Brief Reports

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Stimulated ultraviolet emission from BaF_2 under core-level excitation with undulator radiation

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Photoluminescence (185–240 nm) of BaF_2 has been investigated with use of an intense undulator radiation from the UVSOR ring as a pumping source. It is found that the emission intensity is enhanced and the decay time becomes fast when a mirror is adjusted for best collimation. These facts suggest a possibility of the light amplification due to a population inversion between the valence and outermost-core bands.

Since the first successful lasing[1] in 1960, many different mechanisms have been developed and used widely to obtain laser oscillation. Laser action is well known to be possible in a medium with an inverted population, though a laser without inversion has been proposed recently.[2] In usual cases, the ground state is essentially filled with electrons at thermal equilibrium while the excited states are almost empty. As a result, it is necessary that a large number of electrons should be, optically or electrically, pumped into some excited state until the population inversion reaches a critical value. In the present paper, we propose a new mechanism of laser oscillation for which hole transition plays an important role. That is, two completely filled bands, valence and core bands, in BaF_2 act as laser levels, which can lead to easy formation of a population inversion.

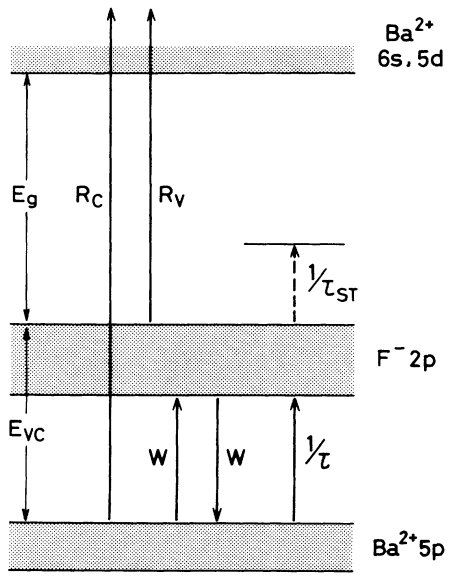

FIG. 1. Schematic energy-level diagram of BaF_2. The pumping, transition, and relaxation rates are also denoted (see text).

Figure 1 shows a schematic energy-level diagram of BaF_2. The conduction band is due to the 6*s* and 5*d* states of Ba^{2+} ions and the valence band is due to the 2*p* state of F^- ions. Below the valence band, there exists an outermost-core band originating from the Ba^{2+} 5*p* state. Here, E_g is the band-gap energy and E_{VC} is the energy difference between the tops of the valence band and the outermost-core band. From the experiments of reflection[3] and photoelectron,[4] we have $E_g = 11.0$ eV and $E_{VC} = 7.8$ eV for BaF_2. In this case ($E_g > E_{VC}$), a core hole created in the Ba^{2+} 5*p* band decays primarily through the radiative recombination with a valence electron, because the nonradiative Auger process kicking up another valence electron into an empty state is energetically forbidden. The resulting luminescence has been called "Auger-free luminescence,"[5] which is characterized by high-temperature stability with a lifetime of the order of 10^{-9} sec. It should be noted that, at thermal equilibrium, both the valence and core bands are completely filled with the same number of electrons. Accordingly, an inverted population between these two levels will be realized at essentially any intensity of excitation through which some electrons are elevated into the unoccupied conduction band from the core band.

In terms of holes, let us consider the change in level populations. The holes are created in the Ba^{2+} 5*p* core

band with a rate R_C by optical pumping. Some degree of valence-band pumping is also inevitable and must be included as R_V in the analysis. The spontaneous and induced transition rates are written as $1/\tau$ and W, respectively. The holes lifted into the valence band subsequently relax into the self-trapped state with a rate $1/\tau_{ST}$. The transition and relaxation processes of Fig. 1 are somewhat analogous to those of a four-level laser system.[6] If the populations of holes in the core and valence bands are denoted as N_C and N_V, then the coupled rate equations to be solved may be given as follows:

$$\frac{dN_C}{dt}=R_C+WN_V-\left[\frac{1}{\tau}+W\right]N_C\ , \tag{1}$$

$$\frac{dN_V}{dt}=R_V+\left[\frac{1}{\tau}+W\right]N_C-\left[\frac{1}{\tau_{ST}}+W\right]N_V\ . \tag{2}$$

Under the equilibrium condition ($d/dt=0$), the difference of hole populations, $\Delta N=N_C-N_V$, is expressed from Eqs. (1) and (2) as

$$\Delta N=\frac{R_C\tau-(R_C+R_V)\tau_{ST}}{1+W\tau}\ . \tag{3}$$

Since $\tau=0.88\times10^{-9}$ sec,[7] $\tau_{ST}=10^{-12}$–10^{-13} sec,[8] and $R_C>R_V$, we have $\Delta N\sim R_C\tau/(1+W\tau)>0$ for BaF_2. This means that, under core-level excitation, the population of holes in the lower Ba^{2+} $5p$ core band is larger than that in the upper F^- $2p$ valence band; in other words, more electrons are populated in the upper level.

The present experiment was performed with use of a beam line 3A1 of the electron storage ring UVSOR in the Institute for Molecular Science, Okazaki, as a pumping source. This beam line provided us with radiation, having a 0.5-nsec pulse width at 11-nsec intervals, from a permanent magnet undulator.[9] The undulator radiation consisted of an intense quasimonochromatic light with $\Delta\lambda/\lambda=5\%$ in full width at half maximum and its higher harmonics. The photon flux of the undulator light at 36.0 eV was estimated to be about 10^{15} photons/sec mm^2. Relatively weak synchrotron radiation was superposed on the undulator radiation. To separate these two beams, a pair of pin holes was inserted between the undulator and a sample.

A 1-mm-thick plate of BaF_2, freshly cleaved from single-crystal ingots obtained from the Union Material Inc. and Horiba Ltd., was mounted on a sample holder installed in a vacuum chamber. The holder was rotatable about its vertical axis. The undulator radiation was incident at nearly 45° on the sample surface with a spot size of 1 mm^2 and a penetration depth of approximately 500 Å. A flat multiple-dielectric coated mirror (100% reflectivity at 217 nm) and a quartz plate were placed close to the sample in the direction perpendicular to the exciting beam; see the inset in Fig. 2. Thus it was possible to form an optical cavity by suitably adjusting the orientation of the dielectric mirror. Without using lenses, the luminescence spectra were observed through the quartz window by means of a detection system composed of a Bausch & Lomb grating monochromator and an R106UH photomultiplier. The entrance slit of the monochromator was 70 cm away from the sample. For decay-profile measurements, we used a microchannel-plate photomultiplier (R2286U-06) whose output signals were detected with single-photon counting techniques using a standard time-to-amplitude converter.[10] All the experiments were carried out at room temperature.

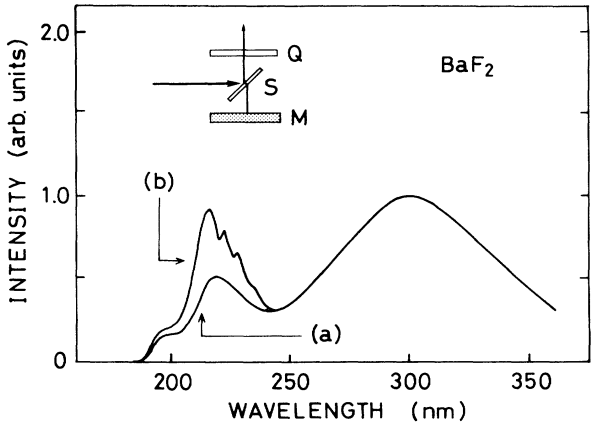

FIG. 2. Luminescence spectra of a BaF_2 crystal excited with undulator radiation of 36.0 eV at 295 K; (a) no collimation and (b) best collimation. Each spectrum is normalized around 300 nm. The inset shows a cavity configuration (Q, quartz plate; S, BaF_2 crystal; M, adjustable mirror). Q and M are separated by 30 mm.

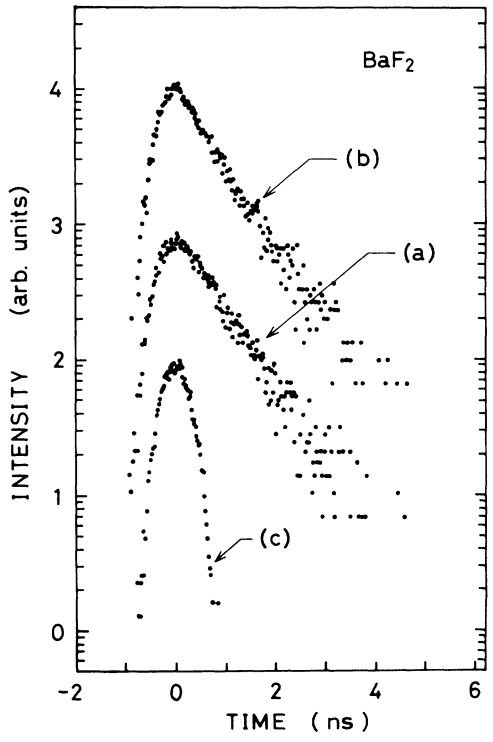

FIG. 3. Decay profiles of the 219-nm band in a BaF_2 crystal, obtained under the excitation with undulator radiation of 36.0 eV at 295 K; (a) no collimation and (b) best collimation. A pulse shape of the exciting light is also shown as (c) for reference. The emission intensity is plotted in a logarithmic scale vs time.

Figure 2 shows luminescence spectra of BaF_2 taken under (a) no collimation and (b) best collimation. The excitation was performed with 36.0-eV photons, corresponding to the interband transition from the Ba^{2+} $5p$ level to the conduction band. No correction of the spectral response of the detection system has been made for the data in Fig. 2. One can see a broadband around 300 nm, which is ascribed to the radiative annihilation of a self-trapped exciton, i.e., an electron bound to a self-trapped hole.[11] In curve (a), two emission bands are also observed at 219 and 195 nm. These ultraviolet bands are due to the interatomic Auger-free transition of the F^- $2p$ valence electron into the Ba^{2+} $5p$ core hole.[12,13] It is clearly seen that the peak intensity of the 219-nm band is enhanced by a factor of 1.7 when the mirror is adjusted for best attainable collimation. An oscillatory structure (210–240 nm) observed in curve (b) corresponds to the spectral change in reflectivity of the multiple-dielectric coated mirror employed.

In Fig. 3 we present decay behaviors of the 219-nm band observed under the core-level excitation with 36.0-eV photons under (a) no collimation and (b) best collimation. A pulse shape of the exciting light is also shown as (c) in the figure. In curve (a), the luminescence decay is single-exponential over two orders of magnitude, with a time constant of 0.8 ± 0.1 nsec. This value is fairly consistent with that reported previously in Ref. 7. By properly adjusting the collimating mirror, however, the transient response of the 219-nm band becomes slightly nonexponential; i.e., it appears that a faster decay component grows up in the peak region, as seen in curve (b). Such a sharpening of the decay profile is a characteristic phenomenon of stimulated emission.[6]

The observations described above suggest a possibility of the light amplification due to a population inversion between the valence band and the deeper-lying core level. In this connection we will make a few comments. All our results had been obtained in the initial stage of the undulator-light irradiation. When a freshly cleaved sample was prolongably exposed, we could not find any effect of the light amplification. This may be attributed to generation of radiation-induced damage which can suppress a laser oscillation, although it is known that the BaF_2 crystals have good radiation resistance.[14] Furthermore, when the intensity of the undulator radiation was reduced to $\sim\frac{1}{3}$ of the maximum value, no appreciable sharpening of the decay profile was observed. It is thus plausible that the pumping power we used is close to that needed for laser threshold. These facts are interpreted as further circumstantial evidence for the amplification of Auger-free luminescence in BaF_2.

In summary, we demonstrated a specific kind of laser action resulting from the formation of holes in the Ba^{2+} $5p$ core band of BaF_2. The amplified radiation was in the ultraviolet region of the spectrum. The present investigation is still deficient in several respects. For example, some unknown irradiation effects may partly contribute to our results. In order to confirm the laser action unambiguously, it will be necessary to do more detailed experiments such as the measurement of the single-pass gain. It is also of interest to extend the present work to other materials showing Auger-free luminescence, e.g., Cs halides, RbF, and KF.[5]

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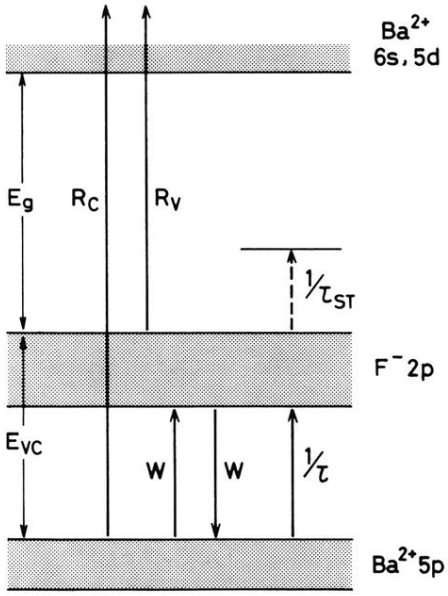

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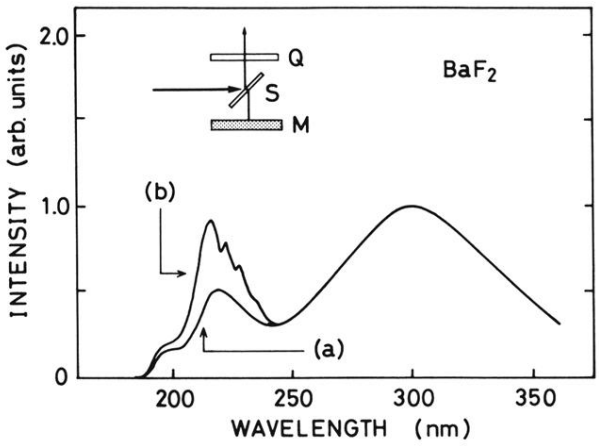

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