Materials Horizons: From Nature to Nanomaterials

M. K. Jayaraj *Editor*

Nanostructured Metal Oxides and Devices

Optical and Electrical Properties

Springer

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Dr. M. K. Jayaraj is currently a Professor at the Department of Physics, Cochin University of Science and Technology (CUSAT), India. He earned his master's and Ph.D. from CUSAT, and completed his postdoctoral research at eminent institutions in India, Italy, France, Japan, and the USA. He is the founder director of the Centre of Excellence in Advanced materials, CUSAT. He is also the mentor of 'Delgado Coating & Technology Solutions Private Limited'. Dr. Jayaraj is a pioneer in the field of thin-film and nanocomposite devices, including sensors/detectors and energy converters, and transparent conductors for photovoltaics. He has more than 180 research publications, several edited books and book chapters, and patents to his credit. In addition, he was honored with the MRSI Medal 2019, conferred by the Materials Research Society of India.

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Chapter 1
Oxide Luminescent Materials

K. Mini Krishna and M. K. Jayaraj

1 Introduction

The emission of light has been a source of fascination, philosophical speculation and scientific investigation since time immemorial. Light emission by matter falls into the two basic categories of **incandescence and luminescence**. Bodies that emit light solely because of their temperature are defined as incandescent. Luminescence refers to light emissions deriving their excitation energy from nonthermal sources.

In 1888, Wiedemann devised the term 'luminescence' from the Latin word meaning 'weak glow' [1]. Vavilov defined 'luminescence' as the emission of light produced by a material over and above its thermal radiation. It generally befalls when an excited electronic state relaxes to a lower energy state, the lifetime of which is much larger than that of light vibrations (10^{-10} s). Luminescence, depending on the mode of excitation, is mirrored in terms such as photo-, radio-, bio-, electro-, chemi-, thermo-, sono- or triboluminescence. In practice, the excitation is most probably via X-rays, cathode rays or UV emission of a gas discharge. Hitherto, the position of the band in a spectral output is seldom dependent on the mode of excitation but on the interlevel spacing. Numerous radiationless processes, arising from interactions with the lattice or a transfer of energy between ions, always compete in reducing the luminescent radiation.

Two other terms quite often used to classify luminescent materials are **fluorescence** ($\tau < 10$ ms) and **phosphorescence** ($\tau > 0.1$ s). The decay law of luminescence is exponential in fluorescence and hyperbolic or still more complicated for phosphorescence. With the advent of quantum theory, they were defined via the emission-based

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quantum mechanical mechanism for the orbital angular momentum multiplicity of the emitted electron. Fluorescence was henceforth defined as a photoluminescent emission that arises from the singlet electronic state and phosphorescence as that originating from the triplet electronic state. The latter, being 10–10,000 times longer than fluorescence, appear to emit much beyond the removal of the excitation radiation.

Delayed fluorescence is yet another singlet state emission with a much longer lifetime than normal. In this rare phenomenon, the electron responsible for the emission crosses over from the singlet state to the triplet state, but eventually returns to the singlet state before emission.

2 Photoluminescence (PL)

The Italian alchemist, Vincenzo Cascariolo, was the first to observe the phenomenon of 'photoluminescence' from the mineral barite on exposure to sunlight. A material photoluminesces when excited by photons (most commonly in the wavelength ranges of infrared, ultraviolet or visible light) with a spectrum broad enough to overlap the ion absorption bands. The fundamental processes involved include excitation, emission together with radiationless transitions. The emission and absorption bands overlap significantly in case of a weak ion–lattice interaction, as is for the f electrons in rare earth (RE^{3+}) ions. A stronger interaction, as the one observed in transition metal ions, causes a redshift in the emission band relative to the absorption band, as explicated by Stokes law [2]. If the system is conducive to radiationless de-excitations, it exhibits an increase in temperature along with a reduced luminescent output.

The phenomenon of photoluminescence is pictorially illustrated in Fig. 1. The configuration curves [3] convey the energy versus interionic distance relation of

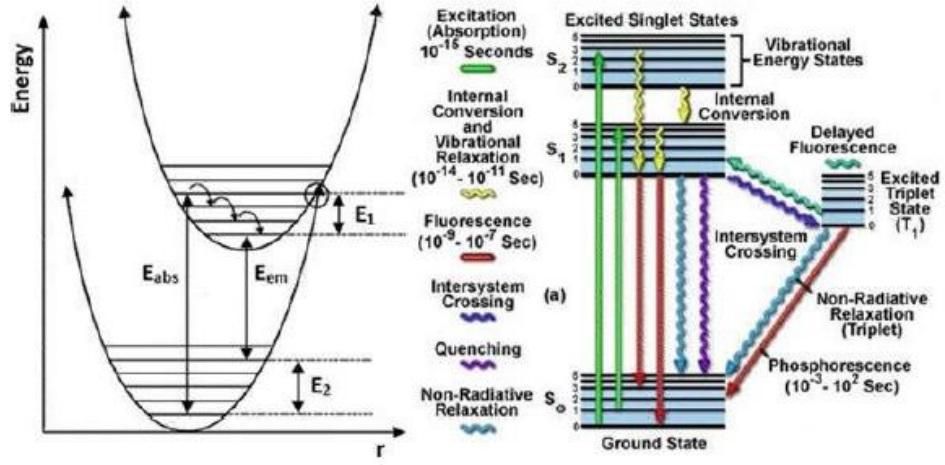

Fig. 1 Configuration coordinate diagram (left) and Jablonski diagram (right)