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Resonant enhancement effect on two-photon absorption due to excitons in alkaline-earth fluorides excited with synchrotron radiation and laser light

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Exciton states in wide-gap materials CaF_2 and BaF_2 have been studied with the technique of two-photon spectroscopy using synchrotron radiation and laser. The two-photon excitation spectrum of CaF_2, and that of BaF_2 as well, exhibited a clear peak on the high-energy side of the $1S$ exciton energy. The peaks are attributed to the $2P$ states of the valence excitons. According to this assignment, the binding energies of the excitons have been determined to be 0.8 and 0.9 eV for CaF_2 and BaF_2, respectively. The signal intensities were larger than that in the case of one-beam excitation by a factor of about 500, which is attributed to a resonant effect on two-photon absorption. [S0163-1829(99)52836-1]

Two-photon absorption (TPA) spectroscopy is an important tool in optical measurements for the investigation of electronic structures in condensed matter[1,2] because it enables the observation of states inaccessible by one-photon absorption. Since the transition probability of TPA is much lower than that of one-photon absorption, intense light from high-power lasers has been used so far. Because of the restriction of laser wavelengths, TPA spectroscopy has not been a widely used technique for the study of wide band gap materials.

Synchrotron radiation (SR) is one of the most important light sources since it provides continuously distributed light in a wide energy range from x-ray to infrared. If the wide spectral range of SR and the high power of lasers are combined, fruitful information on the electronic structures of many materials can be obtained. In this paper, SR-laser combined TPA spectroscopy is applied to two wide-gap materials CaF_2 and BaF_2.

Pizzoferrato *et al.* have performed pioneering experiments of SR-laser combined spectroscopy in TPA,[3–5] studying the $2P$ and $3P$ excitons of alkali bromides and chlorides with the measurements of the transmission difference of SR light under the irradiation of light from a Nd:YAG laser operating at about 10 Hz. However, the upper limit of the scanning range of the energy in their work is as low as the $1S$ exciton energy plus about 1 eV since the SR wavelengths must be located in the transparent region of the samples in their technique. We have recently developed a technique of two-photon spectroscopy that does not have such a limitation.[6–8] Our technique is based on the detection of the luminescence caused by TPA, which is expected to be more sensitive than the transmission method.

From second-order perturbation theory, the two-photon transition probability between the initial and final states, W_{fi}, is given by

$$W_{fi}=\frac{2\pi}{\hbar}\sum_n\left|\frac{\langle f|H_E^{(2)}|n\rangle\langle n|H_E^{(1)}|i\rangle}{E_n-E_i-\hbar\omega_1}+\frac{\langle f|H_E^{(1)}|n\rangle\langle n|H_E^{(2)}|i\rangle}{E_n-E_i-\hbar\omega_2}\right|^2\delta(E_f-E_i-\hbar\omega_1-\hbar\omega_2), \tag{1}$$

where $|i\rangle,|n\rangle$, and $|f\rangle$ are the initial, intermediate, and final states with energies of E_i,E_n, and E_f, respectively, $\hbar\omega_1$ and $\hbar\omega_2$ photon energies of SR and a laser, and $H_E^{(j)}$($j=1,2$) Hamiltonian for the electronic-dipole transition where $\hbar\omega_j$ photons are involved.

When the resonant condition, $E_n - E_i - \hbar\omega_1 = 0$, is realized by SR light, $E_n - E_i$ should be replaced by $E_n - E_i + i\hbar\gamma_n$, where γ_n is the width of the intermediate state n. This results in a simplified form of Eq. (1),

$$W_{fi} = \frac{2\pi}{\hbar}\sum_n \left|\frac{\langle f|H_E^{(2)}|n\rangle\langle n|H_E^{(1)}|i\rangle}{\hbar\gamma_n}\right|^2 \delta(E_n - E_i - \hbar\omega_1)$$

$$\times\,\delta(E_f - E_i - \hbar\omega_1 - \hbar\omega_2). \qquad (2)$$

Since $1/\gamma_n$ is proportional to the lifetime of the state n, W_{fi} will be dramatically enhanced. This resonant enhancement is, therefore, expected to compensate for the weak intensity of SR light in our experiment.

The crystals of CaF_2 and BaF_2 have wide band gaps of about 12 and 11 eV, respectively.[9] They are useful materials as optical windows. The crystal of BaF_2 is also used as a scintillator in high-energy physics, where so-called Auger-free luminescence is detected.[10] Each crystal has the fluorite structure and a cleaved surface exhibits a (111) plane. The valence band consists of the $F^- 2p$ state, and the conduction band originates from the $4s$ ($6s$ and $5d$) states of Ca^{2+}(Ba^{2+}) ions. At low temperatures the lowest Γ exciton is located at 11.2 and 10.0 eV in CaF_2 and BaF_2, respectively.[11] Both have a luminescence band due to radiative decay of self-trapped excitons (STE's) around 4.4 and 4.1 eV for CaF_2 and BaF_2, respectively.

A single crystal of CaF_2 was grown at Oxford University by Hayes and co-workers, and one of BaF_2 was obtained from Horiba Ltd. Cleaved specimens were mounted on a copper holder of a conduction-type cryostat. The sample temperature was kept at 15 K or 295 K. The SR light from the storage ring of UVSOR at the Institute for Molecular Science (Okazaki, Japan) was dispersed through a 1-m Seya-Namioka-type monochromator, and irradiated the samples under the normal incidence. The spectral width of the monochromatized SR light was about 40 meV in the energy range concerned with this study. A LiF filter was used for preventing samples from being exposed to the higher-order light. The repetition rate and the duration of the SR pulses were 90 MHz and 1.6 ns, respectively. The second-harmonic light of a Q-switched Nd:YAG laser ($E_{\text{laser}} = 2.33$ eV) irradiated the samples in the direction opposite to that of the SR light. The duration and the averaged power of the incident laser pulses were about 800 ns and 10 W, respectively. The polarization of the laser light was parallel to that of the SR light. The laser beam was focused on an area of about 2-mm-diameter on a sample surface. Any damage of the specimens due to the laser irradiation could not be observed. The trigger signal for the laser was provided from the master oscillator of the storage ring through a divider which lowered the frequency of the pulses down to about 5 kHz.

The STE luminescence was detected with a microchannel-plate-type photomultiplier tube by using the time-gated photon counting method.[7] Narrow-band filters and a monochromator were used to eliminate the scattered light of the laser. The signal pulses were led to a three-channel gated counter. Channels 1 and 2 were opened for 4 μs just before and after the incidence of the laser pulse, respectively. Channel 3 was used to count the signal all the time. The accumulation time was less than a minute for each data-point. The difference in counts between channels 1 and 2 represents the signal caused by simultaneous excitation of SR and laser light. This signal in the unit of counts per second, normalized by the beam current in the storage ring at 100 mA, is hereafter referred to as an SR-laser signal. Each spectrum was corrected for the spectral distribution of SR. The spectrum obtained through channel 3 was identical with the one-photon excitation spectrum.

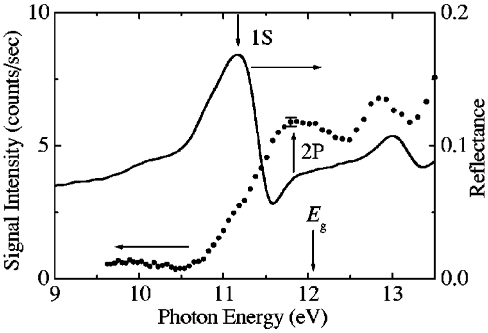

FIG. 1. TPA spectrum of CaF_2 as a function of the sum of the SR- and the laser-photon energies at 15 K (solid circles). The reflection spectrum is also shown by a solid line for comparison. Arrows marked with $1S$ and $2P$ indicate the peaks due to the corresponding exciton states. E_g denotes the band gap.

The dotted curve in Fig. 1 shows the SR-laser spectrum of CaF_2 at 15 K. The abscissa of the figure represents the sum of the photon energies of the SR and the laser light. The reflection spectrum is depicted by a solid line for comparison. The $1S$ peak of the reflection spectrum at 11.2 eV (Ref. 11) is indicated by an arrow. The SR-laser spectrum rises at about 10.6 eV, and reaches a peak at 11.8 eV. We assign this peak to the $2P$ state of the Γ exciton, which is the lowest among the states to which transition is parity allowed. The reflection spectrum also has a shoulder at that energy position. We assign the shoulder to the $2S$ state of the exciton.

The dotted curve in Fig. 2 represents the TPA spectrum of BaF_2 at 15 K. The background, which has the same spectral shape as the one-photon excitation spectrum, is eliminated from the experimentally obtained spectrum. The origin of the background will be discussed afterward in view of the intermediate state of TPA. The spectrum has two peaks at 10.7 eV and 11.2 eV, which correspond to the peaks at 11.8 and

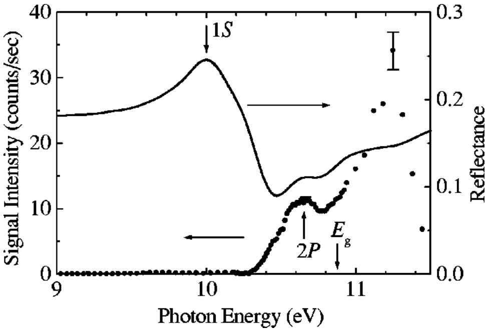

FIG. 2. TPA spectrum of BaF_2 as a function of the sum of the SR- and the laser-photon energies at 15 K (solid circles). The reflection spectrum is also shown by a solid line for comparison. Arrows marked with $1S$ and $2P$ indicate the peaks due to the corresponding exciton states. E_g denotes the band gap.

12.8 eV, respectively, in the spectrum of CaF_2. The solid line represents the reflection spectrum of BaF_2 at 15 K. The peak at 10.0 eV has been assigned to the $1S$ state of the Γ exciton.[11] The 10.7-eV peak is assigned to the $2P$ state of the exciton in the same manner as the case of CaF_2. The reflection spectrum also shows a shoulder at about 10.7 eV, which is attributed to the $2S$ state.

Assuming hydrogenlike energy levels or a simple Wannier exciton picture, the nth level ($n=1,2,3,\dots$) of the exciton, E_n, is given by

$$E_n = E_{\mathrm{g}} - \frac{R^*}{n^2}, \tag{3}$$

where E_{g} is the band gap, and R^* the exciton binding energy. By using Eq. (3), we obtained $R^*=0.8$ and 0.9 eV for the Γ excitons in CaF_2 and BaF_2, respectively.

The values of the binding energy R^* obtained in the present study are about 0.2 eV smaller for CaF_2 and about 0.3 eV larger for BaF_2 than the corresponding values obtained by Tomiki and Miyata.[12] These previous values have been deduced from the band gap energies determined by a Kramers-Kronig analysis of reflection spectra. On the other hand, the present values are based on the clear observation of the $2P$-exciton peaks. This fact makes our values more reliable than the previous ones.

Let us now estimate the intensity of the TPA signal using a TPA coefficient previously obtained, and compare it with the experimentally obtained one. The total amount of SR light absorbed by TPA, I_{TPA}, is given by

$$I_{\mathrm{TPA}} = \int_{x=0}^{d} I(x)\beta I_{\mathrm{laser}} dx < \int_{x=0}^{d} I_0 \beta I_{\mathrm{laser}} dx = I_0 \beta I_{\mathrm{laser}} d, \tag{4}$$

where *d* represents the sample thickness, *x* the distance from the incidence surface, $I(x)$ the intensity of the SR light under the normal incidence at the position *x*, $I_0 = I(0)$, β TPA coefficient, and I_{laser} the intensity of the laser light which is assumed to be independent of *x*.

Since the intensity of the two-photon induced luminescence of STE's, I_{lumi}, is proportional to I_{TPA},

$$I_{\mathrm{lumi}} = \eta I_{\mathrm{TPA}} < \eta I_0 \beta I_{\mathrm{laser}} d, \tag{5}$$

where η represents the quantum yield of the luminescence including the probability of the radiative decay of excitons and the efficiency of the detection system. On the basis of the intensity of the luminescence detected under one-photon absorption, we obtained $\eta \sim 10^{-6}$. Other parameters in the present experiment were $I_0 \sim 10^3$ photons/pulse, $I_{\mathrm{laser}} \sim 0.08$ MW/cm^2, and $d \sim 0.1$ cm.

The TPA coefficient β of BaF_2 has been reported to be 1.1×10^{-4} cm/MW under excitation by a single beam of 5.00-eV photons from a KrF laser.[13] However, the value of β at the $2P$-exciton energy (for 5.35-eV photons) has not been reported as far as our knowledge is concerned. We hence measured β at several photon energies on the low-energy side of the $2P$-exciton energy at 295 K detecting the intensity of the STE luminescence under excitation with a single beam from an excimer-laser-pumped-dye laser. The result is roughly approximated by

$$\beta(2\hbar\omega) \propto \exp(5\times 2\hbar\omega), \tag{6}$$

where $\hbar\omega$ denotes the excitation-photon energy in the unit of eV.

The exponential dependence of $\beta(2\hbar\omega)$ in Eq. (6) is not surprising if the Urbach rule is considered. From Eq. (6) and the value of $\beta(2\times5.00\ \mathrm{eV})$ reported in Ref. 13, we obtain $\beta(2\times5.35\ \mathrm{eV}) = 4\times10^{-3}$ cm/MW. This is comparable to those of alkali halides at the $2P$-exciton energy and above the band gap.[5,14] The value of β at the $2P$-exciton energy may depend on the sample temperature, but the difference should not be so large between 15 and 295 K. Adopting the above value (4×10^{-3} cm/MW) as β of BaF_2 at 15 K, we obtain $I_{\mathrm{lumi}} < 0.02$ counts/sec from Eq. (5).

In the present experiment, we have obtained $I_{\mathrm{lumi}} \sim 10$ counts/sec for both BaF_2 and CaF_2 at 15 K. That is to say, our values of the TPA signals are over two orders of magnitude larger than that estimated above. It should be noted to explain this enhancement that the one-photon excitation spectrum of STE's has a low-energy tail below the $1S$-exciton energy down to 7.5 eV, which may be ascribed to bound states due to unknown impurities and defects.[8] This fact leads us to the conclusion that the enhancement is caused by a real intermediate state rather than a virtual state. A schematic diagram of TPA is depicted in Fig. 3. This resonant effect on the transition probability due to TPA was discussed in acquiring Eq. (2). For a further investigation of the resonant effect, we measured the TPA signal of BaF_2 at 295 K. At high temperatures, lifetimes of bound states are expected to be short because bound excitons can easily escape from these states absorbing phonons. The short lifetime will make the signal intensity small according to Eq. (2). In our experiment, the intensity of the TPA signal measured at 295 K was lower by one order of magnitude than that at 15 K. This fact supports our interpretation based on the resonant effect.

There will possibly exist another absorption process which has energy relaxation in the intermediate state, besides the resonant TPA process: an SR-generated exciton or electron has a chance to be relaxed into a low-lying state, fol-

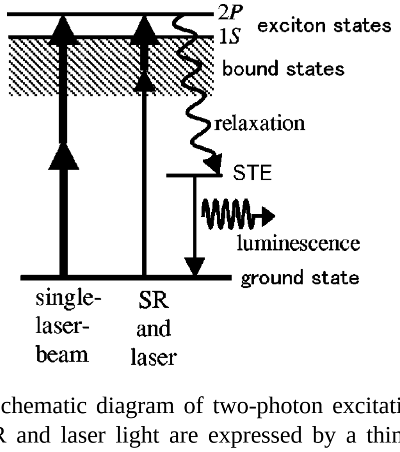

FIG. 3. Schematic diagram of two-photon excitation using SR and laser. SR and laser light are expressed by a thin and a thick arrow, respectively. The SR light is resonant with bound states located below the $1S$ exciton state. STE luminescence caused by relaxation of the $2P$ excitons to the STE state was detected in the present experiment. Two-photon excitation with a single-laser beam, whose intermediate state is a virtual state, is depicted in the left for comparison.

lowed by the laser excitation to induce the STE luminescence. This process is a kind of two-step cascade (TSC) process. We attribute the origin of the background of the TPA spectrum to this TSC process.[8] The coexistence of TPA and TSC required a careful procedure to obtain the TPA spectrum represented by the dotted curve in Fig. 2. We performed the separating procedure for SR-laser spectra at various intensities of the excitation laser in the same manner. The validity of the procedure was confirmed by linear dependence of the intensity of the TPA signal on the excitation laser power.

In Figs. 1 and 2, we found peaks at 12.8 and 11.2 eV in the TPA spectra of CaF_2 and BaF_2, respectively, on the high-energy side of the $2P$-exciton peak. These peaks would seem to be due to P-type exciton states at some critical point different from the Γ point. However, this explanation is ruled out because the corresponding $1S$ peaks cannot be found in the reflection spectra. We propose an alternative explanation that the peaks are related to the conduction-band states forbidden in one-photon absorption and allowed in TPA. The $4p$ state of Ca^{2+} ions for CaF_2 and the $4f$ or $6p$ state of Ba^{2+} ions for BaF_2 are the most probable candidates.

In conclusion, SR-laser combined TPA spectroscopy has been applied to study the exciton states in wide band gap materials CaF_2 and BaF_2. Two-photon induced luminescence of STE's was detected as the SR-laser signal by the time-gated photon counting method. It was pointed out that the TPA signals are resonantly enhanced, which enables the use of SR in extended cases because of compensation for the weak intensity of SR light. The binding energy of the lowest Γ exciton was determined to be 0.8 eV for CaF_2 and 0.9 eV for BaF_2.

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[1] J.J. Hopfield, J.M. Worlock, and Kwangjai Park, Phys. Rev. Lett. **11**, 414 (1963).

[2] D. Fröhlich and B. Staginnus, Phys. Rev. Lett. **19**, 496 (1967).

[3] R. Pizzoferrato, M. Casalboni, R. Francini, U.M. Grassano, F. Antonangeli, M. Piacentini, N. Zema, and F. Bassani, Europhys. Lett. **2**, 571 (1986).

[4] R. Pizzoferrato and M. Casalboni, J. Phys. E **20**, 896 (1987).

[5] M. Casalboni, C. Cianci, R. Francini, U.M. Grassano, M. Piacentini, and N. Zema, Phys. Rev. B **44**, 6504 (1991).

[6] M. Kamada, S. Hirose, S. Asaka, T. Tsujibayashi, M. Watanabe, O. Arimoto, S. Fujiwara, S. Nakanishi, H. Itoh, and M. Itoh, J. Synchrotron Radiat. **5**, 1035 (1998).

[7] S. Asaka, S. Nakanishi, H. Itoh, M. Kamada, M. Watanabe, O. Arimoto, T. Tsujibayashi, S. Fujiwara, and M. Itoh, Rev. Sci. Instrum. **69**, 1931 (1998).

[8] O. Arimoto, S. Fujiwara, T. Tsujibayashi, M. Watanabe, M. Itoh, S. Nakanishi, H. Itoh, S. Asaka, and M. Kamada, J. Electron Spectrosc. Relat. Phenom. **92**, 219 (1998).

[9] K.S. Song and R.T. Williams, *Self-Trapped Excitons* (Springer, Berlin, 1993), Chap. 4, and references therein.

[10] M. Itoh, S. Hashimoto, S. Sakuragi, and S. Kubota, Solid State Commun. **65**, 523 (1988).

[11] G.W. Rubloff, Phys. Rev. B **2**, 662 (1972).

[12] T. Tomiki and T. Miyata, J. Phys. Soc. Jpn. **27**, 658 (1969).

[13] A.J. Taylor, R.B. Gibson, and J.P. Roberts, Opt. Lett. **13**, 814 (1988).

[14] P. Liu, W.L. Simth, H. Lotem, J.H. Bechtel, N. Bloembergen, and R.S. Adhav, Phys. Rev. B **17**, 4620 (1978).