VIVEKANAND COLLEGE, KOLHAOUR (AUTONOMOUS)

LECTURE ON

LUMINESCENCE

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Luminescence

is the emission of light by a substance caused by physical or chemical means. There are several ways to cause luminescence:

Photoluminescence - caused by a beam of photons (light),

Cathodoluminescence - excited by an electron beam (as opposed to a beam of photons).

Thermoluminescence - stimulated by the application of heat, to temperatures below those that result in incandescence.

Chemiluminescence - chemical energy resulting from a chemical reaction.

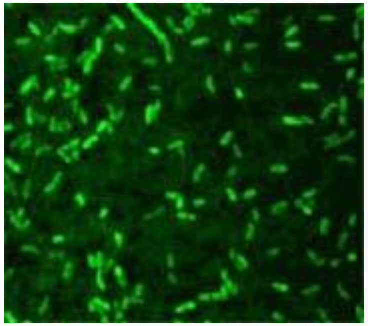
Bioluminescence – a biochemical enzyme-driven reaction with a light producing step.

Triboluminescence - triggered by mechanical energy from a mechanical action such as friction

Resolves such an excited electronic state due to chemical reaction this we term chemiluminescence, or in living organisms, bioluminescence. The most familiar terrestrial example of this "cold light" takes place in the common firefly.

. Bioluminescence is also found in some fungi and earthworms. It is most common, however, in the oceans, where many organisms, from fish to worms living at great depths, have glowing organs.

Radioluminescence is luminescence caused by nuclear radiation. Older glow-in-the-dark clock dials often used a paint with a radioactive material (typically a radium compound) and a radioluminescent material. The term may be used to refer to luminescence caused by X-rays, also called photoluminescence.

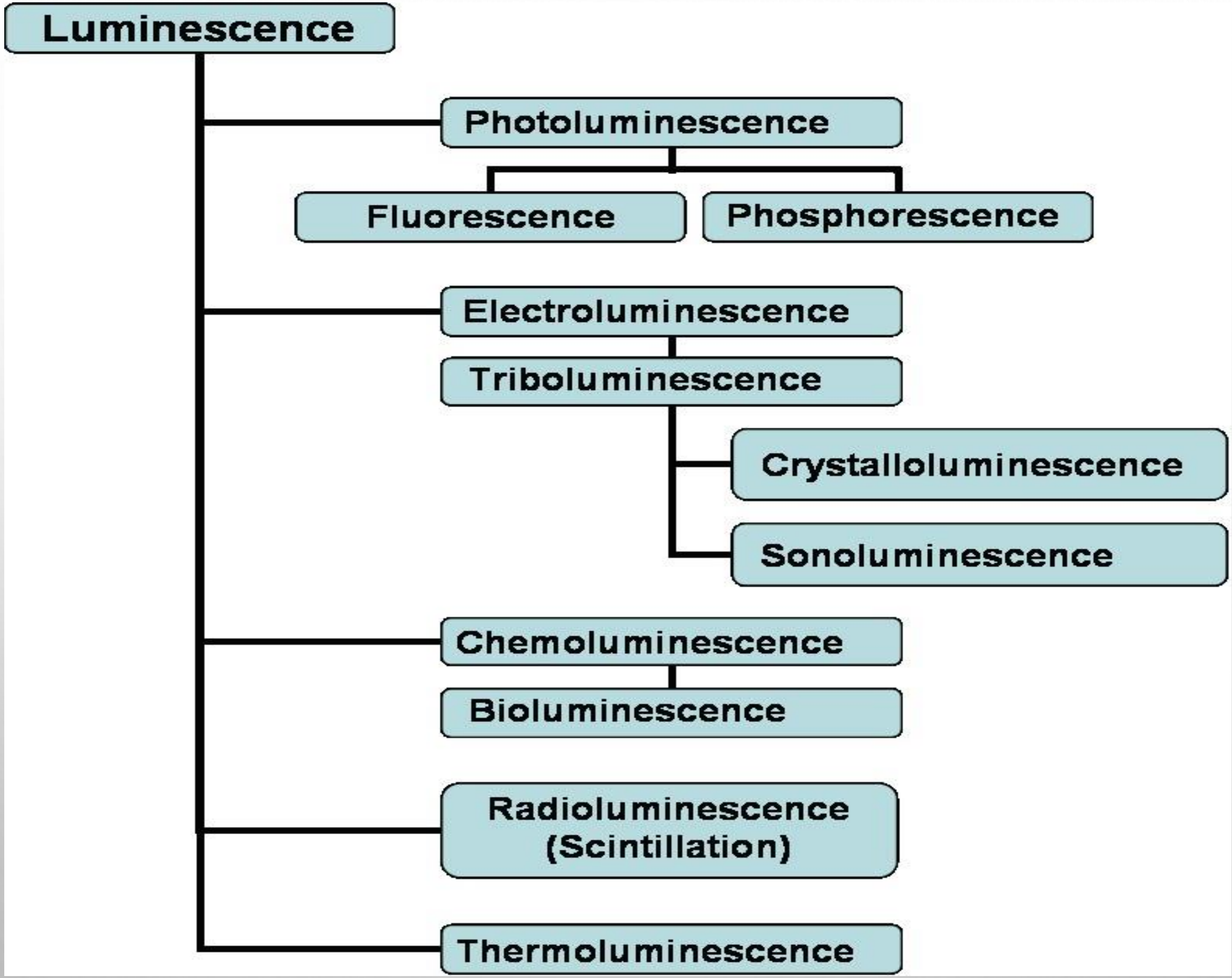


A Classification of luminescence,

	Type	Basis of light emission	Example
A.	Associated with heating (distinct from incandescence)		
1.	Candoluminescence	luminescence of incandescent solids emitting light at shorter wavelengths than expected	heat ZnO
2.	Pyroluminescence	luminescence of metal atoms in flames	yellow Na flame
3.	Thermoluminescence	luminescence of solids and crystals on mild heating (*i.e.*, well below that necessary to produce incandescence)	heat diamond
B.	Associated with prior radiation (fluorescence – short lived; phosphorescence – long lived)		
1.	Photoluminescence	irradiation by UV or by visible light	Bologna stone ($BaSO_4$)
2.	Cathodoluminescence	irradiation by b particles (electrons)	television screen
3.	Anodoluminescence	irradiation by a particles (the nuclei)	zinc sulphide phosphor
4.	Radioluminescence	irradiation by g or X-rays	luminous paint
C.	Associated with electrical phenomena		
1.	Electroluminescence and piezoluminescence	luminescence associated with electric discharges and fields	fluorescent strip light
2.	Galvanoluminescence	luminescence during electrolysis	electrolysis of NaBr
3.	Sonoluminescence	luminescence from intense sound waves in solution	ultrasonic probe in pure glycerol

Table A2. A Classification of luminescence, based on E.N. Harvey.

D.	Associated with structural rearrangements in solids		
1.	Triboluminescence	luminescence on shaking, rubbing, or crushing	gentle agitation of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$
2.	Crystallo(= tribo–) luminescence	luminescence on crystallisation	HCl or ethanol addition to saturated alkali metal halide solutions (NaCl, KCl)
3.	Lyo(= tribo–)luminescence	luminescence on dissolving crystals	LiCl or KCl coloured by irradiation by cathode rays
E.	Associated with chemical reactions		
1.	Chemiluminescence (oxyluminescence)	chemical reaction	luminol + H_2O_2 and peroxidase
2.	Bioluminescence (organoluminescence)	luminous organisms	O_2 + luciferin–luciferase from the sea firefly (*Vagula*)



Luminescence
Photoluminescence
Fluorescence
Phosphorescence
Electroluminescence
Triboluminescence
Crystalloluminescence
Sonoluminescence
Chemoluminescence
Bioluminescence
Radioluminescence
(Scintillation)
Thermoluminescence

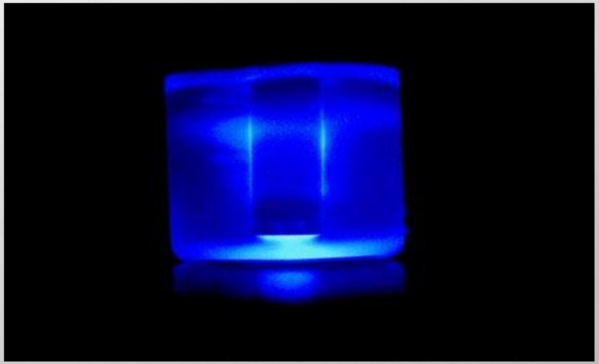
Optically stimulated luminescence is phosphorescence triggered by visible light or infrared. In this case red or infrared light is only a trigger for release of previously stored energy.

Fractoluminescence is the emission of light from the fracture of a crystal.

Fractoluminescence is a subset of the more broad category of mechanoluminescence which is light emission resulting from any mechanical action on a solid

Galvanoluminescence Is the emission of light produced by the passage of an electrical current through an appropriate electrolyte in which an electrode, made of certain metals such as aluminum or tantalum, has been immersed. An example being the electrolysis of sodium bromide (NaBr).

Sonoluminescence is the emission of short bursts of light from imploding bubbles in a liquid when excited by sound.



Bioluminescence

Bioluminescence is the production and emission of light by a living organism as the result of a chemical reaction during which chemical energy is converted to light energy. The name originates from the Greek *bios* for "living" and the Latin *lumen* "light". Bioluminescence may be generated by symbiotic organisms carried within a larger organism. It is generated by an enzyme-catalyzed chemoluminescence reaction, wherein the pigment luciferin is oxidised by the enzyme luciferase. Adenosine triphosphate (ATP) is involved in most instances. The chemical reaction can occur either within or outside of the cell. In bacteria, the expression of genes related to bioluminescence is controlled by an operon called the lux operon.

Artistic rendering of bioluminescent Antarctic krill (watercolor by Uwe Kils)

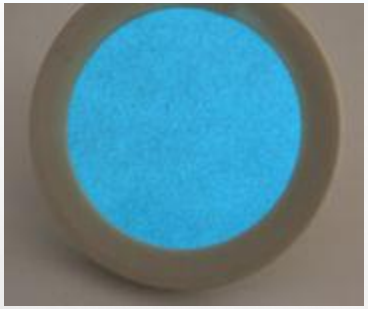
Light is a form of energy. To create light, another form of energy must be supplied. There are two common ways for this to occur, incandescence and luminescence.

Incandescence is light from heat energy. If you heat something to a high enough temperature, it will begin to glow. When an electric stove's heater or metal in a flame begin to glow "red hot", that is incandescence. When the tungsten filament of an ordinary incandescent light bulb is heated still hotter, it glows brightly "white hot" by the same means. The sun and stars glow by incandescence.

Luminescence is "cold light", light from other sources of energy, which can take place at normal and lower temperatures. In luminescence, some energy source kicks an electron of an atom out of its "ground" (lowest-energy) state into an "excited" (higher-energy) state; then the electron gives back the energy in the form of light so it can fall back to its "ground" state.

If you lift a rock, your muscles are supplying energy to raise the rock to a higher-energy position. If you then drop the rock, the energy you supplied is released, some of it in the form of sound, as it drops back to its original low-energy position. It is somewhat the same with luminescence, with electrical attraction replacing gravity, the atomic nucleus replacing the earth, an electron replacing the rock, and light replacing the sound.

Electroluminescence (EL) is an optical phenomenon and electrical phenomenon where a material emits light in response to an electric current passed through it, or to a strong electric field. This is distinct to light emission resulting from heat (incandescence) or from the action of chemicals (chemoluminescence).



An electroluminescent nightlight in operation (uses 0.08W at 230V, and dates from 1960; lit diameter 59 mm)

EL T-Shirt

EL Advertising Panel

Fluorescence

Fluorescence induced by exposure to ultraviolet light in vials containing various sized Cadmium selenide (CdSe) quantum dots.

Fluorescence is a luminescence that is mostly found as an optical phenomenon in cold bodies, in which the molecular absorption of a photon triggers the emission of another photon with a longer wavelength. The energy difference between the absorbed and emitted photons ends up as molecular vibrations or heat. Usually the absorbed photon is in the ultraviolet range, and the emitted light is in the visible range, but this depends on the absorbance curve and Stokes shift of the particular fluorophore. Fluorescence is named after the mineral fluorite, composed of calcium fluoride, which exhibits this phenomenon.

Chemical Process

Fluorescence occurs when a molecule or quantum dot relaxes to its ground state after being electronically excited.

Excitation:

Chemical Process

Fluorescence occurs when a molecule or quantum dot relaxes to its ground state after being electronically excited.

Excitation:

$$S_0 + h\nu \rightarrow S_1$$

Fluorescence (emission):

$$S_1 \rightarrow S_0 + h\nu$$

*h*ν is a generic term for photon energy where: h = Planck's constant and ν = frequency of light. (The specific frequencies of exciting and emitted light are dependent on the particular system.)

State S_0 is called the ground state of the fluorophore (fluorescent molecule) and S_1 is its first (electronically) excited state.

A molecule in its excited state, S1, can relax by various competing pathways. It can undergo 'non-radiative relaxation' in which the excitation energy is dissipated as heat (vibrations) to the solvent. Excited organic molecules can also relax via conversion to a triplet state which may subsequently relax via phosphorescence or by a secondary non-radiative relaxation step.

Relaxation of an S1 state can also occur through interaction with a second molecule through fluorescence quenching. Molecular oxygen (O2) is an extremely efficient quencher of fluorescence because of its unusual triplet ground state. Molecules that are excited through light absorption or via a different process (e.g. as the product of a reaction) can transfer energy to a second 'sensitizer' molecule, which is converted to its excited state and can then fluoresce. This process is used in lightsticks.

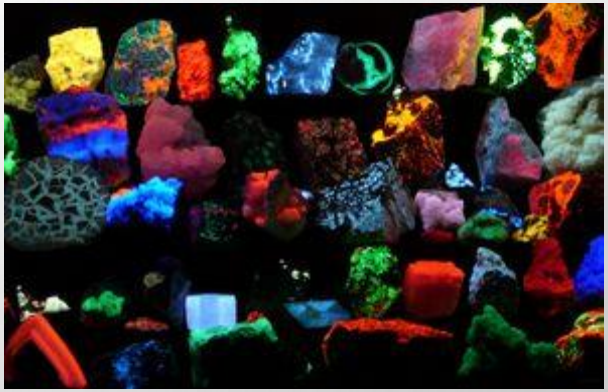
Fluorescence Quantum Yield

The fluorescence quantum yield gives the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\#photons\ emitted}{\#photons\ absorbed}$$

The maximum fluorescence quantum yield is 1.0 (100%); every photon absorbed results in a photon emitted. Compounds with quantum yields of 0.10 are still considered quite fluorescent. Another way to define the quantum yield of fluorescence, is by the rates excited state decay:

$$\frac{k_f}{\sum_i k_i} \qquad [S_1]$$



Fluorescent Minerals

where k_f is the rate of spontaneous emission of radiation and

$$k_i$$

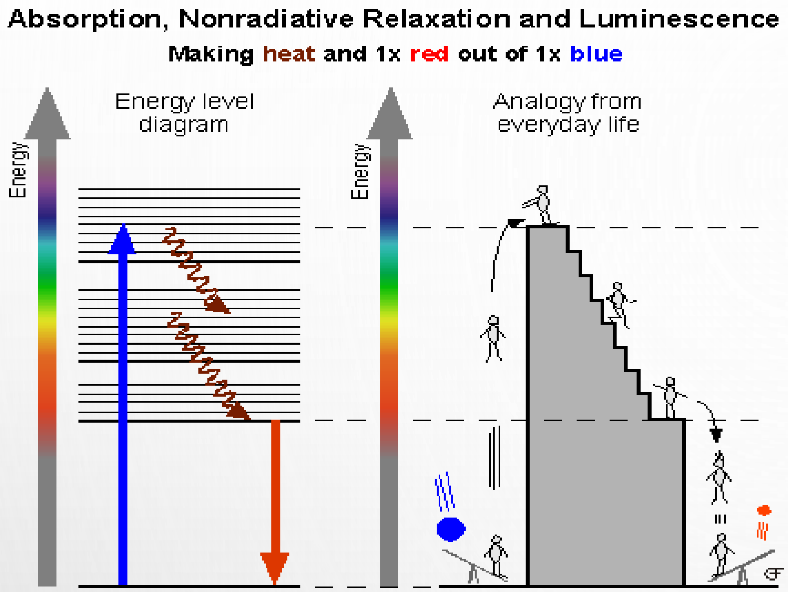
$$\sum_i$$

is the sum of all rates of excited state decay. Other rates of excited state decay are caused by mechanisms other than photon emission and are therefore often called "non-radiative rates", which can include: dynamic collisional quenching, near-field dipole-dipole interaction (or resonance energy transfer), internal conversion and inter-system crossing. Thus, if the rate of any pathway changes, this will affect both the excited state lifetime and the fluorescence quantum yield.

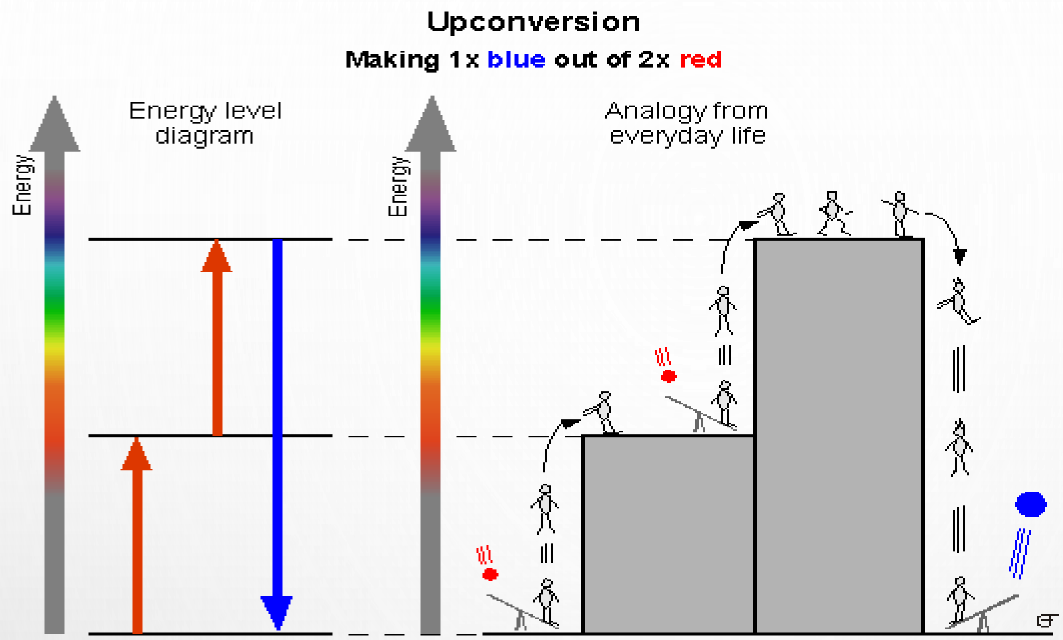
Triboluminescence

Triboluminescence is an optical phenomenon in which light is generated via the breaking of asymmetrical bonds in a crystal when that material is scratched, crushed, or rubbed. This is a variant of luminescence; the term comes from the Greek *tribein* (to rub) and the Latin *lumen* (light).

The process by which triboluminescence was discovered was actually an accident. In the late 1790's sugar production began to produce more refined pure sugar crystals. These crystals were formed into a large solid cone for transport and sale. This solid cone of sugar had to be broken into usable chunks using a device known as a sugar nip. Early American scientists and laymen alike begain to notice that as sugar was "nipped" in low light, tiny bursts of light were visible.



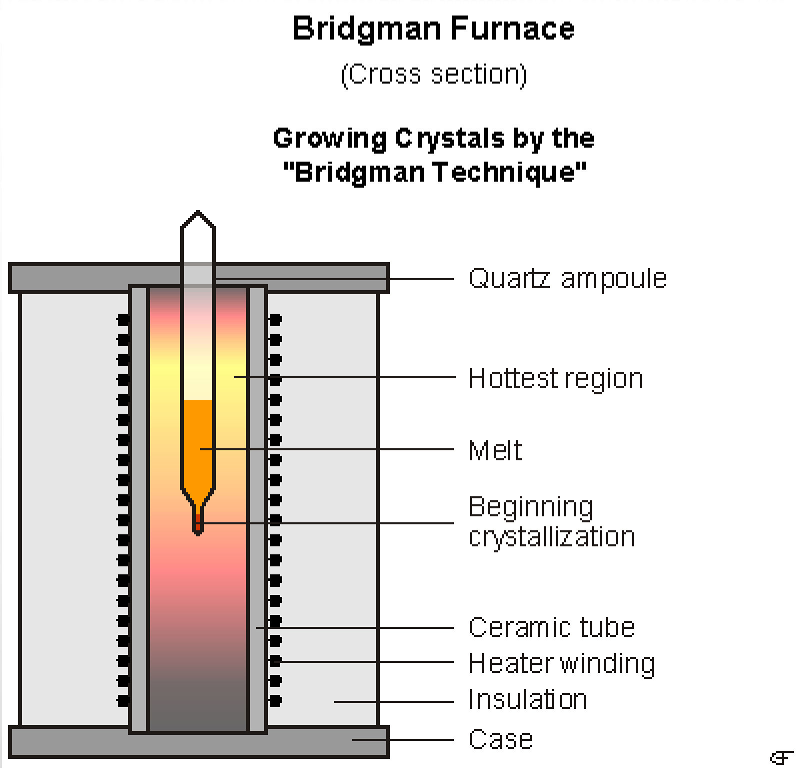
The spontaneous emission of light upon electronic excitation is called photoluminescence.
Luminescence is a rare phenomenon among inorganic compounds. This is due to the predominance of nonradiative relaxation processes. An electronic excitation of a complex or a metal center in a crystal usually ends up as vibrational energy and eventually as heat. In those cases where spontaneous light emission does occur, its spectral and temporal characteristics carry a lot of important information about the metastable emitting state and its relation to the ground state. Luminescence spectroscopy is thus a valuable tool to explore these properties. By studying the luminescence properties we can gain insight not only into the light emission process itself, but also into the competing nonradiative photophysical and photochemical processes.



Photoexcitation at a certain wavelength in the NIR followed by luminescence at a shorter wavelength in the VIS is called NIR to VIS photon upconversion.

This is a rather unusual process since low energy photons are "converted" to higher energy photons. At least two NIR photons are required to generate one VIS photon.

Upconversion can only occur in materials in which multiphonon relaxation processes are not predominant, thus allowing more than one metastable excited state. In rare-earth compounds, the 4f or 5f electrons are efficiently shielded and thus not strongly involved in the metal-to-ligand bonding. As a consequence, electron-phonon coupling to f-f transitions is reduced, and multiphonon relaxation processes are less competitive. The phenomenon of upconversion is therefore most common and best studied in materials containing lanthanide ions. But there are also transition-metal systems and rare-earth / transition-metal combinations which show this phenomenon.



There are several methods of growing crystals. We often use the "Bridgman technique":
The starting material, a powder, is filled into a quartz ampoule, sealed under high vacuum, put into the Bridgman furnace and heated. When the melt is homogeneous, the furnace is slowly moved upwards. Thus the melt is cooling, the narrow tip of the ampoule always being the coldest point. Crystallization will start there, and finally (usually after 10-14 days) the ampoule is filled with one single crystal.

Table A1. Typical colours of incandescence.

Approximate temperature (^{o}C)	Colour observed
525	faint red
700	dark red
900	cherry red
1100	dark yellow
1200	bright yellow
1300	white
1400	blue white

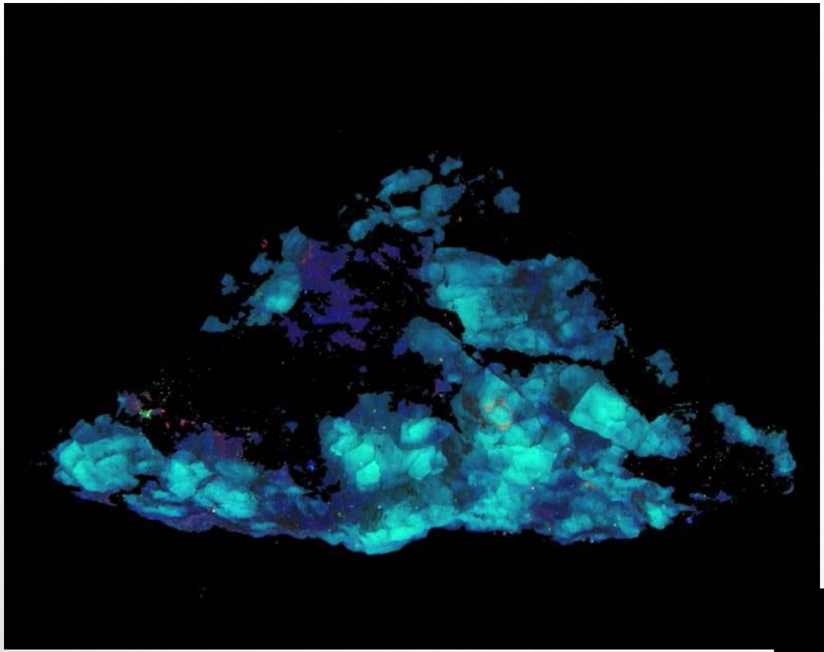


FIGURE 1

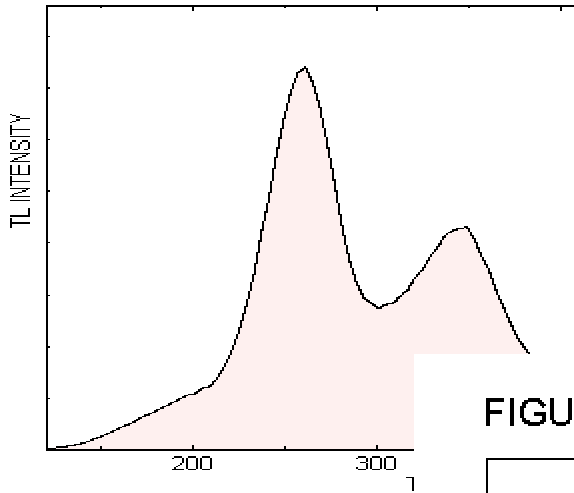


FIGURE 2

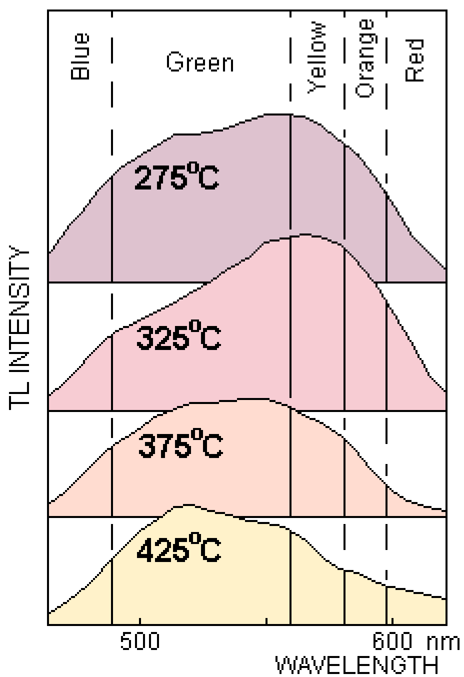


FIGURE 3

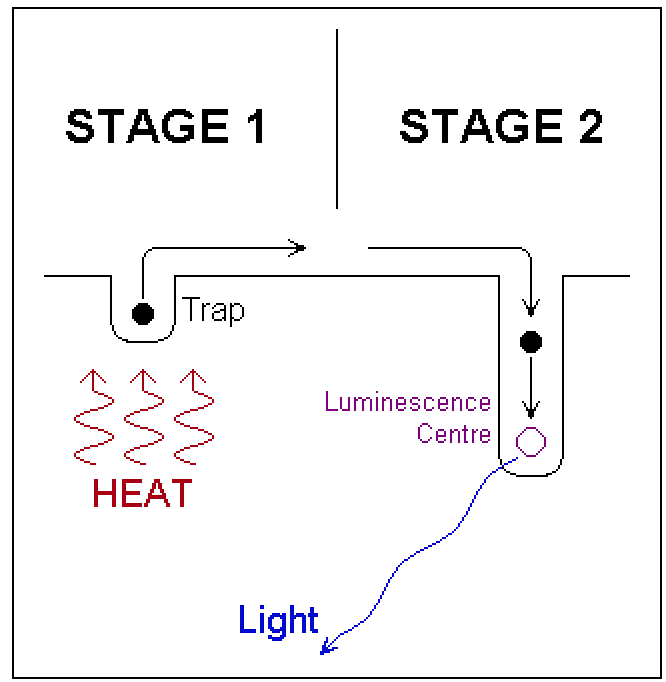


FIGURE 4

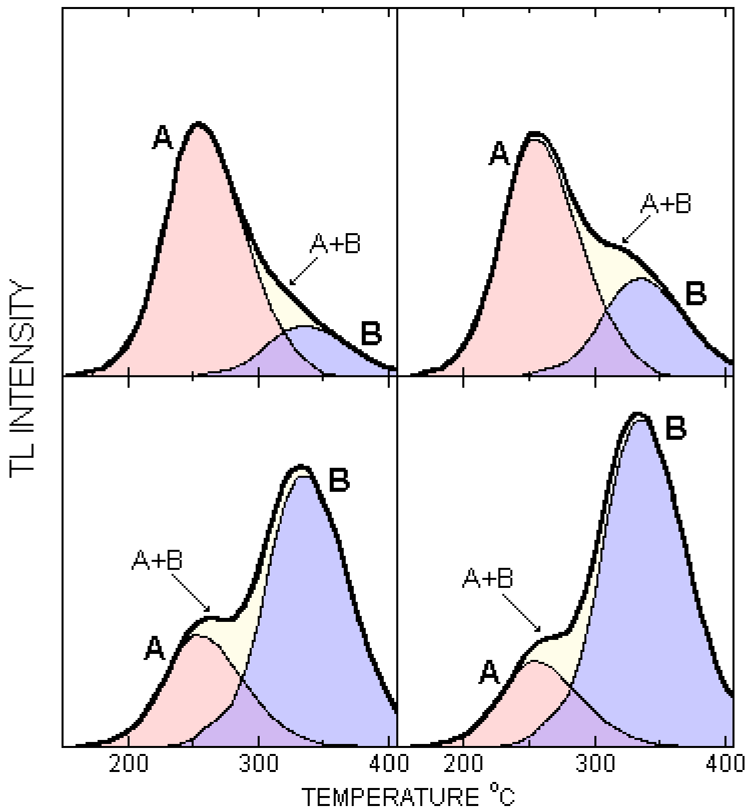
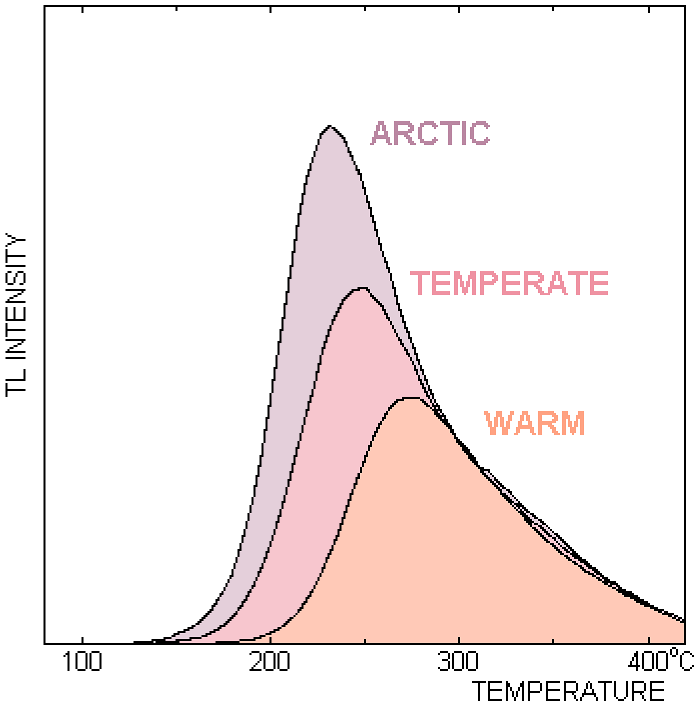


FIGURE 5



THANK YOU