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Excitation-density-dependent competition between radiative and nonradiative annihilations of core holes produced by ion irradiation of a single-crystalline BaF_2

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It was found that the decay time of the Auger-electron-free luminescence of BaF_2 decreases with increasing linear energy transfer (LET) or excitation density. The luminescence decayed exponentially at the initial and final stages, in contrast with a single exponential for photoirradiation. The decay time of a fast component was reduced with increasing LET, while that of a slow component was invariant. A model that Auger-free transitions compete with nonradiative recombinations between core holes and quasifree electrons can explain these experimental results. The recombination rate attained a constant value near the LET of 1.5 MeV/amu Kr ion. The reciprocal of the recombination rate at this LET gives the lifetime of the core exciton.

I. INTRODUCTION

In addition to fundamental luminescence processes due to self-trapped excitons (STE's) and free excitons, another luminescence process has been reported for some of the halides of alkali and alkaline-earth metals recently. Laval *et al.* have found that x-ray-irradiated BaF_2 exhibited a 2200-Å luminescence band with a very short lifetime along with a 3100-Å band with a long lifetime.[1] The latter was assigned to STE's by Williams *et al.*[2] and is a common luminescence feature in alkali halides. The former had a short lifetime in the sub-ns range, which is too short to originate from a singlet STE as is the case for alkali halides. Aleksandrov *et al.*[3] have shown by observing the excitation spectra that the luminescence originates from holes in the inner shell but not from the valence state. Kubota *et al.* showed that the luminescence was due to transitions from the $2p$ orbital of fluorine (valence electrons) to holes with a Ba $5p$ orbital character (the outermost inner shell).[4] This luminescence was named the Auger-free luminescence because the transition does not emit Auger electrons but does emit photons.

We have developed techniques to measure the fast decay of photoemissions from ion-irradiated targets.[5-7] The first motivation to use BaF_2 was to demonstrate the resolution of this equipment, which is now at least 100 ps. The results showed considerable differences from those by photoexcitation: the decay can be decomposed approximately into two exponentials, and the fast component decays faster with increasing particle LET or excitation density. In this report, the decays are measured systematically with several ions, and luminescence dynamics is discussed and a comparison is made with the photoexcitation.

II. EXPERIMENT

Single-photon counting was performed under the condition of the single-ion hit without pile up. To obtain this condition, the ion current was decreased until a rate of one hit per 3000 bunches was achieved. In this way, one can obtain a negligibly short-width pulse of the ion. The decay curves could be obtained using a time-to-amplitude converter (TAC) and an analog-to-digital converter. To provide a fast stop pulse of the ion hit to TAC, a fast secondary electron detector (FASD) has been developed.[5-7] FASD was composed of a 0.01-mg/cm^2 carbon foil and a microchannel plate (MCP). Secondary electrons emitted from the carbon foil by ion penetrating were accelerated up to 5 keV and detected by a MCP, which was model F1551-21 from Hamatsu Photonics.

The start pulses were generated by single-photon counting of photoemission from a sample target. The experimental set up containing FASD, MCP-photomultiplier (R2809U by Hamamatsu Photonics) is essentially the same as previously reported. The resolution was about 100 ps without deconvolution.

Single crystals of BaF_2 were obtained from Horiba Ltd. and from Harshow Chemical Co. He, N, and Ar ions were accelerated up to 1.5 MeV/amu (1 MeV/amu for the Xe ion) by RIKEN linear accelerator. Counting of projectile ions were made by the FASD, whose efficiency was ascertained not to be lower than that of a solid-state detector placed at the position of a target. The monochromator used was model MC-25N from Ritsu Ltd.

III. RESULTS

The time-integrated luminescence spectra of ion-excited BaF_2 displayed only a broad band with a peak at

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3100 Å, but did not display Auger-free luminescence at 2200 Å, in contrast with the case of photoirradiations and electron irradiations, which showed two prominent peaks at 2200 and 3100 Å. The time-resolved luminescence spectra, however, could reveal a prominent peak at 2200 Å. Figure 1 shows a set of dose-normalized luminescence decay curves at room temperature for Ar-ion-irradiated BaF_2, measured with various wavelengths. The figure shows a prominent peak at 2200 Å near time zero due to the ion hit, while at 4 ns no band can be recognized except at 3100 Å. As will be discussed later in detail, each decay can be decomposed approximately into double exponentials in a region of wavelengths from about 2000 to 2500 Å.

In a longer wavelength region, the decay is composed of a nonexponential fast and exponential slow components. The 3100-Å band is similar to the time-integrated luminescence spectrum. This band can be assigned to STE found by Williams *et al.* in the case of electron irradiation.[2] On the other hand, the fast component of the 2200-Å band had a decay time as short as 240 ps. Irradiation with He, N, Kr, and Xe ions showed similar results, although the decay time is not the same. Also, the Ar-ion-irradiated CsBr showed a 2500-Å peak of short decay time, as was seen in photo-induced Auger-free luminescence.[8] As for CaF_2 and NaF, which are known to show no Auger-free luminescences, no extra band due to Auger-free luminescence was observed. From these results, the 2200-Å band observed in the time-resolved spectrum with ion irradiation is assigned to Auger-free luminescence.

The Auger-free luminescence in this case differs considerably from that for photoirradiation. One difference is that the bandwidths for ion irradiations were broader: about 1.5 eV for this case in contrast with 0.74 eV for photoirradiation. The reason for this broadening may be speculated upon as follows. Under the condition of high-density ionizations by ion irradiations, it is likely that the valence electrons adjacent to the core hole Ba^{3+} may be ionized. The transition to give Auger-electron-free luminescence is therefore the superposition of the transitions from filled and partially filled valence bands to the core hole, and hence the bandwidth should be broader than that of Auger-electron-free luminescence for the photoirradiation.

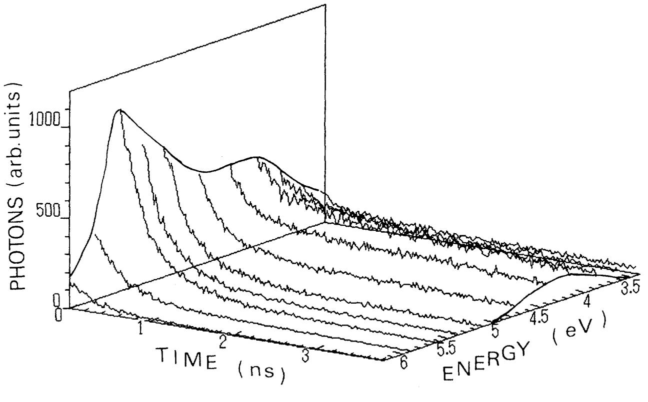

FIG. 1. Dose-normalized luminescence decay of Ar-ion irradiated BaF_2 at room temperature. The peaks of decay curves were regarded as time 0.

The second, a principal subject in this paper is differences for the decay curves compared with those with the photoirradiation. In addition, different ions present different decay curves. A typical decay curve at 2200 Å with Ar-ion irradiation is shown in Fig. 2. The decay curve can be decomposed into two exponentials, whereas the photoirradiation showed a single exponential. Figure 2(A) shows a total decay curve with a linear scale; Fig. 2(B) shows a log-scaled fast component obtained by subtraction of the slow component from the total; Fig. 2(C) illustrates the log-scale plot associated with a linear-line fitting to a slower component. The decay time of the slow component was 800 ps and that of the fast component was 240 ps, which is quite short compared with the 800-ps decay reported[8] in the case of photoirradiation. Table I shows both decay times of the fast and slow components of the decay at 2200 Å obtained for He, N, Ar, Kr, and Xe irradiations along with data reported for electron and photon irradiations. The correct decay times for ion irradiations would certainly be smaller than those in Table I, since deconvolution was not performed. As shown in Table I, decay times of a fast component are short compared with that for photo irradiation, and the decrease has a linear energy transfer (LET) dependence. Here, LET is an ion energy divided by the ion range, where range was calculated by Ziegler's method.[9] By contrast, the decay times of the slow components may be regarded to be invariant, although the value for the He ion is large. LET-dependent shortening of a decay time of the fast component and the independence of the slow component are depicted in Fig. 3.

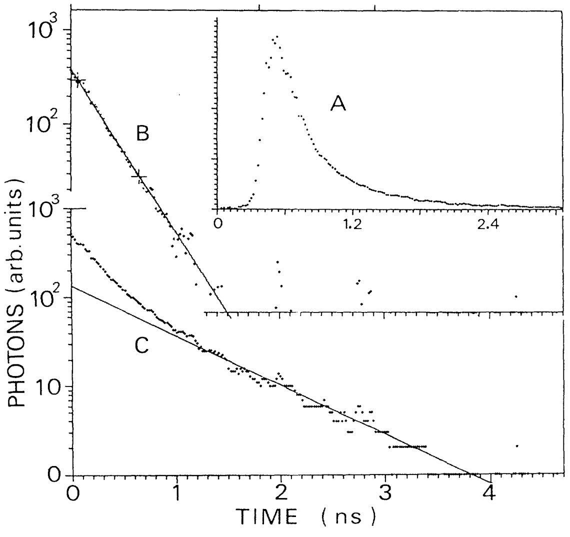

FIG. 2. A typical decay of 2200-Å luminescence of Ar-ion irradiated BaF_2. (A) in a linear scale; (B) log scale of a fast component after subtraction of a slow component; (C) log scale associated with a linear line fitted to a slow component.

TABLE I. LET dependence of decay times of Auger-electron-free luminescence.

Excitation	vuv	light electron	He ion	N ion	Ar ion	Kr ion	Xe ion
LET (MeV cm^2/mg)			0.49	2.91	8.42	14.76	16.16
A fast component (ps)	800[a]	600–800[b]	440	300	240	220	220
A slow component (ps)			1500	814	800	790	840

[a] From Ref. 8.

[b] From Ref. 1 and 8.

IV. DISCUSSIONS

The radiation effect under the present experimental conditions may be considered as follows. Ions whose stopping powers are close to each maximum cannot eject enough energetic secondary electrons to make cascading ionizations.[10] Therefore, the track radius of such an ion is small in spite of its large stopping power, and electrons ejected exist at high density.[6] A large number of positive ions are created through the ionization of the valence electron rather than through the inner-shell ionization. This may be rationalized by the result that STE luminescence is much stronger than that due to Auger-electron-free luminescence. It is therefore reasonable to consider that the core hole in Ba 5p is created through the transient molecular orbital formation proposed by Fano and Lichten[11] rather than through the effect of secondary electrons. Consider now the experimental results regarding the decay. At first, the deactivations due to reactions between the core and core excitons or the core and valence excitons can be ruled out because they constrain the second-order decay of Auger-electron-free luminescence. Furthermore, considering that the hole concerned belongs to an inner shell and is screened by valence electrons, it may be unlikely that ions or excited species react with the core hole through the screen.

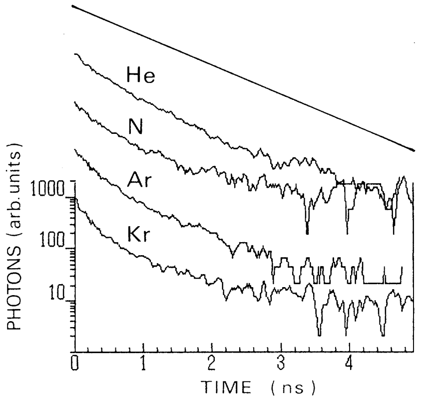

FIG. 3. LET dependent decay of Auger-electron-free luminescence. Incident energies of ions were about 1.5 MeV/amu. The decay, having an equal initial height, was plotted by shifting by an equal level. The uppermost line shows pure Auger-electron-free luminescence.

The electrons ejected may exist at high density for a short period until they recombine with holes of valence bands to be annihilated. They surround a 5p hole of the Ba ion and are attracted toward Ba^{3+} by its 3+ charges. These electrons may be in conduction bands or in high Rydberg states considering the comparatively long lifetime of the luminescence in spite of originating from the core holes. Recombinations between the electrons and the core holes should be nonradiative, or they cannot emit photons near 2200 Å energetically. This process can compete with the Auger-electron-free process. This model, illustrated in Fig. 4, can be expressed by following equations:

$$\mathrm{Ba}^{3+}+e_{\mathrm{F}2p}\xrightarrow{k_1}\mathrm{Ba}^{2+}+\text{photon}\ , \tag{1}$$

$$\mathrm{Ba}^{3+}+e_{\mathrm{cb}}\xrightarrow{k_2}\text{nonradiative}\ , \tag{2}$$

where $e_{\mathrm{F}2p}$ and e_{cb} stand for electrons of 2p orbitals of F atoms and those in the conduction bands, respectively, and k stands for a rate constant. Equation (1) shows the electron transitions from F 2p orbitals to the core holes, and it should be first order. The rate of annihilations of the core holes can be expressed as follows:

$$-d[\mathrm{Ba}^{3+}]/dt=k_1[e_{\mathrm{F}2p}][\mathrm{Ba}^{3+}]+k_2[e_{\mathrm{cb}}][\mathrm{Ba}^{3+}]\ . \tag{3}$$

The solution of this equation is

$$[\mathrm{Ba}^{3+}]=[\mathrm{Ba}^{3+}]_0\exp\{-(k_1+k_2[e_{\mathrm{cb}}])t\} \tag{4}$$

where the subscript 0 denotes time zero. The photon flux observed, $I(t)$, is expressed

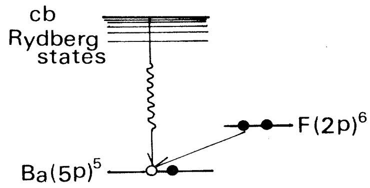

FIG. 4. A competition between nonradiative recombination and Auger-electron-free luminescence.

$$I(t)=k_1[\mathrm{Ba}^{3+}]=k_1[\mathrm{Ba}^{3+}]_0\exp\{-(k_1+k_2[e_{\mathrm{cb}}])t\} \quad (5)$$

or

$$\ln I(t)=\ln(k_1[\mathrm{Ba}^{3+}]_0)-(k_1+k_2[e_{\mathrm{cb}}])t \; . \quad (6)$$

The e_{cb} disappears principally by the recombinations with valence holes F^0 to form STE or color centers:

$$e_{\mathrm{cb}}+F^0 \rightarrow \text{STE or color center} \; . \quad (7)$$

The STE presents the luminescence of a 3100-Å peak whose decay shows large LET dependence attributable to STE-second-order annihilation with STE-STE distance-dependent rate constant. The detailed data and discussion, however, will be given elsewhere. The rate of recombination of Eq. (7) may be assumed to be later than that of Ba^{3+}: the latter is enhanced by Coulombic attraction by 3+ charges; the rise time of 2200-Å luminescence appeared to be faster by 100–200 ps than that of 3100 Å. Also, the latter recombination does not affect the concentration of e_{cb}, since the number of Ba^{3+} is so small compared with that of e_{cb}. As long as the concentration of e_{cb} is considered to be nearly constant near time 0, Eq. (6) is linear for time. This can explain the linearity at the initial stage of a decay curve shown in Fig. 2(c). The apparent rate constant in Eq. (6) $(k_1+k_2[e_{\mathrm{cb}}])$ is larger by $k_2[e_{\mathrm{cb}}]$ than that of pure Auger-electron-free luminescence, which does not have the competing process (2), i.e., k_1.

With time, most of e_{cb} is annihilated by Eq. (7) so that pure Auger-electron-free luminescence remains. In this case, Eq. (6) can be reduced as follows:

$$\ln I(t)=\ln(k_1[\mathrm{Ba}^{3+}]_0)-k_1 t \; . \quad (8)$$

This equation may explain the experimental result that the decay times for the slow component are independent of LET and close to the decay time of pure Auger-electron-free luminescence, 800 ps.

It was assumed above that the core-holes capture e_{cb} faster than than the valence holes do. If this is true, the rise time of Auger-electron-free luminescence in this system should be faster than that of STE luminescence. In fact, the peak of rise of 2200-Å luminescence appeared faster by about 200 ps than that of 3100-Å luminescence.

Also, Eq. (5) or Eq. (6) shows that the decay rate is increased proportionally to the increase in the initial concentration of e_{cb}. Since the density of excitations increases with increasing LET, Eq. (6) can explain the LET-dependent shortening of the decay time of 2200-Å luminescence. By applying reciprocals of 800 ps and the value in Table I to k_1 and $k_1+k_2[e_{\mathrm{cb}}]$, respectively, $k_2[e_{\mathrm{cb}}]$ can be evaluated. Figure 5 shows $k_2[e_{\mathrm{cb}}]$ as a function of LET. The figure shows that the local concentration of e_{cb} increases with increasing LET, since k_2 is independent of LET. The LET effect increases linearly in a region of lower LET, then saturates at high LET due to Kr ion. This first-order increase for LET seems to support the present model. The ceiling of the curve at higher LET may suggest that the rate-determining step is in annihilation of the pair e_{cb}-Ba^{3+} but not in the diffusion of e_{cb} to form the pair. In other words, almost all Ba^{3+}'s can pair with e_{cb} initially under the condition of high-density excitation caused by Kr- or Xe-ion irradiations. Therefore, the ceiling value of $k_2[e_{\mathrm{cb}}]$ may be regarded as the annihilation rate of the pair of e_{cb}-Ba^{3+}, i.e., the core exciton, although the absolute value is certainly larger than the value of Fig. 5 if a deconvolution could be done.

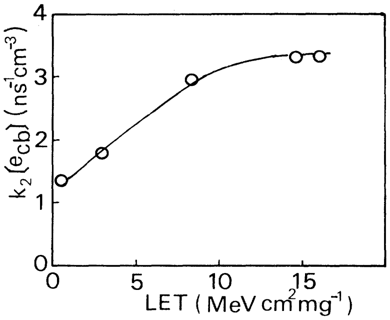

FIG. 5. $k_2[e_{\mathrm{cb}}]$ as a function of LET. The value of 1.14×10^9 s^{-1} was used as a value of k_1, a rate constant of pure Auger-electron-free luminescence (Ref. 8).

Also it is possible to estimate the core holes quenched by recombination with e_{cb}. The initial or total number of the core holes, H_0, could be expressed as I_0/k_1, if there were no decay processes except for that by Auger-electron-free luminescence. The difference between I_0/k_1 and the area under the decay curve of actual luminescence gives the number of quenched core holes. In Fig. 6, normalized values of quenched holes per H_0 are shown as a function of LET. The figure shows that an increase of holes is observed at higher LET. In this expression, the number of quenched core-holes was found to be sensitive to the change of a slope $(k_1+k_2[e_{\mathrm{cb}}])$ in the higher LET regions, which would be understood by using Fig. 3. Although we applied 800 ps as the decay time of the Auger-electron-free luminescence, Kubota and Itoh pointed out from their recent data that the de-

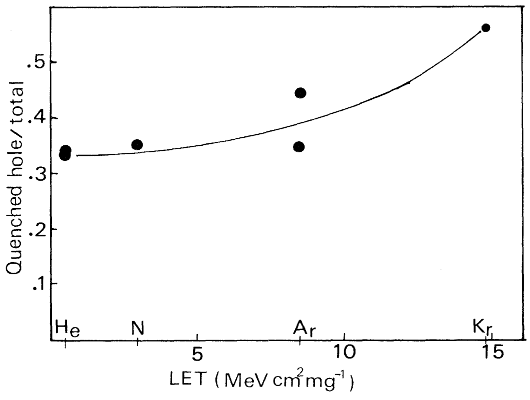

FIG. 6. LET dependence of a rate of quenched core holes to total core holes. The total core holes was assumed to be I_0/k_1.

cay in the case of photoirradiation is slightly beyond a single exponential also. This may be explained by our model if the electron ionized by vacuum-ultraviolet light cannot travel far from the core hole so that its recombination with the parent core-hole competes with the Auger-electron-free luminescence process. If this is true, the decay time, 800 ps, should be corrected to a longer one.

The LET dependence of the yield of H_0 presents an interesting problem. Since our yield data are scattered, we can mention, however, only a tendency that the yield of H_0 has a minimum at the LET due to N ions rather than to a monotonic LET dependence.

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[1] M. Laval, M. Moszynsky, R. Allemeand, E. Cormoreche, P. Guinet, R. Odru, and J. Vacher, Nucl. Instrum. Methods **206**, 169 (1983).

[2] R. T. Williams, M. N. Kabler, W. Hayes, and J. P. Stott, Phys. Rev. B **14**, 725 (1976).

[3] Yu. M. Aleksandrov, V. N. Makhov, P. A. Rodonyi, T. TI. Syreishchikova, and V. N. Yakimenko, Fiz. Tverd. Tela (Leningrad) **26**, 2865 (1984) [Sov. Phys. Solid State **26**, 1734 (1984)].

[4] S. Kubota, M. Itoh, Jian-zhi Ruan, S. Sakuragi, and S. Hashimoto, Phys. Rev. Lett. **60**, 2319 (1988).

[5] K. Kimura, K. Mochizuki, T. Fujisawa, and M. Imamura, Phys. Lett. A **78**, 108 (1980).

[6] K. Kimura, Phys. Rev. A **47**, 327 (1993); K. Kimura, T. Matsuyama, and H. Kumagai, Radiat. Phys. Chem. **34**, 575 (1989).

[7] K. Kimura and H. Kumagai, Radiat. Eff. Defects Solids **126**, 45 (1993).

[8] S. Kubota, J. Ruan, M. Itoh, S. Hashimoto, and S. Sakuragi, Nucl. Instrum. Methods A **289**, 253 (1990).

[9] A computer program was created according to Ziegler's method. J. F. Ziegler, *Stopping Cross-Sections for Energetic Ions in All Elements* (Pergamon, New York, 1977), Vols. 1–5.

[10] F. D. Becchetti, C. CE. Thorn, and M. J. Levine, Nucl. Instrum. Methods **138**, 93 (1976).

[11] U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965).