

CRYSTALLOGRAPHY

Crystalloluminescence

RECENT advances in the analytical techniques applied to the study of faint light sources have made it possible to investigate the nature of the light emitted during processes as diverse as crystallization, nucleation, cracking and various chemical reactions.

The crystalloluminescence observed during the nucleation of alkali halides is now well understood as an impurity phenomenon associated solely with three-dimensional, that is, homogeneous, nucleation¹. Each pulse, several hundreds of photons in size, is emitted as the result of a single nucleation event. A nucleus of critical size, which forms as a disordered, glassy aggregate, eventually 'clicks' over into crystalline form within a few nanoseconds. The energy released during this phase change is converted into fluorescent light with high efficiency provided that suitable heavy-metal impurities are present to act as fluorescent centres. The development of nanosecond pulse techniques has enabled this mechanism to be examined in great detail. Crystalloluminescence, which thus accompanies the birth of a crystal, however, is a comparatively rare phenomenon, and it confirms the validity of Volmer's equation of the rate of homogeneous nucleation as will be shown in a forthcoming publication.

Another phenomenon, described as triboluminescence, is known to occur in numerous solid systems². It is associated with electrical discharges across freshly formed gaps when certain solids are subjected to mechanical or thermal stress, the best-known examples, perhaps, being chlorates, bromates and mixed sulphates, all of which emit light on crystallization, and also ordinary sugar and saccharin, which both show luminescence when crushed. The energy released on cracking need not, of course, be emitted entirely as the long, irregular pulses characteristic of triboluminescence, but may also be converted to fluorescence and phosphorescence (random emission of single photons) in the presence of suitable impurities. Triboluminescence and the crystalloluminescence described in the foregoing are thus basically not related in any way to each other, the first being due to a corona discharge while the second is caused by a molecular rearrangement in which the released energy is converted into light by a mechanism akin to piezoluminescence. Crystalloluminescence shows marked regularities in time and pulse-size distribution depending on supersaturation whereas triboluminescence is invariably random in all respects.

There is a further source of light emission, which sometimes accompanies crystallization events and which appears to have caused some confusion in the past, namely, chemiluminescence. It is usually associated with free-radical recombinations (for example, it is easily observed during the homolytic oxidations of lucigenine, luminol and phenol) and it is also present in many autoxidations (for example, of benzaldehyde, aniline and oleic acid). Thus, the light observed many years ago during the crystallization of molten acetates² was not crystalloluminescence but it was due to free-radical activity caused by the thermally produced acetyl radical and its fragments³. Furthermore, chemiluminescence has more recently been detected⁴ in the course of some heterolytic reactions from which oxygen emerges in the diamagnetic singlet state. As a rule, chemiluminescence can readily be distinguished from both triboluminescence and crystalloluminescence since the light is emitted randomly as single quanta. Nevertheless, it is often more difficult to separate chemiluminescence and low-level phosphorescence.

During the crystallization of non-ionizing organic compounds, the energy changes involved are insufficient to cause genuine crystalloluminescence and the light that is observed occasionally in such systems can be shown to be due to either triboluminescence or chemiluminescence

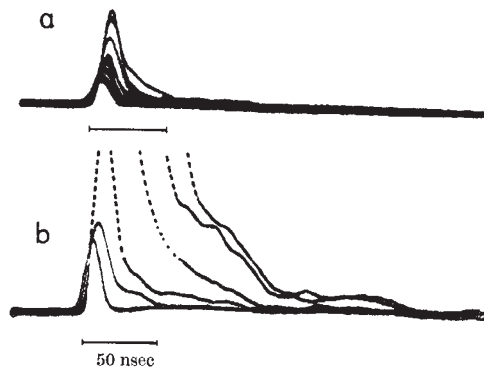


Fig. 1. Triboluminescence pulses observed during the crystallization of benzanilide from alcohol

or both. Thus we have found that the recently reported luminescence during the formation of benzanilide from aniline and benzoylchloride⁵ is essentially caused by the cracking of those crystals appearing first (cf. Fig. 1), which form colourless phosphorescent leaflets and which, since Tschugaeff's time⁶, have been known to be triboluminescent. The groups of triboluminescent pulses shown in Fig. 1a and b were photographed on 'Polaroid' 10,000 ASA using an oscillograph and associated amplifiers with a bandwidth of 75 Mc/s. The composite rise-time of the apparatus, including that of the multiplier photocell, was 9 nsec. The cell possessed a tri-alkali photocathode with a flat response from 1800 Å to 6500 Å and was cooled to -60°C .

Fig. 1a and b indicate, respectively, the lower and upper limits of the size range of the triboluminescent pulses obtained during the crystallization of benzanilide from various organic solvents. The larger pulses seen in b exhibit the irregularities typical of triboluminescence. Owing to a masking effect, much of the triboluminescent light is converted into phosphorescence which does not appear in the photographs but which can readily be observed at higher sensitivities. The fact that both types of pulses shown were due to triboluminescence (rather than to chemiluminescence, phosphorescence, or thermal emission from the photocathode) was confirmed by the detection of the electrostatic discharges, which are invariably associated with triboluminescence, by a method similar to that previously used by Belyaev *et al.*⁷. During both crystallization of benzanilide from solutions and its formation from benzoyl chloride and aniline in ether the multitudes of pulses observed varied randomly in size from 10 to 10,000 quanta.

The very high sensitivity of the techniques used in these laboratories allowed also the observation of a faint glow from the ethereal solutions of the two reagents as well as from pure ether itself. This weak light is, no doubt, due to very slight autoxidation of ether vapour, which may in turn induce secondary oxidation of the solutes.

The many pitfalls for the casual observer, who is likely to confuse one type of light with another, can be avoided by the use of apparatus of sufficient sensitivity and the means of distinguishing between pulses arising from single quanta and those of a more composite nature.

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¹ Garten, V. A., and Head, R. B., *Phil. Mag.*, **8**, 1793 (1963).

² Trautz, M., *Z. Phys. Chem.*, **53**, 1 (1905).

³ Garten, V. A., and Head, R. B. (unpublished results).

⁴ McKeown, E., and Waters, W. A., *Nature*, **203**, 1063 (1964).

⁵ Safonov, J. P., Shlyapintokh, V. Ya., and Entelis, S. G., *Nature*, **205**, 1203 (1965).

⁶ Tschugaeff, L., *Berichte*, **34**, 1820 (1901).

⁷ Belyaev, L. M., Nabatov, V. V., and Martyshev, Yu. N., *Soviet Physics—Crystallography*, **7**, No. 4, 464 (1963).