CHAPTER I

INTRODUCTION

Phosphor materials

A phosphor is a substance that exhibits the phenomenon of luminescence. This includes both phosphorescent materials and fluorescent materials [1]. Phosphorescent materials are known for their use in radar screens and glow-in-the-dark toys as shown in Figure 1, whereas fluorescent materials are common in cathode ray tube (CRT), plasma video display screens, sensors, and white light emitting diodes (LEDs), as shown in Figure 2.

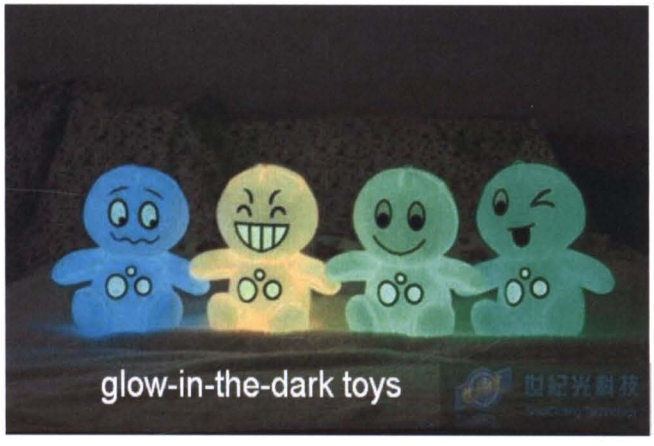

Figure 1 Glow-in-the-dark toys [2]

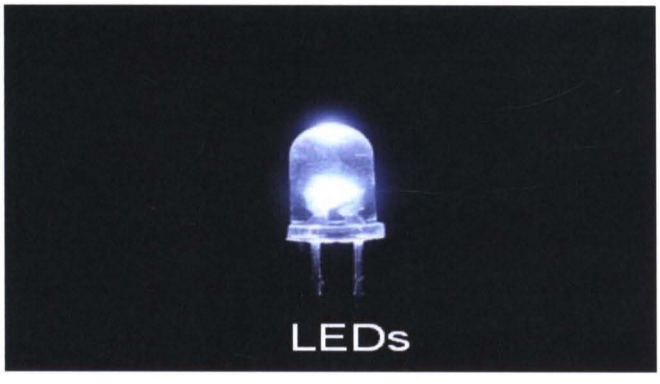

Figure 2 White light emitting diodes (LEDs) [3]

Phosphors are transition metal compounds or rare earth compounds of various types. Their characteristics are high luminescence efficiency, excellent mechanical strength, high flow ability and high packing density.

The phosphor was first found in the early seventeenth century by Vincentuis Casciarola, an alchemist from Bologna in Italy. He found a heavy crystalline stone near a Volcano by firing the stone in a charcoal oven hoping to convert it to a noble metal. Although he was not successful in transforming the elements in the stone but he found that after sintering it emitted red light in the dark if previously exposed to sunlight. The stone was now called the Bologna stone and from modern insights it appears to have been barite ($BaSO_4$). When $BaSO_4$ was fired, it became BaS. Before the discovery of this stone, there is a reference to the preparation of phosphorescence paint from seashells. These seashells were grinded with a rock from a volcano that is ascribed to people living in Japan. This was recorded in a tenth century Chinese document which was written by Xiang-Shun Ye-Lu.

Science research in the field of phosphors is almost 140 years old. In 1886 Theodone Sidot first prepared ZnS crystals by a sublimation method that exhibits phosphorescence in the dark. From present knowledge of phosphors, it seems that Sidot's ZnS contained a small quantity of copper as an impurity, and was the precursor for ZnS-type phosphor.

In the late nineteenth century and early twentieth century, Lenard and co-worker in Germany synthesized phosphors base on alkaline earth sulfides and selenides. They laid down the fundamentals of phosphor research and investigated many phosphors such as ZnS phosphor for use in television tube or cathode ray tube. In addition, they began to study a kind of phosphor constituting of metallic impurities or guest and host material [4].

Type of phosphor materials [5]

1. Electroluminescent Phosphors

Electroluminescence (EL) is the electrical energy which is converted to luminous energy without thermal energy generation. EL was discovered by Destiau in 1936. He observed light emission when a high voltage was applied to ZnS powder and dispersed in castor oil, sandwiched between two electrodes. The types of rare earth and transition metal ions are doped in a wide band gap material. This phosphor layer is sandwiched between two insulators to limit the current and driven with an alternating current at high fields. Phosphor host materials for EL applications must have the following properties as:

(i) A bandgap large enough to emit visible light without absorption

(ii) The possibility of producing an electron avalanche when excited by a high electric field (10^6 Vcm^{-1})

(iii) Lattice that can accept suitable light-emitting dopant

Such host II-VI compounds is ZnS, ZnSe, SrS and CaS. ZnS is now the most widely used host materials. Metal ion suitable for EL devices include Mn^{2+}, Tb^{3+}, Sm^{3+}, Tm^{3+}, Pr^{3+}, Eu^{3+} and Ce^{3+} ions. ZnS lattice doped with Mn (yellow-orange emission at 585 nm) have proved to be one of the best phosphors for EL devices. In a.c. EL cells routine use is made of dielectric insulators often base on amorphous oxides (Al_2O_3, SiO_2, TiO_2 or Ta_2O_7) or ferroelectric materials such as $BaTiO_3$, $SrTiO_3$ and $PbTiO_3$. However a novel low-cost binder for flexible a.c. powder EL panels has recently been found to eliminate the need for insulating layers. This binder is prepared from long chain organic molecule cross-linked by metal ions such as Si, B and Ti added form of alkoxides. Then the phosphor powder was covered with this polymer [4].

The mechanism of thin film electroluminescent (ACTFEL) devices is shown in Figure 3. First, it is tunnel emission of electrons from interfaced states and accelerates of electrons to high energies. Then, it occur impact excitation or impact ionization of the luminescent center. Finally, de-excitation of the excited electron are performed by radiative (photon generation) or non-radiative recombination. This device can be applied to be a flat panel display technology which made thin about 1 mm as the thickness of a glass sheet as shown in Figure 4.

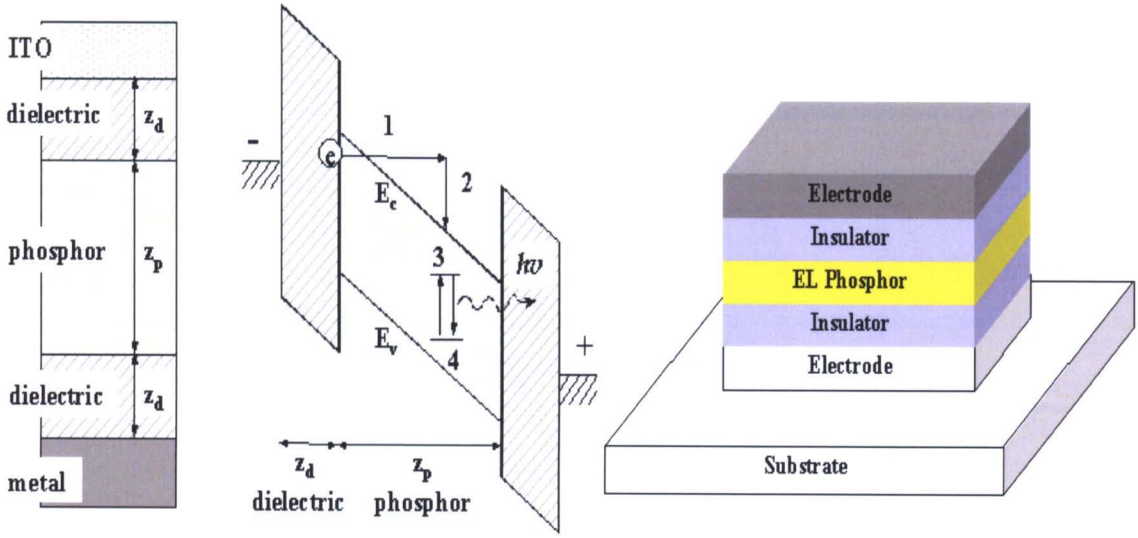

Figure 3 AC thin film electroluminescent (ACTFEL) device mechanisms [5]

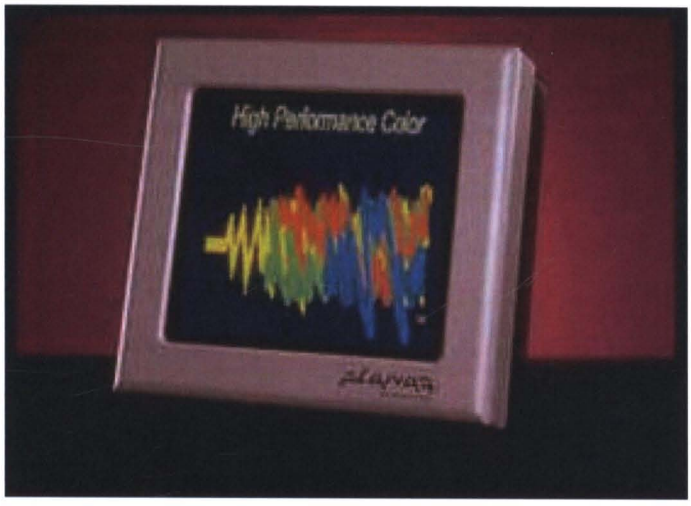

Figure 4 Flat panel ACTFEL displays [5]

2. Cathodoluminescent Phosphors

Cathodoluminescence is a light process which is created from an energetic electron beam. This phosphor is responsible for the light from cathode ray tubes as shown in Figure 5. Generally, Electrons are heated with coil H, go through a hole in the cathode C (-) and are accelerated by an electric field to the anode A (+). The electron gun is also used to focus the beam, and the plates deflect the beam. An energetic electron beam is transferred across the screen and bombards individual

pixels which have powder materials that give off light when the electron beam hits it. This process can be seen in television and computer monitor.

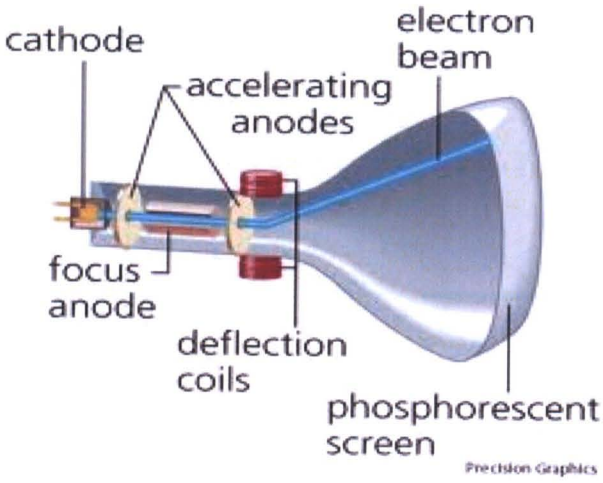

Figure 5 Diagram of cathode ray tube (CRT) [6]

Recently, CRT displays have been a growing interest. When the display size and depth increased that affect on the electron optics needed to address the larger screens. So, the flat panel display technologies were replaced the standard cathode ray tubes. Field Emission Display (FED) is an alternative technology which is fundamentally similar to CRTs as shown in Figure 6.

FED used a thin array of hundreds of tiny little cathode tubes. The tubes are positioned in a flat plane a few millimeters from the phosphor surface. This FED also use less power than a normal CRT and the display is bright and fast. The cathode can be molybdenum microtips, carbon films, carbon nanotube, diamond tips, or other nanoscale-emitting materials. Niobium silicide applied as a protective layer on silicon tip field emission arrays has been claimed to improve the emission efficiency and stability.

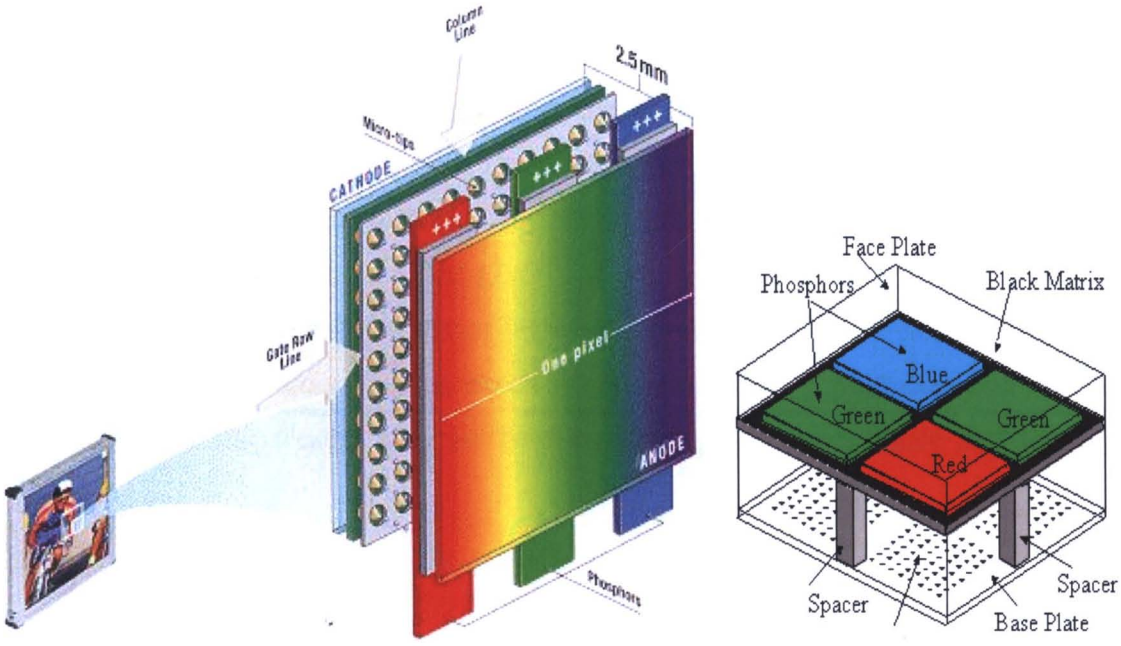

Figure 6 Field Emission Display (FED) [7]

Host and Guest materials

The most of phosphors are composed of host materials doped with rare earth ions. A small amount of activator distributes within the host crystal which absorbs the energy and then transfers energy to guest atom for emitting energy [8]. Figure 7 illustrates the emission of phosphor materials. The ZrO_2 is one type of the host materials which can absorb light in UV and then transfer energy to guest materials, such as Eu. The excited Eu then emits red color.

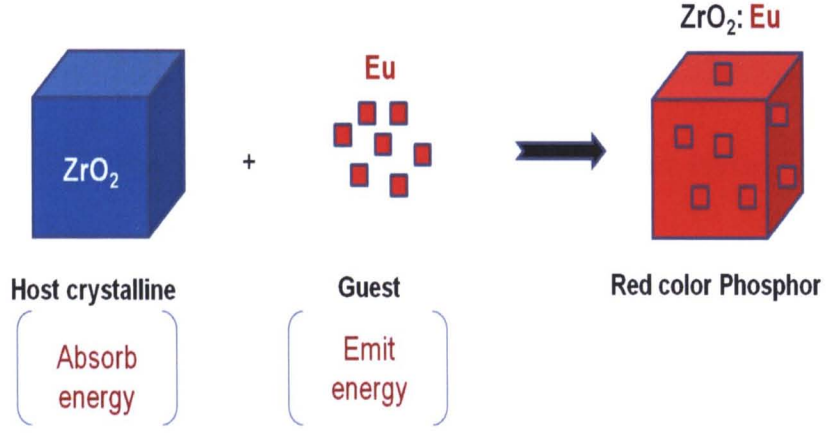

Figure 7 Host and guest materials [8]

1. Host materials

Generally, host materials are transparent and absorb light in UV-visible range. Optical properties of suitable host for phosphors include the high absorption coefficient, high reflectivity and high transmittance. The examples of host material are oxides of transition metal such as TiO_2, ZnO, ZrO_2, WO_3 and SnO_2 [9-11]. Among host materials, zirconium dioxide (ZrO_2), sometimes known as zirconia, exhibits a great potential for being the host of highly luminescence material. This is mainly due to its superior properties such as excellent chemical stability, photochemical stability, high optical transparency, superior hardness, high thermal resistance and low cost [12].

2. Guest materials

For the guest material or luminescence activator, rare earth ions (RE^{3+} ion) are usually used as light-emitting ions in phosphors. These ions such as Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+} ions [13-16] exhibit high luminescent efficiency even at room temperature. RE^{3+} ion has many emission colors. For example, Eu^{3+}, Tb^{3+}, Dy^{3+} ions emit red, green and yellow, respectively, as shown in Figure 8.

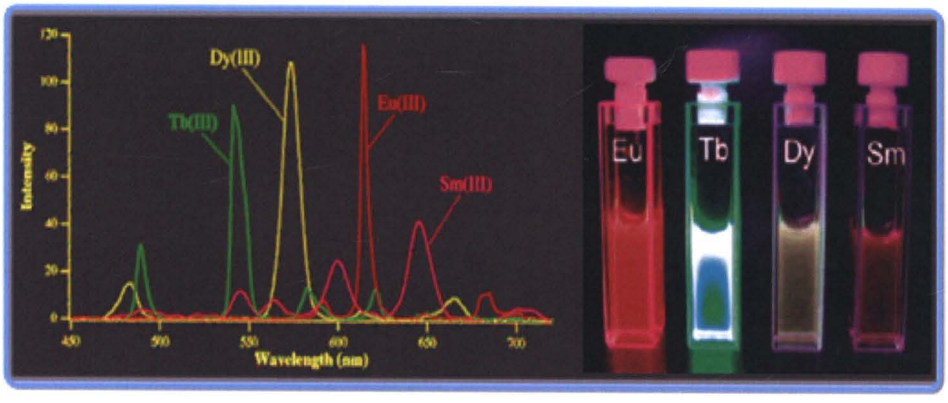

Figure 8 Emission spectra and photograph of rare earth ions [17]

Electronic configuration of RE^{3+} ions

From rare earth (RE) elements have been widely used to activate luminescent and photonic materials. A majority of application involve electronic transitions between states within a $4f^N$ shell configuration of trivalent (or divalent) RE doped into transparent host materials. Figure 9 shows an example partial energy diagram of RE as

Eu^{3+} ion. The diagram indicated splitting of the electron levels due to spin-orbit interaction, which are further split by ligand field (the *J* spliitng). These are composed the transition of $^5D_0 - {}^7F_J$ (J=1, 2, 3, 4) level of Eu.

When a 4f electron is excited into a 5d orbital, the spectroscopic properties of RE in an electronic configuration such as $4f^{N-1}$ 5d are influenced more strongly by the lattice. Therefore, the electronic transitions between the $4f^N$ and $4f^{N-1}$ 5d state, through absorption or emission of photons. The electronic transitions are expected to be characteristically very different from transitions within the $4f^N$ configuration. A modification of the crystal-field theory is necessary from modeling stronger ions-lattice interactions in analysis of the energy level splitting and the excited state dynamics [18].

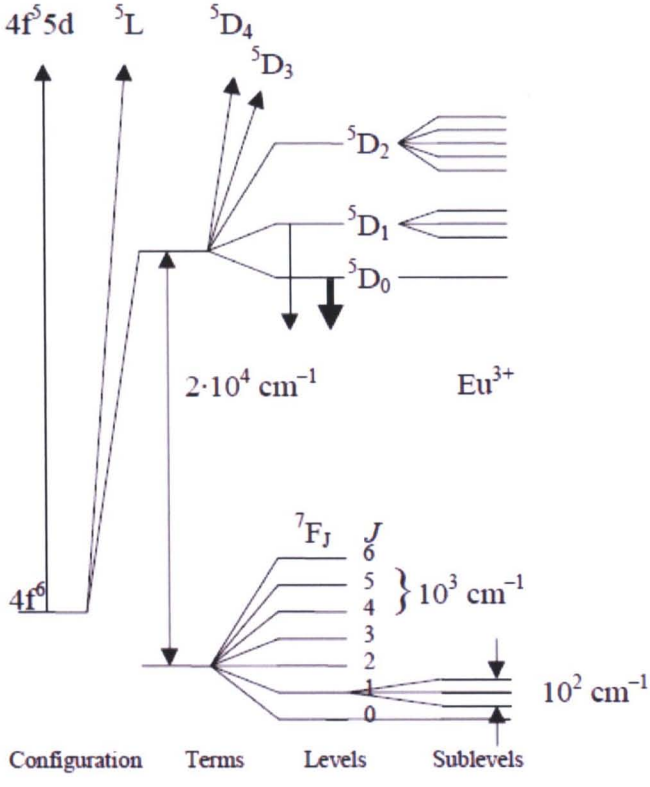

Figure 9 Partial energy diagrams for Eu^{3+} ion [18]

These applications utilize the unique properties of the 4f electrons that have localized states and exhibit weak coupling to ligand electrons and lattice vibrations. The 4f spectroscopic properties include the energy level structure and the dynamic of

the electronic transitions of RE^{3+} ions in solids. Due to these electronic properties, $4f^N$ to $4f^{N-1}$ 5d transitions have become increasingly important in recent year for applications in fast scintillators and ultraviolet laser source.

Energy transfer of ZrO_2: Eu

In the luminescence of solids, the sites of the absorption of incoming radiation and that of the final radiative de-excitation often do not coincide, because the absorbed energy is transferred to a luminescence center even over the distance of many lattice constants. The situation becomes particularly complex when the energy of excitation exceeds the band-gap and the host material is involved. In this case, the energy transfer by excitations as well as by migrating electrons and holes can occur. Various defects of the host can create trapping levels in the forbidden gap and influence the speed and efficiency of all the process. In wide band-gap phosphors, the fast and efficient energy transfer from the host lattice to the emission centers is of the most importance [19].

The example of energy transfer mechanism from host materials to RE^{3+} ions are shown in Figure 10. When ZrO_2: Eu crystals are excited, electrons in the valence band of ZrO_2 absorb the energy and transfer to the conduction band of Eu. Some photos generated electrons return to the valence band from the conductor band of ZrO_2 matrix and recombine with the hole exhibiting the band-edge emission. Other electrons relax to the defect states of ZrO_2 host and recombine with the hole in valence band following a broad luminescence from 400 nm to 600 nm. Since the defect state energy (2.66 eV) of the ZrO_2 is close to the photon energy resonantly excited the $^7F_0$–$^5D_2$ transition of Eu^{3+} ions. Therefore, the Eu^{3+} ions can absorb the energy transferred from the defect emission of ZrO_2 host, resonantly exciting the $^7F_0$–$^5D_2$ transition. Then the electrons transfer from $^5D_0$ state to ^7F_J (J = 0–4) state of Eu^{3+} ions, resulting in a red luminescence as shown in Figure 11.

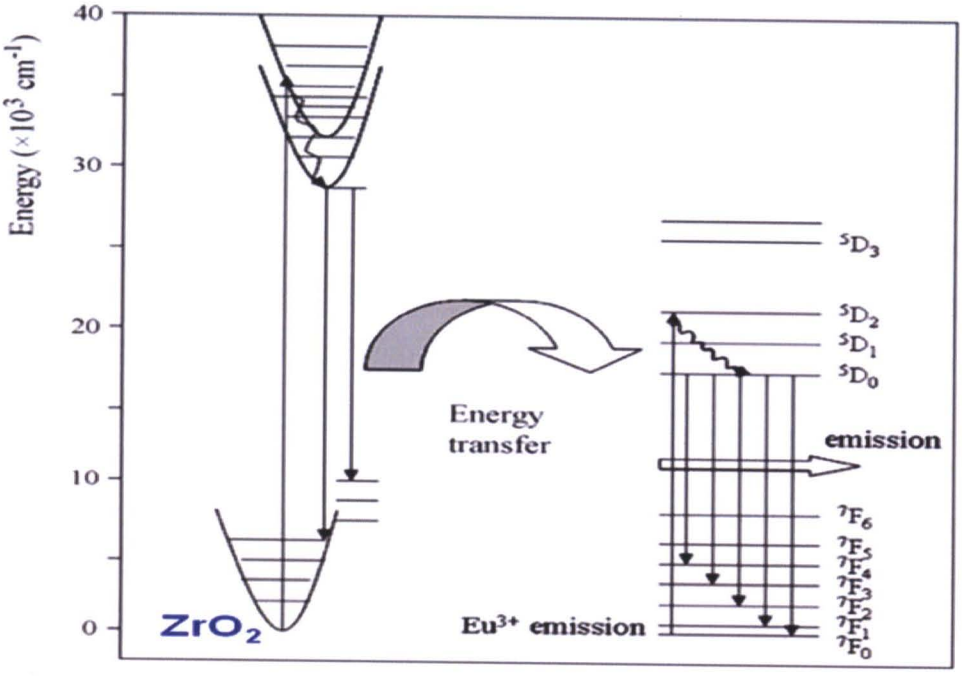

Figure 10 Energy transfer mechanism of ZrO_2 doped with Eu [10]

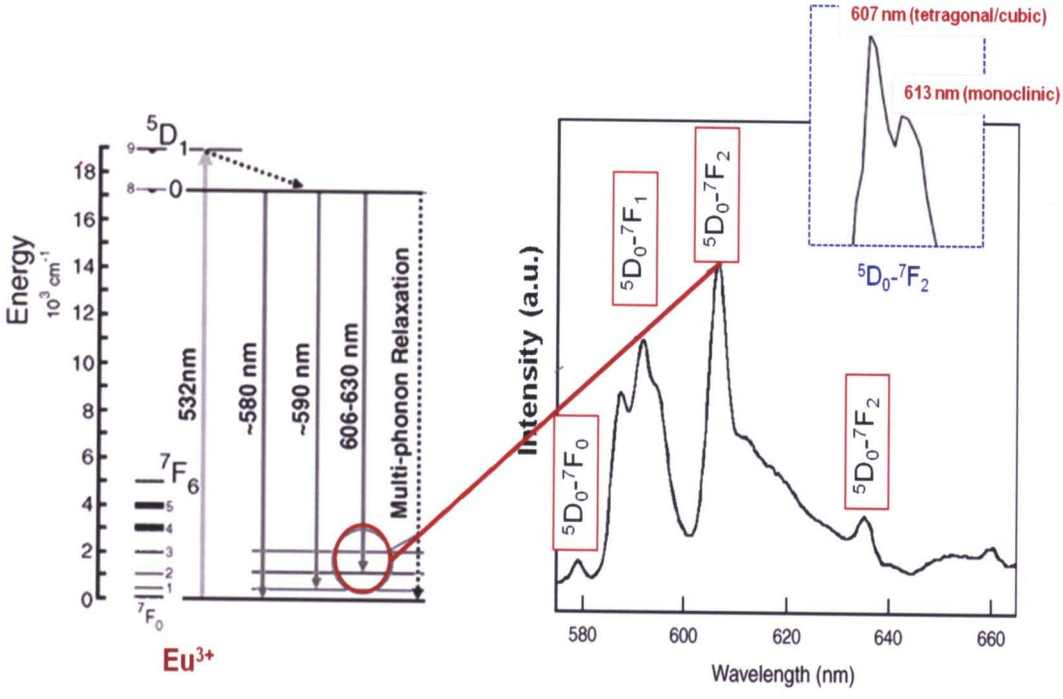

Figure 11 Emission spectra of Eu doped ZrO_2 at different wavelengths [20]

Synthesis of phosphor materials

The synthesis of inorganic phosphor has been the subject of intensive research for over 80 years. Much of synthesis inorganic chemistry includes the coordination chemistry of the metal. These reactions involve molecular rearrangement or substitution of one group or ligand by another. The early syntheses, almost all of inorganic phosphor were synthesized by convention method or solid state reaction. The synthesis details of most phosphor were ascribed below.

1. Solid state reaction

This method was also called a dry media reaction or a solvent less reaction, which was conventional method. Many complex solids can be obtained by direct reaction at high temperature [21]. Most simple binaries are available commercially as pure, polycrystalline powder with typical particle dimensions of a few micrometers. Alternatively, the decomposition of simple metal salt precursors during reaction, leads to a finely divided oxide. The mixtures are then transfer to crucible, normally constructed of an inert materials such as vitreous silica, recrystallized alumina or platinum, and placed in a furnace. The advantages of this method are easy ways, low costs and large-scale productions.

The reaction at high temperatures is slow and typically takes several days. The energies involved in breaking down the structures by overcoming lattice enthalpies. The diffusing of ion through the solid structure over significant distances is very high. A variety of methods can be used to improve reaction rates which include pelletizing and regrinding, the pelletizing of the reaction mixture under high pressure to increase interfacial the contact between reactant particles. For regrinding the mixture introduce reactant interfacial. Both methods, it uses low melting solid that aids the ion diffusion process [22].

The reaction environment may need to be controlled a particular oxidation state which is required or one of the reactants is volatile. Solid state reaction can be carried out in controlled atmosphere, using a tube furnace. Gas can be passed over the reaction mixture during heating. An example of such a reaction is the used of an inert gas to prevent oxidation such as N_2 and H_2. High gas pressure may be used to control the composition of the reaction product.

The drawbacks of solid state techniques are that

(i) It used high temperature for reaction.

(ii) The distribution of the dopant in the host lattice may not be even since the precursors are not mixed on the atomic scale. It causes heterogeneous phase.

(iii) The particle growth cannot be easily controlled and so milling and sieving is necessary. It also produced large particle sizes with broad distribution.

Solid state synthesis of ZrO_2 based phosphors demand controlled heating at high temperatures and long processing times, which often result in inhomogeneous products with low surface areas [22]. So there, various chemical solution methods have been developed for synthesizing these materials

2. Chemical reaction method

As mention above, solid state method have many problems. Therefore, it can be improved by solution chemical reaction method as use solvents to prepare samples. Solution methods are recognized as relatively simple to perform, low-cost, and effective to produce high surface area powders.

The advantage of starting with solution is that the reactants are mixed at the atomic level. Therefore, overcoming the problem associated with the direct reaction of two or more solid phases consisting of micrometer-size particles. The diffusion is fast and diffusion distances are small. Reactions can be carried out at low temperature which minimizes the thermally driven particle growth. As well as the advantages of reduced reaction times, a result of the intimate mixing of the reactants, the final decomposition temperature is lower than the solid state method. The use of a lower temperature can have the effect of reducing the size of the particles formed in the reaction [4]. Thus chemical solution method has been developed for the preparation of zirconia-based ceramics powders, such as co-precipitation [24], spray drying method [25], hydrothermal [26] or solvothermal synthesis [27] and sol-gel method [28].

Co-precipitation process

The co-precipitation process can produce an inhomogeneous compositional distribution because of vastly different solubility of the metal ions. Homogeneous precipitation of phosphors from solution affords the possibility of mixing the dopant into the host lattice at the atom level without depending on high

temperature diffusion. This provides more effective control over stoichiometry in the product. In addition, the size of the final phosphor particle can be controlled by manipulating solution conditions in the co-precipitation process. One successful technique involves the addition of the urea to metal salt in aqueous solution under condition of pH which led to size distribution of phosphors [4].

Combinatorial method

The precursors, as oxides, were dissolved in weak acids and the required amount of each solution was injected by a computer-programmed system into a ceramic container. The solutions were evaporated, the container and residue pulverized and fired. The technique is claimed as a powerful means of increasing the rate of synthesizing [4].

Hydrothermal method

This method use water as solvent. The advantage of hydrothermal method is easy to handle, less expensive, environmentally amicable, large-scale production and Uniform size. For solvothermal treatments were required for the dispersion of crystalline particles into the organic solvent, which affects the growth of particles and large-scale production [4].

Sol-gel method

The sol-gel method has been popular which was used to produce crystalline and high surface area compound. The process involves the addition of metal alkoxide precursors to an alcohol, followed by the addition of water to hydrolyse the reactants. This hydrolysis leads to the gel. This technique used the low temperature processing, low capital investment cost and high homogenous which suitable for preparation thin films. It can react in molecular level that causes small particles dispersed in a liquid with a viscosity well. When the liquid of sol-gel synthesis was burned, the obtained powder was high purity and small particle [4].

RF magnetron sputtering

In RF magnetron sputtering a target is bombarded with fast-moving ion which are generated by an electrical discharge in an inert gas (typically, argon) and directed onto the surface by a strong magnetic field. Momentum transfer results in atom or molecules from the target being vaporized and then deposited in the substrate [4]. The advantage of this method is a cold technique, fast and cheap. It can be used to

prepare films of wide variety of concluding or insulating materials on many types of substrate.

Spray drying method

This method uses a solution of the desired metal ion precursors that is passed through a nozzle using a carrier gas to produce small droplets. These droplets are passed through a high temperature furnace which transforms their contents into spherical metal oxide particles. The technique is also useful for developing particles with controlled morphology and films from colloidal suspensions. Considering the preparation of dispersed crystalline particles also used spray drying method due to controlling of morphology is very simple, low environment temperature, small diameter, phase purity and non-aggregate [4].

Charge liquid cluster beam method

This method is inherently suited to the fabrication of uniform, conformal coating of controlled chemical compositions and stoichiometries. The technique utilizes nanometer-scale charged drops of liquid precursors for thin-film deposition. Moreover, these make use of atomic scale mixing present in these liquids to achieve a film of uniform stoichiometry [4].

Applications

Inorganic phosphors are potential material for modern lighting and display application such as radar screens, glow-in-the-dark toys, cathode ray tube (CRT), plasma display panel (PDP), sensors, white light emitting diodes (LEDs), scintillators, X-ray imaging, optical communication and fluorescence imaging. Figure 12 shows the plasma display panel (PDP). Phosphor material coated on the inside wall of the cell. The phosphors in a plasma display give off colored light when it's excited by UV radiation.

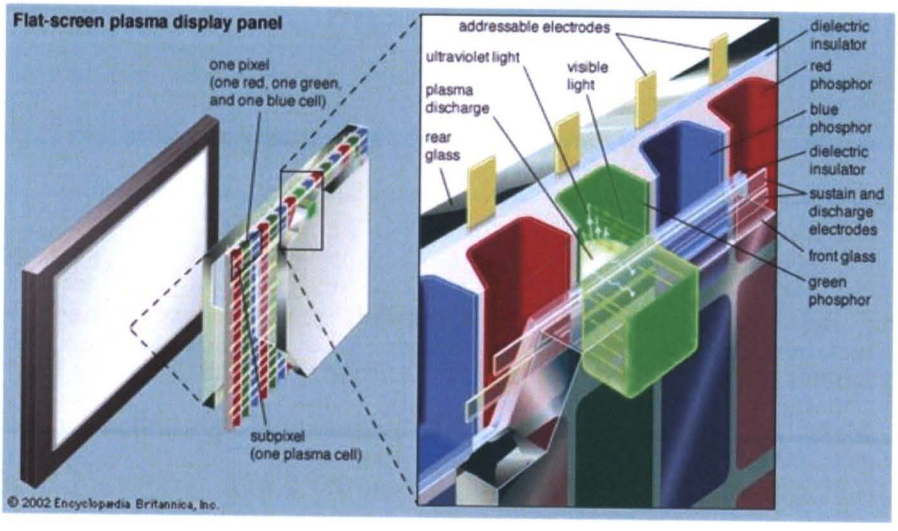

Figure 12 Plasma Display Panels [29]

Summarized

Phosphor compounds are composed of host materials doped with rare earth ions or activators. A small amount of activator distributes within the host crystal which absorbs the energy and then transfer energy to activators for emission color followed by types of rare earth ions. The chemical solution methods are used to prepare these phosphor compounds due to use the low temperature processing, low capital investment cost and high homogenous. Potential material of phosphor can apply for modern lighting and display application.