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Laser-Induced Shock Wave Can Spark Triboluminescence of Amorphous Sugars

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We investigated the triboluminescence (TL) of sugars using an innovative experimental approach: the laser-induced shock wave (LISW) technique. We found that the LISW could induce very bright TL in crystalline sugars, the intensity of which was shown to be 10^5 times higher than that obtained by conventional manual hand rubbing. We also applied the LISW technique to amorphous sugar samples. Although it was supposed that TL could not be excited in amorphous solids of sugars having isotropic structures, we revealed that LISW could induce bright TL in amorphous sugars similar to that induced in crystalline sugars. On the basis of the experimental results showing the dynamic behavior of the sample fracture combined with those of the TL, we discuss these novel TL mechanisms in sugars. We believe that the shock wave technique opens a new channel for investigating the nature of TL.

Introduction

When a mechanical stress (force) is applied to a solid material, visible light emission is occasionally observed. Such light emission is called triboluminescence (TL) and it has been observed for more than a millennium.[1] According to a detailed study by Sweeting, at least 30%, or about 50%, of all *crystalline* materials are predicted to show TL activity, irrespective of whether they are inorganic or organic.[2] Despite the fact that TL is ubiquitous and has a long research history, the fundamental mechanisms underlying TL still remain unclear. According to previous studies on TL, the mechanisms can be classified into the following four categories.[3,4]

(i) Chemiluminescence: molecules are excited by oxidation of the fresh surfaces formed at the fracture.

(ii) Gas-discharge emission: N_2 molecules in the atmosphere are excited by piezoelectrification at the fracture, followed by dielectric breakdown of the surrounding gas.

(iii) Theromoluminescence: molecules are excited by a pyroelectric effect due to thermal energy generated by mechanical rubbing of the sample.

(iv) Deformation luminescence: light is emitted during elastic strain deformation of a solid.

In addition to these, other mechanisms involving photoluminescence, electroluminescence, and cathodoluminescence have been proposed to explain TL.[3]

Of these possible mechanisms, it has frequently been believed that (ii) is the most likely TL mechanism, since a large number of mechanoluminescent crystals belong to noncentrosymmetric space groups. Such crystals should generate electric charge at the fracture surface due to piezoelectrification, and subsequent electron−hole recombination or electric discharge would excite the crystalline molecules or surrounding gas molecules (N_2). However, as Sweeting and other researchers have pointed out, about half of the known mechanoluminescent crystals do not possess noncentrosymmetric space groups, so other possible origins should be considered to clarify the mechanism for TL excitation.[2–4]

One of the experimental difficulties in TL studies is the lack of an adequate means to excite TL in the crystal, and instead of mechanical rubbing by hand, several methods have been proposed so far. In 1979, to explore mechanisms of TL, Hardy et al. proposed a unique technique utilizing pulsed-laser-induced mechanical stress for the first time.[5] Following this study, to access the dynamic behavior of TL, in 2003, we proposed a novel method to excite TL in crystals using a laser-induced shock wave (LISW) and demonstrated that the TL intensity of *N*-isopropylcarbazole crystals was controllable by adjusting the laser power used to generate the shock wave.[6] Furthermore, we succeeded in monitoring the dynamic behavior of TL with the LISW technique. Quite recently, in 2006, on the other hand, Eddingsaas and Suslick reported an intriguing TL phenomenon. They induced TL in sucrose or resorcinol crystals dispersed in oil (slurry) by sonication and observed very intense luminescence of gas molecules (N_2, He, and Ar) dissolved in the slurry.[7] The luminescence was ascribed to TL of the crystals excited by shock waves generated by cavitation in the slurry, and the intensity was much higher than that induced by manual crushing of the crystals. Thus, shock wave methods have significant potential for providing further insight into TL mechanisms.

In the present study, we demonstrate that LISW can induce TL in amorphous solids of sugars, which, in the past, have been regarded as being nonmechanoluminescent. The TL found in the present study would fall into a new category of TL.

Materials and Methods

Commercially supplied (Wako Chemical) sucrose, glucose, or fructose (1 mg) was heated just above the melting point on a thin glass plate and then gradually cooled to ambient temperature for tight adsorption of the sample to the glass plate. After cooling, the sample became a transparent solid and was confirmed to be amorphous by means of polarization microscopy. The amorphous sucrose became crystalline after standing for several days, while the glucose remained amorphous. Crystalline glucose samples were prepared by casting an aqueous glucose solution onto a glass plate and drying, giving glucose

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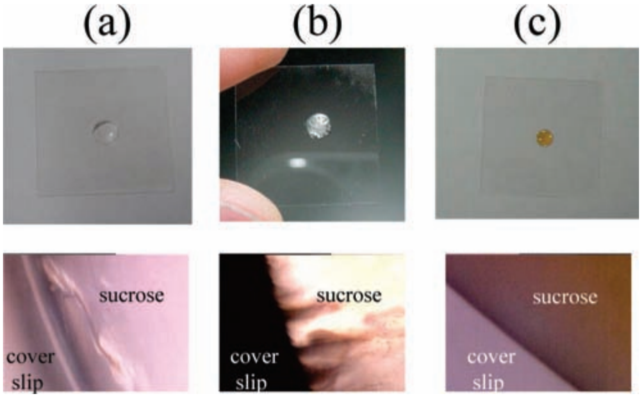

Figure 1. Photographs of sucrose samples adsorbed on coverslips. Upper panels present normal photographs, whereas lower panels present optical polarization micrographs: (a)amorphous sucrose, (b) crystalline sucrose, (c) caramel of sucrose.

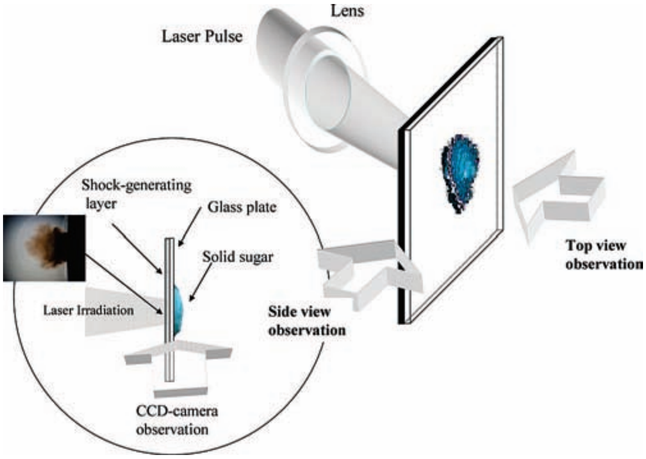

Figure 2. Schematic illustration of experimental arrangements around a sample cell. Two different types of observation methods were employed: side view observation and top view observation.

monohydrate crystals. As representative examples, optical micrographs of sucrose (amorphous, crystal, and caramel) are shown in Figure 1. The transparent sample (Figure 1a) was judged to be amorphous since it did not show a specific rotation, whereas the white cloudy sample (Figure 1b) was found to be crystalline since it did show a specific rotation. Also, heating of sucrose above 200 °C and subsequent cooling gave a caramel-like solid (Figure 1c).

The experimental setup of the LISW system has already been described elsewhere[6] and is briefly presented here using a schematic illustration: Figure 2. The back side of the glass sample plate was coated with a black pigment, which was used as a shock-generating layer for the pulsed-laser irradiation. The fundamental 1064 nm output from a pulsed Nd^{3+}:YAG laser (fwhm $\sim$ 10 ns) was focused onto the shock-generating layer to induce ablation with accompanying shock wave generation. The dynamic fracture behavior induced in the samples by LISW was imaged using a CCD camera and a flash lamp (time duration $\sim$1 μs). The temporal profile and TL spectrum from the sample were recorded with a photomultiplier tube and a gated multichannel photodiode array, respectively. The laser and photodetectors were operated synchronously using a delay generator. All of the measurements were carried out with a single-shot exposure under ambient conditions.

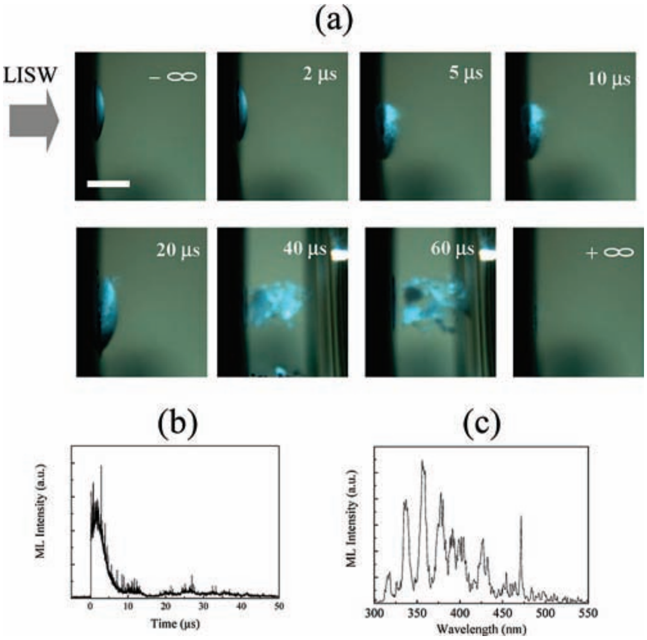

Figure 3. Experimental results on crystalline glucose. (a) Side view images of fracture dynamics. A delay time (Δt) is given in the figure. $\Delta t = -\infty$ and $+\infty$ mean before and after application of the shock wave, respectively. (b) A temporal profile of TL. (c) TL spectrum. Scale: bar = 1.0 mm.

Results and Discussion

TL of Crystalline Sugars. When we applied our technique to sucrose and glucose crystals, TL was, as expected, observed upon fracture of the crystals by the shock wave. Representative experimental results for crystalline glucose are shown in Figure 3. Figure 3a shows temporal images of the view from the side of the sample, and the black band seen in each photograph is a side view of the glass plate. A laser pulse was irradiated from the left-hand side of the black band: see also the Materials and Methods section (Figure 2). The time (t) shown in Figure 3, parts a and b, is the time after laser irradiation, and the origin of the time axis ($t = 0$ μs) is defined as the time at which the shock wave was generated, which corresponds approximately to the laser irradiation time. Fracture of the crystal commenced at <5 μs and continued for more than 50 μs after the application of LISW (Figure 3a). Simultaneously, luminescence was emitted from the sample, and the temporal profile of the emission intensity is shown in Figure 3b. The luminescence (TL) reached its maximum intensity at 3 μs and decayed within 10 μs. Weak TL continued to be emitted until 50 μs. Since it takes <10 μs for LISW to propagate through the crystalline sample, resulting in the generation of numerous microcracks, a large part of the TL was generated during propagation of LISW in the sample.

The TL spectrum displayed in Figure 3c is in good agreement with the second positive band of N_2 luminescence, as reported in a number of publications.[2–4,8] The number of photons emitted in sucrose TL was evaluated to be ca. 10^{20} photons/mol by integrating the temporal TL intensity profile in Figure 3b. This value is 10^5 times greater than that obtained by the high-impact-velocity TL instrument reported by Beese and Zink.[9] Thus, the LISW can induce quite intense TL compared with conventional methods. Similar behavior was also observed for crystalline sucrose.

TL of Amorphous Sucrose and Glucose. As Hardy et al. have reported, there is a clear correlation between the space group of the crystal structure and the TL activity for a series of sugars, and on the basis of such a correlation, the piezoelec-

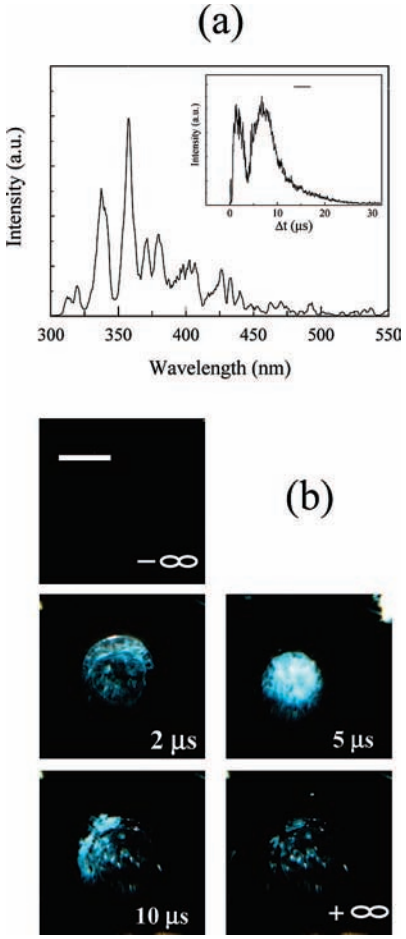

Figure 4. Experimental results on amorphous sucrose. (a) TL spectrum and temporal profile (inset). (b) Top view images of fracture dynamics. A delay time (Δt) is given in the figure. $\Delta t = -\infty$ and $+\infty$ mean before and after application of the shock wave, respectively. Scale: bar = 1.0 mm.

trification mechanism has been put forward as the underlying mechanism for TL in sugars.[10] In practice, it has been reported that the crystal structures of TL-active sucrose and glucose belong to the monoclinic $P2_1$ space group, whereas those of TL-inactive sugars (fructose, galactose, etc.) belong to the orthorhombic $P2_12_12_1$ space group. A similar interpretation is applicable also for TL of crystals of organic aromatics (carbazole derivatives) as we have demonstrated.[11] According to the framework of such a piezoelectrification model, completely amorphous sugars on the nanometer scale and fructose should be TL-inactive.

However, the present technique reveals unexpected behavior, as the results on amorphous sucrose shown in Figure 4 demonstrate. We clearly observed light luminescence from the sample, the spectrum of which is displayed in Figure 4a. The vibronic bands in the spectrum can safely be assigned to the second positive band of N_2 luminescence. That is, the application of LISW induces TL in amorphous sucrose, the mechanism of which is discussed in the following section. A CCD image (top view) at the point of fracture induced by the shock wave is displayed in Figure 4b. Before application of the shock wave, the amorphous sample is not visible in the image, since it is transparent (see also the Materials and Methods section, Figures 1a and 2) and the substrate is seen as black. At 2 μs after laser pulse irradiation ($\Delta t = 2$ μs), the sample can be seen as a bright circle due to scattering of strobe light by the sample, as shown in Figure 4b. Numerous cracks were formed inside the sample by the shock wave, which grew with time ($\Delta t = 5$ μs). At $\Delta t = 10$ μs, the sample started to peel from the substrate. The temporal profile of the TL intensity shown in the inset of Figure 4a has two maxima: The first maximum was observed at $\Delta t \sim 2$ μs, while the second one appeared at $\Delta t \sim 7$ μs. This behavior is interpreted on the basis of the temporal fracture images. The first and second maxima seen in the temporal profile of the TL intensity correspond to generation of TL by the formation of numerous cracks inside the sample (Figure 4b, $\Delta t = 2$ μs) and fracture of the sample (Figure 4b, $\Delta t = 5$ μs), respectively. Furthermore, we found that sucrose caramel (Figure 1c) also emits TL by LISW, although the data are not shown here.

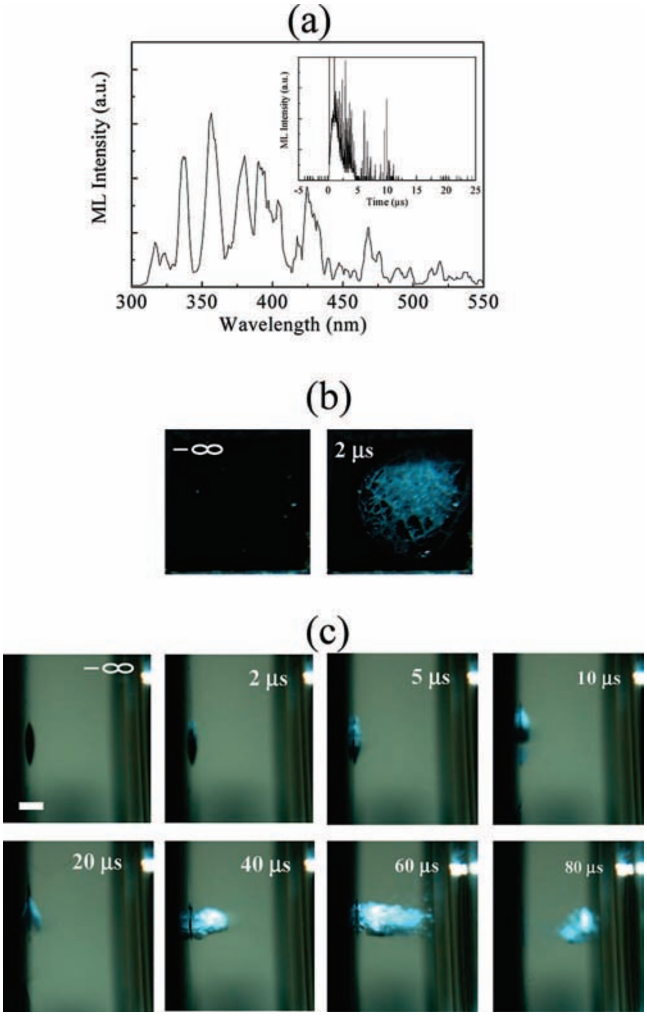

Figure 5. Experimental results on amorphous glucose. (a) TL spectrum and temporal profile of TL (inset). (b) Top view images of fracture dynamics. (c) Side view images of fracture dynamics. A delay time (Δt) is given in the figure. $\Delta t = -\infty$ means before application of the shock wave. Scale: bar = 1.0 mm.

Analogous behavior to that shown in Figure 4 was also observed for an amorphous glucose solid, the results for which are shown in Figure 5. TL assigned to N_2 luminescence can clearly be seen (Figure 5a). The TL intensity reaches its maximum at 2 μs as seen in the inset of Figure 5a. The top view image in Figure 5b demonstrates the formation of numerous cracks in the sample even at 2 μs. The sample solid was somewhat viscous compared with the amorphous sucrose sample, and therefore, the dynamic fracture behavior in the side view images (Figure 5c) was somewhat different from that of sucrose. Even at a stage well after application of LISW ($\Delta t > 40$ μs), the sample has not broken into pieces but has become

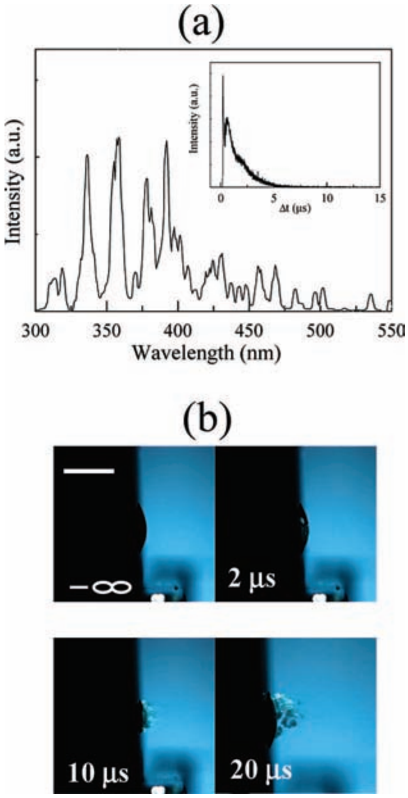

Figure 6. (a) TL spectrum and temporal profile (inset) of amorphous fructose. (b) Side view images of fracture dynamics. A delay time (Δt) is given in the figure. Scale: bar = 1.0 mm.

elongated due to the viscous properties of the solid. In the temporal TL intensity profile, therefore, there is only one peak due to microcrack formation.

Thus, the LISW method has demonstrated that amorphous sucrose and glucose are TL-active. It should be pointed out that the TL intensities of these amorphous samples are comparable to those of the corresponding crystalline samples.

TL of Amorphous Fructose. Since it was also thought that fructose was TL-inactive,[8] we examined the TL of amorphous fructose using the LISW technique. As the results in Figure 6 show, TL of amorphous fructose was clearly observed and the spectrum is composed of N_2 bands (Figure 6a). The shape of the sample was slightly deformed at $\Delta t = 2\ \mu$s, and cracks were observed inside the sample, as confirmed by a top view image (not shown in the figure). The sample started to fracture at $\Delta t > 10\ \mu$s (Figure 6b). On the other hand, the TL had decayed within $\Delta t \sim 5\ \mu$s as shown in the temporal profile in the inset of Figure 6a. At $\Delta t = 10-20\ \mu$s, the sample has clearly fractured into pieces, while the TL has ceased before $\Delta t = 10\ \mu$s. The results indicate that TL in amorphous fructose is initiated during deformation and crack formation of the sample. This is the first demonstration of TL in amorphous fructose.

Mechanistic Aspects of TL Induced by LISW. As reported by Longchambon,[12] and Zink et al.,[8] it was believed that a noncentrosymmetric crystal structure is the necessary condition for generation of TL in sugar. However, the present study demonstrates for the first time that LISW can initiate TL in amorphous sugars. The TL characteristics of amorphous sugars revealed in the present study can be summarized as follows. (I) The TL intensities of amorphous sugars induced by LISW are as high as those of crystalline sugars and are 10^5 times higher than those observed by conventional mechanical rubbing. (II) The TL spectra of amorphous sugars are in good agreement with the N_2 luminescence spectrum, as reported for the TL spectra of crystalline sugars. (III) TL of amorphous sugars commences immediately after application of LISW and concludes before the sample fragments into small pieces.

On the basis of these experimental results, in the following we discuss the mechanisms for TL in amorphous sugars. The TL of the amorphous sugars in the present work is very bright and has never been observed by other TL generation techniques. We propose a novel TL mechanism characteristic of LISW-induced TL in sugars. This mechanism is described below.

The chemiluminescence mechanism (i) described in the Introduction seems to be inadequate for the present case, since the sugars are unlikely to be chemically oxidized. Also, the simple piezoelectrification mechanism (ii) is obviously not applicable for the present amorphous sugars, since amorphous solids have centrosymmetric crystal structures and therefore are piezoelectrically inactive. However, it should be noted that we may have a possibility of TL excitation by piezoelectrification at a very small crystalline domain ($<1\ \mu$m) that cannot be detected by the present polarization microscopy (Figure 1). In addition, the mechanism of frictional piezoelectrification at the interface between the sample and the glass substrate should be excluded, since TL was observed before the sample peeled from the substrate. The thermoluminescence mechanism (iii) is worth considering since heat could be generated at the shock-generating layer upon pulsed-laser irradiation. However, this mechanism is obviously denied since the thermal diffusion length in the glass plate (on which the sample is adsorbed) is very short (1 μm per 1 μs), whereas TL commences immediately after irradiation and before heat can propagate to the sample from the shock-generating layer.

The fourth mechanism (iv), deformation luminescence, for TL in sugars was rejected by Alzetta et al. in 1970.[13] They performed simultaneous measurements of the stress−strain and TL−strain curves for a single sugar crystal. They detected no luminescence emission during elastic deformation of the crystal but observed TL at fracture. However, their experimental conditions are hardly comparable with the present conditions. In their experiments, a mechanical stress of $1-5 \times 10^7$ N/m^2 was slowly applied to the sample. The stress amplitude was of the same order as that in the present study using LISW: the pressure amplitude has been estimated to be $<10 \times 10^7$ N/m^2. In the present LISW experiments, however, since such a high stress was applied to the sample very quickly, the sample would have been subjected to a high pressure for a very short time. Such extreme conditions might induce deformation luminescence in amorphous sugars. The high amplitude produced by the LISW, as high as several tens of megapascals, would induce rapid deformation and subsequent cracking of the solid sample, giving rise to the rupturing of bonds within the sample. Such a situation would result in excitation of the surrounding gas molecules due to the energy released by the rupturing bonds.

Another possible mechanism is TL generation from small crystalline domains existing locally in the amorphous sample. However, this is not plausible since the TL from the amorphous samples in this work is as intense as the TL from crystalline samples and such crystalline domains were not observed by polarization microscopy. Another possibility is a crystalloluminescence process.[14–16] For sugars, the crystalline phase is more stable than the amorphous phase. Amorphous sugars would have been more or less transformed into crystals when lattice motion in the sugar was activated by LISW and the relevant energy subsequently released to excite the sugar molecules. As a result, charge separation or electron ejection would be induced in the domain, resulting in excitation of the N_2 luminescence. The deformation and the crystalloluminescence mechanisms described above do not need fracturing of the sample into small pieces for TL generation. This is consistent with the fracture behavior observed in the present experiments.

Preceding the present work, TL of an amorphous material (silica core fiber) has already been reported by Zink et al., and they suggested the creation of new defect center as a TL mechanism.[17] Furthermore, they also suggest an electron−hole recombination process as a mechanism of TL generated by laser-induced stress wave.[5] Such important processes should be taken into account in the present laser-induced TL. The intense laser shock wave may create numerous defect centers in solid amorphous sugars, and charge separation and/or bond scission could take place in the defect centers.[18] The charge recombination or electric discharge at cracks would excite N_2 luminescence (TL).

In conclusion, LISW can induce very bright TL in both amorphous and crystalline sugars. A novel mechanism is proposed to explain the bright TL of amorphous sugars induced by the rapid application of an intense stress pressure (LISW). We suggest that deformation luminescence, crystalloluminescence, and electron−hole recombination around defect centers together provide a true picture of TL in amorphous sugars. Since such processes are unlikely to occur using the conventional method used to induce TL (i.e., mechanical rubbing by hands), this has not as yet been observed in amorphous sugars. The strong acoustic amplitude of LISW can trigger such processes and spark intense TL.

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