



PII: S0038-1098(97)10166-1

RESONANT THIRD-ORDER OPTICAL NONLINEARITY IN THE LAYERED PEROVSKITE-TYPE MATERIAL $(C_6H_{13}NH_3)_2PbI_4$

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(Received 19 August 1997; accepted 23 October 1997 by T. Tsuzuki)

The third-order nonlinear optical susceptibility, $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$, of the layered perovskite-type material $(C_6H_{13}NH_3)_2PbI_4$ is measured by a transient four-wave mixing technique using a 200-fs-pulse laser source. The maximum $|\chi^{(3)}|$ value is 1.6×10^{-6} esu at the lowest-exciton resonance at 8 K. Longitudinal and transverse relaxation times of the excitons are 7 ps and 0.2 ps, respectively. ©1998 Elsevier Science Ltd

Keywords: A. quantum wells, D. optical properties, E. nonlinear optics.

The nonlinear optical response of excitons in low-dimensional systems has been a subject of extensive research efforts. Semiconductor quantum-dot (zero-dimensional) and quantum-well (two-dimensional) structures have been found to have enhanced exciton binding energies and oscillator strengths, and as a consequence, large third-order nonlinear optical susceptibilities $\chi^{(3)}$. The large family of lead-iodide-based perovskite-type crystals are of great interest because of their unique crystal structures. They are self-organized low-dimensional systems composed of zero-, one-, two-, or three-dimensional networks of corner-sharing $[PbI_6]$ octahedra [1, 2]. Among them the two-dimensional materials, $(R-NH_3)_2PbI_4$, have been most intensively investigated mainly regarding their remarkable excitonic properties [3–6]. It has been shown that excitons are tightly confined in the two-dimensional $[PbI_6]$ well layers and that they form biexcitons under high-density excitations. The excitons and biexcitons have extremely large binding energies (≈ 400 meV and ≈ 40 meV, respectively) [3–5]. We have shown that the two-dimensional $[PbI_6]$ perovskite family have large $\chi^{(3)}$ by an optical third-harmonic generation (THG) measurement at room temperature; [6] $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ of $(C_{10}H_{21}NH_3)_2PbI_4$ is as large as $\approx 10^{-9}$ esu at the three-photon resonance to the lowest exciton, which is comparable to the

largest $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ value of one-dimensional organic polymers. In this communication, we report on the first measurement of the third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ of $(C_6H_{13}NH_3)_2PbI_4$ by a transient four-wave mixing (FWM) technique.

We used $(C_6H_{13}NH_3)_2PbI_4$ instead of $(C_{10}H_{21}NH_3)_2PbI_4$ used in the THG measurement because of the better optical quality of $(C_6H_{13}NH_3)_2PbI_4$ at low temperatures due to the absence of structural phase transitions below room temperature [4]. The samples used in the FWM experiments were 100-nm-thick polycrystalline films spin-coated on optically flat glass substrates. X-ray diffraction studies showed that the films were highly oriented with the inorganic well layers parallel to the substrate surfaces. The thin-film samples have optical properties almost identical to those of a single-crystalline sample for normally incident light. FWM experiments were performed using a two-incident-beam configuration using an optical parametric amplifier seeded by an amplified mode-locked Ti:Al₂O₃ laser as a light source. The pulse duration and the repetition rate were 200 fs and 10 kHz, respectively. The pulsed beam from the pump source was split into two beams with wave vectors k_1 and k_2 with an intensity ratio $I_2/I_1 = 2.7$. The two beams were incident upon the sample with a relative

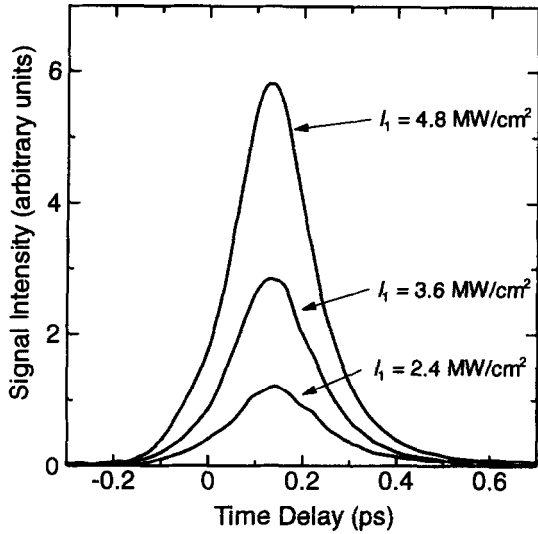


Fig. 1. Intensity of diffracted signal from $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ pumped at 2.344 eV versus time delay measured at 8 K for three different pump intensities. Positive time delay corresponds to k_2 pulse preceding k_1 pulse.

angle of about 6° . The magnitude of diffracted signal beam in direction $k_3 = 2k_1 - k_2$ was detected with a calibrated Si PIN photodiode as a function of the time delay between the two pulses $\tau = t_1 - t_2$. The measurement was performed using a sample with a $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ film in front of the substrate; i.e., the beams first passed through the film and then the substrate.

Figure 1 shows typical time-delay dependence of the diffracted signal intensity for the pump energy resonant to the lowest exciton ($\hbar\omega = 2.344$ eV) measured at 8 K. The diffracted signal intensity increases as the incident pump intensity is increased with its time evolution almost unchanged in the measured intensity range. The signal intensity reaches the maximum at the positive time delay and exhibits an exponential tail on the positive time delay side owing to a finite phase relaxation time [7]. From a numerical analysis on the measured time delay dependence, [8] we conclude that phase relaxation time T_2 of excitons in $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ is 0.2 ps. The maximum signal intensity I_s increases in proportion to the third power of the incident pump intensity up to $I_1 \approx 4$ MW/cm², and saturates at higher intensities as shown in Fig. 2. The cubic dependence of the signal intensity at low pump intensities shows that the response of the excitons is related only to third-order susceptibility. Similar cubic dependence was observed at the low pump intensity ranges in all the measurements with the pump photon energies between 2.31 and 2.41 eV. Figure 3(a) shows the dispersion of $I_s/I_1^2 I_2$ along with the linear absorp-

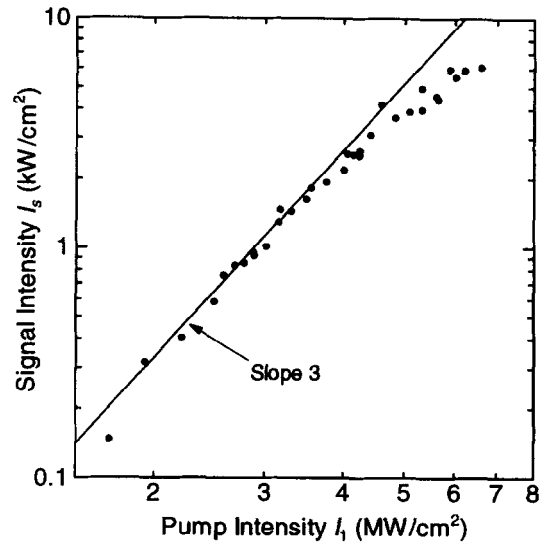


Fig. 2. Diffracted signal intensity versus incident pump intensity for the excitation resonant to the lowest exciton. The nonlinear optical response of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ is in the third-order regime at incident intensities below 4 MW/cm².

tion spectrum measured at the same temperature. The excitonic absorption peak of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ is resolved into sharp multiple lines at low temperatures. The higher-energy lines are tentatively assigned to the phonon sideband of the lowest-energy line [4]. The $I_s/I_1^2 I_2$ spectrum exhibits a broad peak around the lowest-exciton line and a sharp peak at the highest-energy phonon sideband. We determined the $\chi^{(3)}$ values from the $I_s/I_1^2 I_2$ data. An expression for the signal intensity can be obtained by solving the Maxwell equations including linear absorption and third-order nonlinear polarization. The intensity I_s of the signal beam of the wave vector $2k_1 - k_2$ is related to $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ and the intensities of the pump beams of wave vectors k_1 and k_2 (I_1 and I_2 , respectively) by the formula

$$I_s = \frac{3^2 2^6 \pi^6}{c^2 \lambda^2} \frac{e^{-\alpha d} (1 - e^{-\alpha d})^2}{|\tilde{n}|^2 n^2 \alpha^2} |\chi^{(3)}|^2 T_{01}^3 T_{12} T_{23} I_1^2 I_2, \quad (1)$$

where \tilde{n} , n and α are the complex refractive index, the real part of \tilde{n} and the absorption coefficient of the medium at wavelength λ , respectively, d is the sample thickness, and T_{01} , T_{12} , and T_{23} are the power transmission coefficients for the air/sample, sample/substrate, and substrate/air interfaces, respectively. The magnitude of $|\chi^{(3)}|$ of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ was determined using equation (1). Spectral broadening of the incident laser beam (35 meV full width at half maximum) was taken into account by using \tilde{n} , n , and α convoluted with the laser spectrum. Figure 3(b) shows the $|\chi^{(3)}|$ spectrum of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ measured at 8 K. The

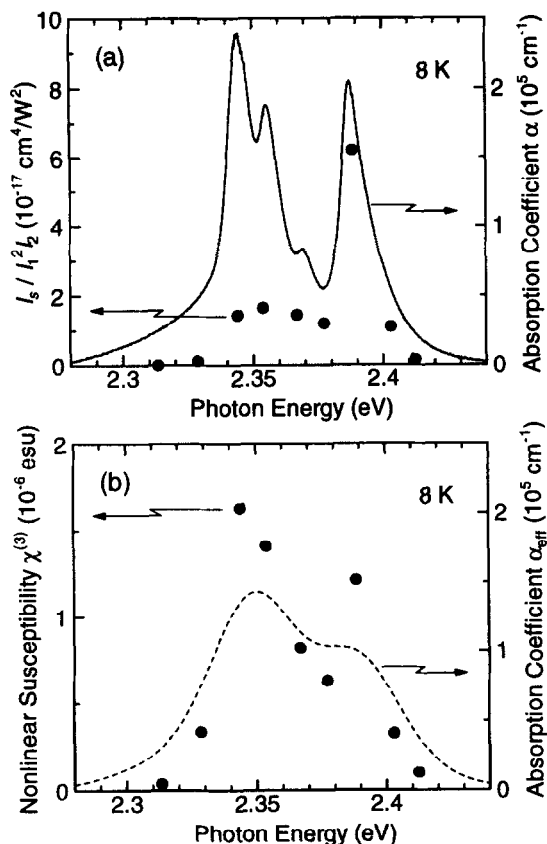


Fig. 3. (a) $I_s/I_1^2 I_2$ and the linear absorption spectra are shown by the closed circles and the solid line, respectively. (b) $|\chi^{(3)}|$ spectrum of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ at 8 K (closed circles). The dashed line shows the effective linear absorption spectrum.

effective absorption spectrum allowing for the spectral broadening of the incident laser pulses is shown by the dashed line for comparison. The $|\chi^{(3)}|$ spectrum has two clear peaks at the resonances to the absorption lines. The maximum $|\chi^{(3)}|$ value is as large as 1.6×10^{-6} esu at the lowest-exciton resonance. Measurements with much narrower spectrum pulses will resolve the fine structures of the $\chi^{(3)}$ spectrum. A FWM measurement using a laser source with a longer pulse duration ($> \text{ps}$) is now underway.

Biexcitons dominate the FWM process when the material is excited with lower-energy photons. A polarization-dependent spectrally-resolved FWM measurement clearly resolved the biexciton contribution to the nonlinear optical processes. The investigation on the biexcitons in $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ will be reported elsewhere [9].

We measured the population relaxation time of the excitons in $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ by a transient grating technique in a box-car configuration of three input pulses. Figure 4 shows the transient grating signals decay measured at 8 K. The observed single exponential

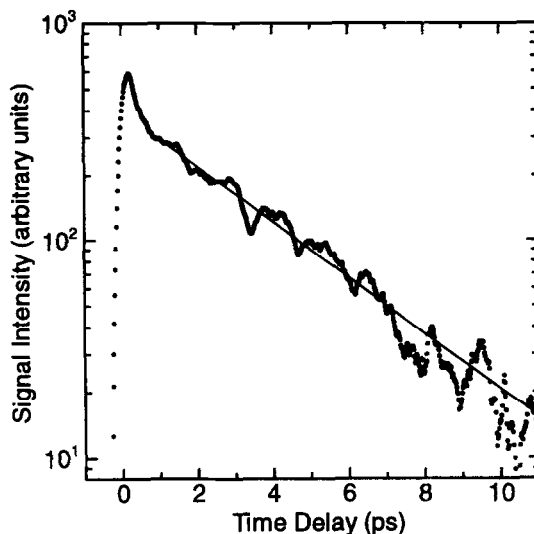


Fig. 4. Transient grating decay curve of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ measured at 8 K (closed circles). The solid line shows the single exponential decay with a time constant of 3.4 ps.

decay with a 3.4-ps time constant shows that the population life time of the excitons is 6.8 ps, because the signal intensity is proportional to the spatially modulated population squared. A beat structure with a period of 1.3 ps superimposed on the exponential decay is presumably due to the exciton-phonon interaction because the corresponding energy of the oscillation, 25 cm^{-1} , agrees well with the energy of a phonon observed in a resonant Raman scattering spectrum of $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ [10].

In summary, a sub-ps transient FWM technique has been used to investigate the nonlinear optical response of excitons in $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$. The measured third-order nonlinear optical susceptibility reaches 1.6×10^{-6} esu at the lowest-exciton resonance. The population and phase relaxation times of the excitons are measured to be 7 ps and 0.2 ps, respectively. Since the excitons in this material are highly stable up to about 100°C , large optical nonlinearity is expected even at room temperatures. The very large $\chi^{(3)}$ and the short response time should make this class of materials promising in resonant nonlinear optical applications.

Acknowledgements—The authors would like to thank Professors Makoto Gonokami and Eiichi Hanamura of the University of Tokyo for stimulating discussions. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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