Technical Physics Letters, 2025, Vol. 51, No. 1

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Triboluminescence of chrysene during mechanical stirring

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Received June 28, 2024
Revised July 22, 2024
Accepted July 28, 2024

The luminescence of chrysene and its isomers (tetracene, triphenylene) during grinding of microcrystals was studied. Triboluminescence of chrysene was detected. Its spectrum coincides with the photoluminescence spectrum. It has been shown that in an atmosphere of air and argon there is no gas component of the triboluminescence spectrum (N_2 and Ar lines). A mechanism for triboluminescence of chrysene is proposed, similar to the electroluminescence of crystals, during the recombination of charge carriers in the electric field of the crystalline layer. It was revealed that the low quantum yield of photoluminescence in centrosymmetric crystals is one of the reasons for the lack of registration of their triboluminescence.

Keywords: triboluminescence, chrysene, quantum yield, photoluminescence.

DOI: 10.61011/TPL.2025.01.60125.20043

Owing to their flexibility, printability, and ease of production of components of the desired shape without additional energy expenditure, organic materials are used widely in various optical devices [1]. Polyaromatic hydrocarbons (PAHs) and metal complexes with aromatic ligands also hold promise for application as triboluminescent compositions for monitoring of mechanical failure of various structural objects [2,3]. Triboluminescence (TL) spectra, representing the glow of crystalline bodies in the course of their destruction, of these aromatic compounds are dominated by the „solid-state" component (i.e., intrinsic luminescence of a crystal). The intensity and position of the maximum in the luminescence spectra may be adjusted by varying the PAH structure complexity. It was demonstrated that the non-centrosymmetry of crystals [2,4], which facilitates efficient separation and recombination of charges during in the process of destruction of crystals, is one of the important criteria of emergence of TL. However, certain centrosymmetric crystals also feature TL [2]. Since most unsubstituted PAHs have a centrosymmetric crystal structure, their TL under impact excitation could not be detected in earlier studies [5]. However, we managed to record TL of a number of PAHs in [6]. The triboluminescence of tetracene remained elusive. Its weakness was attributed to the low quantum yield of photoluminescence (PL): $\varphi = 0.002$ [7]. In this context, comparative studies of TL of isomeric PAHs (chrysene, tetracene, and triphenylene) were carried out in order to identify the influence of both the crystal structure and the quantum yield of PL on TL.

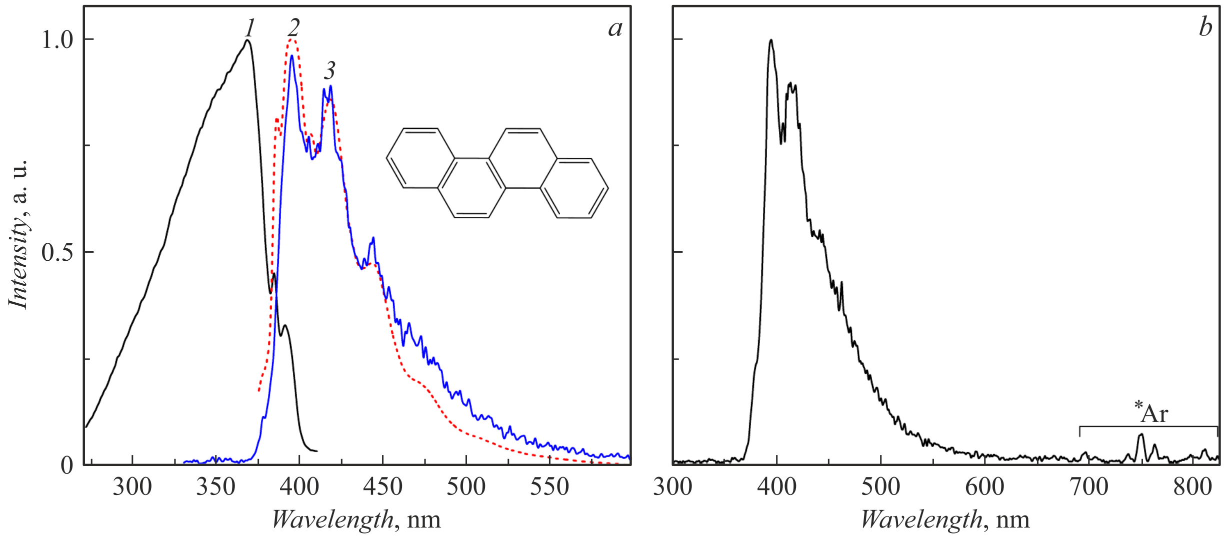
Tetracene, chrysene, and triphenylene (fluorescence grade, Sigma-Aldrich) were used without further purification. High-purity ethanol and benzene were used to prepare the solutions. The equipment and methods of excitation and recording of TL spectra were detailed in [6]. Photoluminescence excitation spectra, photo- and triboluminescence spectra, excited state lifetimes, and PL quantum yields were measured using Fluorolog-3 and Zolix OmniFluo-900 (with an integrating sphere for measuring the absolute quantum yield) spectrofluorimeters.

The spectral-luminescent characteristics of solid samples of the indicated PAHs and the same PAHs in solutions were examined (see the table). Fluorescence bands of tetracene, chrysene, and triphenylene molecules were observed in solutions (electronic transitions $S_1{-}S_0$ [8]); in the case of solid-state PAHs, a redshift of the PL band maxima was noted. The PL quantum yield values (φ) of solid samples and solutions of these PAHs also differ significantly (especially for tetracene microcrystals). The low quantum yield of tetracene PL (see the table) is apparently attributable to the fact that the probability of nonradiative relaxation of its PL increases sharply in the solid phase (due, among other factors, to the effect of increasing polarizability [7]).

We have already detected the TL of triphenylene in the process of grinding of its crystals with a stirrer [9]. Note that no luminescence was observed under impact excitation of solid-state PAHs [5]. At the same time, unlike centrosymmetric tetracene [11] and chrysene [12] crystals, triphenylene is chiral [10]. Accordingly, TL is excited more efficiently in non-centrosymmetric crystals. In addition, the lines of gas atoms are recorded in experiments with mechanical excitation of luminescence in an atmosphere of, e.g., argon or neon [9,13]. In this case, the mechanism of gas-phase luminescence is associated with discharge phenomena during mechanical destruction of solid substances. In contrast, the lack of emission of inert gas atoms [6] indicates that discharges on the surface of crystals do not occur in the process of TL of centrosymmetric PAHs. This suggests that the emission observed during TL is electroluminescent in nature (i.e., it arises in the electric field of a crystalline layer as a result of recombination of charge carriers and is not related to discharges between oppositely charged surfaces of cracks in crystals [5,14]). Compared

Luminescent characteristics of PAHs ($T = 297\,\mathrm{K}$)

PAH	$\lambda_{\max}$ (PL), nm	τ, ns	φ		TL
			Crystals	Solution (10^{-4} mol/l)	
Tetracene	570, 664, 725	4.6	0.008	0.14	–
Chrysene	395, 418, 444	22	0.41	0.14	+
Triphenylene	382, 408, 431, 457	7.2 (9%) 44.8 (91%)	0.33	0.13	+



a — PL excitation spectrum (*1*), PL spectrum (*2*), and TL spectrum (*3*) of chrysene. $\Delta\lambda = 0.5$ (*1*,*2*) and 5 nm (*3*). *b* — TL spectrum of chrysene in an argon atmosphere. $\Delta\lambda = 5$ nm.

to chiral triphenylene, centrosymmetric chrysene crystals are less susceptible to electrification under mechanical impact. As was demonstrated in [6,15,16], TL arises in this case as a result of emergence of local antisymmetry in a solid along the packing planes in crystals and, accordingly, separation of opposite charges in such areas in the course of deformation. However, TL of samarium(III) sulfate was used as an example in [17] to demonstrate that the reason for non-detection of TL is the low quantum yield of its PL. Indeed, TL was not detected in our experiments on mechanical grinding of tetracene microcrystals with a low PL quantum yield (see the table). On the contrary, when chrysene microcrystals with PL quantum yield $\varphi = 0.41$ were ground, fairly intense TL was recorded (see the figure).

Note that the lines of argon atoms in the spectrum are detected at the noise level in TL of chrysene in an Ar atmosphere (see panel *b* of the figure). This confirms that luminescence during mechanical grinding of centrosymmetric chrysene is excited as a result of occupation of luminescence centers (due to charge separation and recombination) in the electric field of PAH microcrystals with subsequent deexcitation in the solid phase.

Thus, a comparative study of luminescence during mechanical grinding of chrysene microcrystals and its isomers was carried out, and TL of chrysene was detected. It was demonstrated that the TL spectrum of chrysene matches its PL spectrum. It was established that one of the reasons for non-detection of triboluminescence in centrosymmetric crystals is the low PL quantum yield. The lack of gas-phase emission in TL of chrysene is indicative of an electroluminescent mechanism of emission of chrysene molecules in the electric field due to charge separation and recombination in a crystalline layer.

Funding

This study was supported by a grant from the Russian Science Foundation (project No. 23-12-20002, https://rscf.ru/project/23-12-20002/).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin