Spectroscopic Studies on $CdBr_2$:Co^{2+} Crystals and Stimulated Luminescence

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1. Introduction

Cadmium bromide crystallize in a ionic layer-type structure, the rhombohedral $CdCl_2$ structure, in which each cadmium ion sheet is sandwiched by two halogen ion sheet [1] A cadmium ion is located at the center of an octahedron composed of six nearest neighbor halogen ions. Cadmium halide crystals provide favorable host crystals for doping divalent metal ions, especially 3-d group transition metals ions, with various concentrations.

In the present work, optical absorption and luminescence spectra have been investigated on $CdBr_2$:Co^{2+} crystals with varying the Co^{2+} concentration. Prominent concentration quenching of the green luminescence is observed in the crystals containing Co^{2+} above 0.1 mol %, which is explained as due to the resonant energy transfer among Co^{2+} ions. By using the crystals doped with Co^{2+} less than 0.1 mol %, dependence of the green emission intensity and decay profile on the excitation density were measured in order to clarify the light emission and amplification mechanism, that is, the change from spontaneous to stimulated emission processes, in the present system.

2. Experimental

Single crystals of $CdBr_2$:Co^{2+} with sufficiently good quality were grown from melt in a sealed quartz ampoule by the Bridgeman method. Absorption and luminescence spectral measurements were conducted with use of the conventional apparatus. Measurements of the dependence of luminescence on the excitation density were performed with pulsed light from a YAG-laser (FHG:4.66 eV), the pulse duration of which was 10 ns. The direction of the excitation pulse light was chosen to be parallel to the crystal c-axis. Luminescence was detected on the same line as the excitation light beam, that is, forward scattering configuration, through a laser cut-off filter, a combination of neutral density filters, a quartz lens and an analyzing monochromator.

3. Results and Discussions

In Fig. 1 is shown absorption spectrum observed in $CdBr_2$:Co^{2+} (0.07 mol %). The absorption structures are attributed to the charge transfer transition from the t_{1u}(Br-$4p$) to t_{2g}(Co-$3d$) states in the O_h crystal field notation. The Co^{2+} ions are supposed to replace the Cd^{2+} ions in $CdBr_2$ and to be subjected to the D_{3d} crystal field of lower symmetry than O_h. Complex structures in the

spectrum are well explained as to come from the level splitting due to the low crystal field and the spin-orbit interaction. Besides these charge transfer structures, many absorption structures due to the so-called d-d transition are observed in the visible and near infrared region, which are very slight ones of absorption coefficient less than 1 cm^{-1}.

Figure 2 shows the green emission spectrum obtained with excitation in the charge transfer absorption region given in Fig. 1. Three groups of emission structures are related to the d-d transitions in the Co^{2+} ions. They are connected to the transitions
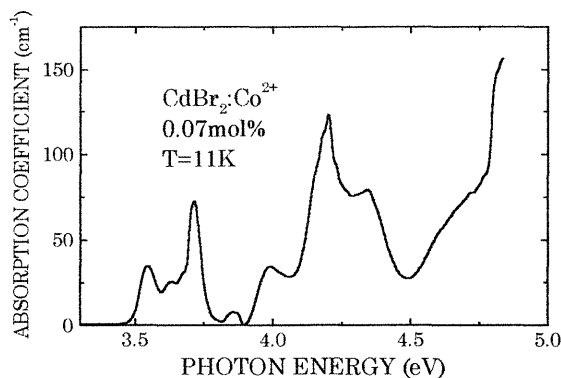

Fig. 1 Absorption spectrum of $CdBr_2$:Co^{2+} observed at 11 K. Structures are attributed to the charge transfer type transitions from bromine $4p$ to cobalt $3d$ orbits.
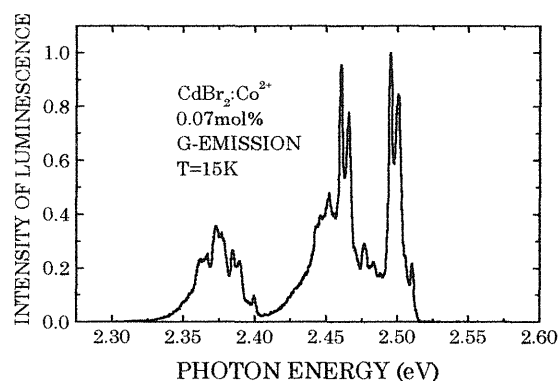

Fig. 2 Emission spectrum observed in the green region under excitation at 3.68 eV at 15 K. The luminescence intensity is normalized as unity at the maximum.

from the $^2T_{1g}(^2H)$, $^2T_{2g}(^2D)$ and $^2T_{2g}(^2H)$ states to the $^4T_{1g}(^4F)$ ground state in order of energy from low to high within the O_h field notations (in the parentheses are given the free ion states of the Co^{2+} ion). Emission structures in each group are assigned to the phonon structures relevant to the phonon emission transitions.

The life-time of the G-emission was determined to be 200 μ s in the case of Co^{2+} concentration less than 0 1 mol % and of week excitation. This lifetime corresponds to the radiative lifetime connected to the spontaneous emission process. With increasing the excitation density, the stimulated emission is expected on the line of the excitation beam to dominate the de-excitation process. In order to elucidate the details of change in the emission process from spontaneous to stimulated one, the luminescence intensity emitted toward the direction of the excitation beam line was observed for the G emission (at 2.49 eV, $^2T_{2g}(^2H)$ to $^4T_{1g}(^4F)$) as a function of excitation density. Excitation was made with FHG (4.66 eV) light pulses from a YAG laser. The result is presented in Fig. 3. The values of n indicated in the figure means the slope of the curve, namely, the power dependence of luminescence (L) on

the excitation density (I_{EXC}), $L = I_{EXC}^n$. Below 0.3 MW/cm^2, $n=1$ where the spontaneous process is dominant. The region between 0.3 and 2 MW/cm^2 where $n=2$ corresponds to the transition region from spontaneous to stimulated processes. Above 2 MW/cm^2, stimulated process become dominant although there appear saturation effects above 10 MW/cm^2 because of the irradiation damage on the crystal surface. These behaviors of the excitation density dependence are understood as the convergence of the emitted radiation onto the direction of the excitation beam line. Figure 4 shows luminescence decay curves for I_{EXC} =0.06 and 2.1 MW/cm^2. In the case of strong excitation, the fast decay component is observed at the initial stage of decay followed by the slow component of 200 μ s which is the radiative decay component due to the spontaneous luminescence. It is possible to reproduce the decay curve through the analysis taking account of both spontaneous and stimulated emission processes.

4. Conclusion

Transition from spontaneous to stimulated emission processes in $CdBr_2:Co^{2+}$ was made clear from the experiments on the excitation density dependence of luminescence under non-cavity condition. This system would be available as microchips for wide energy range laser, amplification and energy conversion.

Reference

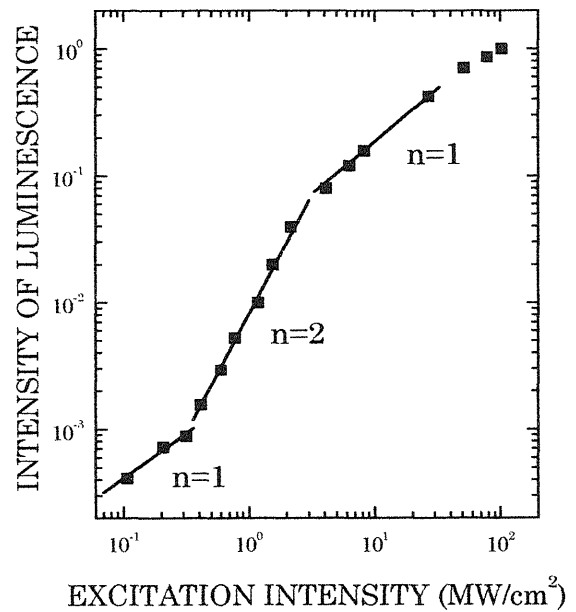[1] H. D. Megaw, Crystal Structures (Saunders, Philadelphia 1973) p.96.

Fig. 3 Dependence of the luminescence intensity on the excitation density obtained at 15 K. Excitation was made with FHG pulses from a YAG laser. Luminescence intensity is given as normalized one.
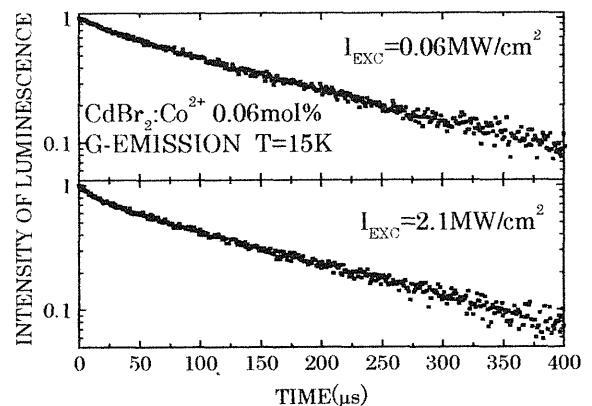

Fig. 4 Decay curves of the G-emission for the week (upper) and the strong (lower) excitation observed at 15 K after 10 ns pulse excitation with FHG(YAG)