CHAPTER III

RESEARCH METHODOLOGY

Preparation of ZrO_2: Y: Eu powder samples

A wet chemical method was used for the preparation of Eu doped yttria-stabilized zirconium oxide crystals. $ZrOCl_2.8H_2O$ (analytical reagent, A.R.), Y_2O_3 (99.99%), Eu_2O_3 (99.9%), citric acid (99.5%) and nitric acid (65%, A.R.) were used as the starting materials. Firstly, $ZrOCl_2.8H_2O$, Y_2O_3 and Eu_2O_3 were dissolved in 2 M nitric acid. The mole ratios of Y and Eu were varied while the mole ratio of Zr is kept constant. Then the citric acid was added into the solution. The mole ratio between metal ions and citric acid was fixed at 1:3. This solution was stirred at room temperature for 1 h and then pH of the prepared solution was adjusted to about 7 by adding conc. ammonium hydroxide. The resulting solution was heated in water bath at 90 °C for 4 h, yielding a transparent gel. Finally, the gel was heated in laboratory furnace at 300 °C for 2 h to burn out organic residues, followed by the calcination at 800 °C for 1 h. This process provides ZrO_2: Y: Eu crystalline sample. The diagram depicting this process is shown in Appendix A.

In this work, the experimental parameters that affect the property of ZrO_2: Y: Eu was studied as follow;

1. The concentration of Eu in ZrO_2 with fixed at 7 mol%

From previous study, it was found that the doping of ZrO_2 lattice with 7 mol% of Y caused the formation of cubic phase [58]. Therefore, in this thesis the content of Y in ZrO_2 was selected at 7 mol% to stabilize tetragonal and cubic phase, which may affect the luminescence of Eu. The contents of Eu were varied from 0 to 10 mol%. The crystal structure and photoluminescence efficiency of the samples were followed as function of Eu concentration.

2. The concentration of Y in ZrO_2 with fixed Eu at 3 mol%

The variation Y content may also affect crystal structure and photoluminescence efficiency of the materials. Therefore, this section investigates the

effects of Y. The material was prepared as described earlier. The quantity of Eu was fixed at 3 mol% whereas the ratio of Y was varied from 0 to 7 mol%.

3. The calcination temperature

The study from literature [54] found that the increasing of calcination temperature affects the particle size or gain size. Therefore, it may affect the luminescence properties. The ZrO_2: 4%Y: 3%Eu crystal was studied further by selecting calcination temperatures at 600, 700, 800 and 900 to 1000 °C.

4. The chelating agents

The chelating agent can form complex with metal ions as shown in Figure 23. The metal was complexed with ethylenediaminetetraacetic acid (EDTA). The strong or weak binding may cause the difference in particle size and structure that affect the luminescence efficiency of the sample. In this study, the different chelating agents which included citric acid, ethylenediaminetetraacetic acid, malic acid and oxalic acid were used. Their chemical structures are shown in Figure 24. These molecules constitute different number of carboxylic groups, which are expected to form complex with metal ions in different manners.

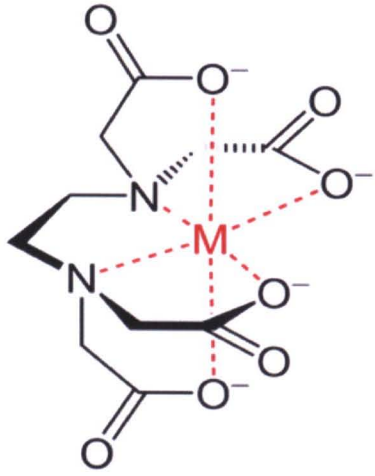

Figure 23 Metal-EDTA complexes

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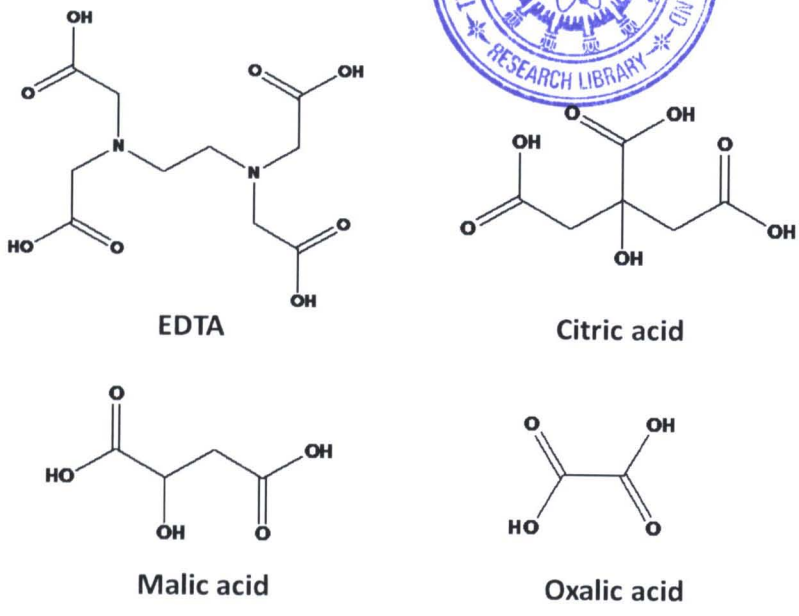

Figure 24 Structure of chelating agents

Preparation of ZrO_2: Y: Eu in polymeric composite films

1. Technique for preparation composite films of ZrO_2: Y: Eu powder samples

Preparations of polymeric composite films have several methods such as drop casting and spin casting. In the drop casting method, a small volume of solution was dispensed on surface and the solvent is allowed to evaporate. The drops were deposited mostly by means of micropipettes onto solid surfaces [60]. In the spin casting method, the mixed solution was deposited onto substrates attached to a spinning machine. When the spin cycle starts, pressure caused by centrifugal force spreads the solution across the substrate. The thin and smooth film forms upon the evaporation of solvent [61]. Both methods were applied to prepare ZrO_2: 4%Y: 3%Eu in polymeric composite films for this research.

2. Composite film of the ZrO_2: 4%Y: 3%Eu in 10% polyvinylalcohol (PVA)

First, ZrO_2: 4%Y: 3%Eu powder with various concentrations at 0.05, 0.1, 0.5, 1 and 2 mol% were dissolved in 5 ml of deionized (DI) water, while 10 wt.% of PVA were dissolved in 10 ml of DI water. The ZrO_2: 4%Y: 3%Eu and PVA solutions were mixed at 1:1 v/v and stirred at 70 °C for 1 h. The mixed solution was used to prepare composite films by using drop casting and spin casting method. The films were characterized by photoluminescence and UV-visible absorption spectroscopy.

3. Composite films of ZrO_2: 4%Y: 3%Eu was also mixed with different polymers such as polystyrene (PS), poly (methyl methacrylate) (PMMA) and poly acrylic acid (PAA).

The different properties of polymers can affect the preparation of composite films and luminescence efficiency of the sample. The PS and PMMA were dissolved in toluene, while PAA acid was dissolved in DI water. The 0.5 mol% of ZrO_2: 4%Y: 3%Eu in dichloromethane was added into the PS and PMMA solutions, while the 0.5 mol% of ZrO_2: 4%Y: 3%Eu in DI water was added into the PAA solution. All solutions were stirred at 70 °C for 1 h. The mixed solution was coated into glass substrates by spin casting method. The spinning was continued for 2 minutes to allow the evaporation of solvent. The composite films were removed from a spin casting machine for characterization.

Technique for characterization of ZrO_2: Y: Eu powder samples

The powder of ZrO_2: Y: Eu crystalline is characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy.

1. Crystal structure

The crystallographic structures of the powder samples were investigated by the XRD and the FT-IR. These techniques can identify of the crystalline structure of a material.

1.1 Powder X-ray diffraction (XRD)

Diffraction is the interference between waves that occur as a result of an object in their part. X-ray are scattered by the electrons in atoms. Diffraction can occur for a periodic array of scattering centre separated by distance similar to the wavelength of the radiation [23]. Scattering is equivalent to reflection from two adjacent parallel planes of atoms separated by a distance d, and then the angle at which constructive interference occurs between waves of wavelength λ is given by Bragg's law:

$$2d\sin\theta = n\lambda$$

Where n is an integer. Thus an X-ray beam impinging on a crystal compound with order array of atoms which will produce a set of diffraction maxima, termed a

diffraction pattern with each maximum, or reflection. Occurring at angle θ correspond to a different separation of planes of atoms in crystal as shown in Figure 25.

X-ray diffraction (XRD) is a technique used to characterize the detailed information and changes about the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples of natural. Powder X-ray diffraction is commonly used to identify unknown substances or heterogeneous solid mixtures to determine relative abundance of crystalline compounds. The Powder X-ray diffraction results of XRD patterns were complied into a database by the Joint Committee on Powder Diffraction Standards (JCPDS).

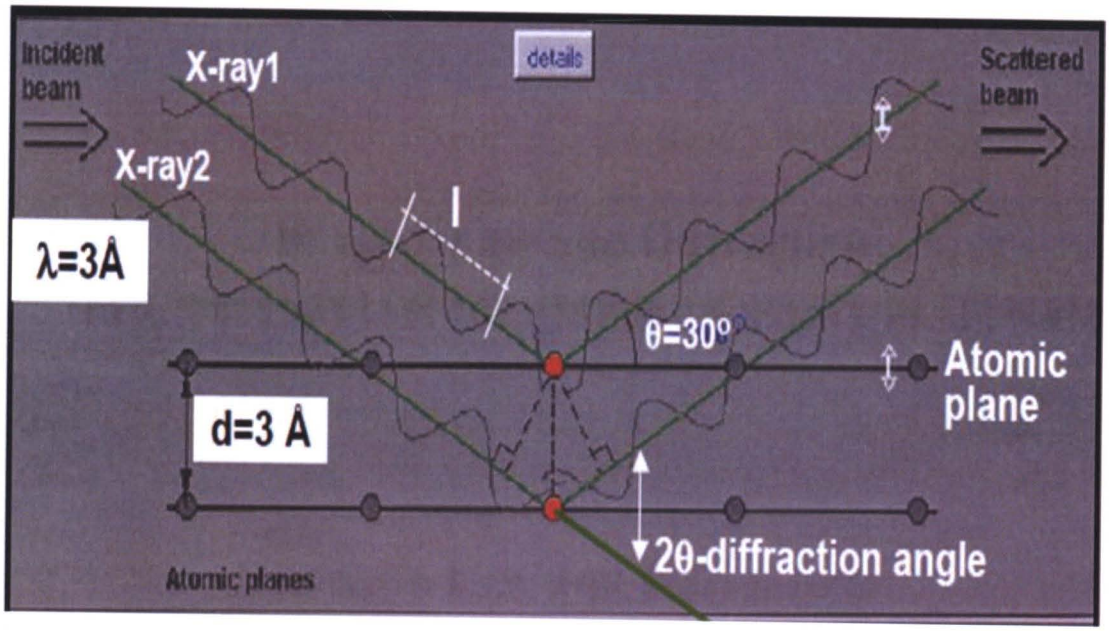

Figure 25 Bragg's equation is derived by treating layers of atoms of reflecting plane [62]

The XRD patterns were recorded using a Philips PW 3040/60 X'Pert-PRO Console with Cu K_α (λ = 0.15418 nm) incident radiation. XRD patterns were recorded from 20 to 80° (2θ) with a scanning step of 0.01°. The particle sizes were calculated from the line broadening of XRD peaks of the sample using the Scherer formula.

$$D = \frac{0.94 * \lambda}{B * \cos\theta}$$

Where D is the average dimension of crystallites, K is Scherrer constant dependent on crystallite shape (0.94); λ is wavelength of X-ray (0.154 nm), B is the full width at half maximum or the difference in angles at half max as B = (2θ High) – (2θ Low); 2θ is the diffraction angle in degree, and base on the half-width of (h k l) reflection of the observed X-ray data, the particle size of the samples can be calculated.

1.2 Fourier transforms infrared spectrometer (FT-IR)

FTIR is vibration spectroscopy which is used to characterize compounds in terms of the strength, stiffness and number of bonds. FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to determine some components of an unknown mixture, to determine a likely structure for compound and to measure properties of bond. It can be applied to the analysis of solids, liquids, and gasses. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. The term FTIR refers to a fairly recent development which the data is collected and converted from an interference pattern to a spectrum [63].

The measurement of the IR spectra was performed using a Perkin-Elmer Model 1600 Series FTIR Spectrophotometer in the wavenumber ranging from 400 to 4000 cm^{-1}. Samples for FTIR can be prepared in a number of ways. For solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. The sample powder 10 mg is finely ground and mixed with approximately 70 mg of dry potassium bromide powder to obtain the pellets. Grinding and mixing can be done with an agate mortar and pestle. Then the mixture is pressed into a transparent disk at sufficiently high pressure for pellets to characterization.

2. Morphology

2.1 Scanning electron microscopy (SEM)

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external

morphology, chemical composition, and crystalline structure and orientation of materials making up the sample [64].

In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample. This approach is especially useful in qualitatively determining chemical compositions. However, SEM samples need to be conductive because electrons can collect on the sample and interact with the electron beam itself. Nonconductive sample must be coated with a thin layer of metal, usually gold or aluminium [65].

The size distribution and morphology were analyzed by scanning electron microscopy (SEM) observation on a LEO 1455 VP scanning electron microscope. The excitation and photoluminescence (PL) spectra were measured using a LS55 luminescence spectrometer equipped with a 150 W Xenon lamp. All the measurements were carried out at room temperature.

2.2 Preparation of ZrO_2: Y: Eu crystal for analysis by SEM

ZrO_2: Y: Eu powders were prepared as shown in Figure 26. The powder was dispersed in water and drops on a silicon wafer as substrate. Then dried and coated with gold to the surface conductive. The system of the LEO 1455 VP was a high vacuum. The sample must be conductive properties before it was analyzed for particle size by SEM.

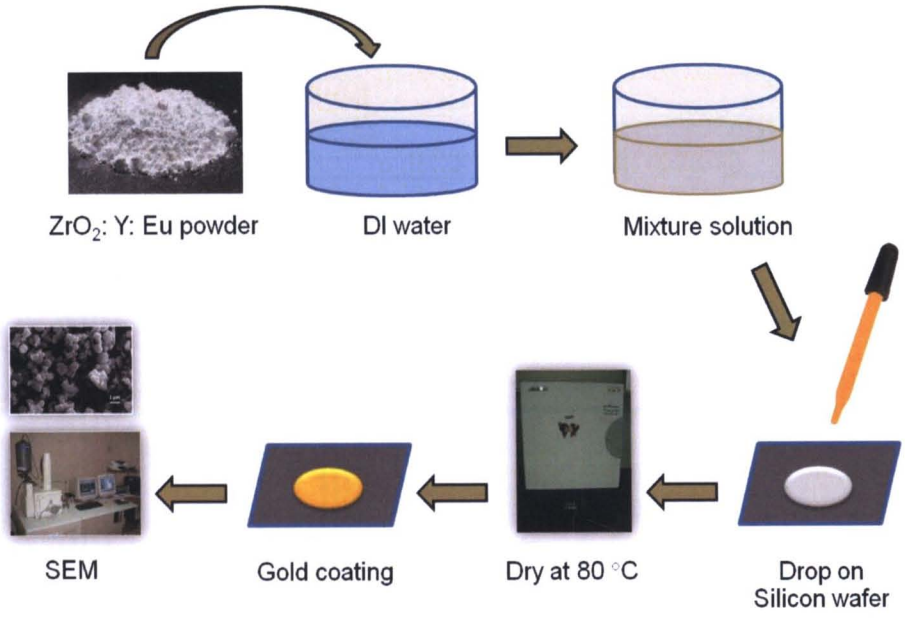

Figure 26 Preparation of powder of ZrO_2: Y: Eu for analysis with SEM technique [65]

3. Photoluminescence

Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons.

3.1 Phosphorescence

Phosphorescence is a specific type of photoluminescence. Phosphorescence is the energy from absorbed photons undergoes intersystem crossing into a state of higher spin multiplicity, usually a triplet state [63]. Once the energy is trapped in the triplet state, transition back to the lower singlet energy states is quantum mechanically forbidden. The result is a slow process of radiative transition back to the singlet state. The average lifetime of the excited triplet state with respect to emission ranges from 10^{-4} to 10 second and sometimes have lasting minutes or hours as shown in Figure 27.

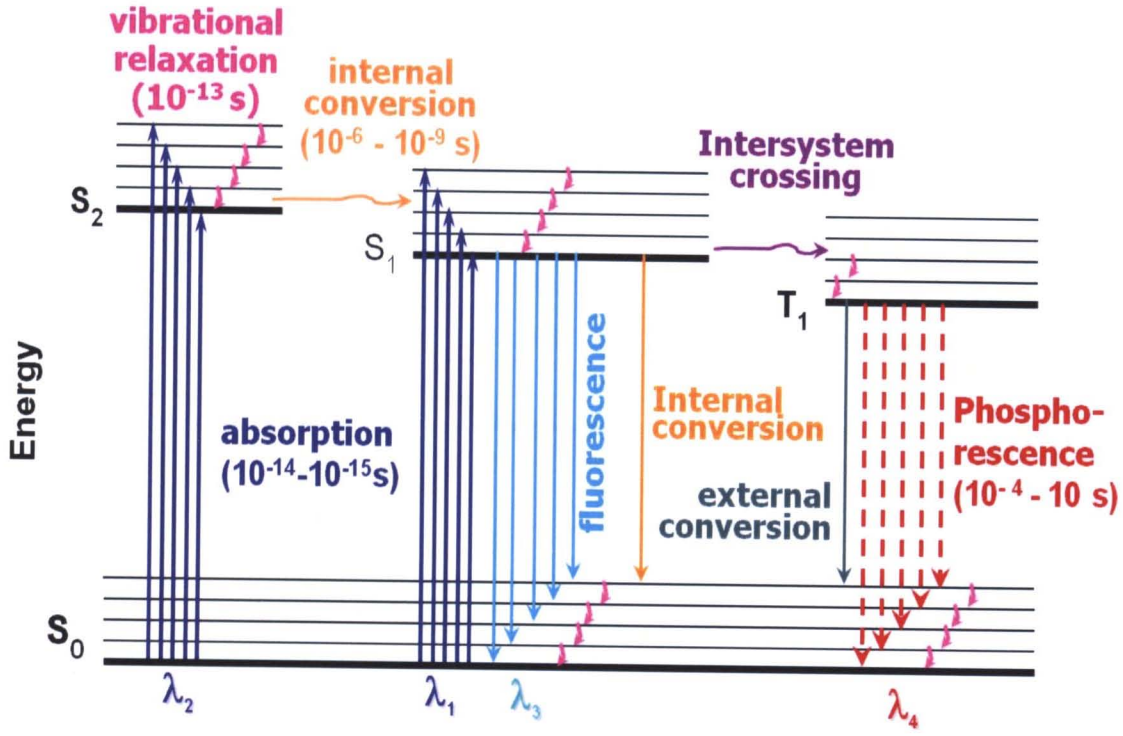

Figure 27 Partial energy diagrams for phosphorescence [66]

The Luminescence spectrophotometer on Perkin Elmer Luminescence LS55 was used for analyzing the emission and excitation spectra. A pulsed-xenon flash lamp is used the source lamp with 20 kW for 8 us duration. Monochromators are the separate Monk-Gillieson excitation covers the wavelength range 200–800 nm with zero order selectable. Combining the instrument's basic proven performance with the FL WinLab software, makes this an ideal tool for applications in areas as analytical chemistry. Computer controlled rationing luminescence spectrophotometer with the capability of measuring fluorescence, phosphorescence and bioluminescence.

The optical diagram of a spectrofluorometer is shown in Figure 28. Several instrument manufactures offer spectrofluorometer capable of providing both excitation and emission spectra. The optical design employs two grating monochromators. Radiation from the first monochromator is split, part passing to a reference photomultiplier and part to the sample. The resulting fluorescence radiation, after dispersion by the second monochromator, is detected by a second photomultiplier.

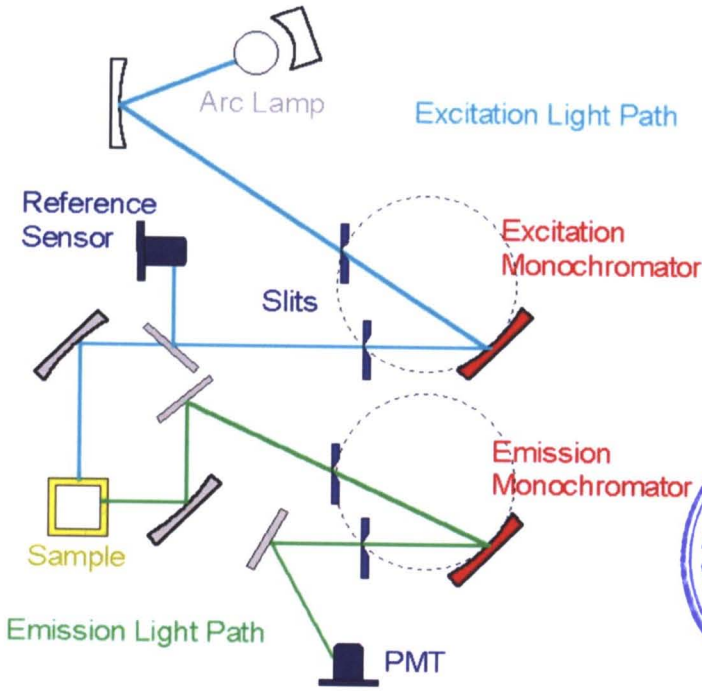

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Figure 28 Optical diagram of spectrofluorometer [63]

3.2 Excitation

Excitation is the addition of a discrete amount of energy (called excitation energy) to a system such as an atomic nucleus, an atom, or a molecule that results in its alteration, ordinarily from the condition of lowest energy (ground state) to one of higher energy (excited state) [67].

The process of excitation is one of the major means by which matter absorbs pulses of electromagnetic energy (photons), such as light, and by which it is heated or ionized by the impact of charged particles, such as electrons. In atoms, the excitation energy is absorbed by the orbiting electrons that are raised to higher distinct energy levels. In a molecule, the energy is absorbed not only by the electrons, which are excited to higher energy levels, but also by the whole molecule, which is excited to discrete modes of vibration and rotation. An excitation spectrum is obtained by measuring luminescence intensity at a fixed wavelength while the excitation wavelength is varied.

3.3 Emission

Emission is the process which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state. Each element emits a characteristic set of discrete wavelengths according to its electronic structure, by observing these wavelengths the elemental composition of the sample can be determined. The frequency of light emitted is a function of the energy of the transition. Since energy must be conserved, the energy difference between the two states equals the energy carried off by the photon. The energy states of the transitions can lead to emissions over a very large range of frequencies. Phosphorescence or emission spectra involve excitation at a fixed wavelength while recording the emission intensity as a function of wavelength [68].

3.4 Preparation of photoluminescence sample

The powder of ZrO_2: Y: Eu was dispersed in potassium bromide powder and the powder sample with the ratio at 70:30 (KBr: Samples). Then the mixed powders were pressed for pellets to characterization with thickness of pellets about 0.50 mm. The irradiation of short wavelength UV light at 260 nm was selected for emission spectra. Addition, the excitation spectra was selected by monitoring the emission at 610 nm.

4. Ultraviolet-visible spectroscopy (UV- visible spectroscopy)

UV- visible spectroscopy is the absorption of electromagnetic radiation in UV and visible regions of the spectrum. The energies and intensities of electronic transitions provide information on electronic structure and chemical environment. UV-visible spectroscopy is among the most widely used techniques for studying inorganic compounds. The process of a UV-visible spectrophotometer is shown in Figure 29. Normally, the beam of incident radiation is split into two; one passing through the sample and the other passing through a cell that is identical except for the absence of the sample. The emerging beams are compared with the detector and absorption is obtained as a function of wavelength. The intensity of UV-visible radiation reflected from the sample is more easily measured than that transmitted through a solid and absorption spectrum is obtained [23].

UV-Visible spectrophotometer on SPECOED S100 UV-Visible spectrophotometer (Analytikijena Specord 100) was used for analyzing the absorption spectra and transmittance.

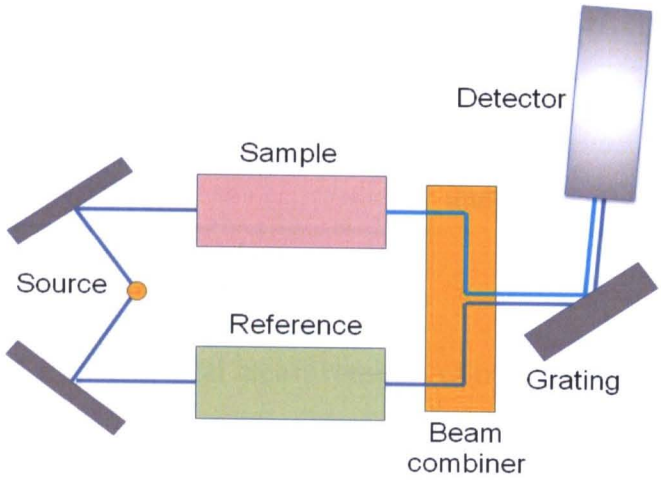

Figure 29 The layout of a typical UV-visible absorption [23]

4.1 Absorption

When atoms or molecules absorb light, the incoming energy excites a quantized structure to a higher energy level. The type of excitation depends on the wavelength of the light. Electrons are promoted to higher orbital by ultraviolet or visible light, vibrations are excited by infrared light, and rotations are excited by microwaves. An absorption spectrum is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its energy level structure, and absorption spectra are useful for identification of compounds. Measuring the concentration of an absorbing species in a sample is accomplished by applying the Beer-Lambert Law [69]. The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

$$A = \varepsilon bc$$

where A is the measured absorbance, ε is a wavelength-dependent absorptive coefficient, b is the path length, and c is the analyze concentration.

Experimental measurements are usually made in terms of transmittance (T), which is defined as $T = I / I_o$, where I is the light intensity after it

passes through the sample and I_o is the initial light intensity as shown in Figure 30. The relation between A and T are:

$$A = -\log T = -\log (I/I_o)$$

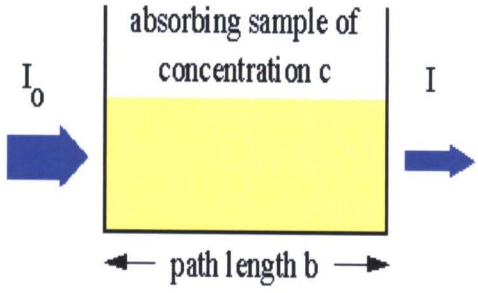

Figure 30 Experimental measurements of transmittance [69]