

## CHAPTER II

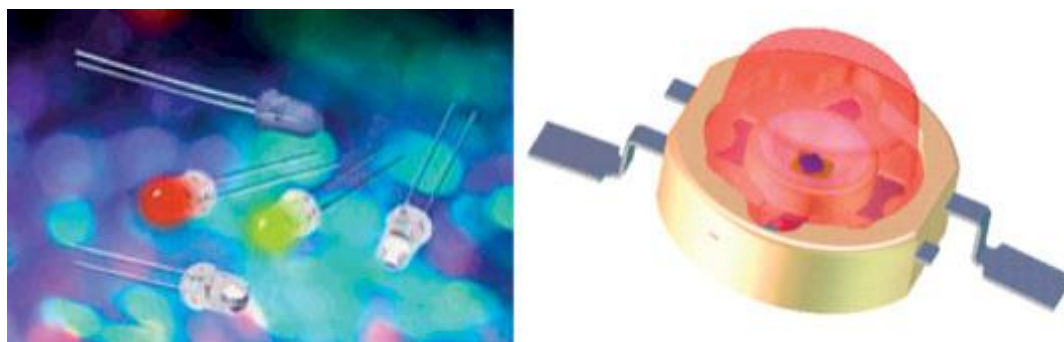
### THEORY AND LITERATURE REVIEWS

#### 2.1 Inorganic Light-Emitting Diodes (LEDs)

Although they have been investigated as possible options for blue LEDs for several years, semiconductors containing group II and VI elements have not succeeded. One example of such a semiconductor is ZnSSe/ZnTe. Nevertheless, Nakamura and his colleagues were victorious in 1993. They decided to use InGaN, a material already demonstrating its potential in solid-state illumination (Nakamura, S. et al., 1997). Because the material is so chemically stable, producing epitaxial layers of sufficient quality for high-efficiency LED operation is challenging. This presents a challenge. On the other hand, the unusually high stability makes achieving exceptionally high current densities possible without damaging the LED material. The lumen package can be increased to values suitable for lighting applications (Figure 2.1). However, the fact that InGaN is relatively immune to flaws is arguably more significant. Standard InGaN LEDs have Figure densities that are noticeably higher than those that would be acceptable when utilizing other material combinations, such as AlGaAs ( $10^9$  cm<sup>-3</sup> to  $10^6$  cm<sup>-3</sup>). Still, because of InGaN slow surface recombination velocity, efficient LEDs can be built from dense layers of defects. This is because InGaN has a slower surface recombination velocity than other materials. Because of the development of long-lasting and dependable blue and UV LEDs, it is now possible to generate white light from solid-state devices by either externally combining the light from blue, green, and red LEDs or by color converting blue LEDs using phosphors.

In semiconductor device literature, the principle of LEDs is extensively described (Nakamura, S. et al., 1997; Zukauskas, A. et al., 2002; Sze, S. M. et al., 1981). Here, we will talk about using LEDs to produce white light and the pertinent characteristics of luminescent materials. Because color conversion is so necessary for

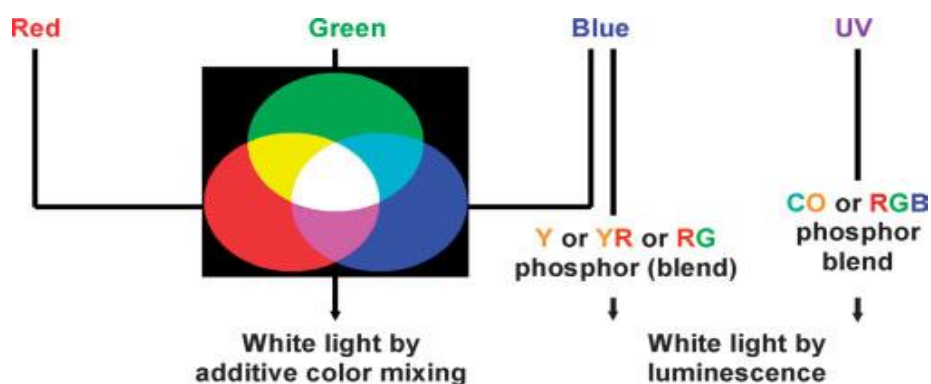
turning LEDs into sources of white light, this section devotes considerable space to discussing the phosphors themselves.



**Figure 1.1** LEDs with a traditional 5-millimeter diameter (on the left) and an LED with a high-power lighting (C. Ronda., 2008).

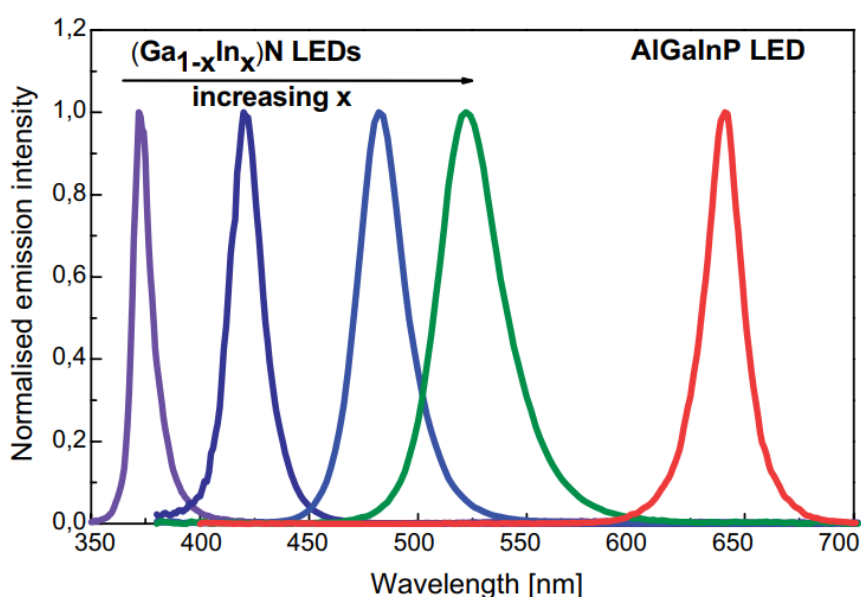
## 2.2 White and Colored LEDs

White light is often composed of a spectrum of colors rather than just one. Combining the blue and yellow/orange primary light sources is the quickest and easiest technique to produce a white light source (Figure 2.2). It may be difficult, at least in the case of small packages, to achieve homogenous mixing of the individual LEDs since the size of the small LED package places size constraints.



**Figure 2.2** Summary of different concepts to generate white light by primary light sources (C. Ronda., 2008).

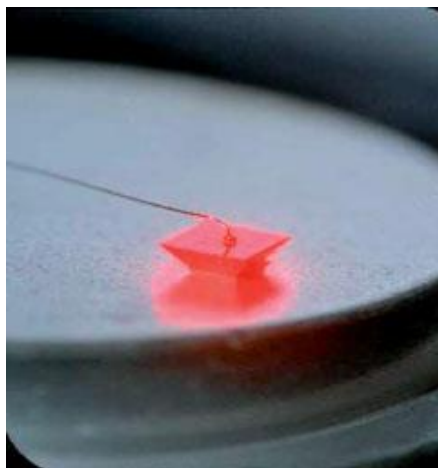
The primary application for colored LEDs as light sources, as opposed to their employment in general illumination, is in settings that require the recreation of pure hues, such as those shown by the spectrum in Figure 2.3. Such environments include traffic signals and the brake or indicator lights on automobiles. In several application areas, filtered white incandescent light bulbs have been replaced by InGaN and AlGaInP LEDs as a result of the former technology's superior efficiency and longer lifetime.



**Figure 2.3** The typical spectrum of a blue InGaN LED, a green InGaN LED, and a red AlGaInP LED (ranging from  $x = 0.0$  to about 0.45) (C. Ronda., 2008).

Because the material has a refractive index more significant than one, the crystal causes any light emitted at an angle more critical than the Brewster angle to be reflected into the crystal. The efficiency is yet decreased due to multiple internal reflections because some residual absorption is still present, such as at the metal contacts or the charge transportation layers. In the past, arranging the semiconductors on an LED so that they formed the shape of a truncated inverted pyramid allowed for the device to achieve the highest level of efficiency possible for a red light source (Figure 2.4). (Krames, M. R. et al., 1999).

This LED's internal and external efficiencies are anticipated to be close to 100%, resulting in a luminous efficiency of  $102 \text{ lm W}^{-1}$ . This figure demonstrates that light emitted by light emitting diodes (LEDs), which are currently the most efficient red-light source available on the market, have the potential to become the dominant source of light in the future.

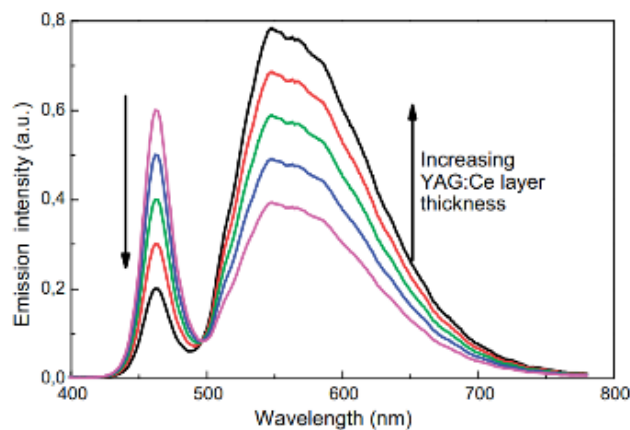


**Figure 2.4** InGaP LED shaped as a truncated inverted pyramid for efficient light extraction (Source: Lumileds).

### 2.3 Phosphor-Converted LEDs

The color point of these phosphor-converted LEDs (pcLEDs) is substantially impacted by the type of phosphor coating and that layer. Because of the high excitation density, which can be as high as  $30 \text{ W cm}^{-2}$  for a 1 W InGaN LED (chip area  $1 \text{ mm}^2$ , external efficiency around 30%), the phosphors that are used have to be able to absorb blue light significantly and have outstanding photochemical stability. The host lattice needs to have a high chemical and thermal stability level for the LED to have a lifetime of more than 10,000 hours (Scott, K., 2002). In addition, the phosphor should have a short decay time to stop saturation from occurring at high drive levels. Because of this, the LED spectrum will change or shift toward the color blue depending on the parameters of the drive. Consequently,  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  are activated when doped into stiff host lattices (oxides, nitrides, and sulfides), which are utilized in the most effective LED converter materials. The most popular phosphor is (Y,  $\text{Gd}_3\text{Al}_5\text{O}_{12}$ : Ce (YAG: Ce) (Nakamura, S. et al., 1997), The optical thickness of the phosphor coating

affects the effective color temperature of the light output from a phosphor-coated LED (pcLED). The first cool white LEDs had a luminous efficiency of roughly  $10 \text{ lm W}^{-1}$  (Bando, K. et al., 1998), translating to a light output of 0.7 lm at a power consumption of 70 mW. The phosphor used in these LEDs was YAG:Ce. As shown in Figure 2.2, the hues shift from a bluish white (cool white) to a yellowish white (warm white) as the layer thickness increases. A high-power LED with a rating of 5 W can generate up to 150 lm even though the efficiency of cool white LEDs is only  $30 \text{ lm W}^{-1}$  (Thornton, W. A. et al., 1971). Using a single yellow phosphor has the disadvantage of preventing the LED from producing low color temperatures (warm white light) with a high color rendering (Muller-Mach, R. et al., 2000). The LED spectrum does not contain any red light. In addition, the driving conditions affect the colors of cool white LEDs. These problems can be remedied using trichromatic white LEDs with two phosphors, the first of which emits light between 520 and 570 nm and the second between 590 and 660 nm.



**Figure 2.5** Emission spectra of a white LED comprising a 460 nm-emitting blue InGaN chip and a phosphor as a function of the optical thickness of the YAG:Ce layer ( Rond, C. et al., 2008).

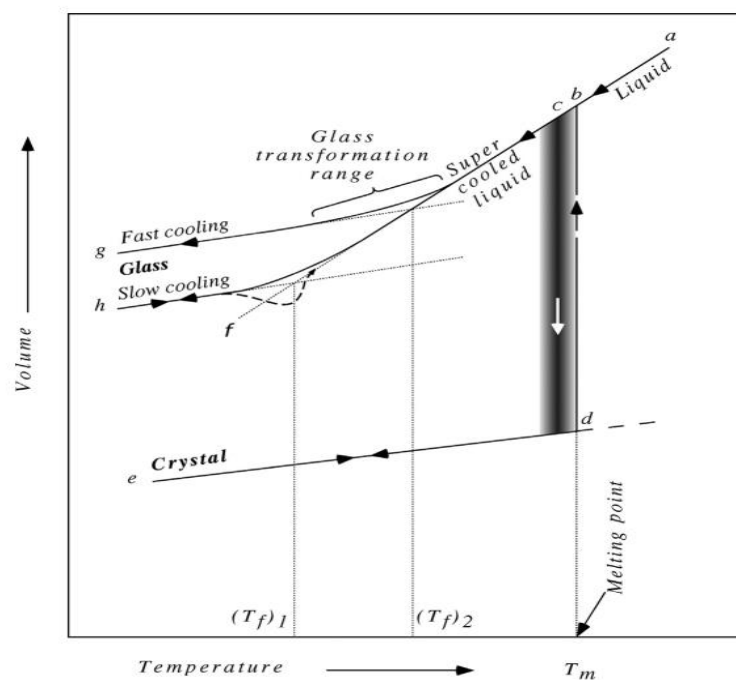
**Table 2.1** Comparison of advantages and disadvantages of LED (Abdelrahman, A. A. et al., 2016).

Advantages	Disadvantages
LED lighting can be fine-tuned to provide a diverse range of color temperatures because it is possible to combine multiple colored LED chips in the same array. The color temperature of the light produced by incandescent and halogen lamps is usually in the range of 2600K to 3000K, with 2700K being the most common of these values. Conversely, LEDs typically have color temperatures ranging from 2700K to 6000K or more.	LEDs are more expensive than other lights.
The efficiency of LEDs is undergoing rapid development at the moment.	There are situations when high voltage can cause LEDs to get damaged.
LEDs are more reliable.	Very little effectiveness across a vast area.
LEDs are more efficient to use under cold temperatures.	LEDs are responsible for reverse heat dissipation.

## 2.4 Composition of the present glass

Glass can be defined as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization." The presence of long-range order in the crystal structure is the primary characteristic that differentiates crystals from glass. (Yamane and Asahara., 2000). The molten liquid is routinely cooled down to make glasses using this method. On the other hand, other techniques aren't used sparingly, such as chemical vapor deposition and the sol-gel process approach. Crystallization

may occur at a liquid's melting point ( $T_m$ ) if the liquid is cooled rapidly from a high temperature. If the crystallization occurs, there will be a sudden shift in the volume and enthalpy at the transition temperature. The heat capacity of the crystal will cause the volume and enthalpy to decline even further if the crystal is allowed to continue to cool after it has already been cooled. When a liquid is chilled below its melting point without crystallization, the resulting state is called a supercooled liquid. Within this zone, the liquid structure continued to reorganize itself even as the temperature fell; nevertheless, there was no sudden drop in volume or enthalpy due to a discontinuous rearrangement of the system (Varshneya., 1994).



**Figure 2.6** The volume-temperature diagram for glass-forming liquid (Varshneya., 1994).

As the liquid is cold, the viscosity of the liquid increases. Because of the rise in thickness, the atoms will not be able to entirely reorganize themselves into the structure of the equilibrium liquid within the allotted amount of time for the experiment. The structure needs to catch up to what would be present if equilibrium were given enough time to develop. When the viscosity of the liquid is so high that its structure is fixed and independent of temperature, the enthalpy starts to deviate from the equilibrium line. It follows a curve with a gradually decreasing slope until the heat

capacity of the frozen liquid eventually determines it. The temperature area, also called the glass transformation region, is located between the boundaries where the enthalpy is that of the equilibrium liquid and that of the frozen solid. The glass transition temperature depends on the heating rate and the sample's prior thermal history. The frozen liquid has transformed into glass at this point. This process of changes in volume/enthalpy with temperature as a supercooled liquid is cooled through the glass transition region (Figure 2.6) (Varshneya, 1994)

In this research, we will focus on three types of glass in which the following components are combined: borate ( $B_2O_3$ ), gadolinium oxide ( $Gd_2O_3$ ), and dysprosium oxide ( $Dy_2O_3$ ) described below.

#### 2.4.1 Borate ( $B_2O_3$ )

Borate is a crucial component, mainly serving as a glass-forming agent and partially as a flux in the current glass components. The following is a synopsis of the twin roles that borate plays in the production and manufacturing processes: Borate was chosen as the material of choice for the current experiment for several apparent reasons, including the ease with which it is available, a low processing temperature, a low glass-forming temperature, and most crucially, its inexpensive cost. The advantage of tolerating extremely high  $Ln^{3+}$  concentrations is offset by the disadvantage that the material's luminous efficiency is decreased by having extremely high phonon energies. Borate is anticipated to work well as a host for  $Ln^{3+}$  activators when combined with other components in a stoichiometrically acceptable ratio.

#### 2.4.2 Gadolinium oxides ( $Gd_2O_3$ )

Gadolinium is particularly significant among the  $Ln^{3+}$  series because it might make transferring energy from the host to the activators and luminescence centers easier. Additionally, it might function as a modifier and effective sensitizer for the dopant  $Ln^{3+}$  in the current glasses. It does not emit visible light to the human eye, and its excitation ( ${}^8S_7 \rightarrow {}^6G_J$ ) and emission ( ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ ) occur in the ultraviolet spectrum. Nevertheless, it can produce visible emission in a host network through a process known as spectrum conversion or by being sensitized by another  $Ln^{3+}$  dopant. It has a more significant energy band gap, better thermal stability, and a higher permittivity (5.4 eV).



### 2.4.3 Dysprosium oxides ( $\text{Dy}_2\text{O}_3$ )

As a glass dopant and effective activator in the current glasses, Dy is a helpful element in the Lanthanides group. Dy has a crucial role in modifying glass and, consequently, in its luminosity. Dy doped glass luminescence requires extensive research in the visible and near-infrared spectrum. Due to the complex electronic structure's arrangement and tightly spaced energy levels, knowing dysprosium spectra was once thought to be essential. As a result, little attention has been given to dysprosium-induced luminescence. Nevertheless, if we pick the right host, we can get the essential  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  transitions from dysprosium. Although much work on spectral studies of  $\text{Dy}^{3+}$  ion-doped materials has been done, it is good optical.

## 2.5 Glass Forming Networks

In general, many elements can form to be glass when they are cooled from the molten state at a rate enough to prevent crystallization. The glass composition can be fundamentally classified into three types; (1) the network formers, (2) intermediates and (3) network modifiers.

### 2.5.1 Network formers

Glass network formers are the elements those form glasses on their own. Several oxides like  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{TeO}_2$ , and  $\text{GeO}_2$  will readily form glass on cooling their melt. The oxides mentioned above compose the element with intermediate electronegativity. Thus, the nature of bonding is typically a mixture of ionic and covalent throughout the glass network.

### 2.5.2 Intermediate

Intermediate oxides will not form glass readily on their own. However, when mixed and melted with some of the glass-forming oxides, they encourage forming of a glass structure. Hence, they are called intermediates which contribute to the formation of glass in association with at least one glass former. Depending upon the network, they are a network former or modifier. T) the cation of intermediates occupies the positions of the glass former during the glass formation. Cations of

elements such as Zn, Ti, Pb, Be, Al, Zr, Th, and Cd act as intermediates in glass formation.

### 2.5.3 Network modifiers

When mixed with glass formers in appropriate proportions, some oxide elements like  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$  change the properties of the glass. These ions are unable to build up a continuous network. Instead, they change the glass structure and hence, the named modifier. The network modifier cations locate randomly in the glass network whose position is close to the non-bridging anions like oxygen, halogens, etc.

## 2.6 Lanthanides

The trivalent state and comparable chemical behaviors distinguish the chemistry of rare earth (RE), abbreviated as RE. RE always occurs as natural mixes, making separating these elements more complicated than it would otherwise be. In the case of lanthanoids, this group exhibits several distinct changes compared to the main group components (Bartolo and Forte, Eds. 2006). The filling of 4f orbitals causes these differences. As can be seen in Table 2.2, the lanthanoids (Ln) are comprised of elements with an atomic number ranging from 57 to 71. In the case of trivalent lanthanoids ( $\text{Ln}^{3+}$ ), electron configurations take the form  $[\text{Xe}] 4f_n$  ( $n = 0-14$ ). In this configuration, the xenon core shows  $5s^2$  and  $5p^6$  filled orbitals, which are radially more external than 4f orbitals. The energy state of  $\text{Ln}^{3+}$  can be shown in a Dieke diagram (Bartolo and Forte, Eds. 2006).

**Table** Error! No text of specified style in document.1 Electron configuration of lanthanide elements and ions (Bartolo and Forte, Eds. 2006).

Atomic number	Element	Symbol	$\text{Ln}^{3+}$	Ground State
57	Lanthanum	La	$4f^0$	$^1S_0$
58	Cerium	Ce	$4f^1$	$^2F_{5/2}$
59	Praseodymium	Pr	$4f^2$	$^3H_4$
60	Neodymium	Nd	$4f^3$	$^4I_{9/2}$
61	Promethium	Pm	$4f^4$	$^5I_4$
62	Samarium	Sm	$4f^5$	$^6H_{5/2}$
63	Europium	Eu	$4f^6$	$^7F_0$
64	Gadolinium	Gd	$4f^7$	$^8S_{7/2}$
65	Terbium	Tb	$4f^8$	$^7F_6$
66	Dysprosium	Dy	$4f^9$	$^6H_{15/2}$
67	Holmium	Ho	$4f^{10}$	$^5I_8$
68	Erbium	Er	$4f^{11}$	$^4I_{15/2}$
69	Thulium	Tm	$4f^{12}$	$^3H_6$
70	Ytterbium	Yb	$4f^{13}$	$^2F_{7/2}$
71	Lutetium	Lu	$4f^{14}$	$^1S_0$

## 2.7 CIE Chromaticity Coordination and Color Correlated Temperature (CCT)

The light color perception by human eyes has frequently been studied using the CIE 1931 chromaticity system. The following equations are used to calculate the tristimulus color values X, Y, and Z as the first step in the process:

$$X = \int_{\lambda}^{\lambda'} \bar{x}(\lambda) P(\lambda) d\lambda \quad (2.1)$$

$$Y = \int_{\lambda}^{\lambda'} \bar{y}(\lambda) P(\lambda) d\lambda \quad (2.2)$$

$$Z = \int_{\lambda}^{\lambda'} \bar{z}(\lambda) P(\lambda) d\lambda \quad (2.3)$$

$P(\lambda)$  is power spectral density, and  $x$ ,  $y$ , and  $z$  are matching functions of color experienced by the eye. Then, chromaticity coordinates ( $x$ ,  $y$ , and  $z$ ) are evaluated utilizing relationships. (Jayasankar, Kumar, and Krishnaiah, 2013)

$$x = \frac{X}{X+Y+Z} \quad (2.4)$$

$$y = \frac{Y}{X+Y+Z} \quad (2.5)$$

$$z = \frac{Z}{X+Y+Z} \quad (2.6)$$

The Chromaticity Diagram's area can typically be plotted, and the emission color determined using only the color ( $x$ ,  $y$ ) coordinate.

## 2.7 Scintillation

When a substance is exposed to radiation, a chain of chemical reactions known as scintillation begins. Both the intrinsic lattice ion and the extrinsic impurities are changed as a direct consequence of this phenomenon. As a result of applying the Coulomb force during a charged particle's contact with matter, the charged particle will slow down due to its energy transfer to the electrons that make up the lattice. This process will continue until the particle has lost its power and ceased moving forward. When electromagnetic radiation interacts with matter, a quantum can either entirely or partially absorb the energy of the radiation. In either case, the situation results in the production of a highly energetic electron. Atoms will experience increased ionization and excitement as a result of this electron. The end consequence

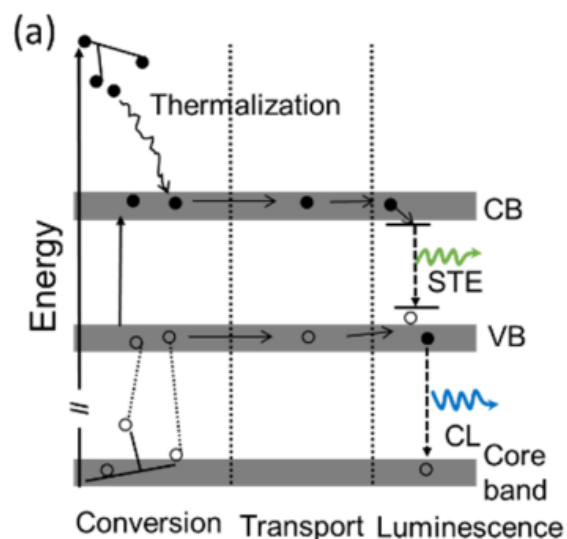
will be secondary electrons and holes, which, in turn, will generate even more energetic versions of both electrons and holes. Last but not least, they will transmit their energy to the centers of luminosity.

Scintillation can be broken down into three distinct stages that occur in order. Figure 2.8 visually represents these steps (Birowosuto, 2007).

1. The process of converting the energy of an incoming radiation or particle into a large number of electron-hole pairs. This can be thought of as an energy transfer. This process involves the interaction of radiation with matter, the production of electrons and holes resulting from that interaction, their relaxation, and their subsequent thermalization.

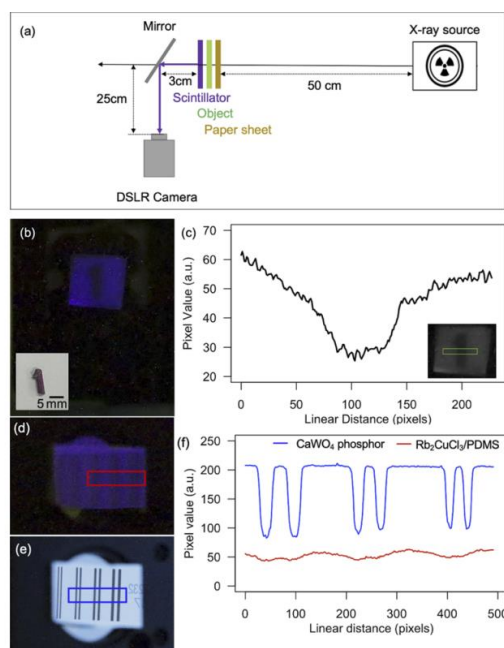
2. The formation of defects and the mechanism of energy transfer that allows the energy of an electron-hole pair to be transferred to the luminous ion participating in the process.

3. The emission process occurs when the luminous ion returns to its ground state after being excited and emits radiation.



**Figure 2.7** A schematic representation of the scintillator mechanism (STE stands for self-trapped excitons; CB stands for conduction band; VB stands for valence band; CL is for cross luminescence; adapted with permission from (Nikl, M., 2006).

(Kopwittthaya, A. et al., 2022) Through the use of the cooling process, synthetic rubidium copper chloride-based flashes were successfully prepared. Depending on the wavelength of the stimulation, the  $\text{Rb}_2\text{CuCl}_3$  that is contained within the PDMS possesses a powerful emission of around 400 nm. The thermal stability has also been investigated using ionizing radiation and ultraviolet light. Fluorescence flashes demonstrate increased heat whenever the temperature is raised, and there is a specific temperature at which quenching is predominated. In the end, the x-ray images produced by our scintillator disclose particular information regarding the object. As shown in Figure 2.8, our research has resulted in developing of a potentially helpful and economically feasible flash phosphor for the X-ray screen business.



**Figure 2.8** (a) A diagram showing how X-ray imaging is set up. (b) An X-ray image was created with a  $\text{Rb}_2\text{CuCl}_3/\text{PDMS}$  scintillator and a 20-second exposure duration. The object seen in the inset is a piece of lead with a thickness of 2 millimeters. (c) The intensity profile of the X-ray image with the contrast ratio is considered. The region of interest (ROI) is depicted here by the inserted green rectangle. (d) an X-ray image of a double-wire IQI with  $\text{Rb}_2\text{CuCl}_3/\text{PDMS}$  scintillator and (e) with a  $\text{CaWO}_4$  phosphor available in the marketplace. (f) Using the results from (d) and (e), a plot of the resolution was constructed (Kopwittthaya, A. et al., 2022).