Picosecond transient absorption rise time for ultrafast tagging of the interaction of ionizing radiation with scintillating crystals in high energy physics experiments

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ABSTRACT: Here we report the first results of a search of a signature for picosecond time stamps of the interaction between ionizing particles and transparent crystalline media. The induced absorption with sub-picosecond rise time observed in a cerium fluoride scintillation single crystal under UV excitation is directly associated with the ionization of Ce\textsuperscript{3+} atoms in CeF\textsubscript{3} crystals, and the very fast occurrence thereof can be used to generate picosecond-precise time stamps corresponding to the interaction of ionizing particles with the crystal in high energy physics experiments.

KEYWORDS: Scintillators, scintillation and light emission processes (solid, gas and liquid scintillators); Instrumentation and methods for time-of-flight (TOF) spectroscopy; Ionization and excitation processes

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1 Introduction

There is an upcoming demand for a new generation of detectors allowing high time resolution. To develop a new generation of ultrafast detectors, especially in experimental particle physics at high luminosity colliders, the processes permitting a measurement precision better than 10–20 ps for the interaction time between ionizing radiation and a detecting medium need to be identified. An important factor when considering the interaction of high-energy charged particles and γ-quanta with detectors is the size of the interaction region. The energy deposit in the detector medium is due to several processes, including ionization, bremsstrahlung, and pair creation along the particle’s trajectory. Moreover, a relativistic particle moving with a speed $v \sim c$ in a transparent detecting medium whose refractive index is greater than unity produces Cherenkov radiation. In order to reduce the interaction region and have a compact experimental setup in high energy physics experiments, one has to use detectors with short radiation $X_0$ and nuclear interaction $R_H$ lengths and small Moliere radius $R_M$. Inorganic scintillation materials meet these requirements in many ionizing radiation detectors [1]. In the last forty years, the application of crystalline scintillation materials in ionizing radiation detectors in high energy physics has played a crucial role in the discovery of the properties of matter and promoted a continuous progress in the detecting techniques. From small detectors based on NaI(Tl), CsI(Na), BaF$_2$, PbF$_2$, and Bi$_4$Ge$_3$O$_{12}$, the experimentalists came to the gigantic Electromagnetic Calorimeter of CMS Collaboration at LHC, consisting of 11 m$^3$ of PbWO$_4$ scintillation crystals. The high quality of the CMS PWO electromagnetic calorimeter and its good performance since the operation start in the LHC irradiation environment has allowed the discovery of a new boson [2]. Nevertheless, the physics of the scintillation development [1] imposes certain limitations on the scintillation materials application in future experiments, especially in high luminosity collider experiments, where a high time resolution of the detectors to mitigate the pileup will be required [3, 4]. The authors of [5] considered some features of the possible emission and absorption of optical photons which appear at the early stages of the interaction process between ionizing radiation and crystalline material. They occur when the density of states has some peculiarities, such as a gap in the bottom of the conduction band. Figure 1 illustrates such distribution of the electron density in a crystalline medium of interest. Here, in addition to possible radiative transitions, such transient states may cause electronic absorption transitions if the crystal is illuminated by an external light source. Thus, in addition to hot intra-band radiative transitions, the absorption transitions can be observed as soon as the population of the lower levels
Figure 1. Hot emission and transient absorption processes in a crystal with a gap in the conduction band. The dark grey area shows the population of the bottom part of the conduction band and light grey shows the density of states (DOS).

of the conduction band is significant, which usually takes place in less than $10^{-12}$ s [1]. Thus, optical absorption from the lowest excited state of the matrix can give a time stamp with a precision close to $10^{-12}$ s, or even better. However, the observation of this absorption must be performed before free carriers are captured by the luminescent centers and/or shallow electron traps. The time scale of this process is comparable to the scintillation rise time of a typical scintillation crystals doped with Ce$^{3+}$ activators and does not exceed 100–300 ps [6]. The observation of such transient absorption and the choice of the proper material need further investigation. It should be mentioned that the fast rising transient absorption in the infrared range was observed at two-photon band gap excitation in CsI crystals [7]. It was associated with the transitions in a self-trapped exciton created after the excitation.

2 Samples, experimental technique and results

In the present work, we choose cerium fluoride, a crystal with short $X_0$ and $R_M$, one of the candidates for detectors at LHC with high luminosity [8]. A CeF$_3$ single crystal has a density of electronic states in the bottom part of the conduction band, which ideally corresponds to the requirements described. The bottom of the conduction band is formed by d orbitals of Ce$^{3+}$ ions with some admixture of f and s states of Ce$^{3+}$. The partially filled f orbital of Ce$^{3+}$ is about 3 to 4 eV higher than the top of the valence band formed by the filled p states of F$^-$ [9]. The authors of [10] measured the optical absorption from the 4f level of Ce$^{3+}$ ions in a CeF$_3$ crystal and identified gap between the 5d Ce$^{3+}$ electronic levels and other bands in the upper part of the conduction band. Five absorption bands in the range from 247 to 194 nm correspond to the absorption transitions from the 4f level of Ce$^{3+}$ to the five components of the 5d level split by the hexagonal crystalline field and vibronic interaction. There is also a transition near 172 nm, assigned to 4f-6s transition [11]. Thus, the bottom state of the conduction band corresponds to the d state of Ce$^{3+}$.
Figure 2. Configuration curves for Ce ions in CeF₃. Arrows indicate different absorption processes: 1 — laser absorption (263 nm), 2 — absorption from the lowest excited state (this transition is also involved in the up-conversion process), 3 — absorption by higher excited states populated after the recombination of Ce⁴⁺ with electrons generated in the up-conversion processes, 4 — emission from the lowest excited state, also a part of the up-conversion process resulting in the ionization of Ce³⁺ to Ce⁴⁺ + e, 5 — fast non-radiative relaxation, 6 — delayed non-radiative relaxation.

with zero-phonon position near 280 nm. The energy of the allowed d (with strong admixture of p)-s transition from the lowest excited d state of Ce³⁺ is expected to be in the range of 400–420 nm. Due to a wide forbidden zone the crystal itself has no optical transitions in the visible range. Figure 2 shows the possible optical transitions in a CeF₃ crystal.

A CeF₃ crystal sample of 3 mm thickness was excited by femtosecond laser pulses in the UV range, the estimated absorption coefficient of the 263 nm radiation was at the level of 5000 cm⁻¹. This excitation provides the excitation of Ce³⁺ ions to the lowest 5d excited level.

The experiment was carried out with a pump-probe spectrometer based on a custom-made original femtosecond Ti:Al₂O₃ pulsed oscillator and a regenerative amplifier, both operating at 10 Hz repetition rate [12]. The pulse duration and the energy of the Ti:Al₂O₃ system after the amplifier were 140 fs and up to 0.5 mJ, respectively, tunable over the spectral range from 770 to 820 nm. The pulses of the fundamental frequency (ω) at the output of the amplifier (790 nm output wavelength was set for the present study) were divided into two parts in a 1:4 ratio (figure 3). The beam with higher intensity was converted to the third harmonic (λ ≈ 263 nm, E up to 12 µJ) and used as the excitation pulse. Pulse energy was chosen to prevent sample surface damage by intense laser pulses. The smaller part of the fundamental frequency, after passing the delay line, was used as a white supercontinuum probe pulse generated by focusing it into a 1 cm long water-containing cell. By using a semi-transparent mirror, the supercontinuum radiation (360–1500 nm) was subdivided into two pulses (reference and signal) of similar intensity, and then they were focused on the sample by means of the mirror optics. The reference pulse is required to eliminate an impact of shot-to-shot instability of supercontinuum. It passes the sample always before the
excitation. Induced change of optical density is calculated by the formula:

$$\Delta D(\lambda, \Delta t) = \lg \left[ \left( \frac{E_{sg}(\lambda)}{E_{ref}(\lambda)} \right) / \left( \frac{E_{sg}^*(\lambda, \Delta t)}{E_{ref}(\lambda)} \right) \right]$$

where $E_{sg}$, $E_{sg}^*$ and $E_{ref}$ are energies of signal pulses passed the sample before and after excitation and the reference pulse respectively.

The sample’s surfaces were carefully polished to prevent the surface damage during the illumination with ultra-short pulses. The beam spot diameter was 0.5 mm. The spectra of both pulses were recorded for each laser shoot and processed by a system including a polychromator equipped with a CCD-camera. The absorption spectra of light from the white supercontinuum were measured in the spectral range from 390 to 700 nm.

Three wide bands were observed in the spectral range from 390 to 700 nm, as seen in figure 4. The narrow dip at 400 nm is due to scattering of the second harmonic of the fundamental frequency and does not relate to the measured sample. It is detected due to the fact that outer absorption filter in the 3rd harmonic generator (figure 3) does not absorb completely the second harmonic of the fundamental frequency. The first peak near 410 nm has a rise which coincides with the rise time of the excitation pulse and is shorter than 1 ps. Assuming that it corresponds to fast populating of the lowest d level of Ce$^{3+}$ ions, following the excitation pulse, we correlate this band to the absorption of the probe pulse from Ce$^{3+}$ d to Ce$^{3+}$ s states. Two other wide bands, peaked near 560 and 630 nm have a slightly higher level of optical density. Figure 5 shows the kinetics of the transient absorption in short (0–200 ps) and long (0–2000 ps) scales. Their intensity profile shows a further growth in the time period (0–400 ps) after excitation, whereas the short wavelength band reaches a constant value of optical absorption in the time scale of 0–200 ps. Approximation of the kinetics curves with sum of exponents showed that long wavelength bands have a rise time at the level of 200–300 ps, so one can conclude that the corresponding electronic levels population is still increasing after the direct excitation.
Figure 4. Transient induced absorption ($\Delta D$) spectra of a CeF$_3$ single crystal obtained for different time delays between the pump and probe pulses. The pump pulse energy is $12 \mu$J.

One possible explanation of this long wavelength absorption is the up-conversion processes resulting in the ionization of the cerium ions and the population of the upper 5d states. The concentration of excited cerium ions is rather high (about $5 \times 10^{17}$ cm$^{-3}$ for the described experimental conditions), and the energy transfer between the excited Ce$^{3+*}$ ions may occur, leading to the ionization of the excited Ce$^{3+*}$: Ce$^{3+*}$ + Ce$^{3+*}$ $\rightarrow$ Ce$^{3+}$ + Ce$^{4+}$ + e. This process is analogous to the concentration quenching of excitons in CdWO$_4$ [13] and is facilitated in CeF$_3$, since the diffusion coefficient of excitations over the Ce$^{3+}$ subsystem is rather high due to the overlapping of the emission and excitation spectra in CeF$_3$. The recombination of the electron with Ce$^{4+}$ has an almost instantaneous component due to the geminate recombination and a delayed component due to the diffusion of the electron to the ionized center. In LiYF$_3$:Ce, this delay can be as long as a few nanoseconds [14]. After the recombination of electrons with ionized Ce$^{4+}$, all 5d levels are populated, thus producing the delayed induced absorption in the long-wavelength domain. Also, we do not exclude that these rising long-wavelength components are connected to shallow traps. They may be due to the population/depopulation of very shallow electron capturing centers created by deformations due to vacancies in the nearest coordinating spheres. Such shallow levels may be created by the d-f states mixture with a predominant f density component. If their depth is less than 0.2 eV, the two observed bands ideally correspond to the electron transfer from their ground state to two upper Stark components of the 5d level of Ce$^{3+}$ ions. Approximation of the kinetics curves by sum of exponents showed that in a longer time range, all bands show a decrease of the optical density with a time constant near 2.5 ns, indicating a decrease in the population of the corresponding level. It correlates well with the time profile of the depopulation of the lowest Ce$^{3+}$ conduction
Figure 5. The transient absorption kinetics of a CeF$_3$ single crystal obtained at different wavelength of the probe pulse: a — on the short ($-2 \div 200$ ps), b — long ($-2 \div 2000$ ps) time range. The time scale is expanded on the inset in the upper figure to show the very fast absorption leading edge.

band level related to the interconfiguration d-f luminescence transition. It is well known that the initial stage of the luminescence kinetics curve of CeF$_3$ crystals contains a short component with a decay constant at the level of 3–5 ns [15].

In order to exploit the observed ultrafast rising transient absorption and create precise time stamps related to the interaction of ionizing radiation with the crystal in forthcoming detectors, CeF$_3$ crystals in the detector have to be probed with 1 to 5 picosecond laser pulses with a wavelength of 400 nm. Wavelength of the probe pulse does not overlap scintillation of CeF$_3$ which peaked at 330 nm [1]. So scintillation and probe pulses can be discriminated by spectrum. Set of
the short laser pulses with a total duration 500–1000 ps consisted of several hundreds 1–5 ps pulses and synchronized with collision of particles is required to scale time intervals between probe pulses at the level of several picoseconds. Frequency of the laser pulse sets should be similar to frequency of the particles collision, of about 40 MHz. Such laser sources can be constructed from commercially available optical components and lasers.

3 Conclusions

We observed the induced absorption with a sub-picosecond rise time in a cerium fluoride single crystal under UV excitation causing the transfer of electrons to cerium excited states. One of the detected bands with a maximum near 400 nm corresponds to the transient absorption from the lowest Ce$^{3+}$ excited state to the upper levels in the conduction band, whereas the two other bands with maxima near 560 and 630 nm most probably appear due to up-conversion processes or the action of shallow electron traps. These processes are directly associated with the ionization of Ce$^{3+}$ atoms of CeF$_3$ crystal and the very fast occurrence of this absorption can be used to generate picosecond precise time stamps of the interaction of ionizing particles with the crystal in high energy physics experiments.

References

[1] P. Lecoq, A. Annenkov, A. Gektin, M. Korzhik and C. Pedrini, *Inorganic scintillators for detector systems*, Springer (2006).
[2] CMS collaboration, *Search for the standard model Higgs boson decaying into two photons in pp collisions at √s = 7 TeV*, *Phys. Lett.* B 710 (2012) 403.
[3] A. Breskin and R. Voss eds., *The CERN Large Hadron Collider: accelerator and experiments*, Volumes 1–2, CERN, Geneva Switzerland (2009).
[4] *International Linear Collider technical design report*, Tokyo, Geneva, Chicago (2013).
[5] P. Lecoq, M. Korzhik and A. Vasiliev, *Can transient phenomena help improving time resolution in scintillators?*, *IEEE Trans. Nucl. Sci.* 61 (2014) 229.
[6] S.E. Derenzo, M.J. Weber, W.W. Moses and C. Dujardin, *Measurements of the intrinsic rise times of common inorganic scintillators*, *IEEE Trans. Nucl. Sci.* 47 (2000) 860.
[7] R.T. Williams et al., *Picosecond studies of transient absorption induced by band gap excitation of CsI and CsI:Tl at room temperature*, *IEEE Trans. Nucl. Sci.* 57 (2010) 1187.
[8] G. Dissertori et al., *A study of high-energy proton induced damage in cerium fluoride in comparison with measurements in lead tungstate calorimeter crystals*, *Nucl. Instrum. Meth.* A 622 (2010) 41.
[9] K. Klier, P. Novák, A.C. Miller, J.A. Spirko and M.K. Hatalis, *Electronic structure of CeF$_3$ and TbF$_3$ by valence-band XPS and theory*, *J. Phys. Chem. Solids* 70 (2009) 1302.
[10] C. Dujardin et al., *Spectroscopic properties of CeF$_3$ and LuF$_3$:Ce$^{3+}$ thin films grown by molecular beam epitaxy*, *Opt. Mater.* 16 (2001) 69.
[11] C. Pedrini, B. Moine, J.C. Gacoin and B. Jacquier, *One- and two-photon spectroscopy of Ce$^{3+}$ ions in LaF$_3$:CeF$_3$ mixed crystals*, *J. Phys. Condens. Mat.* 4 (1992) 5461.
[12] A.P. Blokhin et al., *Femtosecond dynamics of optically induced anisotropy of complex molecules in the gas phase*, *J. Appl. Spectrosc.* 70 (2003) 70.

[13] M. Kirm et al., *Exciton-exciton interactions in CdWO$_4$ irradiated by intense femtosecond vacuum ultraviolet pulses*, *Phys. Rev. B* 79 (2009) 233103.

[14] A. Belsky, K. Ivanovskikh, A. Vasil’ev, M.-F. Joubert and C. Dujardin, *Estimation of the electron thermalization length in ionic materials*, *J. Phys. Chem. Lett.* 4 (2013) 3534.

[15] A. Belsky, private communications.