absorbed across the edge of F which would result in increasing the numbers of F₂⁻ STE formed.

The XEOL of CaF₂:ZnO blended materials are shown figures 2b and 2c. The emission intensity is significantly increased when the Zn or the O edges of ZnO:CaF₂ are excited compared to the Ca and F edges being excited. Heating the sample in air suggests that surface and passivation and not interfacial oxide formation affects the number of STE generated. Because the d orbitals of Zn²⁺ is effectively full, the absorption cross-section of the Zn L_{3,2} edge is low which results in the emission intensity being lower than the O K edge excitation. This increased intensity at the O K edge is due to more secondary processes and radiation tracks are created. The weak O K edge and Zn L_{3,2} XANES is due to reduced x-ray and electron emission from the sample. This correlates very well with the increased STE emission when the O K edge and the Zn L edge are excited. Secondary electrons and x-ray emitted from the ZnO are of sufficient energies to create large numbers of STE in the CaF₂. Effectively, ZnO collects the high energy photons and the final state is from a STE emission from CaF₂.

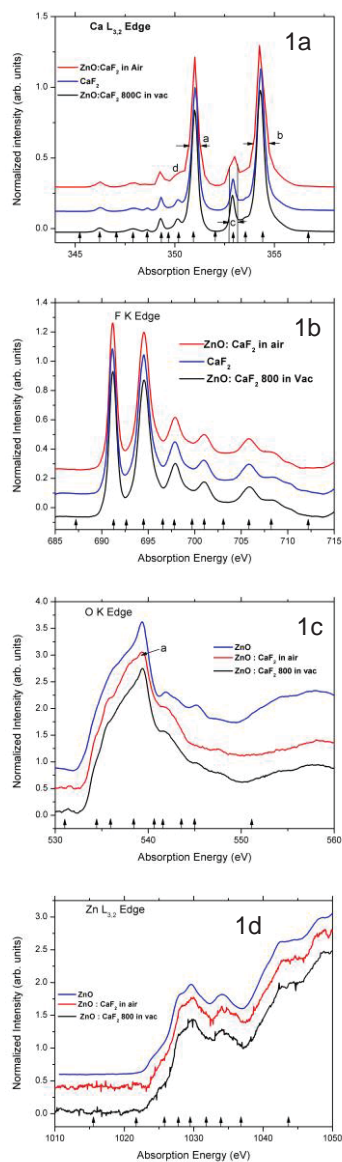


Figure 1: XANES at the Ca L_{3,2} edge, F K edge, O K edge and Zn L_{3,2} edge of ZnO and CaF₂ compared with ZnO:CaF₂ heated in air and in vacuum

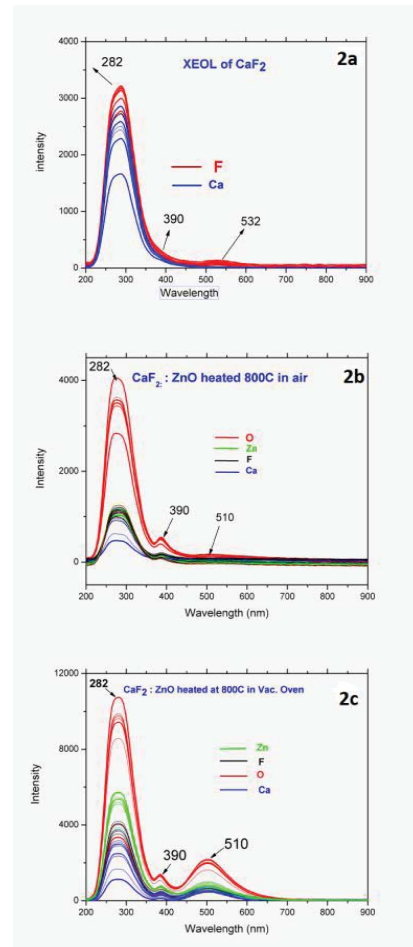


Figure 2: (a) XEOL CaF₂ excited at the F K edge region (670-710 eV) and at the Ca L_{3,2} edge region (330- 360 eV), (b and c) XEOL of ZnO:CaF₂ heat treated in air excited at the Zn L_{3,2} region (1010-1050), O K edge region (520-560 eV) and at the regions for CaF₂

Emission (nm)	CaF ₂	ZnO: CaF ₂ (Air)	ZnO: CaF ₂ (Vac)
282 nm	10 ns, 20% >100 ns, 80%	10 ns, 33% 100 ns, 67%	10 ns, 33% 100 ns, 67
390 nm		<1 ns	<1 ns
510 nm		6 ns, 32% 86 ns, 31% >100 ns, 37%	6 ns, 32% 86 ns, 31% >100 ns, 37%

Table 1: Lifetimes determined from TRXEOL for the three CaF₂ samples.

Annealing of the ZnO:CaF₂ in vacuum results in two processes. First, the CaF₂ nanocrystallites become more ordered and the F₂⁻ anion become more aligned in particular crystal orientations e.g. <111> or <110> resulting in greater overlap with the hole centres. This results in an increased transition probability of the STE and hence higher intensity of emission. Second, the ZnO emission increases because upon annealing, more ZnO is available near the surface to observe the bandgap emission. The results of our TRXEOL investigations are shown in table 1. The lifetime of ZnO emission for both ZnO:CaF₂ samples are the same. The CaF₂ STE emission is different in annealed samples compared to the unannealed CaF₂ which has two main lifetimes (10 ns and >100 ns). For both materials containing ZnO, there was 20% at 10 ns and 80% with lifetime greater than 100 ns. Lifetimes for CaF₂ were determined to be 33% at 10 ns and 67% at >100 ns. Annealing in air resulted in a decrease in intensity of STE emission due to surface passivation but the lifetime relative to vacuum annealed sample does not change, suggesting that the STE emission from the CaF₂ nanocrystals are not from just surface sites. The shorter lifetimes of the annealed samples are a result of an increase in order in the nanocrystals.

4. Summary

XEOL of CaF₂ is an efficient method to produce UV photons for biological applications if the CaF₂ nanomaterials are close to the biomaterial of interest. By mixing the CaF₂ with x-ray collectors such as ZnO, the intensity of CaF₂ emission is significantly increased. Annealing the samples in air and in vacuum shows that surface oxidation attenuates the CaF₂ STE emission intensity but increases the percentage of fast emission. Overall, the CaF₂ STE emission can be increased by mixing with a collector material and annealing at 800C in vacuum.

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6. References

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