Fast electron–hole plasma luminescence from track-cores in heavy-ion irradiated wide-band-gap crystals

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Abstract

Measurements of fast luminescence decays and time-resolved spectra reveal novel ultra-short-lived luminescence (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 characterized by its super-linear increase to excitation density, non-tailing decay, sample dependence and temperature-insensitive decay and yield. The luminescence can not be attributed to known excited species, but vigorous interaction among dense electron–hole pairs, i.e. plasma. © 2002 Published by Elsevier Science B.V.

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1. Introduction

We have seen so far no studies on direct observations of initial ion tracks. To do this, photon detection is one of the fastest and the most sensitive methods. We have developed a single ion single photon coincidence technique (SISP) to measure fast luminescence decays and time-resolved spectra (TRS) [1–5]. We have so far reported following phenomena attributed to the track core, which suggest vigorous interactions among primary intermediates such as free excitons in KBr [2] and rare gases [3], saturation of exchange interaction rate of self-trapped excitons (STE) in BaF$_2$ [4], stimulated emission of the excited F$^+$-center and very recently, novel ultra-fast luminescence (UFL)

was found in α-alumina [5]. The UFL was proposed to originate from electron–hole plasma (e–h plasma) under extremely high-density-excitation. If it is true, it is the first finding about the substantial phenomenon in incipient and isolated ion tracks. As for e–h plasma, there have been many reports for laser irradiated semiconductors [6] and a few recent reports for ion irradiated metals [7]. In these substances, however, excitons or plasmons have the sufficient lifetimes and yield to migrate and to aggregate, while in wide-gap materials, free excitons can not be formed or their yields are very small and cannot migrate because of immediate self-trapping by the strong electron–lattice coupling. Even recent powerful laser is still insufficient to produce e–h plasma in wide-gap materials. In contrast, a heavy ion can deposit sufficient energy density to form e–h pairs adjacently. Following rough estimations for excitation densities (ED) may be meaningful. Presuming the core radius tentatively to 5–10 Å, the ED for Xe ion in the

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present materials is about 6–20 eV/Å^3. In contrast, the corresponding ED of the laser is at most 5×10^{-2} eV/Å^3 even by the powerful soft X-ray laser with the specification, 6×10^{12} photons of 58.5 eV/pulse [8]; the high power electron pulse [9], e.g. 1000 Å/cm^2, 0.5 MeV electrons, is 8×10^{-2} eV/Å^3. Thus, heavy-ion irradiation is by a few orders higher in excitation density. Deposit energy per atom attains to 200–660 eV in the case of a lattice constant of 4 Å.

2. Experimental

He-, N-, Ar-, Kr- and Xe-ions as excitation sources were accelerated to 2.0 MeV/nucleon, by the heavy-ion linear accelerator of our institute (RILAC) and collimated to parallel beams of the size, 0.5×0.5 mm^2. Ions of 2.0 MeV/nucleon have stopping powers near the maximum, while they eject little energetic δ-rays: at this incidence energy, the ejection rate of electrons with energy >2 KeV (the lower limit of energetic δ-rays) has been evaluated to about 5% of the deposit energy [10]. Therefore, irradiation effects in track cores appear dominantly, while so-called halo part is minor. Equal ion velocities give nearly the equal track radii, since ranges of secondary electrons are determined principally by ion velocity and the radius of a track core is proportional to ion velocity [11]. Hence, without data of the radius, we can estimate a ratio of ED due to different ions, since it is equivalent to the ratio of the deposit energy/range. This approximation is valid as long as ED-dependence of the objective quantity is large enough. The irradiation was carried out with low ion current (100 K ions/s) and low ion fluence (5×10^9 cm^{-2}) so as to satisfy the condition of single ion hit and observe the isolated track effect free from overlapping of the tracks. Therefore, a time-correlated output signal from SISP corresponds to a single event in a single ion-track. Plates of crystals, NaF, LiF, NaCl, KCl, CsCl, KBr, KI, RbI, CsI, BaF$_2$, MgO, α-alumina, diamond and SiO$_2$, were mounted in a cryostat (modified Oxford type CF250) and also were slid during irradiation to get a fresh surface. The optical system was calibrated although not absolute.

3. Results and discussion

The SISP revealed novel UFL for all heavy-ion irradiated crystals except for a diamond and a SiO$_2$. The UFL's for a group of KCl, NaF, LiF, CsCl and MgO could be discerned easily because the known luminescence has peaks at quite different wavelengths and has much longer lifetimes [12]. Fig. 1(a), an example of this group, is a three-dimensional display of wavelength-dependent decay curves of a KCl single crystal irradiated by Xe-ions at 6 K; 'specific I' means intensity per ion, which is not absolute but its scale is the same through all figures in the text. The figure shows ultra-fast decay components, i.e. UFL in the UV-light region. Their decay times are within 100 ps; deconvolution gave a decay time of 80 ps. Fig. 1(b), TRS's display of Fig. 1(a), shows that the UFL has a peak max round 300 nm (4.13 eV) and the band width, 1.6 eV; the dent near the center of
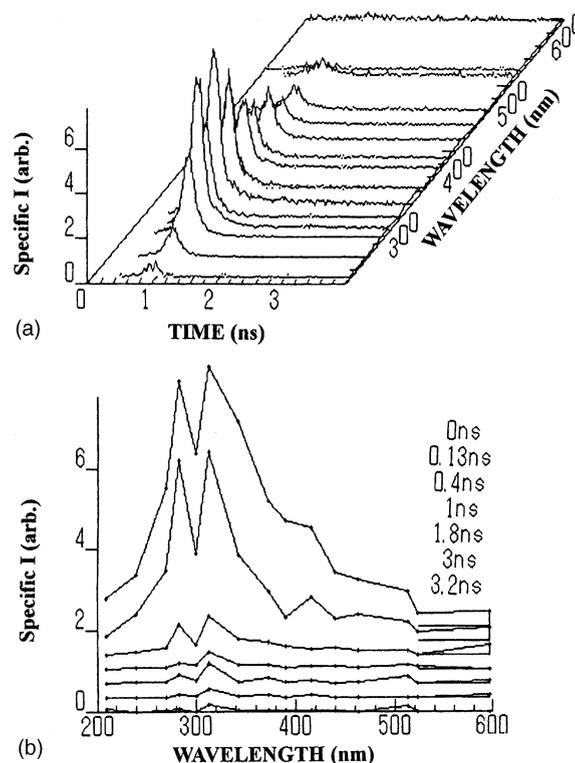

Fig. 1. Decay curves and TRS of Xe-ion irradiated KCl at 6 K: (a) wavelength-dependent decay curves and (b) TRS's.

the band is ascribed probably to an accidental error. By contrast, the known luminescence for KCl is only due to the π-STE of lifetime of 5 ms and peak at 534 nm (2.32 eV). This is too weak to be recognized in this short time range of 4 ns. The UFL's for heavy-ion irradiated LiF, NaF, CsCl and MgO had similar lifetimes of several tens ps and were spread round 4.0, 3.4, 4.4 and 4.0 eV, respectively. On the other hand, the peaks and lifetimes of known luminescence bands are 3.44 eV and 5.9 ms, 2.65 eV and 0.34 ms, 2.9 eV and 12 ms, for LiF, NaF, CsCl [13], respectively; MgO, 4.9 eV and 3.3 eV with lifetimes of the order of μs [14]. In another group of NaCl, KBr, KI, RbI, CsI, BaF_2 and α-alumina, intense bands were overlapped. For example, RbI is known to have strong σ-STE luminescence at 318 nm of which decay time is 3 ns at 4.2 K [15]. Fig. 2(a) shows a three-

dimensional display of equal-height decay curves of Xe-irradiated RbI at 6 K. One can see the UFL evidently around the σ-band. The TRS's are given in Fig. 2(b) and a TRS at time 0 (due to the decay peak) can be decomposed as shown in Fig. 2(c) by Gaussian fitting. Figures show that the UFL spreads to both sides of the σ-band. So-called Ex band [12] is too weak at 6 K to be detected within 4 ns and the known π-STE at 400 nm was not observed also because of its long lifetime, 22 μs [12]. The similar UFL's were observed clearly for all crystals of this group except for diamonds and quartz. It is only noted at present without further discussion that the latter two are constructed mainly by covalent bonds. Now that the UFL were observed for a number of samples, it seems reasonable to deduce that the UFL is a common phenomenon to many insulators, except for some kinds of materials such as diamonds and quartz. Why only we could observe the UFL in spite of many other studies should be owing to the following technical and experimental conditions. Our SISP has the high-sensitivity and time-resolution of 80 ps. We have used heavy-ion excitation under the conditions to observe track core exclusively from the halo track where the irradiation effect is equivalent to electron irradiation, which is much lower in ED.

Now, let us consider origins for the UFL with further experiments. At first, luminescence of isolated free excitons, STE and the other excited centers like F^{+*} can be omitted from the candidates of the UFL, from large differences in the lifetime, the appearance wavelength, the temperature dependence and the band width [12]. Accidentally fast atomic transitions, as proposed for CsI [16], can be ruled out from the fact that the UFL were observed for a wide range of samples. From similar reason, the hot band of the STE can be ruled out. Moreover, this cannot explain the result that the UFL's for KCl and NaF of the group 1 appear at quite different wavelength from the π-STE which is only one origin for the hot band if it were. Auger free luminescence [17] can be ruled out, because the UFL's were observed even for CsI, RbI, KCl, LiF, etc., which are known to have no Auger free luminescence. Transition radiation cannot explain the large sample dependence which was shown
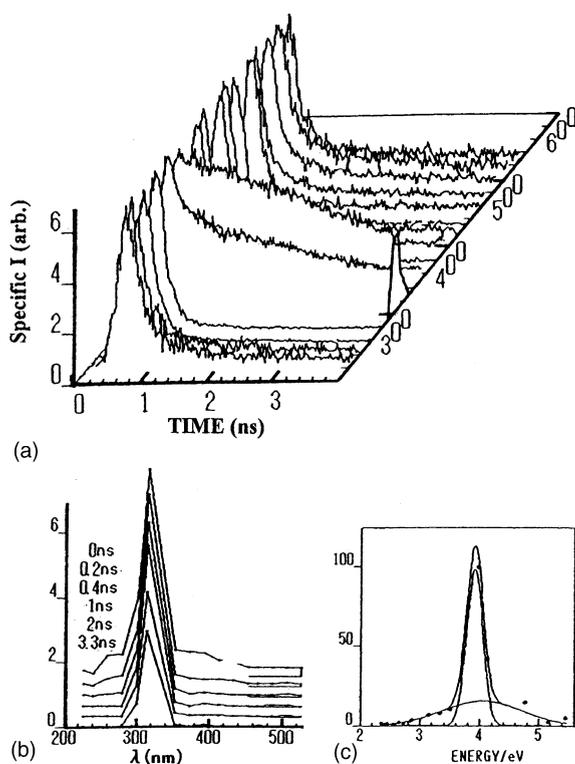

Fig. 2. Decay curves and TRS of Xe-ion irradiated RbI at 6 K: (a) wavelength-dependent decay curves in equal-height, (b) TRS's and (c) decomposition of the TRS at time 0 (at a peak) into two Gaussians.

afore and will be shown in the last paragraph in this text. Also, present ion current, sub pA, seems too small to observe it. Moreover, the light image measured on a plane normal to the light axis was a simple centrifugal-pattern but not a hollow-pattern characteristic to the optical transition radiation. Consequently, we may concentrate only multiple interactions among e–h pairs or their excited derivatives. We need to consider no new isolated excited states, since relaxation processes after e–h pair formation are determined by nature of the sample crystal.

In Section 1, it was mentioned that e–h pairs could be produced adjacently. Under such condition of high density, the decay curve can be sharpened by vigorous interactions among the excited species. In fact, we have observed extreme sharpening of the decay curves. Here two examples are presented. One of the two, F^{+*} of α-alumina, showed the sharpening and the stimulated emission [5]. The other, the STE of BaF_2, was the sharpening with quenching [4]. Accordingly, it may be necessary to check whether the UFL can be explained by such sharpening. In general, the decay curve under the interaction of the species, however, must be followed by a tail longer than the lifetimes of the excited species subsequent to initial shortening, since the species can interact throughout their lifetimes and also the time-retarded formations become slower with passing time because of a decrease in the concentration of charged species as the origin. Resultant decay must tail at least for few ns. However, the UFL had no tail as shown in Fig. 1. In addition, the tailing should have pronounced temperature dependence, since the charged species become mobile more at higher temperatures, as shown actually [4]. No temperature dependence was observed.

Thus, STE's and excited centers can be excluded. In cases of most alkali halides, the decay rates of σ-STE's were observed to be independent of ED and nearly equal to those by photo-irradiation. Therefore, non-tailing decay with half life-time shorter than 100 ps restricts species under the interaction to the ones with shorter lifetimes than that of the UFL. Such short-lived ones are e–h pairs and free excitons.

If the UFL originates from multiple interactions among the constituents, the UFL must increase in higher order than the first for the concentration of the constituent or ED. Fig. 3 shows ED dependence of the specific intensity of the UFL, where ED's were changed by using different ions, He-, N-, Ar-, Kr- and Xe-ions. Now, let us look over the curves for alumina and RbI. No UFL could be detected by He ions irradiation
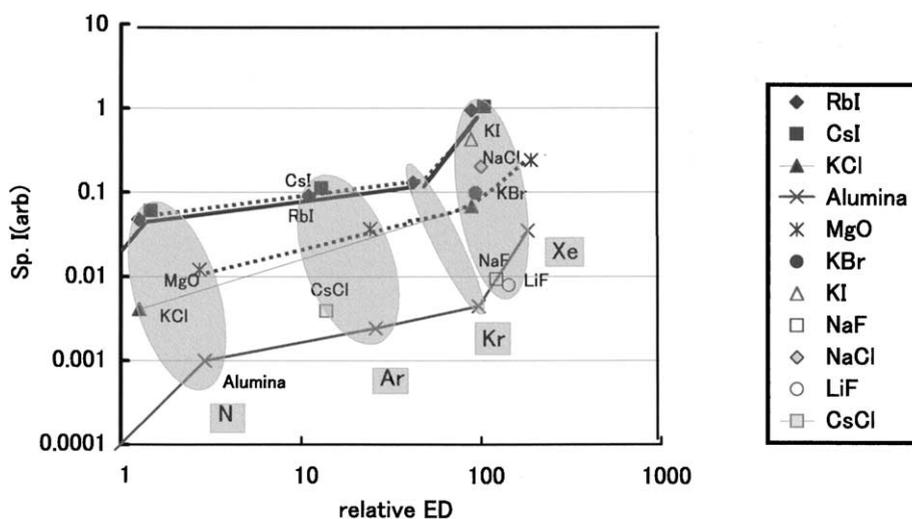

Fig. 3. ED-dependent specific intensity of the UFL at 6–11 K.

of which ED's are 0.052 and 0.115 for RbI and alumina, respectively, but both curves increase by the rate of third order towards N-ion irradiation, thereafter, they ascend moderately towards Kr-ions, however, they rise abruptly in the third order towards Xe-ions from Kr-ions. The curve for CsI looks similar to that of RbI since measured points are close to those for RbI although the curve lacks Kr- and He-ion irradiation. The increase for MgO, which is mild, may look essentially similar to the above three samples. The samples other than these four have similar intensities although they have only a single point for ED. Three-step increase is an interesting phenomenon, but we remark here only super-linear increase of about the third order. This may prove that the UFL originates from multiple interaction or bindings among constituents.

Adjacent e–h pairs, having open shell structures, can interact or combine immediately like adjacent H atoms, even if the e–h pairs are short live. Large screening effect by dense e–h pairs works in favor of interaction or binding since it suppresses immediate recombination among electrons and holes, as the e–h plasma in semiconductors does [6]. Thus, in track cores of heavy ions, e–h pairs may prefer to combine each other and to form a kind of instantaneous clusters. We call them e–h plasmas also analogous to the case of semiconductors. In general, the binding may induce the gigantic oscillator strength [6,18]. Thus, the UFL may be attributed to e–h plasma and to recombination luminescence between an electron and a hole, again, as is in semiconductors. Whereas e–h plasma in semiconductors is consisted of free excitons, free-exciton complexes are unlikely in insulators, because free excitons have been observed rarely and they have very low quantum yields. Also, it is unreasonable if adjacent e–h pairs do not interact until they relax into free excitons.

The UFL was mostly insensitive to temperature both in the intensity and the decay rate, quite different from the known facts that exciton and defect luminescence are quenched largely with increasing temperature; slow processes like thermo-luminescence are not the case. Such temperature-insensitivity suggests that the UFL is created before self-trapping with strong temperature dependence. This supports e–h plasma.

The UFL peaks showed red shifts as large as several eV from band gaps. This may be understood by following dynamics in the track-core. Ion-ejected electrons expand to radial direction out of the ion trajectory, lose the energy and return back to the holes, that takes 10^{-14}–10^{-13} s [19]. Since major ionization occurs directly or indirectly in valence electrons of the form of X^- (X = halogen or oxygen atom), holes, X's are formed densely in the track core so that the core region is subjected to strong Coulomb repulsive force by a lot of excess M^+'s: the field is estimated as large as 10^8 V/cm at a distance of 5 Å even in an 1 MeV He^+ ion [19]. Consequently, the track core may be expanded somewhat, but so-called ion-explosion [20] and thermal spike models cannot be realized within this time interval [16,19]. On the other hand, since X's are free from Coulomb force by M^+, there may occur reactions or displacements, $X + X^- \rightarrow X_2^-$, $X + X \rightarrow X_2$, $X + X + X^- \rightarrow X_3^-$, etc. These products or intermediate states become new holes, which are the counter holes of electrons along with X when e–h plasma is relaxed. Recombination luminescence with such holes causes the large red shift like Stokes shift as seen in the STE and broadens luminescence. Also, the binding energy between e–h pairs could be significantly large by considering the Morse curve at short distances, which gives red shift also. By the way, we have often seen reports that the track core is amorphousized [21]. This may be related with track expansion and hole displacements in the incipient tracks aforementioned.

The UFL has considerable sample dependence, as shown in Fig. 3. Comparing halides with the same alkali metal at the same ED, the one with the larger halogen ion has the larger specific intensity. The extent is such that the maximum specific intensity is about ten times of the minimum. Similar tendency is seen in STE's in halides with larger metal ions [8]. This phenomenon is interpreted as halogen ions of the smaller sizes have the larger probabilities to form defects because of the larger free space of the movement. Analogously, the e–h plasma of smaller halogen ions may have larger probabilities of non-radiative processes.

Now, we stand just at the starting point of the study on e–h plasmas in insulators and on a new type of track effect. Many problems are left unsolved. Although we cannot argue sufficiently for e–h plasma model, there may be no doubt that we could observe novel fast luminescence.

Acknowledgements

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