Laser-Driven Shock Wave-Induced Triboluminescence of an Organic Crystal: Toward a Semiquantitative Study

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Received: April 7, 2003; In Final Form: June 13, 2003

A novel technique for studying triboluminescence (TL) of organic crystals is proposed. *N*-Isopropylcarbazole (NIPCz) crystals were fixed onto a glass plate, whose reverse side was coated with a black pigment that was used as a shock-generating layer. A single fundamental pulse from a Nd^{3+}:YAG laser (1064 nm, fwhm ∼ 10 ns) was irradiated onto the shock-generating layer to generate a shock wave, and this resulted in both crystal fracture and TL from the NIPCz crystals. The TL spectrum was almost the same as the fluorescence spectrum of the NIPCz crystals. The dynamic behavior of the crystal fracture and the transient intensity of the TL were shown to be interrelated with each other. The generation of the TL commenced 200 ns after the laser exposure, and this was reproducible irrespective of the NIPCz samples, indicating that the generation and detection timings for TL are controllable with high accuracy by the present technique. In addition, the TL intensity increased with increasing amplitude of the shock wave, as well as the laser fluence. The results presented here demonstrate that the present method provides novel means of investigating TL phenomena semiquantitatively in a noncontact mode.

Introduction

The application of mechanical stress to solids occasionally results in the emission of visible luminescence. This phenomenon is known as either triboluminescence (TL) or mechanoluminescence (ML) and has a long research history.[1] To date, a wide variety of materials such as organic/inorganic crystals, natural fibers, and biomolecules have been reported to exhibit TL.[2] As is widely known, TL activity is correlated with the crystal structure,[3] and most TL-active materials belong to a noncentrosymmetric space group, suggesting that piezoelectrification followed by electric discharge or electron−hole recombination is the origin of the excitation that leads to TL. However, the fundamental mechanism underlying the TL processes, and in particular its dynamics, is far from being well understood.[4−6] One crucial problem in the study of TL has been the lack of a quantitative method for its generation and detection. TL is commonly generated in solids by the mechanical rubbing or fracture of a sample using a glass rod with an optical fiber attached to it for the purpose of detection.[6,7] Although TL might be detected efficiently using this technique, it is obviously difficult to control the TL intensity and the timing of the detection after the application of mechanical stress. Because of the limitations of such a methodology, studies on transient TL behavior have rarely been explored. Therefore, it is desirable to establish a novel methodology that would enable us to control the generation and detection timings of TL in order to elucidate the fundamental TL mechanisms.

Here, we propose the "laser-driven shock wave" technique for a semiquantitative study of TL. The number of studies into laser-driven shock wave effects on the physicochemical processes of solids have hitherto been limited.[8,9] In relation to the present study, laser-induced ML has already been reported for certain metals (Cu, Ag, Au, and so on).[10,11] However, it is worth noting that the present work is totally different from these studies in its implementation. For example, when studying the TL/ML emitted by a sizable metal disk in the studies mentioned above, the sample is irradiated directly by intense laser pulses (fluence ∼ 20 J/cm^2), and the TL/ML generated by the shock waves is detected from the reverse side of the disk. Such a method is readily applicable to nontransparent and/or nonemissive solids, but for many TL active organic/inorganic crystals such as carbazole[12−16] and anthracene[17] derivatives, europium complexes,[18,19] and so forth, the crystals themselves are semitransparent and show relatively intense photoluminescence (PL). The direct irradiation method mentioned above is clearly not applicable for this class of materials. Therefore, for these organic samples, an indirect but semiquantitative TL excitation method should be developed.

In the present study we developed a novel TL generation/detection system by utilizing "laser-driven shock waves", and applied the methodology to the TL of *N*-isopropylcarbazole (NIPCz) crystals. Because NIPCz exhibits a high TL activity, as both Nowak et al. and ourselves have already reported,[13−15] it is a very suitable compound for the proposes of the present study. The shock-wave-induced TL behavior of NIPCz was investigated systematically by means of photoacoustic, μs-time-resolved imaging, and spectroscopic measurements.

Experimental Section

Anthracene-free NIPCz was synthesized and purified according to the method in the literature.[15] A sample cell was prepared as follows (see also Figure 1). NIPCz crystals (∼1 mg) were heated above the melting point (mp ∼ 380 K) to be melted on a thin glass plate (Matsunami Glass, 24 × 24 mm^2, thickness = 0. 15 mm) and then gradually cooled under ambient condition. Thus, the crystals were tightly adsorbed on the glass plate and covered with a holed slide glass (Matsunami Glass, 24 × 24

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10.1021/jp034904t CCC: $25.00
Published on Web 07/09/2003

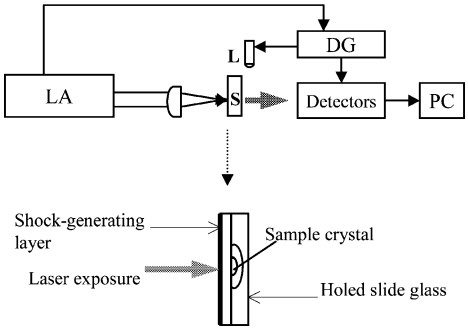

Figure 1. Experimental setup for the laser-driven triboluminescence generation/detection system. LA, pulsed Nd^{3+}:YAG laser; L, pulsed Xe lamp; DG, delay generator; PC, computer; S, sample cell. For detectors, further details are given in the text. Enlarged illustration of the sample cell is also shown in the figure.

Figure 2. Microsecond images of fracture of NIPCz crystalline aggregates induced by the laser-induced shock wave. Laser fluence (F) was set at 1.5 J/cm^2. The scale bar represents 1 mm. t denotes the delay time after laser irradiation. Fracture (cracking) is marked by the arrows (see main text).

mm^2 with a hole diameter of 15 mm and a depth of 0.6 mm). The reverse of the glass sample plate was coated with a black pigment (Asahipen, black lacquer 420), which was used as a shock-generating layer. The layer has 50 μm thickness and can absorb 1064-nm-laser-pulses completely (transmittance at 1064 nm = 0%).

The experimental setup developed for the present study is shown schematically in Figure 1. The fundamental output (1064 nm) from a nanosecond (ns)-pulsed Nd^{3+}:YAG laser (Spectra Physics, PRO-250−30, fwhm ∼10 ns) was focused onto the shock-generating layer (spot radius = 3 mm) of the sample cell through a spherical lens (f = 50 mm). Irradiation of stray light onto the crystals was carefully avoided. The amplitude of the shock wave was measured by using a PZT transducer coupled with an amplifier and a digital storage scope (LeCroy, 9354C), as described in our previous works.[20,21] The dynamic fracture behavior induced in the crystals by the shock wave was imaged using a CCD camera (PCO, SensiCam), whereas a pulsed Xe lamp (Hamamatsu, C4479, duration time ∼ 1 μs) was used as a gated illuminator. Temporal profiles and spectra of the TL were obtained using a photomultiplier tube (Hamamatsu, R928) and a multichannel photodiode array (Hamamatsu, PMA 11), respectively. The CCD camera, the pulsed lamp, and the photodiode array were electrically coupled with the laser through a delay generator (Stanford, DG535). All of the measurements were carried out with a single-shot exposure under ambient conditions.

Results and Discussion

Our μs-time-resolved images of fractures in the NIPCz crystalline aggregates are displayed in Figure 2, where t represents the delay time after laser irradiation (fluence (F) = 1.5 J/cm^2); −∞ and +∞ correspond to the periods before and after irradiation, respectively. As seen in the figure, the aggregates are obviously fractured by laser irradiation (t = +∞). Simultaneously, we observed blue visible luminescence, as in the spectrum shown in Figure 3. It is worth noting that the observed spectrum agrees very well with the TL spectrum that we have reported and resembles the photoluminescence (PL) spectrum (also shown in Figure 3, dotted line, excited at 355 nm). No other spectral components were detected, such as luminescence from molecular nitrogen.[5,22] The TL spectrum exhibited a slight red shift when compared to the PL spectrum. Very recently, Duignan et al. reported in detail the spectral differences between TL and PL for sixteen compounds (both metal complexes and purely organic compounds)[23] and demonstrated that the primary origin of a spectral red shift in TL compared to PL is the self-absorption of the crystal luminescence. Because the NIPCz crystals show a small Stokes shift and the absorption spectrum overlaps significantly with the fluorescence (PL) spectrum, we consider that the self-absorption effect in TL is a possible reason for the red-shift in the present case. However, because the PL lifetime of NIPCz crystals is sufficiently short (<20 ns),[24] we cannot preclude completely a contribution from pressure-induced (i.e., shock wave) changes in the Franck−Condon factors that affect the spectral shift in TL, as discussed in detail in the literature.[23] Irrespective of the reason for the red shift in the TL, it is concluded that the laser-driven shock wave can certainly generate TL in NIPCz crystals. When an intense laser pulse is irradiated onto the surface of a material beyond a certain fluence threshold, ablation takes place, accompanied by the propagation of an intense pulsed-acoustic wave (i.e., shock wave) in the material. Because the amplitude of the laser-driven shock wave has been reported to be in the order of GPa,[8,9] the shock wave is enough to induce TL in NIPCz crystals (discussed again later).

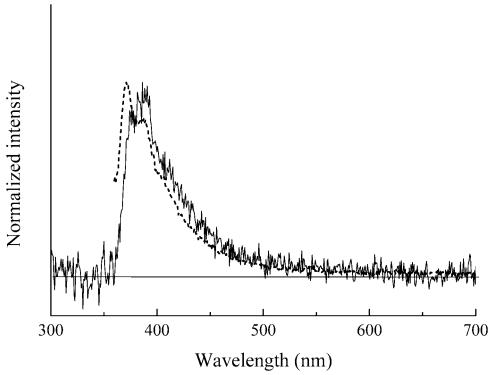

Figure 3. Normalized PL (broken line) and TL (solid line) spectra of NIPCz crystals. The PL spectrum was measured using 355-nm laser excitation.

In Figure 2, crystal fracture is seen at t = 40 μs, as shown by the arrows. Furthermore, although the data are not shown here, fracture started at $t \leq 2$ μs, which was the time-resolution limit of the present imaging system. To obtain more detailed information, temporal profiles of TL at several laser fluences (F = 0.4−1.5 J/cm^2) were investigated, and the results are displayed in Figure 4. At F = 0.4 J/cm^2, we could not observe any fracturing of the crystals, and hence no TL signal was obtained. At $F \geq 0.78$ J/cm^2, both crystal fracture and TL were observed simultaneously, and the TL intensity increased with increasing F, owing to the generation of a stronger shock wave at the higher F value. Besides the TL intensity, the increase in F resulted in a longer TL duration time, and the TL continued up to ∼40 μs at F = 1. 5 J/cm^2. Phenomenologically, these results are consistent with those in Figure 2. Additionally, as seen in the data inserted in Figure 4, TL appeared at $t \sim 200$ ns after the laser pulse irradiation. A rough calculation indicates that the time necessary for the shock wave to propagate to the

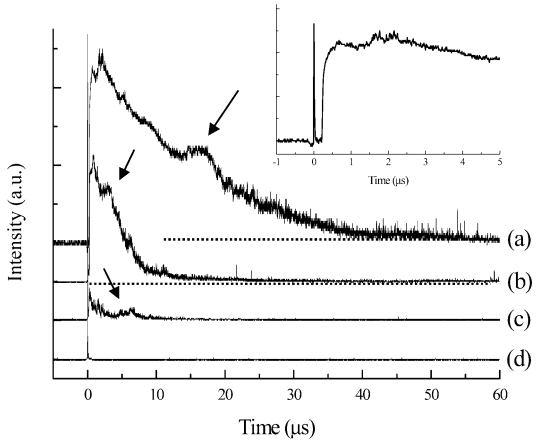

Figure 4. Temporal profiles of TL in the μs region. Zero in the abscissa is defined as the onset of laser irradiation. *F*, (a) 1.5, (b) 1.2, (c) 0.78, and (d) 0.40 J/cm^2. Inset: Enlarged profile of (a) at an early stage after laser irradiation. The spike at $t = 0$ is due to stray light from the laser pulse. The additional rise (bump) in the profiles is marked by arrows (see main text).

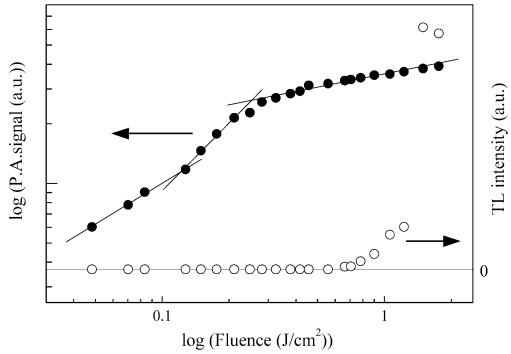

Figure 5. Fluence dependencies of the amplitude of the acoustic/shock wave (closed circle, on a semilogarithmic scale) and the TL intensity (open circle, on a normal scale).

NIPCz crystals through the glass plate of the sample cell is ~100 ns,[25] so the observation of an induction period of $t \sim 200$ ns before the TL observed after laser irradiation (Figure 4) will be also a reasonable consequence. The long duration time of up to 40 μs and the induction period of ~200 ns obviously distinguish the present luminescence (i.e., TL) from PL excited by stray light from the laser.

Chandra and Zink have investigated the temporal behavior of TL for several organic crystals by using an air-driven steel piston.[4,5] For a coumarine crystal, the duration time of the TL generated by this method was submillisecond in order, owing to superposition of several individual TL pulses produced during the motion of multiple cracks in the crystal. On the other hand, the laser-driven shock wave method can apply stress energy to solids quite rapidly;[8,9] the time for the shock wave to pass through the crystalline aggregates is estimated to be submicrosecond. This is the origin of the short duration time of the TL in the present study.

It may be worth pointing out that each of the temporal profiles in Figure 4 showed a bump during the total time decay of the TL, as indicated by the arrows. Although the time delay after the laser irradiation for the bump to be observed was dependent on *F*, the observation of the bump was not fortuitous, and analogous results with those in Figure 4 were confirmed repeatedly for many samples. At the present stage in the investigation, we suspect that the appearance of the bump is related to crack formation in the crystal sample and/or peeling of the crystals from the glass plate. The simultaneous observation of both time-resolved crystal images and transient TL intensity will provide more detailed information, measurements of which are currently being undertaken in our research group.

The present laser-driven shock wave method was shown to have a high potential to induce TL. To show the generality of the present method toward TL phenomena, the relationship between the amplitude of the shock wave and the TL intensity should be revealed. Therefore, we studied the dependencies on *F* of both of the TL intensity and the amplitude of the acoustic/shock wave, as shown by the data summarized in Figure 5. The total TL intensity at a given value of *F* was estimated by integrating temporal profiles analogous to those in Figure 4. When analyzing the *F* dependence of the amplitude, two inflection points were observed at 0.13 and 0.25 J/cm^2. This type of dependence has frequently been observed for laser ablation.[20,21] The signal increases gradually with increasing *F* because of normal photoacoustic effects (where the slope is unity), and the slope then increases abruptly beyond the first inflection point (0.13 J/cm^2). This fluence is regarded as the threshold for ablation of the shock-generating layer, and the abrupt increase in the signal is attributed to the generation of the shock wave. The slope decreased beyond the second inflection point, because of the shielding effects with respect to laser light caused by the ablation plumes. On the other hand, when examining the *F* dependence of the TL intensity, the intensity value remained at zero when $F \leq 0.7$ J/cm^2. Above this fluence, the TL intensity increased very sharply, indicating that this fluence is the threshold value for TL generation as well as for the fracture of NIPCz crystals. In practice, when *F* was below the threshold (0.7 J/cm^2), no crystal fracture was observed, which was in good accordance with the results in Figure 4. A certain amplitude of shock wave is necessary to induce crystal fracture. These results indicate explicitly that the TL intensity can be controlled by varying *F*, which is one of the advantages of the present technique.

The above discussion is concerned not with the shape (temporal profile) of the shock wave but only with its intensity. For the shapes of laser-driven shock waves, Dyer and Srinivasan reported a compressive stress signal (~5 ns rise time and ~20 ns decay time, total duration time ~40 ns) in polymer ablation induced by irradiation of intense ns-excimer laser pulses.[26] On the other hand, McGrane et al. developed a method of generating shock waves with 10 ps rise time followed by >200 ps constant pressure (i.e., flat-top waveform) utilizing irradiation of spectrally chirped femtosecond laser pulses to Al films.[27] Unfortunately, our PZT transducer does not have temporal resolution in the ns−ps temporal region. Therefore, we cannot directly follow the temporal profiles of the present shock waves. On the analogy of the result of ns-pulsed laser ablation by Dyer and Srinivasan, we deduce that the temporal profile of our shock wave is close to a Gaussian-type-waveform with several tens of ns duration. Anyhow, because the present TL process takes place in much longer temporal region (<100 μs) than the duration time of the shock waves, we consider that the TL behavior is not affected by the temporal profile of the shock wave.

Next, we will briefly discuss the TL mechanisms of NIPCz crystals. The coincidence and correspondence between the images of crystal fracture and the temporal profile of the TL intensity in Figures 2 and 4 respectively indicate that the generation of TL requires fracturing to occur to create a fresh crystal surface. NIPCz crystals belong to a polar space group (orthorhombic, *Iba*2),[14] and the crystals have piezoelectric properties.[28] Therefore, piezoelectrification at fresh crystal

surfaces followed by electrical discharge and/or electron−hole recombination would give rise to the formation of the excited singlet state of NIPCz; TL. In addition to the creation of fresh surfaces, the shock wave also induces peeling of the crystals from the glass surface, as seen in Figure 2, and this also generates TL. We consider that these processes are reflected on the complicated temporal behavior of the TL intensity in Figure 4.

Conclusion

We developed a novel laser-driven shock wave technique that enables the semiquantitative analysis of TL behavior in NIPCz crystals for the first time. The dynamic behavior of fracture and TL in the crystals was observed directly in a microsecond regime. The combination of fast imaging of the crystals fracturing, accompanied by the transient TL measurements, is very novel in terms of TL studies and will shed further insights into TL mechanisms. Furthermore, the technique enables the control of the detection timing and intensity of TL, so that semiquantitative studies on the TL phenomena of other TL-active crystals will be further progressed. Owing to the characteristics of the methodology, it would be possible to obtain time-resolved TL spectra by coupling a laser system with a gated-photodetector apparatus. In particular, the laser fluence dependencies of the strength of the shock wave and the TL intensity indicate that the technique has a high potential for comparative studies of the TL yields of various crystals.

Acknowledgment. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (No. 13750669).

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