

Time resolved luminescence of solids excited by femtosecond VUV pulses and synchrotron radiation

M. Kirm¹, V. Babin¹, E. Feldbach¹, V. Nagirnyi¹, S. Vielhauer¹, S. Guizard², B. Carré³, M. De Grazia³, H. Merdji³, A. N. Belsky⁴, N. Fedorov⁴, and P. Martin⁴

¹ Institute of Physics, University of Tartu, 142 Riia Street, 51 014 Tartu, Estonia

² Lab. des Solides Irradiés, CEA/DSM/DRECAM-CNRS, Ecole Polytechnique, 91 128 Palaiseau, France

³ CEA/DSM/DRECAM/Service des Photons, Atomes et Molécules, 91 191 Gif-sur-Yvette, France

⁴ CELIA, CNRS-CEA, Université de Bordeaux I, 33405 Talence, France

Received 31 July 2006, revised 22 November 2006, accepted 22 November 2006

Published online 9 March 2007

PACS 41.60.Cr, 42.65.Ky, 61.80.Ba, 61.80.-x, 61.82.Ms, 78.47.+p, 78.55.Hx

Time-resolved luminescence spectroscopy has been widely used in studies of electronic excitations and their dynamics in insulators. Present paper discusses the potential of vacuum ultraviolet spectroscopy applied for wide band gap crystals using classical synchrotron radiation as well as more recently developed pulsed femtosecond short-wavelength light sources. Optical spectroscopy using novel free electron lasers and laser systems based on higher harmonic generation process allow detailed investigation of the interaction between electronic excitations and behaviour of solids under extreme radiation conditions. Significant changes in the quantum yield and emission decay kinetics as well as surface damage of single crystals were observed for CdWO₄ and CaWO₄ crystals studied in the temperature range of 8-300 K. However, in the range of excitation densities applied, up to $\sim 10^{12}$ W/cm², the nature of luminescence centres and their characteristic emission spectra remained similar to those observed at low excitation densities.

phys. stat. sol. (c) 4, No. 3, 870–876 (2007) / DOI 10.1002/pssc.200673876

Time resolved luminescence of solids excited by femtosecond VUV pulses and synchrotron radiation

M. Kirm^{*,1}, V. Babin¹, E. Feldbach¹, V. Nagirnyi¹, S. Vielhauer¹, S. Guizard², B. Carré³, M. De Grazia³, H. Merdji³, A. N. Belsky⁴, N. Fedorov⁴, and P. Martin⁴

¹ Institute of Physics, University of Tartu, 142 Riia Street, 51 014 Tartu, Estonia

² Lab. des Solides Irradiés, CEA/DSM/DRECAM-CNRS, Ecole Polytechnique, 91 128 Palaiseau, France

³ CEA/DSM/DRECAM/Service des Photons, Atomes et Molécules, 91 191 Gif-sur-Yvette, France

⁴ CELIA, CNRS-CEA, Université de Bordeaux I, 33405 Talence, France

Received 31 July 2006, revised 22 November 2006, accepted 22 November 2006

Published online 9 March 2007

PACS 41.60.Cr, 42.65.Ky, 61.80.Ba, 61.80.-x, 61.82.Ms, 78.47.+p, 78.55.Hx

Time-resolved luminescence spectroscopy has been widely used in studies of electronic excitations and their dynamics in insulators. Present paper discusses the potential of vacuum ultraviolet spectroscopy applied for wide band gap crystals using classical synchrotron radiation as well as more recently developed pulsed femtosecond short-wavelength light sources. Optical spectroscopy using novel free electron lasers and laser systems based on higher harmonic generation process allow detailed investigation of the interaction between electronic excitations and behaviour of solids under extreme radiation conditions. Significant changes in the quantum yield and emission decay kinetics as well as surface damage of single crystals were observed for CdWO₄ and CaWO₄ crystals studied in the temperature range of 8–300 K. However, in the range of excitation densities applied, up to $\sim 10^{12}$ W/cm², the nature of luminescence centres and their characteristic emission spectra remained similar to those observed at low excitation densities.

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Storage rings (synchrotrons) are well-established short-wavelength light sources, which are widely exploited for various spectroscopic techniques characterising structural properties as well as electronic excitations of various materials. Synchrotron radiation (SR) has played an important role in the development of luminescence spectroscopy and in the investigation of dynamical processes as reviewed recently by Zimmerer [1]. As a tuneable source, along with its inherent time resolution and high repetition rate (a few MHz) SR allows revealing complicated relaxation processes induced by vacuum ultraviolet (VUV) photons in wide gap materials. The pulse duration of SR is typically ~ 100 ps and the photon fluxes generated reach $\sim 10^{12}$ photons per second. These are sufficient for spectroscopic purposes, but not for direct observation of effects due to high density of electronic excitations reported for the irradiation by ion beams [2] or by pulsed nanosecond electron beams [3].

The development of new generation VUV light sources with extremely high peak power and brilliance, based on the free electron laser (FEL) concept [4] as well as on principles of higher order harmonic generation (HHG) in a gas [5], has opened new possibilities in investigation of luminescence properties of solids [6, 7]. Due to the ultra-short pulses such sources are perfect tools for studies of relaxation dynamics of electronic excitations and for investigation of interactions of matter with the intense light pulse itself [8]. Tuneable short-wavelength laser radiation provides convenient excitation of electrons both from the valence band and inner-shell levels to the conduction band [9, 10], while ultra-short pulse duration makes it also attractive for pump-probe experiments in VUV region.

* Corresponding author: e-mail: marco.kirm@ut.ee, Phone: +00 372 737 4603, Fax: +00 372 7383 033

The aim of the present paper is to discuss challenges, advantages and limitations of modern light sources (SR, HHG, FEL) in the studies of various properties of electronic excitations by means of luminescence spectroscopy in various solids. The examples, which will be presented below, were selected in a way to expose the strongest sides of each light source applied in luminescence studies.

2 Spectroscopy using synchrotron radiation Low temperature luminescence spectroscopy has been extensively used in the investigation of electronic structure of rare earth ions in wide gap hosts because of their importance for such applications as scintillating and light generating materials. Recently, the properties of $4f^2 \rightarrow 4f^15d$ transitions of Pr^{3+} ions doped into Cs_2KYF_6 host with elpasolite structure were evaluated. This system has potential as a down-conversion phosphor, where after absorption of one VUV photon up to two photons can be emitted in the UV – visible range [11]. Fig. 1 shows excitation and emission spectra recorded for this sample at 10 K using the SUPERLUMI station of HASYLAB at DESY [1]. Time resolved luminescence spectra can be recorded within a time window Δt delayed by an interval of δt in respect of excitation pulse due to periodic nature of SR. According to [11] the excitation into the 5d bands of Pr^{3+} at 180 nm results in numerous narrow emission lines, which are typical of $4f^2 \rightarrow 4f^2$ transitions expected in the case when the $^1\text{S}_0$ state is located below the 5d bands. However, as depicted in Fig. 1b the time resolved emission spectrum shows broad structures, which are features of the $5d \rightarrow 4f$ radiative transitions to the ground state (emission at 230 nm) as well as to the higher $4f^2$ states as found in many Pr^{3+} -doped fluoride compounds [12]. As shown in Fig. 1b, there is no slow emission typical of $4f^2 \rightarrow 4f^2$ transitions detected in any time window. Moreover, the decay time of the emission centred at 230 nm is 14.8 ns being in a good agreement with analogous data for the allowed $5d \rightarrow 4f$ transitions of the Pr^{3+} ions doped into other complex fluorides as reported in [12].

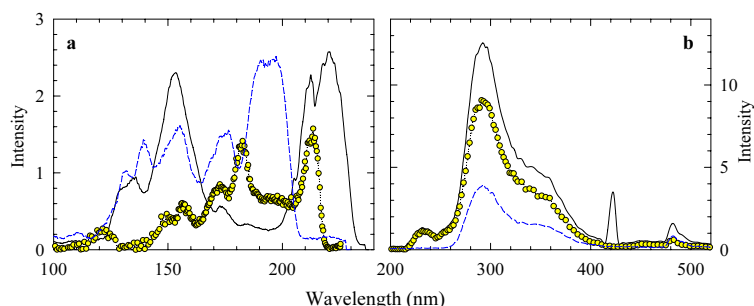


Fig. 1 (a) Time integrated excitation spectra of emissions detected at 320 nm (black solid line), 230 nm (symbols) and 408 nm (blue dashed line) from a $\text{Cs}_2\text{KYF}_6:\text{Pr}$ (0.5 mol%) crystal at 10 K. (b) Emission spectra of the same crystal excited by 211 nm photons and recorded in time integrated mode (black solid line) and within short (symbols) and long time-window (blue dashed line) with the following parameters $\delta t_1 = 11$ and $\delta t_2 = 33$ ns; $\Delta t_1 = 33$ and $\Delta t_2 = 115$ ns, respectively (see text for details). The sharp peak at 422 nm in the time integrated emission is due to the second order of the excitation at 211 nm. The excitation spectra are scaled for the best visibility.

The excitation spectra recorded for various emissions show different onsets (see Fig. 1a). The emission bands due to the $5d \rightarrow 4f$ transitions recorded at 320 and 230 nm are excited at wavelengths shorter than 233 and 219 nm, respectively. The excitation of the $4f^2 \rightarrow 4f^2$ emissions shows a threshold at 208 nm. The $^3\text{H}_4 \rightarrow ^1\text{S}_0$ transition (~ 213 nm) was not revealed, which is masked by strong $4f \rightarrow 5d$ absorption in this energy range. Theoretical calculations performed in [11] confirmed interpretation of the experimental data based on assumption that Pr^{3+} ions occupy all three cation sites of the host. The crystal field is strongest for Pr^{3+} ions located in the sites of small Y^{3+} and K^+ ions that causes a considerable splitting of 5d bands into two groups and shifts their onsets above 210 nm (Fig. 1a). The crystal field is weakest for a Pr^{3+} ion substituted into the Cs^+ site because of the larger cation-fluorine distance. As a result the $^1\text{S}_0$ is the lowest level wherefrom the usual $4f^2 \rightarrow 4f^2$ transitions take place. Using high-resolution time-resolved luminescence spectroscopy under SR it was possible to clarify the nature of overlapping intra- and inter-configurational transitions of rare earth ions and to investigate their excitation mechanisms.

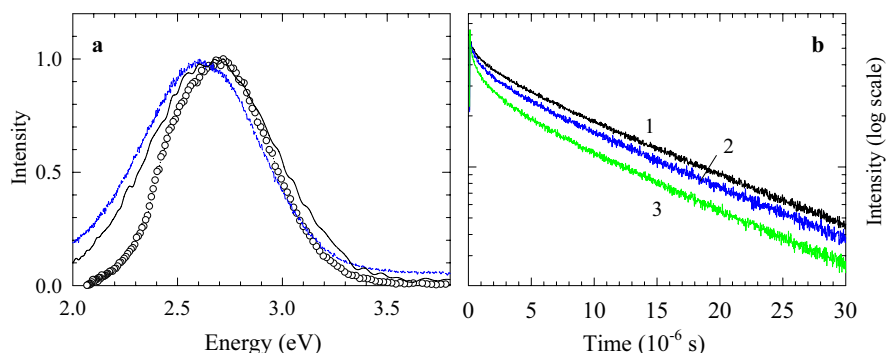


Fig. 2 (a) Time integrated emission spectra of a CdWO_4 crystal at 300 K excited by 4 eV SR (symbols), by multiphoton excitation using 800 nm (blue dashed line) and by HHG VUV (black solid line) femtosecond pulses. A small red shift in the luminescence spectra is due to the sensitivities of the different detector-spectrometer combinations. Spectra are normalised at their maxima. (b) Emission decay curves recorded at 2.47 eV for the same crystal at 300 K excited by HHG femtosecond pulses in VUV at different focal spot sizes: 1 – 107 μm , 2 – 56 μm , 3 – 15 μm .

3 Spectroscopy using high-order harmonic generated femtosecond VUV pulses The non-linear HHG of short wavelength radiation is realised by focussing of a high power (in TW range) laser beam in a gas cell (see [5] and references therein). In such processes multiple odd harmonics are produced, which cover the energy range of several tens of eV. The photon flux for the whole spectrum can be as high as $\sim 10^{10}$ per shot as shown for Ar in [13], exceeding the respective value of SR by a factor of $\sim 10^4$.

The PFLA (French acronym for tuneable femtosecond laser platform) facility of the Saclay Laser-Matter Application Centre (CEA, Saclay, France) was applied in the present study. The 800 nm pulsed fundamental beam (35 fs pulse length, 13 mJ pulse energy, 1 kHz repetition rate) of a Ti-Sapphire laser was loosely focussed into an Ar filled gas cell with a length of 4 cm. The VUV radiation was separated from the fundamental beam by a pair of SiO_2 plates either reflecting or transmitting the former and the latter radiation, respectively. Finally, an Al filter of a 100 nm thickness, transmitting in the energy range of 15 – 72 eV, was applied. The lowest photon energy reaching the sample was determined by the filter transmission, while the highest energy was limited by the wavelength of 27th harmonic generated (29.8 nm or 41.6 eV). A parabolic mirror was used to focus beam down to a $\sim 15 \mu\text{m}$ spot on the sample. The size of the spot was monitored by a special CCD camera from the image of the fundamental laser beam. The excitation density was varied by moving samples out of a focal plane. However, by applying such an optical scheme only $\sim 1\%$ of the generated VUV photons ($\sim 1 \text{ nJ}$ or $\sim 10^8$ photons per pulse) reached the sample resulting in a maximum fluence of $\sim 0.6 \text{ mJ/cm}^2$. The emission spectra were recorded by means of the TRIAX190 spectrograph equipped with a CCD detector. A R3809 (Hamamatsu) photo multiplier tube (PMT) was applied in decay measurements carried out in time correlated single photon counting mode. Single shot experiments are not favoured by using the HHG source.

Figure 2a demonstrates emission spectra recorded from CdWO_4 at different excitation conditions at 300 K. Irrespective of the excitation regime used, the resulting luminescence spectra had the shape and spectral characteristics typical of the intrinsic emission due to the radiative transitions within oxyanionic complex, forming Frenkel type small radius self-trapped excitons (STE) in CdWO_4 (see [14] and references therein). Single photon excitation by SR and multiphoton excitation by the fundamental frequency of the Ti-Sapphire laser (4 eV or 1.55 eV, respectively) create preferentially excitons, while the HHG VUV excitation ($\geq 15 \text{ eV}$) results in electron-hole pair formation. In the latter case, no changes in the shape of emission spectrum were observed at varying excitation density, only the luminescence intensity was decreased. Hence, the luminescence of CdWO_4 crystals under HHG VUV excitation is similar to that observed under low excitation densities and no new kind of emission centres are introduced in the range of power densities up to $\sim 10^{11} \text{ W/cm}^2$ achieved at the PFLA facility.

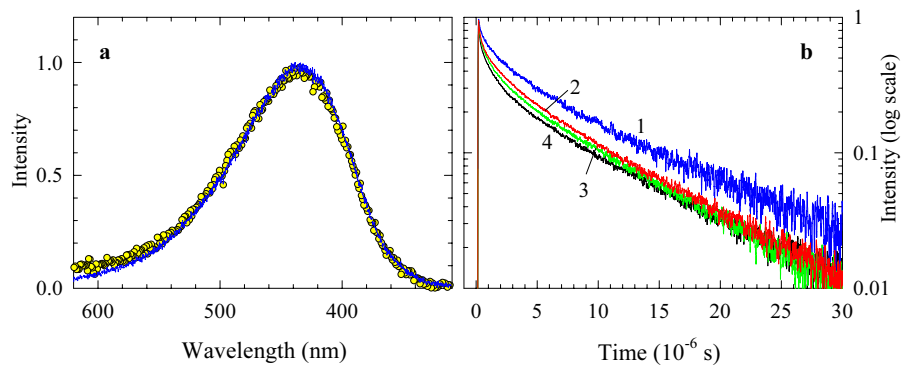


Fig. 3 (a) Time integrated emission spectra of a CaWO_4 crystal at 300 K excited by 89.8 eV (13.8 nm) photons generated by FEL. Blue line represents the spectrum under maximum fluence ($\sim 8 \mu\text{J}$) and symbols 26 % of that. (b) Decay curves of the main emission of the same crystal at 300 K excited by 89.8 eV photons at different fluencies: 1- 16 % (blue), 2 – 26 % (red), 3- 57 % (green), 4 – 100% (black).

The study of luminescence decay kinetics is a very sensitive method to investigate nature of electronic excitations and their mutual interaction [1]. A drastic shortening of decay times along with a decrease in a quantum yield above the threshold value of 10^{16} photons/s cm^2 was reported for a number of inorganic scintillators excited by high power polychromatic (3-62 keV) SR in [15]. A powerful XUV plasma laser providing $\sim 10^{12}$ monochromatic photons of 58.5 eV in a 80 ps pulse ($\sim 10^9$ W/ cm^2) quenched luminescence of CsCl and CsI considerably [16]. However, an interval of 20 minutes between shots of plasma laser is neither favourable for study of luminescence spectra nor decay kinetics. The HHG source with its high repetition rate has been successfully applied in studies of acceleration of decay kinetics of various emissions in BaF_2 and anthracene by means of time correlated single photon counting [7].

Despite of a relatively slow emission decay, but thanks to their high efficiency some tungstate crystals (e.g. CdWO_4 and ZnWO_4) are used as scintillators in industrial applications. In [17, 18] the observation of short and long decay components (~ 1 and $15 \mu\text{s}$; ~ 0.1 and $25 \mu\text{s}$; for CdWO_4 and ZnWO_4 , respectively) was reported without further clarifications. The ratio of their intensities depended on the excitation source. Whereas the short component is observed under excitation by ionising radiation, it is absent under optical excitation [19, 20]. The studies in μs range do not set so high demands on speed of detector response, and possible changes in the decay kinetics are easier to reveal than those observed in sub-nanosecond range in BaF_2 [7], which finally motivated choosing a CdWO_4 crystal for the present study.

Figure 2 b demonstrates the decay curves of CdWO_4 crystal at 300 K. The variation of excitation density by a factor of 50 resulted in increasing deviation from the exponential decay law within the first few microseconds, whereas after $10 \mu\text{s}$ the decay follows the single exponential with a lifetime of $15 \mu\text{s}$. The similar value was obtained for the same CdWO_4 crystal using a flash lamp based laboratory set-up (low excitation density) described in [20]. The reason for such a drastic behaviour in the initial phase of the decay is mutual interaction of elementary intrinsic excitations. For a detailed discussion of quenching of luminescence by high local density of electronic excitations we refer to [21]. In CdWO_4 the absorbed energetic VUV photons create free electron-hole pairs ($E_{\text{th}} = 5$ eV [22]), which after relaxation form self-trapped molecular excitons of Frenkel type. It is obvious that a dipole-dipole interaction of closely spaced self-trapped excitons is the main cause for the non-radiative decay channel responsible for non-exponential behaviour of decay kinetics in the initial phase. Using conventional laser radiation (≤ 90 mW/ cm^2) similar changes in the decay kinetics were revealed and also explained via mutual interaction of STE in CeF_3 [23] using one photon excitation as well as in PbWO_4 [24] and CaWO_4 [25] by two-photon excitation. However, in our case femtosecond VUV pulses produce a substantially larger amount of non-relaxed mobile electron-hole pairs. Their interaction with the self-trapped excitons can contribute

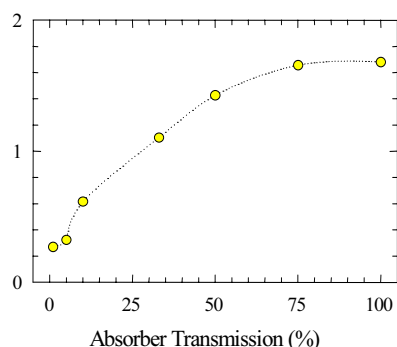


Fig. 4 Luminescence intensity of intrinsic emission of CaWO_4 single crystal at 300 K as a function of the excitation density. The FEL operated at photon energy of 48.4 eV (25.6 nm) with a maximum fluence of $\sim 30 \mu\text{J}$. The size of focal spot is still under determination. Therefore the relative absorber transmission is used as a convenient measure of incident power.

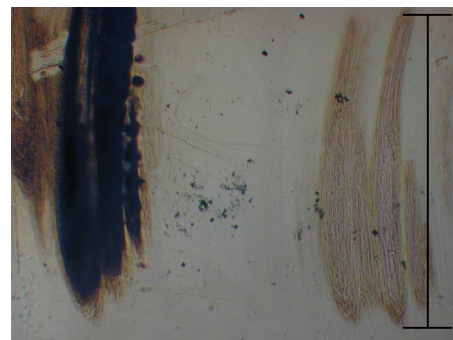


Fig. 5 A microphoto of surface damage of a CaWO_4 crystal after exposure to the FEL radiation. The deeper craters are observable on the left and the initial erosion stage is visible on right. The shape corresponds to the image of FEL radiation on the sample. The bar shows the length of vertical structures ($\sim 0.7 \text{ mm}$), which is mainly due to the sample movement caused by thermal expansion of the cryostat during the several series of measurements at different temperatures.

to this process as well. The quantitative analysis of the results obtained using theoretical approaches described in [26] (and references therein) will be published separately [27].

4 Spectroscopy using free electron laser FLASH Since August 2005 the free electron laser FLASH of HASYLAB at DESY started user operation in the wavelengths below 32 nm [28]. Here we report on our recent results on studies of CaWO_4 carried out in May 2006 at BL1. The FLASH operated at 25.6 and 13.8 nm in a single bunch mode providing 25 fs pulses at 5 Hz repetition rate. The pulse energies were as high as $30 \mu\text{J}$ ($\sim 10^{12}$ photons at 25.6 nm) recorded by a gas monitor detector. In addition to the inherent fluctuation of FEL radiation, a N_2 filled gas absorber was used to attenuate the incident beam by up to two orders of magnitude from the maximum estimated value of $\sim 10^{12} \text{ W/cm}^2$ (the size of a focal spot is taken from a ray-tracing calculation). The actual size of the focal spot is still under evaluation, which prohibits precise determination of numerical values for several important physical quantities in this paper. Luminescence spectra, typically averaged over 2000 FEL pulses, were analysed by a Spectra-Pro308i spectrograph equipped with a CCD detector. Single shot decay curves were recorded through a set of band-pass filters using a XP2020Q PMT and stored by a digital oscilloscope.

Fig. 3a shows emission spectra of CaWO_4 at 300 K excited by femtosecond FEL pulses being in good agreement with our unpublished data under XUV excitation with SR as well as with those reported for UV excitation [25]. Hence, up to the power densities of $\sim 10^{12} \text{ W/cm}^2$ the nature of luminescence is similar to that observed under excitation by conventional low intensity light sources. Like under HHG excitation the decay curves exhibit a strong non-exponential behaviour (see Fig. 3b) within the first ten microseconds for similar reasons as discussed in Sec. 3. Thereafter, the decay is described by a single exponential component with a characteristic lifetime of $\sim 8.6 \mu\text{s}$, which is in the range typical for CaWO_4 (see [25] and references therein). A detailed quantitative analysis is a subject of forthcoming publication.

Another important issue is the saturation effects in light emission leading to the non-proportionality in scintillator response (see [26] and references therein) or possible distortion of images of fluorescent screens used in visualization of intense FEL and HHG beams [28,29]. Fig. 4 demonstrates a sublinear response of a CaWO_4 crystal. The 48 eV photons penetrate into the crystal deep enough to decrease the role of surface losses, which contribute significantly to the non-radiative decay of electronic excitations at lower energies. Therefore, the main cause for such behaviour is the excitation density effects as discussed in [3] for cross-luminescence in BaF_2 where quenching starts on the formation of $\sim 10^{18}$ elec-

tron-hole pairs in 1cm^3 . The powerful FEL allows the direct study of high-density excitation effects in solids.

Figure 5 shows surface damage of CaWO_4 crystal induced by the FEL beam. This raises the following important questions: which part of the surface area illuminated by FEL is emitting and is there any considerable role of damage in the decrease of quantum yield? Presently, these issues remain still open for further studies. However, we monitored the luminescence intensity as a function of FEL radiation dose and also by varying incident intensities using the gas absorber. These results indicate that there is some damage depending on the radiation resistance of the crystal, but in the latter experiment the recovery of luminescence intensities occurred to the level below, but still comparable with the initial yield of the non-irradiated crystal. Obviously, XUV photons are absorbed deep enough in the crystal avoiding influence of surface damage and the power density of $\sim 10^{12}\text{ W/cm}^2$ is still tolerable for tungstate crystals.

5 Summary In multibunch mode, SR sources being tuneable in wide energy range provide photon beam characteristics well suited for luminescence investigations of solids with high spectral as well as temporal resolution in sub-nanosecond time range. HHG based light sources generate fs pulses with a high repetition rate covering wide excitation energy range, which makes them attractive for studies of fast dynamical processes and effects due to high excitation density under many excitation pulses. Tuneable free electron lasers combine fs pulse lengths with a high brilliance enabling single shot spectroscopy under extreme conditions. All light sources are complimentary with their advantages and drawbacks.

Acknowledgements Financial support by the Access to Research Infrastructures activity in the FP6 of the EU (contracts RII3-CT-2003-506350, FOSCIL, Laserlab Europe and RII3-CT-2004-506008, IA-SFS) the HRM Activity of the EU, Marie Curie Action XTRA RTN, the New Emerging Science and Technology contract TUIXS (NEST-012843) and by the Estonian Science Foundation (Grants 6538 and 0548J) for research are gratefully acknowledged.

References

- [1] G. Zimmerer, *J. Lumin.* **119/120**, 1 (2006).
- [2] K. Kimura, J. Kaneko, S. Sharma, W. Hong, and N. Itoh, *Phys. Rev. B* **60**, 12 626 (1999).
- [3] M. Kirm, F. Savikhin, A. Lushchik, and Ch. Lushchik, *Radiat. Meas.* **33**, 515 (2001).
- [4] V. Ayvazyan et al., *Phys. Rev. Lett.* **88**, 104802 (2002).
- [5] P. Salières, A. L'Huillier, Ph. Antoine, and M. Lewenstein, *Adv. Atom. Molec. Opt. Phys.* **41**, 83 (1999).
- [6] M. Kirm, A. Andrejczuk, J. Krzywinski, and R. Sobierajski, *phys. stat. sol. (c)* **2**, 649 (2005).
- [7] P. Martin, A. N. Belsky, E. Constant, E. Mével, and F. Salin, *IEEE Trans. Nucl. Sci.* **48**, 1137 (2001).
- [8] R. Sobierajski, J. Krzywinski, A. Andrejczuk, U. Hahn et al., *Rev. Sci. Instrum.* **76**, 013909 (2005).
- [9] F. Quéré, S. Guizard, P. Martin et al., *Phys. Rev. B* **61**, 9883 (2000).
- [10] J. Gaudin, G. Geoffroy, S. Guizard et al., *Appl. Phys. B, Lasers and Optics* **78**, 1001 (2004).
- [11] D. Schiffbauer, C. Wickleder, G. Meyer, M. Kirm et al., *Z. Anorg. Allg. Chem.* **631**, 3046 (2005).
- [12] S. Kück, I. Sokólska, M. Henke, T. Scheffler, and E. Osiać, *Phys. Rev. B* **71**, 165112 (2005).
- [13] S. Kazamias, F. Weihe, D. Douillet et al., *Eur. Phys. J. D* **21**, 353 (2002).
- [14] V. Nagirnyi et al., in: *Proc. 8th Internat. Conf. on Inorganic Scintillators and their Use in Scientific and Industrial Applications*, Alushta, Ukraine, 2005 (Nat. Acad. of Sciences, Kharkov, 2006), pp. 36–39.
- [15] V. A. Pustovarov, A. L. Krymov, and E. I. Zinin, *Nucl. Instrum. Methods A* **359**, 336 (1995).
- [16] P. Jaeglé, S. Sebban, G. Jamellot et al., *J. Appl. Phys.* **81**, 2406 (1997).
- [17] Y. C. Zhu, J. G. Lu, Y. Y. Shao et al., *Nucl. Instrum. Methods A* **244**, 579 (1986).
- [18] C. L. Melcher, R. A. Manente, and J. S. Schweitzer, *IEEE Trans. Nucl. Sci.* **36**, 1188 (1989).
- [19] M. J. Lammers, G. Blasse, and D. S. Robertson, *phys. stat. sol. (a)* **63**, 569 (1981).
- [20] V. Nagirnyi, L. Jönsson, M. Kirm et al., *Radiat. Meas.* **38**, 519 (2004).
- [21] A. N. Belsky, R. A. Glukhov, and I. A. Kamenskikh, *J. Electron. Spectr. Relat. Phenom.* **79**, 147 (1996).
- [22] V. Nagirnyi, M. Kirm, A. Kotlov, A. Lushchik, and L. Jönsson, *J. Lumin.* **102/103**, 597 (2003).
- [23] M. Nikl, J. A. Mares, M. Dusek et al., *J. Phys.: Condens. Matter* **7**, 6355 (1995).
- [24] M. Itoh, M. Horimoto, and M. Fujita, *J. Phys.: Condens. Matter* **15**, 193 (2003).
- [25] V. B. Mikhailik, H. Kraus, D. Wahl, M. Itoh, M. Koike, I. K. Bailiff, *Phys. Rev. B* **69**, 205110 (2004).

- [26] A. N. Vasil'ev, in: Proc. 8th Internat. Conf. on Inorganic Scintillators and their Use in Scientific and Industrial Applications, Alushta, Ukraine, 2005 (Nat. Acad. of Sciences, Kharkov, 2006), pp. 1–6.
- [27] A. N. Vasil'ev et al., in preparation.
- [28] V. Ayvazyan et al., Eur. Phys. J. D **37**, 297 (2006).
- [29] C. Valentin, D. Douillet, S. Kazamias et al., Opt. Lett. **28**, 1049 (2003).