Time-Resolved Luminescence Measurements on Upconversion Phosphors for Electron Beam Sterilization Monitoring

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ABSTRACT

We present our recent investigations on time-resolved measurements of alterations in the temporal luminescence decay of upconversion phosphors induced by electron beam treatment. The latter is a promising alternative to low-temperature and dry sterilization of surfaces for sensitive packaging materials. Especially in the food and medical sector regulations concerning sterility are increasingly tightened. For this, a secure proof for electron-beam-assisted sterilization is required. However, no non-destructive and *in situ* method exists up to now.

Our approach to provide a secure proof of sterilization is to place a suitable marker material based on rare-earth-doped phosphors inside or on top of the packaging material of the respective product. Upon electron irradiation the marker material changes its luminescent properties as a function of applied energy dose. We verified the energy dependence by means of time-resolved measurements of the luminescent decay of different upconversion materials.

In our experimental realization short laser pulses in the near-infrared range excite the marker material. The emitted light is spectrally resolved in a monochromator, collected via a silicon photo diode, and analyzed with an oscilloscope. As the main results we observe a reduction of luminescence lifetime due to electron beam treatment dependent on the emission wavelength. Hence, the electron beam induces changes in the particles' up- and down- conversion properties from which the applied energy dose can be derived.

Keywords: nondestructive testing, upconversion, lanthanides, electron beam sterilization, time-resolved luminescence analysis

1 INTRODUCTION

The development of new sophisticated materials and combination of medical devices with electronics lead to a substantial need for alternative sterilization techniques in life sciences. For this, electron beam treatment is a promising alternative to classical sterilization methods as are e.g. heat, steam or chemical routines. Hence, a secure proof for the surface sterility is an important issue in many economic sectors. Especially for food, medical, pharmaceutical and consumer goods asepsis is very significant to avoid dangerous infections[1]. The authors present in this paper a new optical technique to prove electron beam sterilization with an optical active material based on sodium yttrium fluoride doped with Thulium.

2 BACKGROUND

2.1 Electron beam sterilization

Electron beam irradiation is a promising option to classical sterilization methods due to its advantages such as safety, high speed processing and applicability to sensitive materials. It depends on the absorbed dose and the acceleration energy. The technique relies on its effect on microbial germs on e.g. surfaces of medical products or food packaging. Interaction of electrons with microorganisms leads to generation of radicals and result in dead by DNA chain cleavage [2]. Electrons are generated under high vacuum in an electron accelerator similar to a Braun tube. Their high kinetic energy enables the electrons to penetrate the exit window and can thus sterilize the product surface under atmospheric pressure. The correlation between depth and dose depends on the acceleration voltage. By setting parameters according to individual requirements, electron beam irradiation is even possible through the polymer foil wrapping the medical product. This special feature facilitates one of the biggest advantages of this technique: to be integrated into in line processing.

Regarding reliability for sterility it is indispensable to ensure that a sufficient dose was applied. Currently, the deposition of a lethal dose is tested by means of film dosimeters and validated by microbiological methods in combination with fluorescence microscopy. The main drawback of a microbiological approach is the highly time-consuming cultivation of germs for several hours to investigate their proliferation. Further, the packaged product needs to be opened, so sterility is no longer given. But even after validation of film dosimetric approaches by microbiological methodologies, evaluation of film dosimeters still takes at least half an hour. Hence, the advantage of integration of electron beam irradiation into in line processes for sterilization purposes is lost,

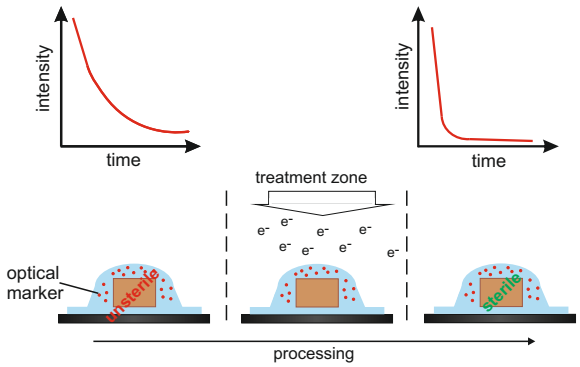

Figure 1: Concept of the electron beam sterilization process and the monitoring approach

when completing investigation is the retarding step.

The novel methodology presented here is to apply an optical marker material into the packaging material which changes its optical properties upon electron beam irradiation as depicted in figure 1. A certain change of defined optical properties as for example luminescence lifetime of excited states can be interrogated fast and contactless and therefore nondestructively at any time during and after the sterilization process. In addition to the change of optical properties, qualified materials require to be nontoxic, mechanically and chemically stable and integrable into packaging materials. One material class which fulfills the requirements are upconversion phosphors based on lanthanide-doped host lattices.

2.2 Upconversion phosphors

Upconversion (UC) refers to a transformation of two or more pump photons in the near-infrared *via* intermediate long-lived states into one emitted higher-energy photon in the visible range. There are different models to explain the processes of upconversion. In general, three mechanisms can be differentiated: excited state absorption (ESA), energy transfer upconversion (ETU) and photon avalanche (PA) [3, 4, 5]. In the case of ESA at least two photons of same energy are sequentially absorbed by the activator (A) to reach the excited state. However in case of ETU, the absorption of the first photon by the activator is followed by an energy transfer from the neighboring sensitizer (S) which results in population of the higher excited state (E^{**}). ETU was first described independently by Auzel, Ovsyankin, and Feofilov in 1966 [6, 7, 8]. ESA and ETU should be distinguished from the two non-linear optical processes of two-photon absorption and second harmonic generation which only occur efficiently by coherent excitation with enough power [4, 5].

The efficiency of upconversion mainly depends on a well-defined coordination between host lattice, activators and sensitizers, the doping concentration, and a long lifetime of the intermediate state. The choice of the host lattice therefore determines distance and collocation between doping ions. For that reason, host lattices based on sodium yttrium fluoride proved to be very suitable for efficient upconversion [9].

In this paper the authors present time-resolved up- and downconversion results on $NaYF_4$:Yb^{3+},Tm^{3+} exhibiting a blue luminescence in the visible range and a strong upconversion around 800 nm.

3 EXPERIMENTAL DETAILS

3.1 Electron beam exposure

Samples of the powder material were prepared on a cover slide and enclosed with adhesive tape. To ensure a reproducible material amount the powder the volume was defined by a small plastic ring on top of the slide. Particles were processed in a Reamode at the Fraunhofer Institute for Plasma and Electron Beam Technology. An electron acceleration voltage of 160 keV and doses of 30 kGy, 50 kGy, 100 kGy, 150 kGy and 300 kGy at the sample surface were applied.

3.2 Optical measurements

For the optical measurements samples could be used after the electron beam exposure without any further preparation. Steady state spectra are recorded with a Horiba Jobin-Yvon iHR 550 spectrometer and a CCD camera. The investigated optical parameter is the lifetime of excited states, so time-resolved measurements were performed with the two following set ups.

3.2.1 Laboratory set up

In figure 2 the schematic view for the acquisition of spectrally resolved data is shown. Irradiation at 976 nm was carried out with a diode laser (Visotek Inc. Smart Laser Tools DL-50) that was pulsed by a pulse generator (BNC 555 pulse/delay generator). Samples were installed directly in front of a spectrometer (Horiba Jobin-Yvon iHR 320). Emitted light after sample irradiation was spectrally separated in the monochromator and collected via a silicon photo diode. The time-resolved electric current was amplified and displayed in an oscilloscope. Data were acquired in LabVIEW and analyzed with MatLab (R2011b version 7.13). Spectral resolution was about 10 nm. In association to the luminescence spectra several wavelengths were picked and luminescence decay was measured for each wavelength.

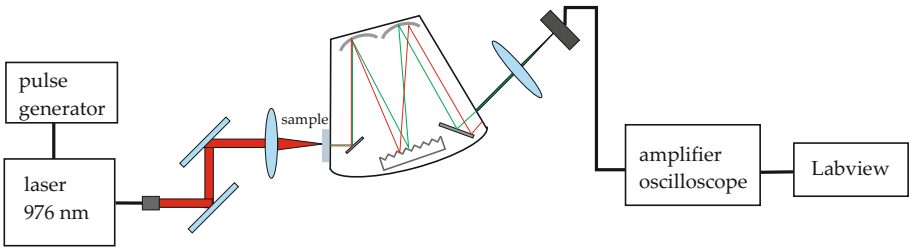

Figure 2: Schematic view of optical set up built up on an optical table

3.2.2 Set up for handheld device

Envisaging a commercial application there is a need to develop a simple but suitable set up to perform time-resolved measurements on e-beam irradiated samples. For this, particles are excited with a 50 mW laser diode at 980 nm that is controlled by a microcontrol unit. Light emitted from the sample is collected via a silicon photo diode situated next to the laser; afterwards the signal is amplified and digitalized via microcontroller, submitted to an external analysis unit and finally analyzed with LabVIEW or Matlab.

3.3 Data analysis

The luminescence lifetime is obtained by fitting the time-resolved data to a single exponential decay function (equ. 1). To avoid the influence of the laser on the decay curve, fitting starts only with a precisely defined delay. For each wavelength 10 slopes were collected and averaged.

$$I(t) = I_0 e^{-t/\tau} + C \tag{1}$$

4 RESULTS AND DISCUSSION

4.1 Time-resolved data of several wavelengths

The upconversion spectra of non-treated marker material is depicted in figure 3. It shows no distinguishable differences to the treated powder (data not shown). However, the time-resolved data of certain wavelengths collected with the laboratory set up described in chapter 3.2.1 reveal notable differences in lifetime for visible and near-infrared emission (data not shown). For all wavelengths, electron beam exposure leads to a sizable effect on luminescence lifetime as shown in figure 4. The change of luminescence lifetime is similar for the wavelengths in the visible range, but τ is significantly higher in the near-infrared. Also the change of lifetime is remarkably higher there. Decrease for all wavelengths is

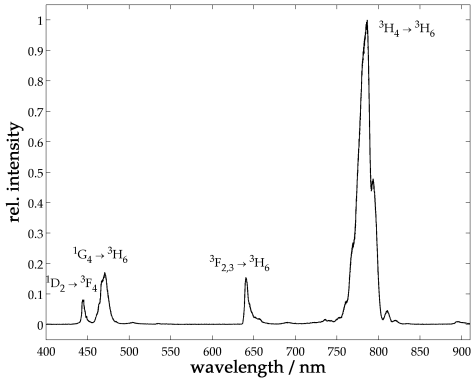

Figure 3: Upconversion spectra of $NaYF_4$:Yb^{3+},Tm^{3+} irradiated at 980 nm

at least 250 μs, and hence clearly exceeds the inaccuracy of approximately 5 % of the time-resolved electric current measurements. In figure 5 τ of the 1000 nm emission wavelength is plotted over the applied dose. Even though, no clearly dependence can be assigned, first hints are given. Varieties in sample preparation and sample positioning may lead to deviations. Further, there may also occur fluctuations in lateral dose application at the sample surface.
Changes in luminescence lifetime remain stable over several months. Nevertheless, the mechanism behind the revealed changes in luminescence lifetime is not yet completely understood. No variation in the crystal structure is indicated by X-ray diffraction (XRD). The authors assume changes in population of excited states and the fine structure of the doping agents that affect the transition rates between electronic states. Notwithstanding, further experiments are required to clarify the causes.

4.2 Integrated time-resolved data

In comparison to the time-resolved data discussed in chapter 4.1 decay curves collected with the set up described in chapter 3.2.2 were acquired over the whole range the photodiode is sensitive to. Hence, the decay time is a mixture of all emitting states which explains

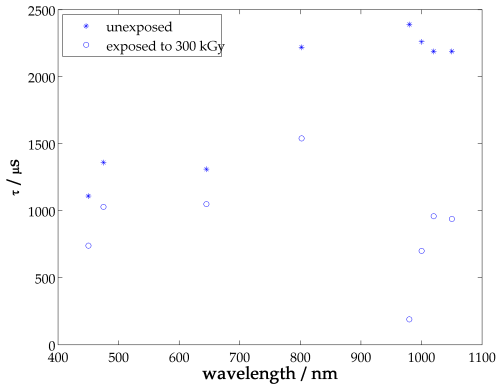

Figure 4: Comparison of luminescence lifetime at different emission wavelengths for untreated material and material exposed to 300 kGy

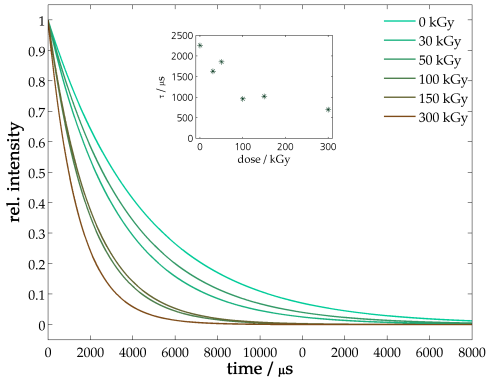

Figure 5: Alterations of luminescence decay at 1000 nm emission wavelength by irradiation at 980 nm

the differences in absolute lifetime to the spectrally resolved data. Nevertheless, a distinct reduction of luminescence lifetime can be observed with increasing dose as depicted in figure 6. So far, no clearly proportional dose - decay time dependence was revealed, but measurements show first evidence. Additional evaluation is therefore needed.

5 CONCLUSION AND PERSPECTIVES

In this contribution the authors showed the suitability of $NaYF_4$:Yb^{3+},Tm^{3+} as an optical marker material for electron beam sterilization. The material shows an evident decrease of luminescence lifetime due to the exposure. Further, the data revealed first hints for a dose dependence, but additional experiments are required. As the luminescence decay occurs over a rather large time scale (up to 2 ms) and the electron beam induced lifetime decrease is sizable, the change in luminescence

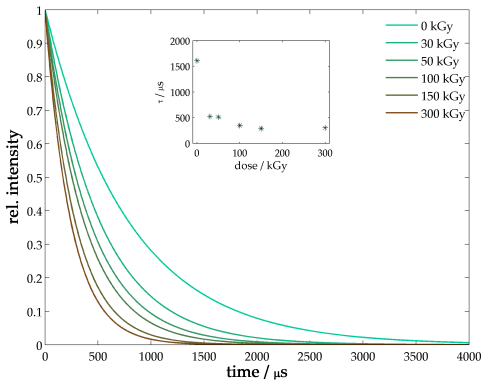

Figure 6: Alterations of luminescence decay collected with handheld device by application of different doses

decay can be measured with rather simple electronics as shown by the authors.

6 ACKNOWLEDGEMENT

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