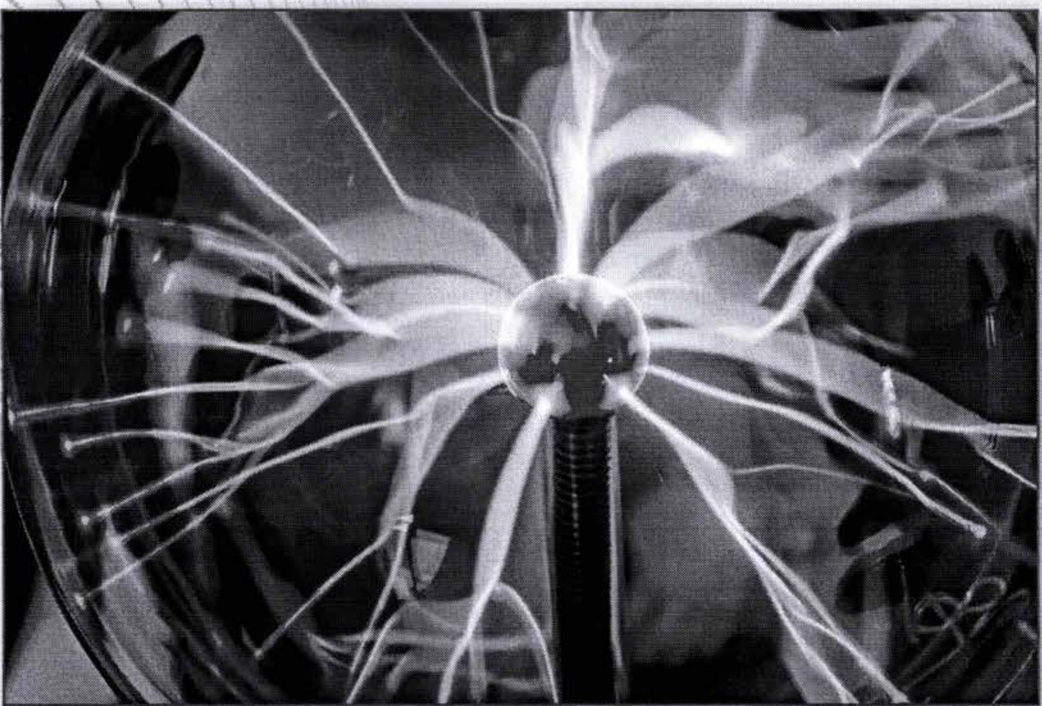
BORATE PHOSPHORS

Processing to Applications



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9 Borate Phosphor: Mechanoluminescence and Lyoluminescence Phosphors

V. R. Raikwar

9.1 HISTORICAL BACKGROUND

9.1.1 MECHANOLUMINESCENCE (ML)

Luminescence is a phenomenon of light emission by certain materials caused by some external parameters such as chemical reaction, incident light, applied pressure, force, temperature or electric current. The type of luminescence induced by any mechanical action on solids is known as mechanoluminescence. This mechanical action can be elastic deformation, plastic deformation and fracture of solids. The light emissions induced by these actions are respectively called elastico ML (EML), plastico ML (PML) and fracto ML (FML) [1]. Nearly 50% of all inorganic salts and organic molecular solids show FML; however, only a few solids exhibit EML and PML. Although the phenomenon of ML is known for a long time, up to the end of 20th century no remarkable practical application of mechanoluminescent materials could be made because of the low ML intensity and lack of reproducibility. In earlier days, ML was known as triboluminescence [2]; nowadays it corresponds to luminescence due to the contact of two dissimilar materials. Mechanoluminescence was a known phenomenon as light was generated from striking stone or quartz. But, the first discovery of ML was reported by Francis Bacon (1605) [3]. It was mentioned in his work on "The advancement of learning, divine and human", the scraping of the hard sugar with a knife; "it is not the property of fire alone to give light...loaf-sugar in scraping or breaking". In 1664, Robert Boyle reported that a particular diamond, when pressed upon with a steel bodkin, produced a short-lived bright glow [4]. For several centuries, the phenomenon of light emission associated with rock breaking in mines and during earthquakes has been reported. The sugarcane production was taken by the people worldwide from hundreds of years. In earlier days, a sugar product was very hard. The process to separate it from the container might have produced a tinkling spark, which is nothing but ML. This was a period that was before the invention of photomultiplier tube (PMT), where most observations were carried out with the observer's naked eyes who might be efficiently trained for taking observations in the dark. The observations and conclusions which were in 17th-century and 18th-century research articles mostly included a number of minerals and pottery materials, sugar, rock salt, agate and jasper. The workers in this field concluded that these materials were capable of holding light that they receive and release it when fractured. By the end of 1920, there were nearly 500 known ML materials. Longchambon recorded the ML spectra of sugar and other crystals for the first time [5]. In 1925, Longchambon in his pioneer work on organic compounds, reported ML in 70% of 305 aromatic compounds and in 20% of 90 alkaloids. Longchambon suggested that ML emission arises from the dielectric breakdown of surrounding gases (although the spectra may contain additional lines if the materials can be excited to photoluminescence by ultraviolet in the gas discharge) [5]. Bhatnagar et al. [6] reported the ML of saccharin crystals. Inoue et al. [7] recorded the ML spectra of sugar and tartaric acid crystals. Carriere, in 1946 [8], studied the ML produced during the stretching of rubbers.

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Hoff and Boord [9] found that cis-4-octane shows ML, while trans-4-octane does not when they are both subjected to rapid cooling by immersing a test tube containing these compounds in liquid air. The ML of II–VI semiconductors, particularly ZnS:Mn, coloured alkali halide crystals and Si were also reported during the first generation of Jenny reported triboluminescence in semiconductors [10]. The leading workers during the first generation of ML were: Tschugaeff [11], Trautz [12], Garnez [13], Longchambon [5] and Wick [14]. The PMTs were used for ML studies after 1950. As per the literature survey, very few reported ML research in the 17th, 18th and 19th centuries. About this important phenomenon of ML, the workers showed interest in 20th century and with the advancement of technology and possibility of using ML in applications in various fields of life, published around 372 research papers. In the 21st century, more than 500 research papers have been published to date. That shows the importance of ML in myriad applications from sensing to displays [15]. Many materials were discovered, which depicted ML and they were tried and tested in various applications. ML materials can be conductors, semiconductors and insulators. Several materials have been discovered or synthesised, after the development of photomultiplier tube in the mid-20th century, with one-half of inorganic crystals and almost one-third of organic compounds showed ML [16]. In the last three decades (mostly in 1990s), a range of materials have been discovered that emit an intense and repeatable EML during their elastic deformation without any destruction [17–33].

Major applications of ML are listed here: as a stress sensor, "the real-time visualization of the stress distribution in solids", for the visualization of internal defects in a pipe, in the analysis of artificial legs, for the "real-time visualization of quasidynamic crack-propagation" in solids, to determine crack-growth resistance and other parameters of crack propagation, as a novel "ML-driven solar cell" system, for the "real-time visualization of the stress field near the tip of a crack", as a source of ML light, in the determination of laser and ultrasonic powers, in writing secret messages, as a "EML-based safety-management monitoring system", in the non-destructive testing of materials, in radiation dosimetry, in mechanoluminescence damage sensors, in fracture sensors, in impact sensors, in pigments and paints for security printing and fracture studies, in a "fuse-system for army warheads", in the evaluation of the design of a milling machine, in "online monitoring of grinding processes", as a potential earthquake indicator, in the determination of several parameters of solids, and a triboluminescence X-ray unit has been designed in which X-ray imaging can be performed [34]. A new era of application includes artificial tooth, artificial skin, encrypted communication in a defence system, information storage, patient care and health monitoring [35].

The progress in mechanoluminescence has been relatively slow because of multiple reasons, such as low emission of light by the crystals in the aggregate state and absence of proper explanation of an intrinsic mechanism of this special type of light emission. One of the possible reasons of light emission in ML can be the electrons (along with ions and neutral species) were emitted from the surface of crystals when the ML crystals were fractured by external force stimulus. Subsequently, the luminescent centres could be excited by electron bombardment to yield mechanoluminescence.

9.1.2 Lyoluminescence (LL)

Lyoluminescence is a form of chemiluminescence in which the emission of light occurs when a pre-irradiated solid is dissolved into a specific liquid solvent. In general, lyoluminescence effect is observed, when solid samples are irradiated heavily by ionizing radiation and later they are dissolved in water. The total amount of light emitted by the material increases proportionally with the total radiation dose received by the material up to a certain level called the saturation value. "Many gamma-irradiated substances are known to be lyoluminescent; these include spices, powdered milk, soups, cotton and paper". Several organic substances and halide crystals produce a glow when lengthy exposure to high-energy radiation like X- rays, γ-rays, etc. is followed by immersion in a liquid solvent. This glow is called the "lyoluminescent glow". The first reported phenomenon of lyoluminescence was by Wiedemann and Schmidt, who observed lyoluminescence in glucose [36].

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