Available online at www.sciencedirect.com
ScienceDirect
Current Applied Physics 7 (2007) 1–5
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

High intensity photoluminescence of microcrystalline $CsPbBr_3$ films: Evidence for enhanced stimulated emission at room temperature

S. Kondo [a,*], K. Takahashi [a], T. Nakanish [a], T. Saito [a], H. Asada [b], H. Nakagawa [c]

[a] *Research Center for Development of Far-Infrared Region, Fukui University, Bunkyo, Fukui 910-8507, Japan*
[b] *Department of Applied Physics, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910-8507, Japan*
[c] *Department of Electronics, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910-8507, Japan*

Received 10 May 2005; received in revised form 5 August 2005; accepted 15 August 2005
Available online 11 October 2005

Abstract

Photoluminescence of microcrystalline $CsPbBr_3$ films grown from the amorphous phase shows stimulated emission not only at cryogenic temperature but also at room temperature, in great contrast to the case for bulk $CsPbBr_3$ single crystals, where no stimulated emission occurs even at 4.2 K. This is the first demonstration of room temperature stimulated emission from metal halide compounds.

The stimulated emission is so strong that single-path-light-amplification stimulated emission across the film thickness is observed at relatively low threshold excitation intensities of $\sim$50 kW cm^{-2} at 77 K and $\sim$100 kW cm^{-2} at 295 K suggesting a large optical gain. The physical origin of the stimulated emission is assigned as due to free exciton-free exciton inelastic collision. The large-gain mechanism is attributable to giant oscillator strength effect characteristic of excitonic superradiance recently reported in this issue.

PACS: 78.66.−w; 42.70.Hj; 78.55.Hx; 78.68.+m

Keywords: Film; Luminescence; Stimulated emission; Exciton; Mesoscopic; $CsPbBr_3$

1. Introduction

Nanodimensional particles of semiconductors have attracted much attention over the last two or three decades owing to mesoscopic enhancement of linear and nonlinear optical properties. Various efforts have been made to obtain nanodimensional particles according to the object of investigation. In the study of quantum size effect on excitons, which is one of the most attractive mesoscopic properties exhibited by nanodimensional particles, the particles are usually embedded in a glass or crystal matrix. The mole fraction of the particles is generally very small, typically of the order of 0.1 mol% or less. Preparation of a specimen containing nanoparticles with a high concentration is not merely desirable for the basic research of their mesoscopic properties, but also for their application studies.

We have shown that many metal halide semiconductors such as silver [1], thallium [2], copper [3], lead [4] and cadmium [5] halides, including their mixed systems [6], can be rendered amorphous by quench-deposition yielding film samples. The amorphous films have a well-defined, characteristic crystallization temperature at which their absorption spectra drastically change in outline. The films, when crystallized at temperatures just above the crystallization temperature, are generally in a microcrystalline state, and change into polycrystalline state when they are subsequently annealed at higher temperatures. Many of the crystalline films produced via the amorphous phase, whether they are microcrystalline or polycrystalline in nature, show very high transmittance compared with polycrystalline films directly deposited onto hot substrates. The microcrystalline films may provide alternative, extremely densely

---

[*] Corresponding author. Tel.: +81 776 27 8659; fax: +81 776 27 8770/8750.
E-mail address: d930963@icpc00.icpc.fukui-u.ac.jp (S. Kondo).

1567-1739/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2005.08.001

nanoparticle-dispersed specimens for studying mesoscopic enhancement of optical properties.

Concerning $CsPbCl_3$ and $CsPbBr_3$, which are known to be one of the most luminescent semiconductors [7], we recently reported in this issue [8] that the microcrystalline/polycrystalline films prepared by crystallization from the amorphous phase show enhanced photoluminescence. In particular, the microcrystalline films exhibit more than an order of magnitude stronger free exciton emission than the polycrystalline films, as well as than bulk single crystals. A possible explanation for this phenomenon is given in terms of excitonic superradiance. Very recently, we found furthermore [9] that highly photo-excited microcrystalline films of $CsPbCl_3$ show stimulated emission at cryogenic temperatures originating from exciton–exciton inelastic collision at very low threshold excitation intensities of the order of $10\ \mathrm{kW\,cm^{-2}}$ (polycrystalline $CsPbCl_3$ films did not show stimulated emission). At higher excitation intensities above $50\ \mathrm{kW\,cm^{-2}}$, single-path-light-amplification stimulated emission across the film thickness is observed suggesting a very large optical gain. The large-gain mechanism is attributable to giant oscillator strength effect characteristic of excitonic superradiance. In the present study, similar measurements have been carried out for microcrystalline $CsPbBr_3$ films prepared by crystallization from the amorphous phase. Stimulated emission is observed not only at cryogenic temperatures but also at room temperature in great contrast to the case for bulk $CsPbBr_3$ single crystals, for which no stimulated emission is observed even at a very low temperature of 4.2 K [10].

2. Results and discussion

Figs. 1 and 2 show examples of luminescence spectra measured at 77 and 295 K, respectively, for a microcrystalline $CsPbBr_3$ film (thickness, ~150 nm) under N_2 laser-light excitation (wavelength, 337.1 nm; pulse duration, 0.5 ns) with various excitation intensities. The microcrystalline $CsPbBr_3$ film was achieved (from the amorphous phase) in a way somewhat different from those employed in [8] and [9]. In short, an amorphous film prepared by quench-deposition onto a cooled (to 77 K) silica-glass substrate in a vacuum of about 9×10^{-6} Pa was rapidly heated up to 500 K, annealed at that temperature for 15 min, cooled again to 77 K, and annealed at 400 K for 17.5 h and subsequently at 500 K for 30 min. The confinement-induced blue shift of the peak energy of the free exciton emission band (mentioned later, Fig. 3) relative to that for polycrystalline films, both measured under ordinary-light-source excitation, was 21 meV, which corresponds to a microcrystal size of about 7.6 nm as determined in the same way as that reported in [8]. The luminescence measurements were carried out in an optical configuration of back scattering normal to the film. The incident angle of the exciting light was 45° with respect to the film and its spot at the film surface had a dimension of about $2 \times 2\ \mathrm{mm^2}$. The maximum intensity (100% excitation) of the exciting light was $142\ \mathrm{kW\,cm^{-2}}$ at 77 K (Fig. 1) and $247\ \mathrm{kW\,cm^{-2}}$ at 295 K (Fig. 2). F band is due to free exciton emission and S band is a new band. Notably the latter band increases in intensity rapidly with excitation intensity above ~30% excitation exhibiting a very narrow line width at both temperatures.

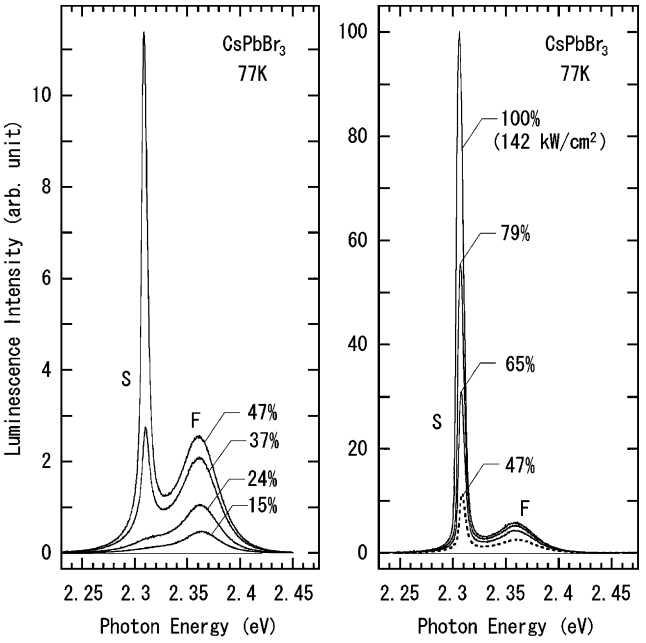

Fig. 1. Photo-excited luminescence spectra of a microcrystalline $CsPbBr_3$ film measured at 77 K under various percentages of excitation intensity, with the 100% intensity corresponding to $142\ \mathrm{kW\,cm^{-2}}$.

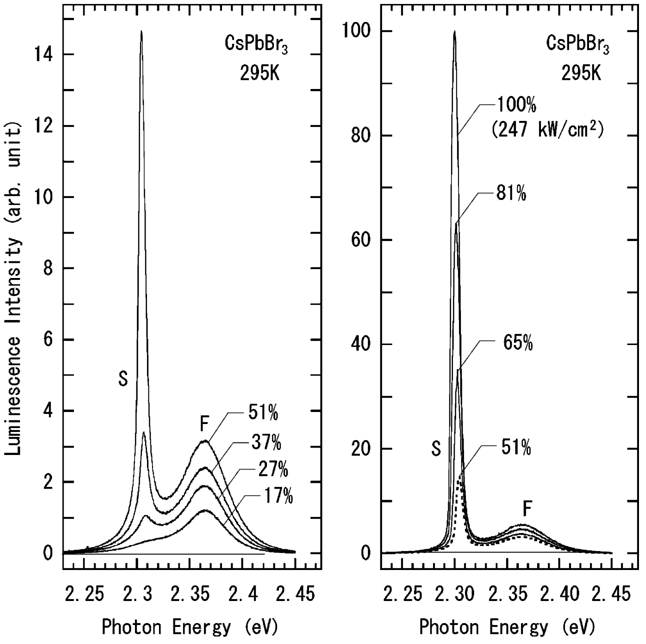

Fig. 2. Photo-excited luminescence spectra under various excitation intensities with the 100% intensity corresponding to $247\ \mathrm{kW\,cm^{-2}}$, measured at 295 K for the same microcrystalline $CsPbBr_3$ film whose luminescence spectra at 77 K are shown in Fig. 1.