History of Luminescence from Ancient to Modern Times

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Abstract

Luminescent phenomena have fascinated mankind since the earliest times. The light from the aurora borealis, glow worms, luminescent wood, rotting fish and meat are all examples of naturally occurring luminescence. E. Newton Harvey's 770 page volume "A History of Luminescence: From the Earliest Times until 1900" is a classic which narrates interesting stories from ancient cultures to modern times. The earliest written account of a solid state luminescent material comes from a Chinese text published in the Song dynasty (960–1279 A.D.). The Buddhist sacred jewel, called "hashi-no-tama" in Japan, is alleged to be self-luminous and to shed a brilliant light on its surroundings. In the Svetasvatara Upanishad, probably recorded at some time before the sixth century BC, we find a mention of fire-flies as one of the manifestations of Brahma.

Knowledge of luminescence in ancient India must not be concluded without mention of the luminous cobra-stone of India and Ceylon. Prof. Hensoldt caught fifty cobras in Ceylon without finding a stone. However, evidence of cold light was first reported by the Greeks. Aristotle knew of the luminescence of dead fish and flesh and also of fungi.

Robert Boyle reported to the Royal Society of London on 28 October, 1663 his observation: "Eleventhly, I also brought it some kind of glimmering light by taking it (natural diamond) into bed with me and holding it a good while upon a warm part of my naked body." Robert Boyle's principal luminescence studies began with diamonds, extended to shining wood, fish, and flesh, and ended with the element phosphorus. Boyle was probably the first to describe phosphorescence, thermoluminescence, electroluminescence, and triboluminescence in a single substance, a diamond.

The word luminescence was first used by a German physicist, Eilhardt Wiedemann, in 1888. In Latin 'Lumen' means 'light'. The materials exhibiting this phenomenon are known as 'Luminescent materials' or 'Phosphors' meaning 'light bearer' in Greek. The term phosphor was coined in 17th century by an Italian alchemist named Vincentinus Casciarolo of Bologona. Eilhard Wiedemann (1888) was the first to classify different classes of phosphors according to the type of excitation. Wiedemann and Schmidt (1895) were probably the first to report the thermoluminescence (TL) of at least two of the modern materials widely used, viz. fluorite and CaF_2:Mn. Oldenberg (1705) described the phenomenon of TL in the mineral, fluorite. But the real boost to research was given by the pioneering work of Farrington Daniels and his group (1940-50) at the University of Wisconsin (USA).

Bhuwan Bhatt has traced the history of "Luminescence Dosimetry Work in India" during one of NCLA Conferences. It also highlights the pioneering work in the field of thermoluminescence in the early 1950's by Prof. S.N. Bose and his group at Khaira Laboratory, Calcutta University and by Prof. H.N Bose and his group at IIT, Kharagpur. The present review will also focus on TL applications in Indian context.

Keywords:History of luminescence, Persistent luminescence, Luminescence dosimetry, Indian scenario

1. LUMINESCENCE PHENOMENON IN ANTIQUITY

Luminescent phenomena have fascinated mankind since the earliest times. The light from the aurora borealis, glow worms, luminescent wood, rotting fish and meat are all examples of naturally occurring luminescence. It is unfortunate that primitive man has left no written record of his observations but only crude pictographs of the more striking objects of his environment. We cannot but believe that the Neanderthaler knew of many luminescences—the aurora borealis, glow worms, or luminous wood. Perhaps he had seen the glow of luminous bacteria growing on meat or fish. Ever on the alert, a new sight at night must inevitably have caught his attention and directed all faculties into further exploration of the phenomenon. The contrast of light and darkness is so striking that many races have adopted

some story of the origin of light in the history of creation. Such stories are found in Bible, Vedas and Sri Guru Grantha.

***Mythical Tales from Ancient India*:** Occasional references to the firefly and glow worm are to be found in the holy writings of ancient India, the Vedas, and in the Indian epic poems. In the Svetasvatara Upanishad, probably recorded at some time before the sixth century BC, we find a mention of fire-flies as one of the manifestations of Brahma.

Fog, smoke, sun, fire, wind,
Fire-flies, lightning, a crystal, a moon—
These are the preliminary appearances,
Which produce the manifestation of Brahma in Yoga

The Sanskrit word, *khadyota*, meaning firefly or glowworm, occurs a number of times. In one of the books, the Anugita, we find, "As those who have eyes see a glow-worm disappear here and there in darkness, so likewise do those who have eyes of knowledge. Such a soul the Siddhas see with a divine eye, departing [from the body] or coming to the birth or entering into a womb."In another book of the Mahabharata, the Vana Parva there is the story of Saryati and Sukanya, who mistook Cyavana's eyes for glowworms and a description of "the Lord, like a fire-fly at night time during the rainy season. ..." Finally, at a later period, in the Sarvadarsana Sangraha, a treatise dealing with various schools of philosophy in India, by the celebrated scholar of the fourteenth century a. d., Madhava Acharya, we find the expression "many firefly-like pleasures." This is apparently a comparison of pleasures to fireflies, both of which are transient.

Knowledge of luminescence in ancient India must not be concluded without mention of the luminous cobra-stone of India and Ceylon, although the date of the legend is unknown, and the story sounds highly improbable but completely fascinating. The best account has been related by Professor H. Hensoldt, who obtained one of the stones, called "Naja-Kallu," during a stay at Point de Galle, Ceylon. It is said that about one cobra in twenty carries around in its mouth a small luminous stone that it places in the grass at night to attract fireflies, which the cobra then proceeds to eat. Hensoldt caught fifty cobras without finding a stone but one night in the field with a Tamil coolie he saw a cobra resting by what he thought was a luminous spot. He wished to kill the cobra at once but the Tamil implored him not to because the snake is alleged to be particularly dangerous when watching the Naja-Kallu. However, on the next night the Tamil saw the cobra in the same place and obtained the stone by climbing a tree and throwing ashes over it. The ashes were collected and sifted after the snake had left. The stone was "a semi-transparent water worn pebble of yellowish color, about the size of a small pea, which in the dark, especially when previously warmed, emitted a greenish phosphorescent light." Chemically it was a fluorite, some varieties of which (chlorophane) are said to be sufficiently phosphorescent to shine all night long after exposure to the sun's rays. The pebble no doubt existed but the part played by the cobra is reminiscent of another more recent story regarding the Indian baya-bird or bottle-bird (Ploceus baya) , which is alleged to stick fireflies in the mud-pellets of its bottle-shaped nest in order to scare marauding animals from the eggs and young birds [1].

Stories from China and Japan: Both in China and in Japan there are many ancient stories of mysterious lights or fires seen over water, fields, or mountains, ascribed to dragons or caused by the gods. Sacred trees often emitted light. History of Tsin Dynasty describes a poor but diligent student who could not afford to buy oil, and, because of his poverty collected fireflies

and used them to pursue his studies in the evening. A painting of this quaint scene has been made by the Japanese artist, Ka-no Tan-yu (1602-1650). In Japan firefly collecting very early became a popular pastime, like the observation of autumn coloring. The firefly festival on the Ugi River was an important event in the neighborhood of Kyoto. The Buddhist sacred jewel, one of the seven treasures, called "hashi-no-tama" in Japan, is alleged to be self-luminous and to shed a brilliant light on its surroundings, a symbol of the enlightenment of Buddha's teaching.

There is a story concerning an interesting painting which was presented to the second emperor of the Sung dynasty. On the painting was a cow which appeared during the day as eating grass outside a pen but at night as resting in it. When it was shown to the court, none of the officials could offer an interpretation. The monk Tsan-ning, however, said that the ink [or color] which was shown only in the night was mixed with drops from a [special kind of] pearl shell and the ink [or color] which was shown only during the day was made by grinding a rock which had fallen from a volcano to the seashore [1].

Observations by the Greek Philosophers: The early Greeks observed the aurora borealis and there is somewhat uncertain indication of knowledge of inorganic luminescence. A passage of Euripides (480-406 b.c.) in his tragedy Bacchae described how the Bacchantes "carried fire on their hair without being hurt." The "fire" has been interpreted by J. P. Jorrissen (1948) as a phosphorescent material, but the evidence is far from convincing. It is with Aristotle (384-322 b. c.) that a fairly wide knowledge of cold light is revealed. Aristotle knew of the luminescence of dead fish and flesh and also of fungi. The evidence on which this is based comes from a discussion of light and color in De Anima (Book II, Chap. 7).

That there is light in the eyes of fishes, and in eyes in general, has been noted by many subsequent writers. Such a light could be merely reflection of external light, as from the eye of a cat or the eye of a man. Homer, in describing Achilles rushing into battle, wrote:

Grief and revenge his furious heart inspire
His glowing eyeballs roll with living fire.

Human experience also shows that pressure on the eyeball or a blow to the eye gives the sensation of light. This is that, when the eye is pressed or moved, fire appears to flash from it. This naturally takes place in darkness, or when the eyelids are closed, for then too, darkness is produced. There is also a passage in De Mundo which might refer to sea phosphorescence. Speaking of the characteristics of the ocean, Aristotle wrote: "Often too, there are exhalations of fire from the sea."

Many other classic derivations appear in the nomenclature of luminescence or of luminous animals in Greek literature—Pyrophorus, fire-bearing, from the Greek "pyr," fire, and "phero," to bear; also horn, the Greek "phos," light, there is phosphor, light giving; from the Latin, "lux, lucis," light, comes lucifer, light bearing. Greeks called the morning star, "Phosphoros," Romans called it "Lucifer." There is satisfaction in the fact that the words "phosphorescence" and "luciferin" have such poetic connotations. During the Dark and Middle Ages, no new discovery or new phenomenon important for the history of luminescence had been made [1].

2. LUMINESCENCE PHENOMENON IN HISTORICAL TIMES

The first artificial phosphor described in Western literature dates from 1603. Then, the Italian shoemaker and alchemist Vincenzo Cascariolo used the natural mineral barite (BaSO4), found near Bologna, in an effort to create gold. After heating the ground stone under reducing condition he–obviously – did not obtain gold, but a persistent luminescent material. This so-called Bolognian stone became famous and a subject of study and admiration for decades to come. It is not clear which dopant or dopants were actually responsible for the persistent luminescence, but the host material definitely was BaS. While not made intentionally but by serendipity, BaS thus is the first sulfide phosphor ever synthesized [2].

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In the following centuries, many scientists synthesized and investigated luminescent materials, but it was too early for a systematic study. However, the synthesis of CaS as a phosphor in 1700 by Friedrich Hoffmann and of SrS in 1817 by J. F. John are worth mentioning. Curiously enough, the luminescent properties of ZnS, which was going to become one of the most important luminescent hosts in the 20th century, were not recognized until 1866, when the so-called Sidot blend (hexagonal ZnS) was developed by Theodor Sidot [2, 3].

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When Wiedemann (1888) recognized luminescence as the antithesis to incandescence, he also classified luminescences into six kinds according to the method of excitation. No better basis of classification is available today. He recognized photoluminescence, thermoluminescence, electroluminescence, crystalloluminescence, triboluminescence, and chemiluminescence. The designations are obvious, characterized by the prefix. Photoluminescence of solids is excited by light itself and is subdivided into fluorescence and phosphorescence. Thermoluminescence is light from gentle heating. Electroluminescence appears from gases in electrical fields; crystalloluminescence and triboluminescence occur when solutions crystallize or when crystals are crushed or broken, and chemiluminescence may appear during chemical reaction. All bioluminescences are examples of chemiluminescence. Although present ideas of the mechanism by which light is emitted have changed and many more types of luminescence have been recognized, the new varieties all belong to the six categories of Wiedemann [1]. In Germany, between late 19th and early 20th centuries, Philip E.A. Lenard and colleagues worked on phosphors. They used different rare earth ions in addition to heavy metal ions as luminescent ions in different host materials [5].

3. Luminescence Scenario in India

Investigations on Luminescence in India [6] seem to have started around 1920; the main centres were Bangalore, Calcutta and Dacca, and 21 research papers were contributed during national and international journals from these centres during 1923-1940. Studies on luminescence of dye-stuffs, organic compounds, rare earth compounds and natural minerals like ruby, diamond and corundum, etc. exposed to ultra-violet and visible radiations were reported in these papers. After 1940, the studies on the luminescent properties of phosphors excited by X-rays, UV, cathode rays and ionising radiations were undertaken by Indian scientists. During 1970s, BARC scientists made notable contributions to the field of thermoluminescence dosimetry and PRL group in the area of archaeological dating. We can claim to have made substantial contribution of standard quality by our scientists in the field of luminescence during the last four decades.

BC Bhatt has reviewed the Indian scenario in the field of Luminescence Dosimetry in his recent review paper [7]. The author reports: "Last five decades have witnessed tremendous progress in the field of luminescence dosimetry in India. During this period development of new and sensitive phosphors and dosimetric techniques was reported. Applications of these phosphors were exploited in different fields, such as personnel and environmental monitoring, medical dosimetry, high dose dosimetry, accident and retrospective dosimetry, and archaeological/ geological dating. Commensurate with these developments, progress in the related readout instrumentation also took place. Along with these developments, the ongoing R&D work by different research groups in the field of dosimetry helped in putting the dosimetry programmes, including the nationwide personnel and environmental monitoring programme, on a firm footing."

HS Virk has highlighted Indian scientific contributions to the field of Luminescence in his latest volume [8], "Luminescence Related Phenomena and their Applications" covering Luminescence Dosimetry (N. Chahan); Thermoluminescene (KVR Murthy); TLD Materials (SK Omanwar et al.); Elastico-Mechanoluminescence of TL Crystals (BP Chandra et al.); TL Phosphors for Radiation Dosimetry (Bhatt & Kulkarni); Retrospective Accident Dosimetry (AS Pradhan et al.) and ZnS:Cu/ZnS Nanophosphors (AS Pannu & M. Sharma).

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