Luminescence from defect centers with monomolecular- and bimolecular-type configurations in C₇₀ crystals

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Abstract

We have investigated luminescence spectra, decay behaviors and their temperature dependence in C₇₀ crystals prepared by different annealing procedures. The spectra have been measured with one-photon excitation, two-photon excitations and excitation below the HOMO–LUMO band gap. We have found two types of defect-related luminescence band with different activation energies: the radiative recombination of Frenkel-like excitons weakly localized at monomolecular-type defects existing near the sample surface and the radiative recombination of excitons trapped at bimolecular-type defects.

Keywords: A. Fullerenes; D. Optical properties; D. Electronic states; E. Luminescence

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1. Introduction

The discovery and synthesis of fullerenes on a macroscopic scale, especially C₆₀, have led to a number of spectroscopic studies [1–5]. C₇₀ has also received great attention because of the availability of high-purity and large-quantity samples. The absorption and luminescence bands observed near the fundamental absorption edge in C₇₀ molecules in solution are assigned to optical transitions between the ground and first excited singlet states with molecular vibration modes of the C₇₀ molecules [6–9]. The absorption spectrum for C₇₀ thin films shows a feature quite similar to that observed in solution, and the observed peaks are assigned to the same electronic transitions as in solution. Starukhin et al. [4] have investigated luminescence properties of C₇₀ in solid, and assigned the luminescence bands to the radiative recombination of Frenkel excitons. In the previous paper, we have reported that the luminescence spectrum in the visible region consists of two components with different decay times [5]. The observed spectrum has been ascribed to the radiative recombinations of Frenkel excitons and self-trapped states of charge-transfer (CT) excitons. However, luminescence spectra of C₇₀ solids are strongly dependent on the samples and excitation conditions, which means that the origin of photoluminescence is still controversial. Recently, Akimoto et al. have reported that the luminescence spectrum of C₆₀ single crystals can be explained in terms of a superposition of luminescence bands due to trapped states resulting from fluctuations of the intermolecular orientational correlation in a pair of C₆₀ molecules [3]. This result suggests that there exist defect centers associated with orientational disorder, and leads us to reexamine luminescence properties considering a role of such defects for C₇₀ crystals.

In this paper, we report on luminescence spectra and decay behaviors in C₇₀ crystals prepared by different annealing procedures. From the results measured under various excitation conditions, we have found two types of defect-related luminescence band: the radiative recombination of Frenkel-like excitons weakly localized at defects which are associated with the molecular orientational disorder existing near the sample surface and the radiative recombination of excitons localized at defect-related traps consisting of adjacent molecules.
2. Experimental

The synthesis and purification of C\(_{70}\) was accomplished using the Kratchmer-Huffman method [10]. The purity of C\(_{70}\) powders is better than 99.9\%. C\(_{70}\) crystals were prepared from powders by a sublimation method. A typical size of the prepared crystal was \(\approx 0.5 \times 0.5 \times 0.5 \text{ mm}^3\). Luminescence spectra were measured using a grating monochromator equipped with a cooled charge-coupled device as a detector. An Ar ion laser (2.410 eV) was used as a one-photon excitation source. A femtosecond optical parametric amplifier (1.240 eV) was used as a source for a two-photon excitation. For the excitation below the band gap, a cw Ti sapphire laser (1.780 eV) was used. Time-resolved luminescence spectra were measured by means of a time-correlated single photon counting method using second harmonic light of a mode-locked Ti sapphire laser. The time resolution of luminescence decay behaviors was \(\approx 50 \text{ ps}\).

3. Results and discussion

Fig. 1 shows the luminescence spectra of three different as-grown C\(_{70}\) crystals measured at 77 K with a one-photon excitation at 2.410 eV. Although some common luminescence bands are observed at 1.818, 1.729 and 1.682 eV for all the samples studied here, the spectral shape strongly depends on the sample. In spectra (a) and (b), the luminescence band around 1.82 eV is suppressed, and the spectra are featureless.

Here, we measured luminescence spectra at 4.2 K, changing excitation conditions: one-photon and two-photon excitations. As the absorption coefficient of C\(_{70}\) solid at 2.410 eV is \(\approx 2 \times 10^7 \text{ cm}^{-1}\), the skin depth of the one-photon excitation light is as small as 50 nm. The broken curve in Fig. 2(a) shows the luminescence spectra of an as-grown C\(_{70}\) crystal (Fig. 1, sample (c)) at 4.2 K with one-photon excitation (2.410 eV). The luminescence spectrum shows a vibrational structure with peak energies of 1.818 (marked by closed circle), 1.790, 1.749, 1.729, 1.665 and 1.636 eV. The peak energy of 1.818 eV is slightly lower than the absorption peak (1.83 eV) due to the optical transition of Frenkel excitons [5]. Assuming the 1.818 eV band as the 0–0 transition, all other peaks can be assigned to the phonon sidebands because the energy shifts measured from the 1.818 eV band are very close to the frequencies of \(a_1^0\) modes in a C\(_{70}\) molecule. Hereafter, we refer to these bands as the type-S luminescence bands.

To measure luminescence spectra with a volume excitation utilizing a two-photon absorption process, we used a femtosecond-pulse laser with a photon energy of 1.240 eV. The solid curve in Fig. 2(a) shows the luminescence spectrum of the as-grown sample measured by two-photon excitation (2.480 eV). The type-S bands are not observed, while broad luminescence bands are observed at \(\approx 1.69 \text{ (closed triangle)}\) and \(\approx 1.54 \text{ eV}\). This result suggests that the luminescence centers which give rise to the type-S bands are located near the sample surface, while the centers related to the 1.69 eV band exist in the whole volume of the sample.

To confirm the assignment to the defect-related luminescence, we prepared samples in which defects were intentionally introduced. C\(_{70}\) crystals were annealed at \(\approx 300^\circ\text{C}\) for 24 h in vacuum and rapidly cooled to room temperature (thermal quenching). The solid curve in Fig. 2(b) displays the luminescence spectrum of the quenched sample with two-photon excitation. The 1.69 eV band with a vibrational structure is observed, and the intensity is stronger by a factor of about 70 than that observed for the as-grown sample. This

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Fig. 1. Sample dependence of luminescence spectra for as-grown C\(_{70}\) crystals measured at 77 K.

Fig. 2. (a) Luminescence spectra of a C\(_{70}\) crystal measured at 4.2 K under one-photon excitation (broken curve) and two-photon excitation (solid curve) conditions; and (b) luminescence spectra with two-photon excitation (solid curve) and excitation below the gap (broken curve) for the quenched sample.
result indicates that the 1.69 eV band is related to defect states. Observed peak energies are 1.685, 1.653, 1.620, 1.590 and 1.535 eV, and they are assigned to the phonon sidebands associated with \( \epsilon_2 \) modes, if we assume the 1.685 eV peak (marked by closed triangle) as the 0–0 transition. We note that the vibrational mode seen in this series of luminescence is in contrast to the \( a'_1 \) mode which is observed for the type-S bands. We also measured the luminescence spectrum of the quenched sample by excitation with a photon energy below the HOMO–LUMO gap. As shown by the broken curve in Fig. 2(b), the spectrum feature is similar to that observed with the two-photon excitation; the luminescence peaks are observed at the same energies in both spectra. We refer to this spectrum as the type-D.

To investigate energy level structures of defect centers, we measured variations of emission intensities with temperature. The closed circles in Fig. 3(a) display the temperature dependence of emission intensity measured at 1.800 eV for the as-grown sample; and (b) temperature variation of the type-D emission intensity measured with two-photon excitation (closed circles). Open triangles display the luminescence decay behaviors of the type-D bands measured with one-photon excitation. The intensity decreases with increasing temperature: \( \tau = 0.4 \) ns at 4.2 K and \( \tau = 0.07 \) ns at room temperature. Using the Arrhenius-type model of recombination processes, the intensity \( I \) and decay time \( \tau \) are expressed as,

\[
I \propto \tau \propto \left[ a + b \exp\left(-\frac{E_1}{k_B T}\right) + c \exp\left(-\frac{E_2}{k_B T}\right) \right]^{-1},
\]

where \( k_B \) is the Boltzmann constant, \( a, b \) and \( c \) are constants and \( E_1 \) and \( E_2 \) are thermal activation energies. We analyzed the experimental data using Eq. (1), and the result is shown by the solid curve in Fig. 3(a). We obtained thermal activation energies of \( E_1 \) and \( E_2 \) for the type-S band to be 3 \( \pm 1 \) and 40 \( \pm 10 \) meV, respectively.

Closed circles in Fig. 3(b) show the temperature dependence of emission intensity of the type-D band for the quenched sample measured at 1.460 eV with two-photon excitation. The intensity decreases with increasing temperature. Shown in the inset of Fig. 3(b) is the luminescence decay kinetics of the type-S component as a function of the inverse of temperature. The decay time becomes shorter with increasing temperature: \( \tau = 0.4 \) ns at 4.2 K and \( \tau = 0.07 \) ns at room temperature. Using the Arrhenius-type model of recombination processes, the intensity \( I \) and decay time \( \tau \) are expressed as,

\[
I \propto \tau \propto \left[ a + b \exp\left(-\frac{E_1}{k_B T}\right) + c \exp\left(-\frac{E_2}{k_B T}\right) \right]^{-1},
\]

where \( k_B \) is the Boltzmann constant, \( a, b \) and \( c \) are constants and \( E_1 \) and \( E_2 \) are thermal activation energies. We analyzed the experimental data using Eq. (1), and the result is shown by the solid curve in Fig. 3(a). We obtained thermal activation energies of \( E_1 \) and \( E_2 \) for the type-S band to be 3 \( \pm 1 \) and 40 \( \pm 10 \) meV, respectively.

Now, we discuss the origin of two luminescence components which give rise to the 1.818 eV (type-S) band and 1.685 eV (type-D) band. Fig. 4(a) shows the type-S spectrum in which we see the vibrational structure with the \( a' \) mode. This mode is also observed in the vibrational structure of luminescence spectrum for C70 molecules in solution. The luminescence spectrum for C70 molecules in methylcyclohexane solution is shown in Fig. 4(b). The 0–0 band of \( S_1 \rightarrow S_0 \) transition is observed at 1.904 eV, and the vibrational structure indicated by the solid bars is attributed to the \( S_1 \rightarrow S_0 \) transition with emission of \( a' \) mode vibrations. The fact that the \( a' \) mode is observed for both cases suggests that the wavefunction of the excited state giving rise to the type-S band has the symmetry similar to that of the \( S_1 \) state of C70 molecules. Indeed, in C60 crystals, the selection rule of the observed vibrational mode has allowed to distinguish
localized states with different symmetries [1,3]. Accordingly, we attribute the luminescence center for the type-S band to a monomolecular-type localized state. Such a localized state may originate from the molecular orientational disorder, i.e. misorientation of long axis of a C70 molecule in the fcc lattice. The activation energies of $3^{\pm 1} \text{ and } 45^{\pm 10} \text{ meV}$ correspond to the energy difference between the defect state and the free Frenkel exciton state, and the energy difference between the defect state and the free electron–hole pair state, respectively. The monomolecular-type defect center is regarded as a weakly localized Frenkel-like exciton, because the activation energy to the free Frenkel exciton is very small ($\lesssim 3 \text{ meV}$). Fig. 4(c) displays the type-D spectrum in which the observed vibrational structure is not the $a'_{1}$ mode but the $e'_{2}$ mode. This result indicates that the luminescence center giving rise to the type-D bands has a configuration different from that of the type-S bands. For C60 crystals, there exist excitons trapped at the two types of defect-related trap: monomolecular and bimolecular-type defects. Such trapped excitons have been observed by electron spin-echo [11] and luminescence measurements [1–3]. In the luminescence spectra of C60 crystals, the vibrational structures with Raman active $a_{u}$ and $h_{g}$ modes and a Herzberg–Teller active $t_{1u}$ mode have been observed. Considering the close similarity of C70–C60 in molecular and crystal structures, there may exist similar defects in C70 crystals. Here, we attribute the type-D band to an exciton state trapped at a bimolecular-type defect. Such a defect with the bimolecular-type configuration may be associated with orientational or distance disorder of a pair of molecules in the lattice. The activation energies of $14^{\pm 7} \text{ and } 45^{\pm 15} \text{ meV}$ corresponds to the binding energies of the bimolecular-type defect center measured from the free Frenkel exciton state and the free electron–hole pair state, respectively.

Using the obtained activation energies, we estimate a binding energy of free Frenkel excitons. The estimated values are $37^{\pm 10} \text{ and } 31^{\pm 17} \text{ meV}$ from the type-S band and type-D band, respectively. Although these values should be the same, they are in agreement with the value of $30 \text{ meV}$ which was obtained by electroabsorption spectroscopy [12], taking account of the experimental errors.

Finally we briefly mention the assignment which was reported in our previous paper [5]. We have observed two luminescence components with different decay times, and assigned the fast decay component to the radiative recombinations of Frenkel excitons and the slow one to self-trapped states of CT excitons [5]. The experimental results presented here, however, lead us to revise the assignment reported in the previous paper. The fast and slow components should be assigned to the monomolecular-type luminescence (type-S band) and the bimolecular-type luminescence (type-D band), respectively. The self-trapped state of CT exciton is caused by the strong exciton–phonon interaction, and such a localized state is extended over adjacent molecules. The configuration of the self-trapped CT exciton thought to be similar to that of the bimolecular-type defect state. The observation of the type-D band with the excitation below the HOMO–LUMO gap strongly supports the assignment of the defect-related luminescence band.

4. Conclusions

We have investigated luminescence spectra, decay behaviors and their temperature dependence in C70 crystals. We have observed two types of defect-related luminescence bands showing different vibrational structures. The 1.818 eV band (type-S) is assigned to the radiative recombination of Frenkel-like excitons weakly localized at monomolecular-type defects existing near the sample surface. The 1.685 eV band (type-D) originates from the recombination of excitons trapped at bimolecular-type defects. We have obtained the binding energy of free Frenkel excitons ($\lesssim 30 \text{ meV}$) from the measured activation energies of the trapped states.

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References