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Time-resolved photoluminescence of hydrogen-bonded ferroelectrics $PbHPO_4$

T. Fuyuki, K. Sasaki[1], N. Ohno*

Division of Electronics and Applied Physics, Graduate School of Engineering, Osaka Electro-Communication University, Hatsu-cho, Neyagawa, Osaka 572-8530, Japan

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Abstract

The time-resolved photoluminescence spectra of ferroelectric $PbHPO_4$ (LHP) have been examined from 6 to 320 K. The spectra were obtained under two-photon excitation by using 4.66 eV light pulses from a *Q*-switched Nd:YAG laser. A Stokes-shifted broad PL band has been observed at around 2.8 eV. The peak energy shifts from 2.69 eV in 30-ns delay spectrum to higher energy at 2.94 eV in 10-μs spectrum. It is found that the luminescence bands investigated at temperatures from 6 to 320 K have been decomposed into two luminescence bands peaking at 2.69 and 2.94 eV with lifetimes of 400 ns and 45 μs, respectively. The influence of ferroelectric properties on the exciton states and exciton relaxation in LHP crystal is discussed on the basis of obtained temperature-dependent time-resolved PL spectra.

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1. Introduction

$PbHPO_4$ (lead hydrogen phosphate; LHP) is one of hydrogen-bonded ferroelectric materials. The LHP crystal undergoes a second-order phase transition from monoclinic Pc in the ferroelectric phase to monoclinic P2/c in the paraelectric phase at transition temperature $T_C = 310$ K [1]. The spontaneous polarization P_S rises slowly with temperature below T_C to saturation at $\sim T_C$–130 K (180 K). The advantage of targeting LHP is that the hydrogen bond linking PO_4^{3-} tetrahedra in quasi-one-dimensional network are separated by Pb^{2+} ions [1], which is in contrast to the well-known KDP with three-dimensional linkage of the hydrogen bond. This simple crystal structure of LHP has been taking an appeal to many researchers as a reference material to understanding of proton ordering in hydrogen-bonded ferroelectrics [2–5].

*Corresponding author. Tel./fax: +81 72 825 4684.
E-mail address: n-ohno@isc.osakac.ac.jp (N. Ohno).
[1]Present address: Harison Toshiba Lighting Corp.

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Recently, optical properties of LHP have been investigated by our group [6–8]. The dichroic first exciton transitions are observed at 5.7 eV. The exciton transitions have been assigned as the cationic excitation in Pb^{2+} ions. The fundamental absorption edge at 10 K is located at 5.1 eV. It is found that Urbach's rule holds for the fundamental absorption edge [6,7]. Furthermore, temperature dependence of the steepness parameter is well scaled to that of spontaneous polarization P_S. The temperature behavior of the steepness parameter in LHP has been well explained in terms of the Stark effect on exciton states under the local electric field due to the hydrogen ordering [10]. The small value of the high-temperature steepness parameter $\sigma_0 = 0.78$ suggests that self-trapped states are stable for excitons in this ferroelectric material.

When the LHP crystal is photo excited at the exciton band, a broad photoluminescence (PL) band with a large Stokes-shift is observed at 2.8 eV [8,9]. The photo-excitation measurement of the PL band reveals that the 2.8 eV band is intrinsic in origin, probably due to the radiative decay of self-tapped excitons. These results have suggested that the exciton is a sensitive probe for a study of the ferroelectric structural phase transition. Above T_C the internal electric field-induced polarization of exciton is smeared out because of randomization of the proton ordering. Below T_C, on the other hand, a net polarization appears, implying that the inversion symmetry of exciton is broken. An investigation on the effect of the electric field induced by surrounding proton ordering on the exciton states and exciton relaxation is an interesting problem.

In the present study, time-resolved PL spectra of LHP crystal have been investigated from 10 to 320 K under the one- and two-photon excitations using a pulsed laser in order to investigate the excitonic states under the local electric field. The influence of the local electric field on the exciton states and exciton relaxation in LHP is discussed on the basis of the temperature dependent TRPL spectra.

2. Experiment

The single crystals of LHP grown from the conventional gel-grown method [2] were used for PL measurements. The sample was mounted on the copper cold finger of a cryogenic refrigerator, where the temperature could be controlled within 1 K between 6 and 320 K. TRPL spectra induced under two-photon excitation were measured using fourth harmonics (4.66 eV) from a Q-switched Nd:YAG laser (pulsed light width; 5 ns, repetition rate; 10 Hz) and an image-intensified CCD camera (gate width; 2.5 ns). The TRPL spectra induced under one-photon excitation were excited by the second harmonics (5.65 eV) from dye laser (Coumarin 460) excited with third harmonics (3.49 eV) from a Nd:YAG laser. These PL spectra have been corrected for spectral response of the detection system.

3. Results and Discussion

The time-integrated PL spectrum of LHP induced under two-photon excitation is almost the same as the PL spectra under the usual one-photon excitation above the bandgap energy [8], although it is located at slightly higher energy. The PL band peaking at 2.82 eV has a large Stokes shift with 0.6 eV full-width at half-maximum at low temperatures (see the bottom spectrum of Fig. 2), assigned as radiative annihilation of self-trapped excitons (STEs) [8].

The temperature dependence of two-photon excited PL spectra was investigated at temperatures from 6 to 320 K. In Fig. 1, the spectral-integrated intensity of the 2.82 eV band is plotted by closed circles against the crystal temperature. The observed temperature behavior of PL intensity is quite different from that induced under one-photon excitation process (open circles). Here, a conventional CW deuterium lamp was used as an exciting light source and the excitation energy of dispersed light was 6.35 eV. Intensity of the one-photon excited PL band (open circles) is almost constant at the low temperatures, decreasing slightly at ~50 K, and begins to decrease rapidly above 180 K. The temperature dependence of the intensity can be described by a usual two-step thermal activation process. On the other hand, the PL intensity for two-photon excitation starts to decrease at low temperature. It is noteworthy that