Novel ultra-fast luminescence from incipient ion tracks of insulator crystals: electron–hole plasma formation in the track core

K. Kimura *, S. Sharma, A.I. Popov

RIKEN, The Institute of Physical and Chemical Research, Hirosawa 2-1 Wako-shi Saitama 351-0198, Japan

Abstract

Measurements of fast luminescence decay and time-resolved spectra revealed novel ultra-fast luminescence with the lifetime of several tens ps in heavy-ion-irradiated single crystals of LiF, NaF, NaCl, KCl, KBr, KI, RbI, CsCl, CsBr, CsI, α-alumina, and MgO. The luminescence is furthermore characterized by a super-linear increase in the efficiency with increasing excitation density, non-tailed decay curve, and temperature-insensitive decay-rate and yield. The results mean that the luminescence neither originates from localized excited states such as self-trapped excitons, free excitons, excited defects, and excited impurity centers nor their interaction. A process which does not contradict the experimental results is the formation of the e–h plasmas and the luminescence from them.© 2001 Elsevier Science Ltd. All rights reserved.

Keywords: High-density excitation; Heavy ions; Time-resolved luminescence spectra; Electron–hole plasma

1. Introduction

During the studies for primary processes of ion tracks, we have always encountered the result that novel, interesting, and substantial phenomena characteristic in ion irradiation, originate from the track core, e.g. vigorous interactions among primary intermediates such as free excitons in KBr (Kimura et al., 1980) and rare gases (Kimura, 1993), saturation of exchange interaction rate of self-trapped excitons (STE) in BaF_2 (Kimura and Wada, 1993; Kimura and Hong, 1998), stimulated emission of the excited F^+-centers and the novel ultra fast luminescence decay component (UFLDC) from the track core in α-alumina (Kimura et al., 1999). This finding of the UFLDC in α-alumina motivates us to assign it and to investigate whether it is general for many other wide-band gap materials. It is however necessary to measure the luminescence decay and the time-resolved spectrum (TR-spectrum) with the time resolution less than 100 ps in

order to discern the UFLDC from known luminescence like excitons and excited centers. For this purpose, we have used the single ion single photon coincidence technique (SISP) developed by us (Kimura, 1994), which has the time resolution of about 80 ps.

2. Experimental

He-, N-, Ar-, Kr-, and Xe-ions were accelerated to 2.0 MeV/nucleon by the heavy-ion LINAC of our institute and collimated to 0.5×0.5 mm^2. Ions of 2.0 MeV/nucleon have stopping power a round the maximum and does not eject such energetic secondary electrons in order to work as δ-rays: At this energy, the ejection rate for the electrons of energy > 2 keV, the lower limit of energetic δ-rays, has been estimated to be about 5% of the deposit energy (Becchetti et al., 1976). This means that the track of the present incident ion energy can be regarded as comprising only the core part approximately, namely the so-called halo part can be neglected. Equal ion energy or ion velocity has

* Corresponding author.
E-mail address: kkimura@postman.riken.go.jp (K. Kimura).

the following meaning. Since the track radius is proportional to the ion velocity (Brandt and Ritchie, 1974), ions of the same velocity have nearly the same track radius. Hence, in our case, we can use the so-called linear energy transfer (LET: An energy integral of electronic stopping power divided by the range) as the relative excitation density (ED): ED is approximately proportional to LET.

The ion fluence per one decay curve was usually at most 5×10^9 cm^{-2}. The rate of ion hitting was around 100 K counts per s (cps), while the rate of photon counting was at most a few hundred cps. Each coincident signal, output from the time-to-pulse-height convertor (TAC), corresponds to a single event in a single ion-track. Such low ion current and fluence satisfy the measurements for the single track effect free from a pile up of damages.

Sample crystals used were NaF, LiF, NaCl, KCl, CsCl, KBr, KI, RbI, CsI, BaF$_2$, MgO, α-alumina, diamond, and SiO$_2$. The sample plates were mounted in a cryostat (modified Oxford type CF250) and were also slid during irradiation by a remote control in order to get a fresh surface. Measurements by SISP were made in the same manner as those in the previous one (Kimura et al., 1999).

The optical system was calibrated using two monochromators, a calibrated photo-diode, and standard deuterium- and tungsten-lamps.

3. Results and discussion

The SISP with heavy-ion irradiation revealed the UFLDC for almost all alkali- and alkaline-earth halide crystals, and insulator metal oxide crystals, except for diamond and SiO$_2$. It is obvious that the UFLDC is a novel luminescence but not the known luminescence due to excitons and excited centers (Song and Williams, 1995), because the UFLDC has as short lifetime as 100 ps (several tens ps by deconvolution) and appears in a wholly different wavelength region from known luminescence bands (KCl, NaF, LiF, CsCl, and MgO), or even in the case of NaCl, KBr, KI, RbI, CsI, BaF$_2$, and α-alumina in which known ones superpose; the UFLDC could be easily distinguished by an entirely different bandwidth and lifetime. Now let us show an example of the latter category. Fig. 1a is a three-dimensional display of wavelength-dependent decay curves of an RbI single crystal irradiated with Xe-ions at 6 K; specific I means intensity per ion, which is in arbitral unit but relatively universal through the text. One can recognize fast decays due to the UFLDC appearing in both wavelength regions of intense but slower decays at 320 nm which are due to the σ-STE (Song and Williams, 1995). The UFLDC becomes much clearer by equi-height plot in Fig. 1b. Fig. 1c shows time-resolved spectra (TRS), which are the cross-sectional views along the wavelength axis of Fig. 1a at fixed delay times. Fig. 1d shows the decomposition of the TRS at 0 ns into two bands due to the UFLDC and the σ-STE. Thus, the results show the UFLDC with the lifetime of about 30 ps (by
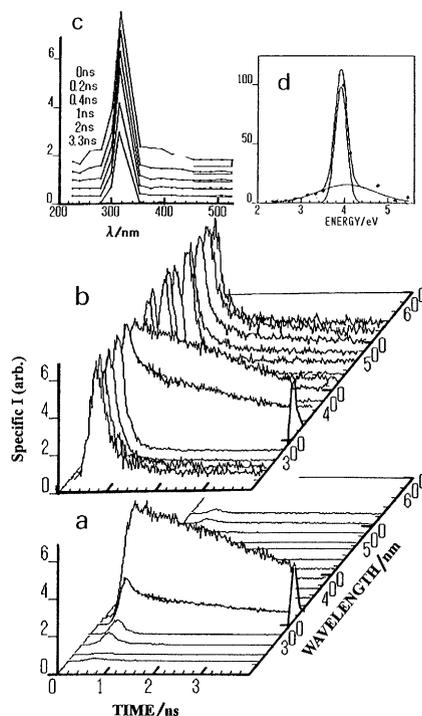

Fig. 1. Decay curves and TR-spectrum of RbI under irradiation with Xe ions at 6 K. (a) Wavelength dependent decay curves; (b) equi-height plots of (a); (c) a TR-spectrum; (d) decomposition of the TR-spectrum at 0 s of (c) into two gaussians.

deconvolution), the peak at 4 eV, and the width at 1.5 eV. The similar UFLDCs were observed for other aforementioned crystals. The UFLDCs for samples of the former category were quite obvious since the known luminescence bands do not overlap. Thus, the finding of the UFLDC was general in all crystals used except for diamonds and quartz that are formed mainly by covalent bonds. It may be deducible that the UFLDC is the general phenomenon in many insulators. Our finding is owing to the following techniques. At first, our SISP has the high sensitivity and a time-resolution of 80 ps. Secondly, we used a heavy-ion excitation and extracted the track core exclusively from the halo track, where the irradiation effect is due to electron irradiation. Otherwise, the UFLDC should be concealed in intense known bands. The result that only heavy-ion irradiation can give rise to the UFLDC, suggests the important role of high ED.

Now, let us roughly evaluate high ED by heavy-ion irradiation. Assuming the core radius tentatively to be 5–10 Å, the ED for Xe ion in the present materials is about 6–20 eV/Å^3. In contrast, the corresponding ED of the laser is at the most 5×10^{-2} eV/Å^3 even by the most powerful soft X-ray laser with the specification, 6×10^{12} photons of 58.5 eV/pulse (Jaegle et al., 1997); the high power electron pulse (Vaisburd and Semin, 1981), e.g. 1000 Å/cm^2,

0.5 MeV electrons, is 8×10^{-2} eV/Å^3. Thus, heavy ion irradiation is most powerful. The deposit energy is spent initially to form electron–hole pairs (e–h pairs) at very high density that their distances can be lattice constants. As far as the ED is concerned, lasers and electron pulses seem to be insufficient to produce multiple e–h pairs adjacently. Adjacent formation is a necessary condition for the interaction between e–h pairs to take place. In the present crystals, the strong electron–phonon coupling does not allow diffusional encounters of the pairs. Thus, the situation is quite different from excitons in indirect semiconductors which are long-lived and mobile that easily form exciton molecules and drops even if they are separated by several tens of Å .

The UFLDC was mostly insensitive to both specific intensity and decay rate to the change in temperature, which is quite different from those known regarding exciton and defect luminescence.

At this step, we can omit free excitons, self-trapped excitons and excited centers produced by recombination between electrons and holes (comprising trapped ones) from candidates of origins of the UFLDC, by reason that the latter is characterized by the lifetime as short as several tens ps, the different appearance-wavelength and the much broader band. Accidentally, fast atomic transitions can be ruled out from the fact that the UFLDC can be observed commonly for a wide range of samples and its bandwidth is also extremely broad. From these results, Auger free luminescence (Kubota et al., 1988), with the lifetime of sub-ns, is not the case. Apart from the isolated-excited states mentioned so far, one may consider the interactions between excited states to enhance the luminescence or quench under the condition of present high-density excitation and result in the shortening of the lifetime. For example, the excited F^+ for α-alumina is stimulated (Kimura et al., 1999) and the STE luminescence in BaF$_2$ is quenched (Kimura and Hong, 1998) with the increasing ED. In general, the decay curve of this case must have a longer tail, succeeding the initial fast decay and in accordance with the lifetime of each excited state, since an average distance determining the rate constant increases with the depletion of the centers with increasing time. Such tailing should be much more prominent at higher temperatures at which the centers become more mobile, as is shown typically (Kimura and Hong, 1998; Kimura et al., 1999). However, the observed UFLDC has no tail even by the changing temperature. Therefore, interactions between excited states such as STEs and excited centers cannot be origins of the UFLDC. We will discuss this with regard to free-exciton complex later.

The most decisive influence to the yield of the UFLDC was brought about by ED. Fig. 2 shows relative specific-intensity of the UFLDC for various crystals as a function of ED due to He-, N-, Ar-, Kr-, and Xe-ions. Now, let us look at the curves for RbI and alumina. No UFLDC could be detected by He-ion irradiation of which EDs are as small as 0.115 and 0.052 eV/Å for alumina and RbI,
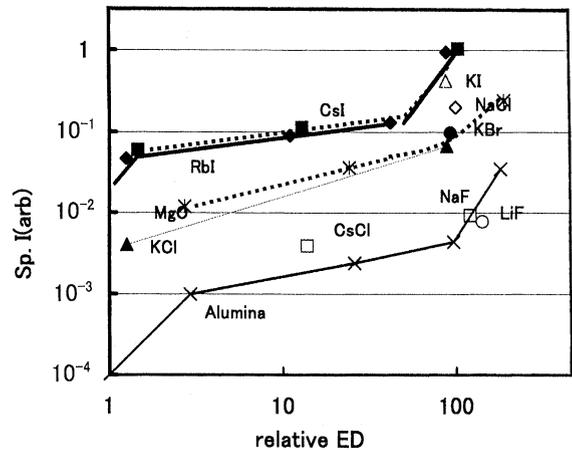

Fig. 2. Excitation-density dependence of specific intensity of the UFLDC. The ED on the abscissa is scaled in the unit of eV/Å but this scale is available also in eV/Å^3 since the radius is nearly the same to all ions.

respectively, but it increases by a rate of third order for ED towards N-ion irradiation, thereafter, both curves ascend moderately towards Kr-ions, however, they rise abruptly with the third order from Kr-ions to Xe-ions. The curve for CsI, although it lacks Kr- and He-ion irradiation, seems to depict a similar curve. The MgO curve looks mild in the rising rate, however, it may be smeared because of accidental poor time resolution of the SISP. Anyhow, the common tendency of the samples is that the specific intensity of the UFLDC increases with increasing ED and moreover its rate is super-linear. This super-linear increase strongly suggests that the UFLDC originates from the multiple interaction or bindings among excited states or their precursors. In addition, non-tailing decay curves of the UFLDC indicate that these states or precursors must be short-lived similarly to the UFLDC by the same reason as that described in the previous paragraph. Namely, the constituents of the UFLDC seem to be limited to e–h pairs or free excitons.

As described in the previous part, heavy-ion irradiation can produce e–h pairs at a very high density that their distances are dimensions of the lattice constants. They may be bound like adjacent H atoms. The large screening effect generated by dense e–h pairs should weaken the individual nature of the pairs, as the e–h plasma in semiconductors (Klingshirn and Haug, 1981). Thus, the core track can give rise to the e–h plasma rather than the recombination between electrons and holes that occurs independently. Furthermore, the binding may induce the gigantic oscillator strength of the e–h plasma on the analogy of the case of semiconductors (Rashba, 1975). Therefore, the UFLDC may be ascribed to the e–h plasma luminescence. The free-exciton complex is unlikely because they are observable only in limited alkali halides and with very low quantum yields and in case of ion irradiation, the binding

between the e–h pairs seems to occur before relaxation into the free exciton.

The peaks of the UFLDC position around 4 eV, while those of 1s free excitons are from 5.3 to 13 eV and band gaps are from 6 to 13.7 eV. One may doubt the spectral shift of this e–p plasma to be as large as several eV, different from the case in semiconductors. This may be interpreted as follows. Simultaneously with ejection, the electrons expand toward radial direction of the ion trajectory, loss of energy, and return to the holes. Time spent for these processes may be estimated at 10^{-14}–10^{-13} s by Ritchie and Claussen (1982). During the travel of the ejected electrons, the remaining track core is rich in positive charges so that the core region is expanded by Coulomb repulsion and deformed largely from the original crystal structure. The field at a distance of 5 Å is as large as 10^8 V/cm even in the case of a light-ion track such as 1 MeV He^+ according to Ritchie's estimation. However, the so called ion-explosion (Fleischer et al., 1975) and thermal spike models cannot be realized within this time interval (Ritchie and Claussen, 1982). We can see the similar estimation in a recent study (Yavlinskii, 2000). Such an expansion deforms the crystal structure largely so that the band gap is reduced since it is determined at a coordinate largely displaced from the equilibrium position (imagine the position shifted largely from the origin on the so-called configuration coordinate). Also, in this expanded core, a bond between halogen atoms and halogen ions may occur so that holes of the e–h pairs are molecules or molecular anions. In addition, the binding energy should be significantly large by considering the Morse curve with the short distance. They all work to reduce the photon energy of the e–h plasma luminescence. Thus, the present e–h plasmas seem significantly different from those in semiconductors produced by laser light.

The UFLDC has shown large sample dependence. As seen in Fig. 2, it expands to a few orders by the difference in the samples. Picking up alkali halides with the same alkali metal at the similar ED, the one with the larger halogen ion has the larger specific intensity. This tendency can also be seen in case of the quantum yields of STE's luminescence, although there exists ambiguity for light metal ions (Song and Williams, 1995). This phenomenon is understood by the alkali halides with the smaller halogen ions that have the larger probabilities to form Fraenkel defects, because of the larger free space for the movement. Analogously, the e–h plasma also is expected to have larger probabilities in non-radiative processes for smaller halogen ions.

Transition radiation can be ruled out by the aforementioned large sample dependency, in spite of similar dielectric constants. Moreover, the present experiments were done in ion current as low as sub-pA. Thirdly, the light image perpendicular to the photon-emission axis was a simple centrifugal-pattern and not a hollow one characteristic of the optical transition radiation.

4. Conclusion

The UFLDC has been observed commonly for many wide-band gap crystals excited by heavy-ion excitation. This finding is what we like to remark initially. It was observed that the UFLDC originates from the interactions among multiple excited constituents having a lifetime less than several tens ps. We proposed e–h plasmas as the origin of the UFLDC. There remain, of course, many questions for the e–h plasma in these materials. We are just at the starting point. Fast multi-channel TR-spectra are developed to take more precise spectral shapes and absolute intensities. It would be important to know the enormity of the yield of the UFLDC to the deposit energy. Also, we are interested in the defects or products that the e–p plasmas leave, because the processes for the production are considered to be due to a collective manner.

Acknowledgements

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