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Life-time resolved emission spectra in $CdBr_2$ crystals

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Abstract

Decay curves of the Y-emission were measured at 60, 100 and 140 K by varying emission energy in the range of the Y-emission. The observed decay curves were decomposed into three or four exponential decay components. These decay components were named τ_1, τ_2, τ_4 and τ_5. The emission spectrum for each decay component, i.e., life-time resolved emission spectrum, was obtained by analyzing the observed decay curves. At 60 K, three bands at 1.95, 2.24 and 2.47 eV are obtained for the τ_5, τ_4 and τ_1 components, respectively. For the τ_2 component, sharp peaks appear around 2.30–2.50 eV. At 100 K, a dominant band of the τ_4 component is seen at 2.25 eV. In the low-energy side, a weak band of the τ_5 component is located at 1.95 eV. At 140 K, only a single band of the τ_4 component is observed at 2.27 eV. The origin of emission bands in life-time resolved emission spectra is discussed.

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Keywords: Two-photon excitation; Layered structure

1. Introduction

Cadmium bromide ($CdBr_2$) crystallizes in the $CdCl_2$-type structure with the space group D_{3d}^5, belonging to the divalent metal halide crystals with layer structure [1]. The top of the valence band consists mainly of bromine 4*p* orbitals with admixture of cadmium 4*d* character and the bottom of the conduction band mainly of cadmium 5*s* orbitals [2–4]. Optically created excitons are immediately localized as self-trapped excitons (STEs) through strong exciton–lattice interaction. The STE states are believed to be equivalent to the excited states of a $[Cd^{2+}Br_6^-]^{4-}$ complex molecular ions with D_{3d} symmetry. This model for the STE was proposed on the basis of fairly strong covalency between the central divalent Cd^{2+} ion and surrounding halogen ions and of experimental results on absorption and electron paramagnetic resonance (EPR) spectra in the neutron-irradiated crystals which show behaviors similar to those of Cu^{2+} or Ag^{2+} centers doped in cadmium halide crystals [5].

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Fig. 1 shows typical emission spectra of $CdBr_2$ at 9 K (solid curve) and 100 K (broken curve). Two types of emission bands appear at 3.28 eV (UV) and 2.25 eV (Y). The UV- and Y-bands have been interpreted as radiative annihilation of STEs. With increasing temperature, the UV-band dominant at 9 K decreases its intensity rapidly around 60 K, and then it is replaced at 60 K by the Y-band, which is predominantly observed at 100 K. Such a replacement of the UV-band by the Y-band was explained by the population transfer due to thermal activation process of STEs from the UV-emission state to Y-emission state. The UV-emission is connected with the parity allowed transition from the A_{2u} state to the ground A_{1g} state. It has been cleared that the initial state of the UV-emission comprises the three sub-levels arising from the triplet STE [6]. Decay curves of the Y-emission have been investigated by Nakagawa and Kitaura [6]. It is found that the decay curves consist of four decay components. They were assigned to intrinsic luminescence from STEs. However, there still remains an ambiguity whether each decay component is of an intrinsic origin of $CdBr_2$ or not. This subject will be cleared from an analysis of the emission spectra for the decay components, i.e. life-time resolved emission spectra.

In the present study, the life-time resolved emission spectra were determined from the decay curves of Y-emission at various photon energies. The origins of each decay component are discussed on the basis of the life-time resolved emission spectra. Furthermore, the initial states of intrinsic decay components in the Y-emission band are explained by means of the excited states of a $[Cd^{2+}Br_6^-]^{4-}$ complex molecular ion.

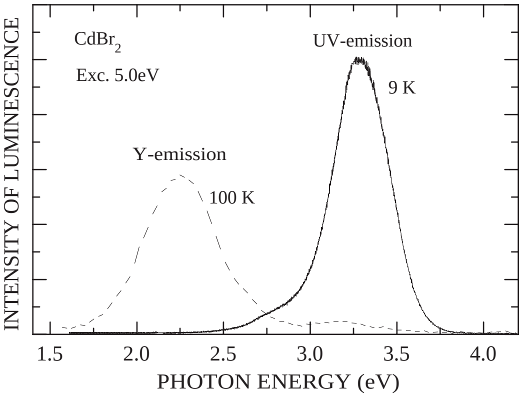

Fig. 1. Luminescence spectra of $CdBr_2$ observed at 9 K (solid line) and 100 K (broken line) under one photon excitation in the fundamental absorption region.

2. Experimental

Single crystals of $CdBr_2$ were grown from melt in a sealed quartz ampoule by the Bridgeman method. Special reagent grade powder of 99.99% purity of dehydrated $CdBr_2$ was purchased from Kojundo Chemical Laboratory Co., Ltd. Samples were cut in the size of $6 \times 6 \times 5\,mm^3$ from the crystal ingots with a razor blade. The crystal sample was mounted on the copper holder of a closed-cycle He refrigerator, and then was cooled down to 9 K in vacuum. The temperature was monitored by a silicon diode sensor and was controlled by an electric heater. Decay measurements were performed by means of two photon excitation with pulsed third harmonic generated light from a YAG-laser (THG at 3.49 eV with pulse duration of 10 ns). Luminescence was observed using a combination of a prism, a focusing quartz lens, a cut-off filter (Toshiba L39), a monochromator (SPEX 270M), a photomultiplier (Hamamatsu R955), a digital storage oscilloscope (Tektronix TDS520C) and a personal computer. The spectral and time resolutions were set to 1.5 nm and 1 μs, respectively.

3. Results and discussion

Figs. 2(a)–(c) show the decay curves of $CdBr_2$ observed at 1.95, 2.25 and 2.46 eV, respectively. They are decomposed into three or four exponential decay components, as indicated by thin straight lines. The decay components labeled by τ_1, τ_2 and τ_4 are reported in Ref. [6]. The decay component τ_5 is newly found instead of the τ_3 component in Ref. [6]. In the present experiment, the existence of the τ_5 component is confirmed from the decay curve observed at 1.95 eV and at 60 K. The ratios of time-integrated intensities of