

# **Chapter 3**

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Experimental

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# CHAPTER- 3

## Experimental

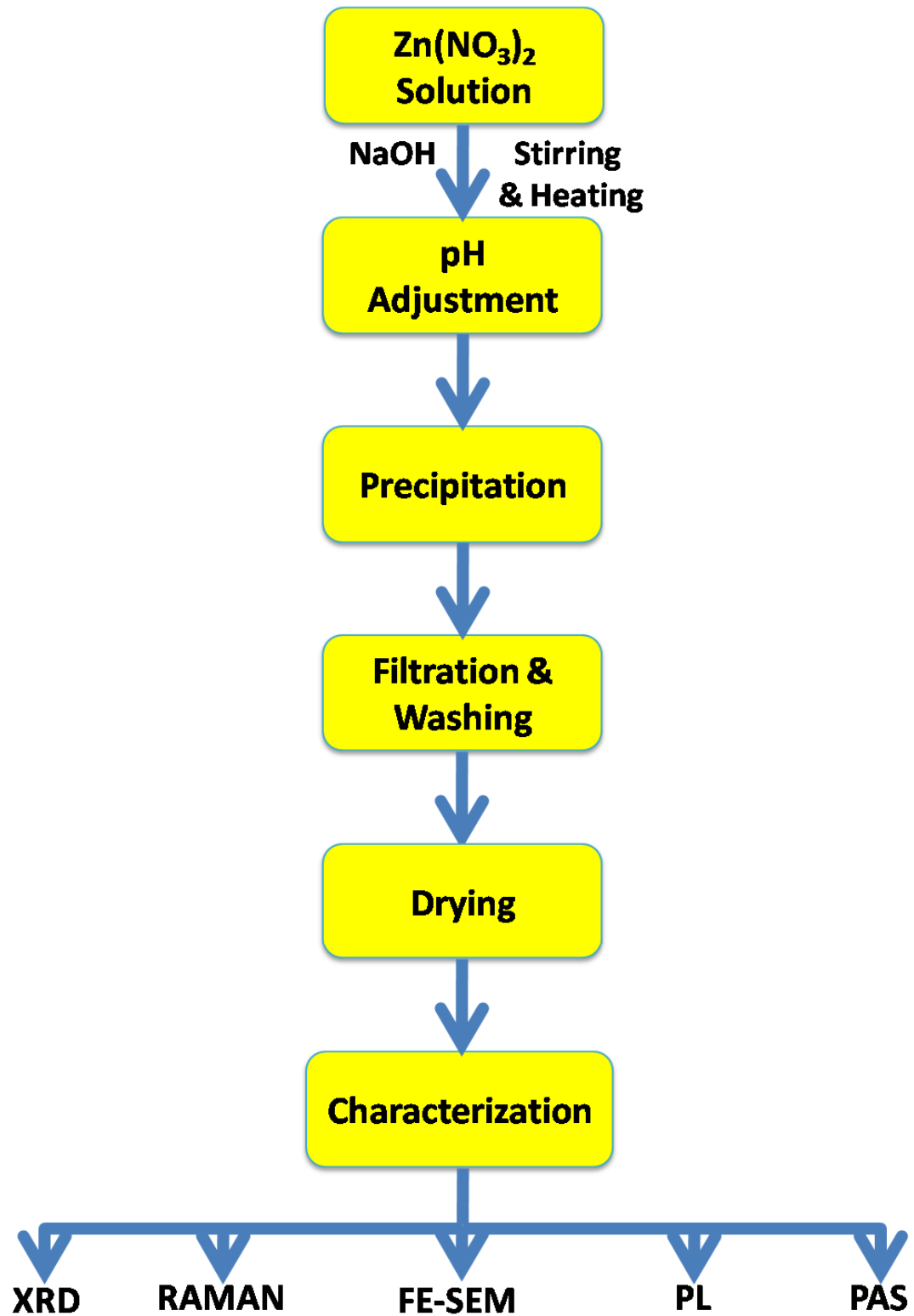
This chapter describes the methodology to prepare the samples and the experimental techniques used to analyse them. Details about the different synthesis techniques which are used in the present work for the preparation of ZnO, doped and codoped ZnO and ZnO based composites are discussed in Section 3.1 to Section 3.3. A brief description with specifications about the various characterisation techniques used in the present work are appended in Section 3.4.

### 3.1 Synthesis of ZnO Nanoparticles

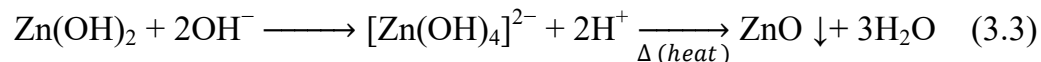
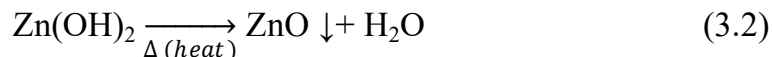
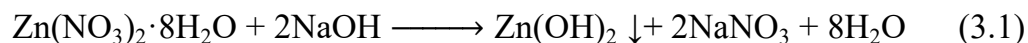
ZnO was synthesised through coprecipitation, combustion and sol-gel techniques. As prepared ZnO powder samples were further calcined at different temperatures and subjected to different characterisations.

#### 3.1.1 Co-precipitation Technique

To synthesise ZnO nanopowder through the conventional coprecipitation technique, the desired quantity of Zinc nitrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (Himedia, 99.0 %)] of 1M solution was taken in a beaker. Aqueous solution of NaOH (Merk - AR) of 1M was added drop wise with constant stirring to the zinc nitrate solution till the required  $p\text{H}$  of the precipitation is attained. A white product was obtained after filtering and washing the precipitate several times with distilled water followed by acetone. Finally, the product was dried at 80 °C for 24 h in a vacuum oven. The ZnO samples were synthesised at 6 different  $p\text{H}$  such as 5.5, 7, 9, 10, 11.5 and 13. Further, all samples were dried at 250 °C for 5 h. A flowchart for the synthesis of ZnO nanoparticles through coprecipitation route is shown in Fig 3.1 and the mechanism of the reaction is given in equation (3.1 to 3.3), where equation 3.1 and 3.2 were followed at lower  $p\text{H}$  ( $\leq 10$  pH) of solution, however, equation 3.3 represent the reaction at higher  $p\text{H}$  ( $\geq 10$  pH) of solution.



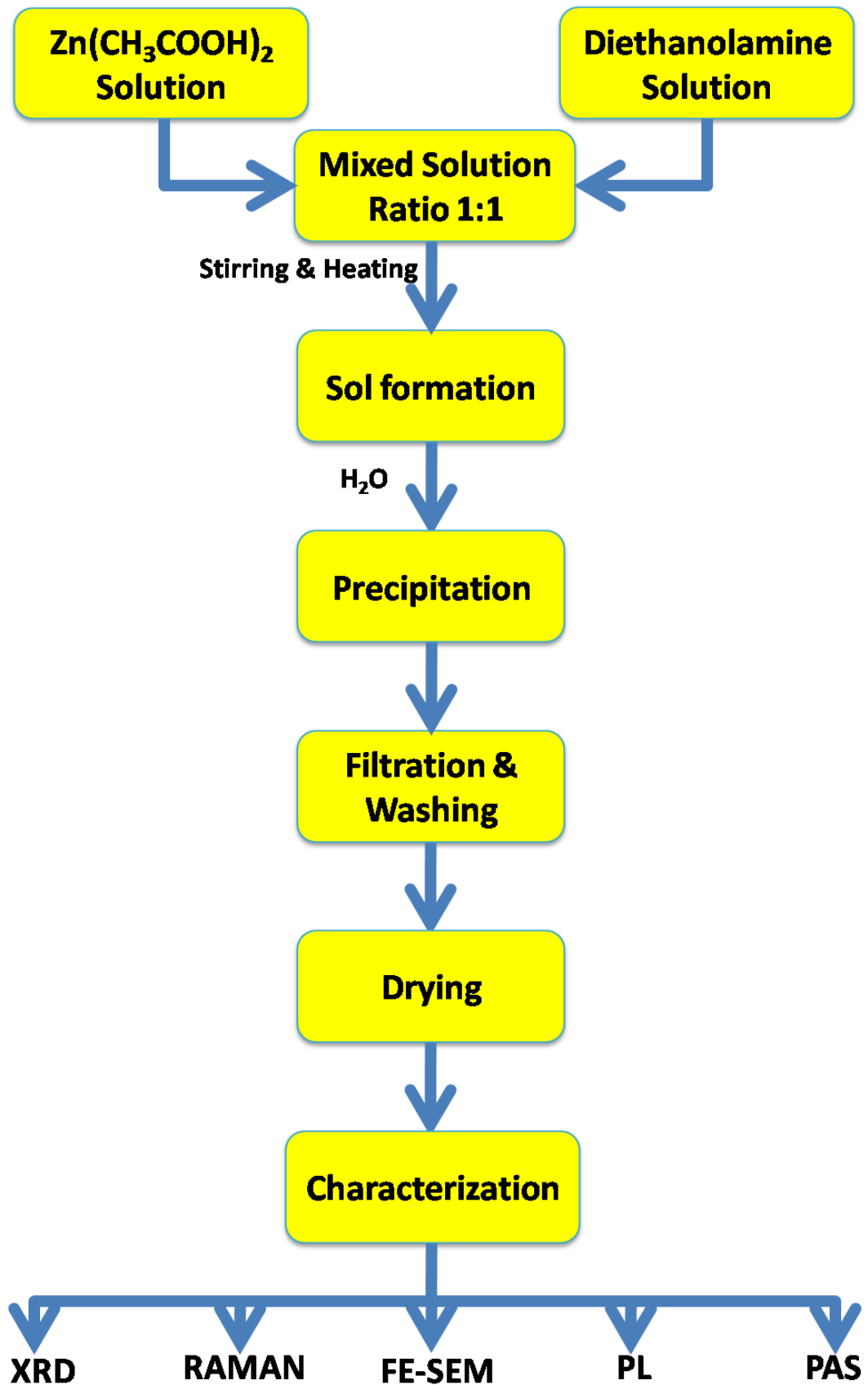
**Figure 3.1** Flow chart of the synthesis of ZnO through co-precipitation technique.



The samples dried at 80 °C and 250 °C were subjected to various characterisations like; X-ray diffraction, Raman spectroscopy, Field emission-scanning electron microscopy, PL spectroscopy and positron annihilation lifetime spectroscopy.

### 3.1.2 Sol-gel Technique

In sol-gel method, ethanol (Merk - absolute) was used as a solvent, and diethanolamine [ $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$ , (DEA), Merk – AR] as a sol stabiliser. Zn of 0.5 M molar solutions were prepared by dissolving zinc acetate 2-hydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , (Himedia, 98.0 %)] in 0.1 L of ethanol in a 250 mL conical flask. All materials were of analytical grade. After vigorous stirring of ethanolic solution for 30 minutes and simultaneous heating at 80 °C, DEA was added drop by drop under constant stirring. The molar ratio of DEA/Zn was fixed at 1:1. In the presence of DEA, the milky solution of zinc acetate became transparent after stirring for 5 minutes. The solution was left for 12 h stirring. The final solution was transparent without any suspension of particles. This transparent organic complex precursor solution was used to prepare ZnO powder. These complexes underwent hydrolysis and inorganic polymerisation leading to the formation of transparent sols consisting of zinc oxide nanoparticles. When water was added drop wise with constant stirring to the solution, precipitation occurred readily. A white product was obtained after filtering and washing the precipitate several times with distilled water followed by ethanol. Finally, the product was dried at 80 °C for 5 h in a vacuum oven. As prepared ZnO sample was calcined at 250, 600, 800 and 1000 °C for 5 hours and were probed through different characterisations such as; X-ray diffraction, Raman spectroscopy, Field emission-scanning electron microscopy, Photoluminescence spectroscopy and positron annihilation lifetime

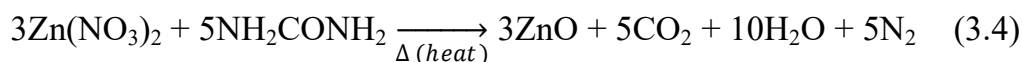


**Figure 3.2** Flow chart of the synthesis of ZnO through sol-gel technique.

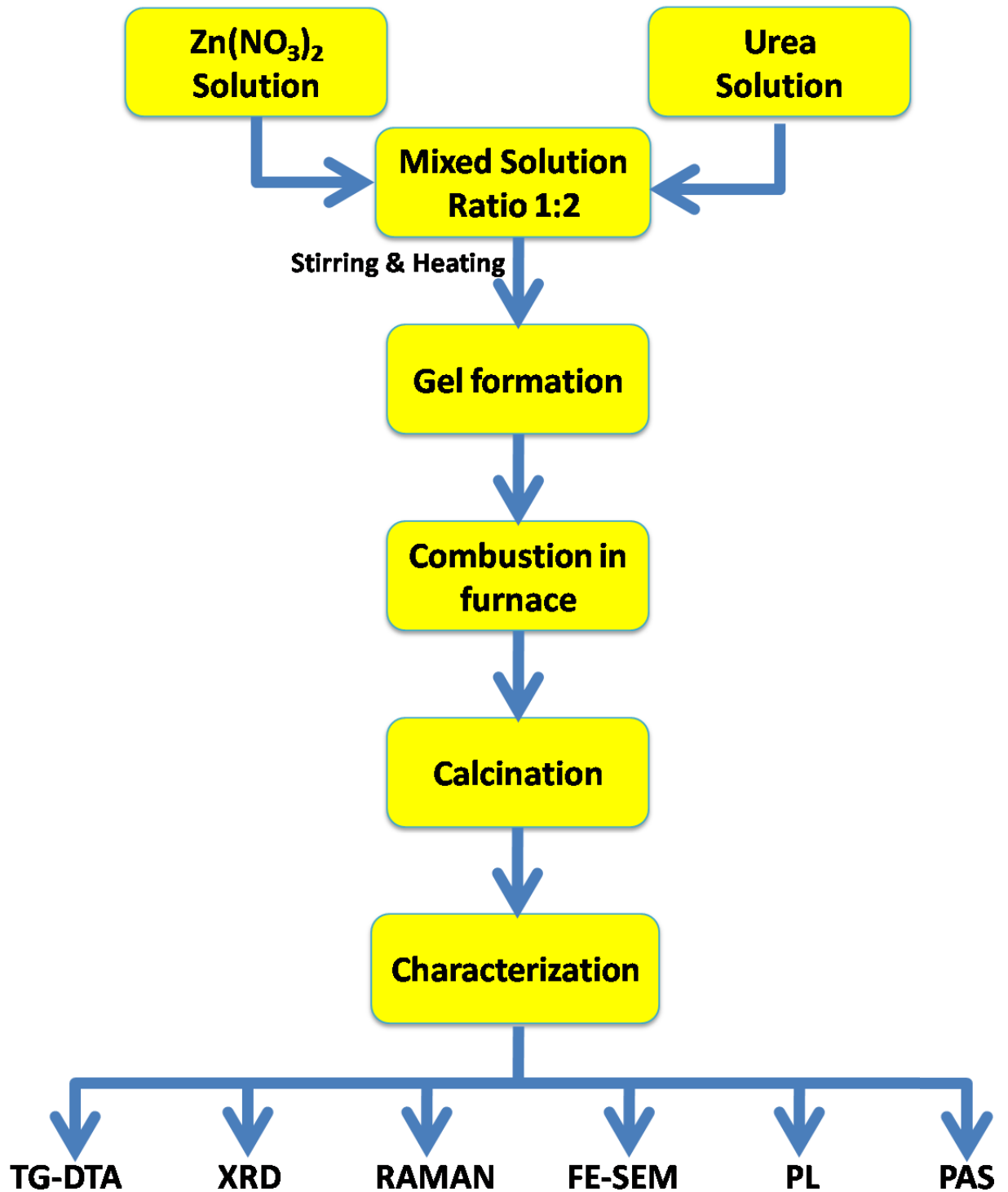
spectroscopy. The flow chart for the synthesis of ZnO through sol-gel technique is shown in Fig 3.2.

### 3.1.3 Combustion Technique

In solution-combustion route, 1M Zn solution was prepared by dissolving Zinc nitrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (Himedia, 99.0 %)] in deionised water. Urea [ $\text{CO}(\text{NH}_2)_2$ , (Himedia - AR)] dissolved in water, was used as a combustion fuel, where its combustion heat is about  $-2.98$  kcal/g. All materials were of analytical grade. The appropriate amount of Zinc nitrate and urea solution were mixed in a beaker and vigorously stirred under a constant heating at  $80$  °C until it became gelatinous. The precursor solution was then poured in a crucible and introduced in a furnace maintained at  $600$  °C. Vigorous exothermic combustion reaction between Zinc nitrates and urea took place. Initially, the solution underwent dehydration and then spontaneous ignition occurred followed by smoldering combustion with enormous swelling. This process produced foamy and voluminous product followed by large amounts of gases. The whole process took hardly 5 to 6 minutes. The synthesis technique utilised the heat energy released by redox exothermic reaction at a relatively low ignition temperature between metal nitrates and urea. The process lasted for a relatively short time, so that the particles could be maintained to the nanometer scale. The flow chart of ZnO synthesis through combustion route is shown in Fig 3.3. The mechanism of the reaction is given below in equation (3.4).



The prepared ZnO sample through combustion route was further calcined at  $600$ ,  $800$ ,  $1000$  and  $1200$  °C for 5 hours and subjected to various characterizations; Thermogravimetry-differential thermal analysis, X-ray diffraction, Raman spectroscopy, Field emission- scanning electron microscopy, Photoluminescence spectroscopy and positron annihilation lifetime spectroscopy.

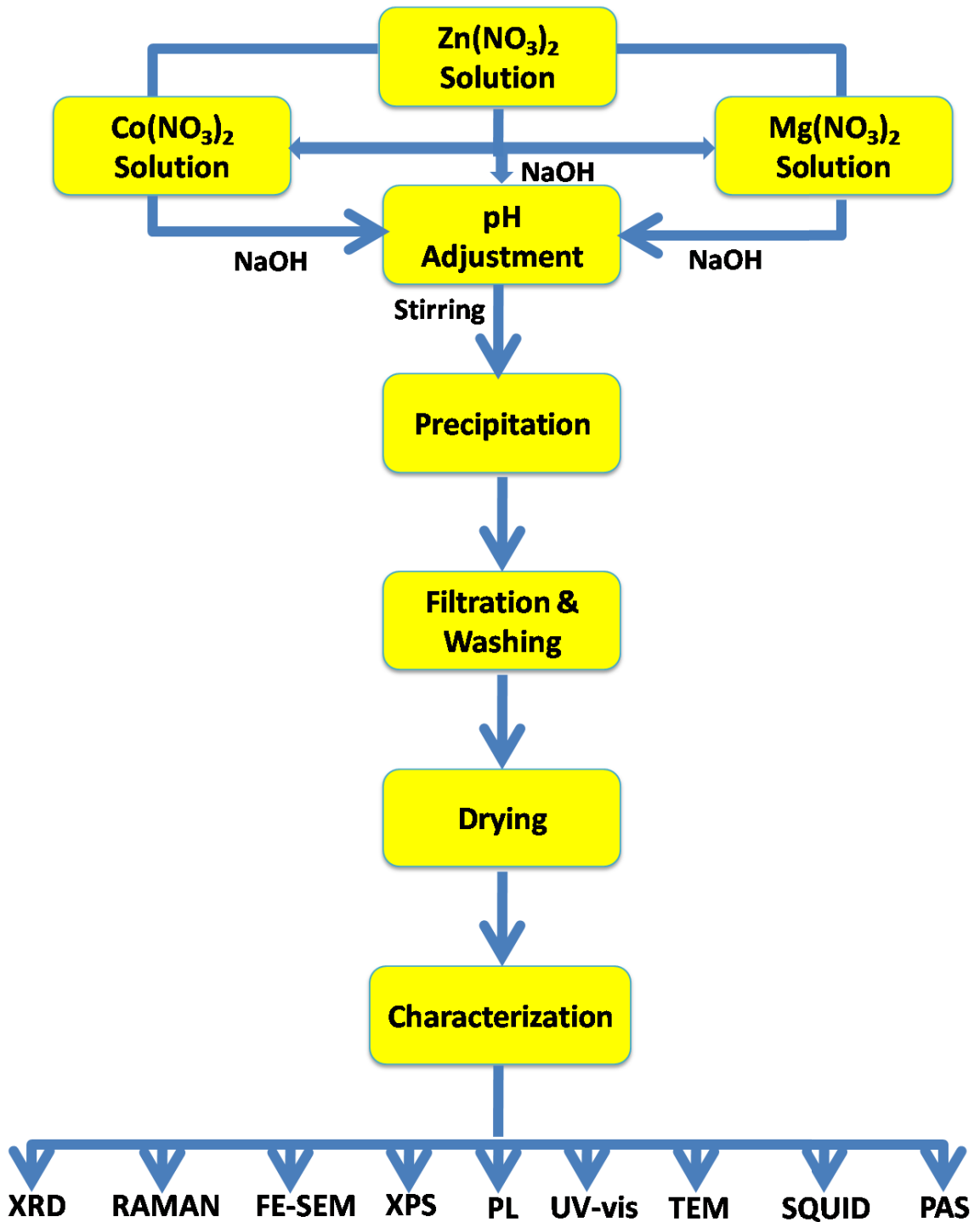


**Figure 3.3** Flow chart of the synthesis of ZnO through combustion technique.

### 3.2 Synthesis of Mg/Co Doped or Mg and Co Codoped ZnO

Mg doped ZnO were synthesised through coprecipitation technique. The calculated amount of  $\text{Mg}(\text{NO}_3)_2$  solution (1M) were mixed with  $\text{Zn}(\text{NO}_3)_2$  (1M) solution in accordance to the composition of  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  ( $x = 0, 0.04, 0.08, 0.12, 0.10$  and  $0.15$ ) and stirred for half an hour for homogenous mixing. 2 M aqueous solution of NaOH was added to the mixed solution drop wise till the final  $p\text{H}$  of the solution attained 11. A white hydroxide powder was precipitated out after filtering and washing the sample several times with distilled water followed by acetone. Finally, the samples of Mg doped ZnO was obtained after drying the precipitate at  $250\text{ }^\circ\text{C}$  for 12 h. Mg/Co doped or Mg and Co codoped ZnO samples were also synthesised through the same coprecipitation technique at  $p\text{H}$  11. The calculated amount of  $\text{Mg}(\text{NO}_3)_2$  and/or  $\text{Co}(\text{NO}_3)_2$  solutions were mixed with  $\text{Zn}(\text{NO}_3)_2$  solution, respectively to synthesise  $\text{Zn}_{1-x-y}\text{Mg}_x\text{Co}_y\text{O}$  with  $x=0.04, y=0$ ;  $x=0.04, y=0.05$  and  $x=0, y=0.05$ . After precipitation, washing, filtration and drying were done to get the desired Mg/Co and Mg, Co codoped sample. Finally, the products of  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  and  $\text{Zn}_{1-x-y}\text{Mg}_x\text{Co}_y\text{O}$  were ground and subjected for different characterisations. The schematic representation for the preparation of  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  and  $\text{Zn}_{1-x-y}\text{Mg}_x\text{Co}_y\text{O}$  samples through co precipitation method is shown in Fig 3.4. Mg doped ZnO was investigated through X-ray diffraction, Transmission electron microscopy, Raman spectroscopy, PL spectroscopy, Fourier transform infra-red spectroscopy, X-ray photoelectron spectroscopy and positron annihilation lifetime spectroscopy. The characterisations like X-ray diffraction, Field emission- scanning electron microscopy, Raman spectroscopy, UV-visible Spectroscopy, Positron annihilation lifetime spectroscopy and Superconducting quantum interference device were used for the analysis of Mg, Co doped and Mg, Co codoped ZnO samples.

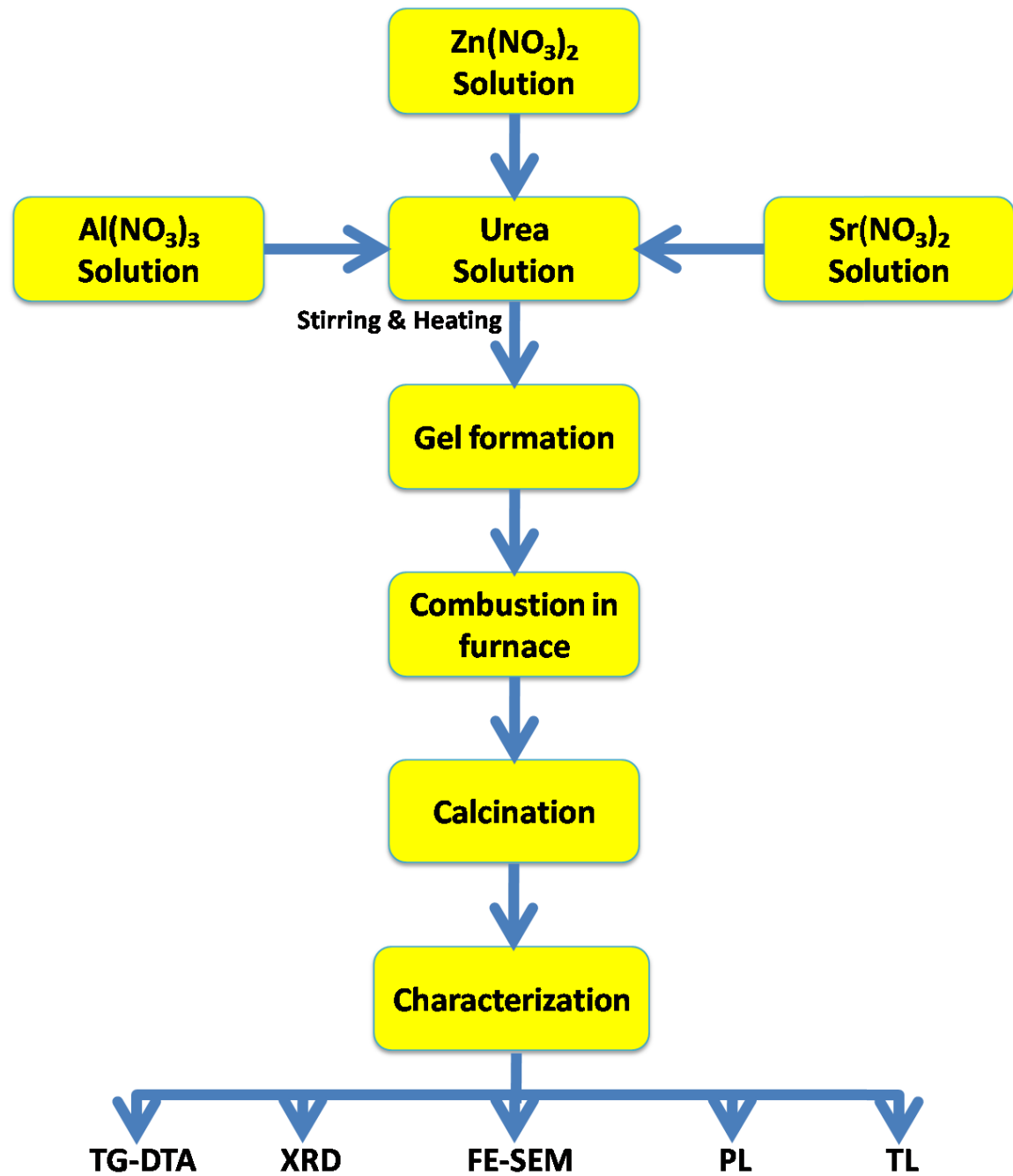




**Figure 3.4** Flow chart of the synthesis of Mg/Co doped or Mg and Co codoped ZnO through co-precipitation technique.

### 3.3 Synthesis of ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> Composites

ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composites were synthesised through combustion technique. Calculated amount of Al(NO<sub>3</sub>)<sub>3</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> solutions were mixed with Zn(NO<sub>3</sub>)<sub>2</sub> solution in a beaker in accordance to the compositional ratio of Al, Sr and Zn present in ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composite, where, ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composite were synthesised by varying ZnO concentrations from 2.5 % to 20 %. In addition, the appropriate amount of urea was mixed with nitrate solution in the same beaker and vigorously stirred at 80 °C until it became gelatinous. The precursor solution was then poured in a crucible and was introduced in a furnace maintained at 700 °C. Vigorous exothermic combustion reaction between metal nitrates and urea took place. The whole process of combustion reaction lasted for 5 to 10 minutes and final product of ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composite were obtained. Further, the composites were calcined at 700, 800, 1000 and 1200 °C for 3 hours. The schematic representation for the synthesis of ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composite using combustion method is shown in Fig 3.5. The characterisations of the materials were carried out through thermo gravimetry-differential thermal analysis, X-ray diffraction, Field emission scanning electron microscopy, X-ray photoelectron spectroscopy, Photoluminescence and Thermoluminescence spectroscopy.



**Figure 3.5** Flow chart of the synthesis of ZnO(%)SrAl<sub>2</sub>O<sub>4</sub> composite through combustion technique.

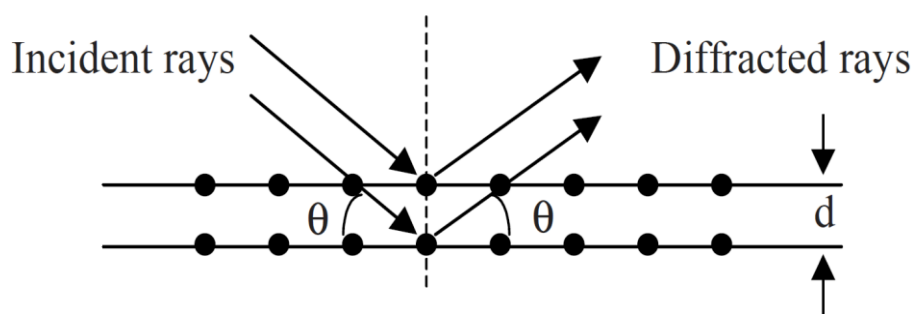
### 3.4 Characterisation Techniques

#### 3.4.1 X-ray Diffraction (XRD)

X-ray diffraction utilises the electromagnetic waves with a wavelength of the order of one angstrom. Because, the lattice constant of the different crystals are the same order of magnitude as the wavelength of the X-rays, which is the first requirement of diffraction. When the X-rays were incident upon a sample, diffraction from different atoms takes place. Diffracted x-rays interfere with each other. In crystals, because the atoms are distributed in periodic manner, the diffracted waves form sharp interference maxima (peaks) with regard to the symmetry of atoms present in crystal. The peaks maximum in an X-ray diffraction pattern is directly related to the atomic distances. Therefore, by measuring the distribution of diffraction pattern one can deduce the crystal structure of a material. According to Bragg's law, if diffraction occurs from a given set of lattice planes where 'd' is the inter-planer distance, the given condition should be followed:

$$2d \sin\theta = n\lambda \quad (3.5)$$

Where, 'θ' is the incident angle, 'λ' is the wavelength of the x-ray, and 'n' is an integer representing the order of the diffraction. This process is shown schematically in Fig. 3.6.



**Figure 3.6** Schematic of diffraction of x-rays by a crystal.

X-ray diffraction experiments were performed using an 18 kW rotating anode (Cu  $K\alpha$ ) based Rigaku powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam. The generator was operated at 40 kV and 150 mA. The powder samples

were placed on a grooved quartz sample holder with the help of a glass slide and scanned from  $20^\circ$  to  $80^\circ$  diffraction angle ( $2\theta @ 4^\circ/\text{min}$ ) at room temperature to explore the crystallinity and structure of pure ZnO, doped/codoped ZnO and ZnO(%) $-\text{SrAl}_2\text{O}_4$  composites.

### 3.4.2 Raman Spectroscopy

In Raman Spectroscopy, when the photons (through laser) were incident upon a sample, they got scattered. The scattering could be either elastically (Rayleigh scattering) or inelastically (Raman scattering). In elastic scattering, the energy of the emitted photon remained same as the incident photon. However, in inelastic scattering, the energies of the scattered photons were different from the incident photons. This phenomenon of inelastic scattering was used in Raman spectroscopy. Therefore, in an inelastic scattering, when incoming photons scattered through the lattice, which either generate a phonon in crystal lattice and re-emitted at a lower energy (anti-Stokes scattering) or annihilated with a phonon from crystal lattice and was re-emitted at a higher energy (Stokes scattering). These inelastically scattered photons (light) were collected, and information about the energy levels (phonon energy of crystal lattice) for a sample could be figured out from the energy change in the light.

Raman scattering of ZnO and doped/codoped ZnO were performed on a micro-Raman setup of Renishaw, UK equipped with a grating of 1800 lines/mm and a peltier cooled charge coupled device (CCD) detector. The  $\text{Ar}^+$  laser (514.5 nm) was adopted as the excitation source. A microscope from Olympus (Model: MX50 A/T) was attached with the spectrometer, that focuses the laser light onto the sample. The GRAM-32 software was used for data collection.

### 3.4.3 Fourier Transform Infra-Red Spectroscopy (FT-IR)

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range of IR is measured as wave numbers typically over the range  $400 - 4000 \text{ cm}^{-1}$ .

FTIR spectra of ZnO and Mg doped ZnO were obtained using a FTIR (*SHIMADZU-8400S* and *JASCO-470 plus*) in the range of 400-4000  $\text{cm}^{-1}$ .

### 3.4.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a technique which provides the valuable information regarding the crystallography and high-resolution images of samples by using electron beam as a source. TEM is operational in two basic modes, image mode and diffraction mode. In TEM, electron beam originate thermionically from the electrons gun and are accelerated to high voltages (in excess of 100 keV). With the help of a condenser lens, the electron beam is subjected onto the sample. When the electrons beam hit the specimen, two types of scattering took place: elastic and inelastic. Elastic scattering involves no loss of energy, while in inelastic scattering, electrons lose some energy. By using elastically scattered electrons, diffraction patterns can be obtained while inelastically scattered electrons give rise to a spatial variation in the intensity of the transmitted beam. The magnification of TEM is directly related with the wavelengths of electron beam. In TEM the wavelengths of electron beam could be vary directly by changing the voltage of electrodes according to Equation (3.6):

$$\lambda = \frac{h}{\sqrt{2m_0eV}} \quad (3.6)$$

For instance, if the voltage of 100 keV is applied across the electrodes, the wavelength will be as small as 0.0386 Å.

In present study, TEM was used to observe the morphology of ZnO and Mg doped ZnO samples. TEM images were obtained using a *TECNAI 20G<sup>2</sup> FEI* operated at an accelerating voltage of 100 kV. During the sample preparation for TEM characterisation, <1µg sample were ground and mixed with 5 ml of methanol. After that, the suspended solution was sonicated to make uniform dispersion of the sample in methanol. Then 1-2 drops of the suspended solution was dived over carbon coated copper grid (Holey Carbon type) by using a faucet to hold a TEM grid. Then the grid was dried (by heater) in air before using in TEM experiment.

### 3.4.5 Scanning Electron Microscopy (SEM)

In a Scanning electron microscope (SEM), electrons were used as a source for the characterisation of samples. Either by thermionically or via field emission process, the electrons were emitted from a tungsten cathode, which were focused by two successive condenser lenses into a very narrow intense beam. With the help of two pairs of coils, the beam of electrons was focused over the sample surface. Upon encroaching on the sample, the primary electrons transmit their energy inelastically to the atomic electrons of crystal lattice. Several scattering processes took place on the sample surface, some electrons managed to leave the surface to be collected by a detector facing the sample. Basically, these electrons were the secondary electrons. Finally, by using photomultiplier tube (PMT) to amplify the signal and modulating this signal with the intensity of a cathode ray tube (CRT), the image of sample was produced. The research quality SEMs are generally able to produce images with a resolution of  $\sim 50 \text{ \AA}$ .

The morphology of ZnO, doped/codoped ZnO and ZnO(%) $-\text{SrAl}_2\text{O}_4$  composites were investigated by using scanning electron microscope (SEM). The surface morphology of the samples was examined with a FESEM ZEISS SUPRA<sup>TM</sup> 40 instrument operated at 5 kV. All the samples were used in powder forms for the observation in SEM.

### 3.4.6 Energy Dispersive Spectroscopy (EDS/EDX)

In EDS, high energy electron beam is used as a source to excite core level electron from the inner orbital (e.g. the  $1s$  shell) of atom present in the sample. Due to the release of inner core electron, formation of hole takes place in a lower shell of atom. Therefore, to fill the hole in a lower shell an electron from an outer shell of atom (e.g. the  $2s$  shell) releases its energy, which consequences in the form of x-ray emission. This x-ray emission is the characteristic of the particular atom present in the sample. Therefore, one could recognise the exact atom present in the sample by analysing the x-ray spectral lines of atom. To analyse the x-ray, cooled Si(Li) detector with an ultrathin

(diamond) x-ray window (lithium drifted silicon detector) is used in EDS. In most of the cases, EDS systems are attached with SEM and utilise the same electron beam source to excite x-rays from the sample subjected for analysis.

The compositional details of Mg/Co doped or Mg and Co codoped ZnO samples were investigated by using EDS of Oxford x-ray system integrated with Scanning Electron Microscope (SEM). The Oxford x-ray system was controlled by software known as INCA. INCA allows users to acquire an x-ray spectrum from a specified point or area.

#### **3.4.7 Thermogravimetry-Differential Thermal Analysis (TG-DTA)**

TGA is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled rising temperature program. On the other hand, the DTA method consists of measuring the heat changes associated with physical or chemical transformations occurring during the gradual heating of a substance. Thermal changes, such as dehydration, crystalline transition, lattice destruction, oxidation and decomposition, are generally accompanied by an appreciable rise or fall in temperature and are amenable to DTA investigation. Mutually the TGA and DTA facilitate as TG-DTA equipment and consist of a furnace, a temperature regulator, a specimen block, sensitive weighing machine, thermocouples, and a temperature-recording system.

The thermal properties of the samples synthesised through combustion technique such as ZnO, SrAl<sub>2</sub>O<sub>4</sub> and ZnO(20%)- SrAl<sub>2</sub>O<sub>4</sub> composite were measured using a Mettler 832 *TG-DTA* instrument. The melting temperature, crystallisation temperature and heat of fusion of all samples were undertaken at a scan rate of 10 °C min<sup>-1</sup>.

#### **3.4.8 X-ray Photoelectron Spectroscopy (XPS)**

In the XPS technique, low-energy x-rays are used as a source. When the x-ray is focused onto the sample, the electrons are ejected by absorbing the photon in accordance to photoelectric effect. The energy of the ejected electron is as follows as shown in Eq. (3.7):



$$E_{KE} = h\nu - E_{BE} \quad (3.7)$$

Where,  $E_{KE}$  is the energy of the ejected electron,  $h\nu$  is the energy of the incident photon, and  $E_{BE}$  is the energy of the involved bound electron state. Therefore, we can measure the photoelectron energy (binding energy) as well as identify the particular atom, since the values of binding energy are element specific. Moreover, XPS is sensitive regarding the concentration of different elements in multi-component samples and show relative peak intensities proportional to the concentration of the element.

To identify the chemical bonding and valency of ions in ZnO, Mg doped ZnO and ZnO-SrAl<sub>2</sub>O<sub>4</sub> composite, X-ray photoelectron spectroscopy (XPS) study was carried out at a base pressure better than  $5 \times 10^{-9}$  Torr. The measurement was done by using an Mg and Al twin anode x-ray gun with Mg-K <sub>$\alpha$</sub>  and Al K <sub>$\alpha$</sub>  radiations of incident energy 1253.3 eV and 1486.6 eV, respectively. Graphitic C-1s peak (284.6 eV) has been used as an internal reference to calibrate the shifts in binding energies of core levels due to charging effect.

### 3.4.9 UV-visible Spectroscopy

UV visible spectroscopy utilises the UV as well as visible light spectrum for the measurement. During the measurement, the UV/visible light beam was incident upon the sample subjected for study and a reference sample, simultaneously. The absorbed/transmitted/reflected light from the sample was collected by a photodetector through a spectrometer. This collected light intensity was compared with the intensity coming from the reference sample and plotted as a function of wavelength. In this way the absorbance/transmittance/reflectance of the sample subjected under study can be obtained as a function of wavelength. In semiconductor, the band-to-band absorption as a function of wavelength obtained through UV visible spectroscopy can also be used to calculate the bandgap. The relationship (Equation (3.8)) among the absorption coefficient  $\alpha$ , the light energy  $E$ , and the bandgap energy ( $E_g$ ) is shown in following expression:

$$\alpha = [A(h\nu - E_g)^{m/2}]/h\nu \quad (3.8)$$

Where,  $m = 1$  for a direct transition and  $m = 4$  for an indirect transition and  $A$  is a constant.

UV-visible absorption spectra of the ZnO and doped/codoped ZnO were recorded by using Shimadzu (*UV-2600*) spectrophotometer operating in the spectral range of 200-800 nm.

### 3.4.10 Photoluminescence Spectroscopy (PL)

Photoluminescence (PL) spectroscopy is a non-destructive method of probing the optical properties of materials. In *PL* study, when light was focused (through Laser or Xenon lamp) onto the sample, the electrons in the sample at ground state absorbed the energy and got excited to some permissible excited states. This process is called “photo-excitation”. After that, the excited electrons relaxed back to their equilibrium states and the absorbed energy was released through emission of light. This emitted light was then collected by a photo detector through a spectrometer. Many useful information can be extracted out of PL spectra:

1. We can determine the bandgap of semiconductors by collecting the photon emission through radiative transition in between the conduction and valence band states.
2. If the impurity and defects are present in semiconductors, then there will be defect energy levels in between the conduction and valence band. These energy levels work as metastable state and the radiative transitions associated with these levels can be used to identify specific impurity and defect.

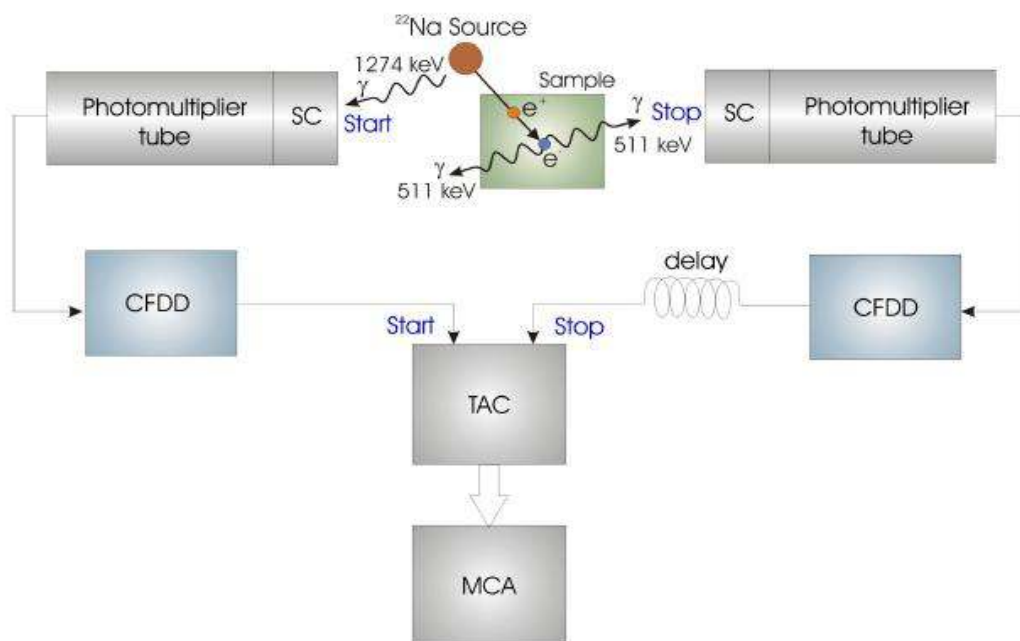
PL study was carried out to study the emission spectra of ZnO, Mg doped ZnO and ZnO(%)-SrAl<sub>2</sub>O<sub>4</sub> composites by using third and fourth harmonic of a pulsed Nd: YAG laser (Spitlight600, Innolas, Germany,) as a light source (355 and 266 nm wavelength) with Ocean Optics QE65000 as dispersing device. Xenon lamp in wave length range 280-900 nm (Horiba Jobin

Yvon Spectrofluorometer, FluoroMax®-4), was used for recording the excitation spectra of ZnO(20%)-SrAl<sub>2</sub>O<sub>4</sub> composite calcined at 1200 °C.

### 3.4.11 Positron Annihilation Spectroscopy (PAS)

Positron annihilation spectroscopy (*PAS*) utilizes positron as a source. Positron ( $e^+$ ) is the antiparticle of electron ( $e^-$ ). During the measurement, PAS consists of inserting positrons into a sample and measuring their lifetime spectrum. The  $\beta^+$  radioactive isotope <sup>22</sup>Na, the most widely used positron source which was used for positron annihilation. The advantage of this isotope is that, its most numerous decay channel is the emission of a  $\gamma$ -ray of 1274 keV in concurrence with the positron. The emission of a  $\gamma$ -ray with photon energy 1274 keV gives the signal which points out the birth of the positron. After that, the positron loses rapidly their energy by scattering through matter. Therefore, due to thermalisation through matter, the initial kinetic energy of positrons drop below 0.1 eV and positrons annihilate in cationic vacancy by emitting another  $\gamma$ -ray with photon energy about 511 keV. This  $\gamma$ -ray with energy 511 keV gives another signal of annihilation of positron and therefore, we can measure the thermalisation time (life time)  $t_{th}$  by measuring the difference in between the birth time and annihilation time of positron. Thus, to facilitate the calculation of positron lifetime, one basically needs two scintillation detectors (SC) attached to a time analyser. The two detectors feed, through single-channel analysers (SCA) accurately synchronised for the energies of the two photons, a time-to-amplitude converter (TAC) with a positron birth signal (the 1274 keV photon) and a positron annihilation signal (one of the two 511 keV photons). The output of the TAC, which is a pulse of height proportional to the time delay between start and stop signals, was then counted and classified by multi channel analyser (MCA). A simplified block diagram of PAS is shown in Fig 3.7.

Different abbreviations used in flowchart are described as: SC, Plastic scintillator, CFD; Constant fraction discriminator, TAC; Time to amplitude converter, MCA; Multi channel analyser.



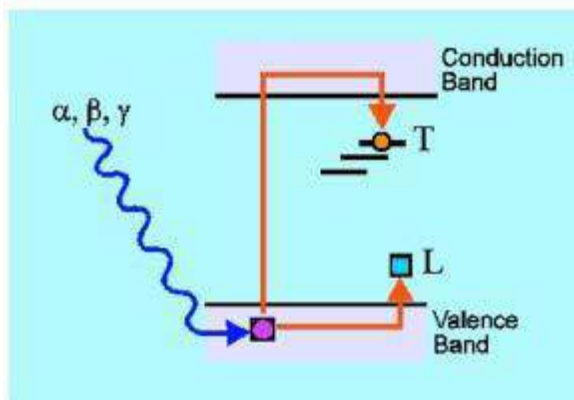
**Figure 3.7** Flowchart for PAL spectrometer.

In this work, Positron annihilation lifetime (*PAL*) measurement was carried out to detect the cationic defects in ZnO and doped/codoped ZnO by using a fast-fast coincidence system consisting of two 1 in. tapered off BaF<sub>2</sub> scintillators coupled with XP 2020Q photomultiplier tubes. The prompt time resolution of the system using a  $^{60}\text{Co}$  source with  $^{22}\text{Na}$  gate was 298 ps. The lifetime spectra were deconvoluted using the code PATFIT 88.

### 3.4.12 Thermoluminescence Spectroscopy (TL)

When the sample is exposed to the ionised radiation, the electrons and holes (vacancy of an electron) are produced in pairs: they can be captured in the electron traps (denoted as L) and holes traps (denoted as T), as shown in Fig. 3.8. These traps are metastable, and usually their lifetime is very long at room temperature. When such irradiated samples are heat treated, the stimulation of trapped electron ‘L’ from a metastable level to the conduction band take place. Further, electron ‘L’ in conduction band annihilate with the hole ‘T’. This process of recombination of electron with a hole is known as thermoluminescence. Thermoluminescence is important since the study of the temperature dependence of the afterglow intensity and spectrum, permits one to

draw conclusions about the depths at which impurity or defects levels lie in solids.



**Figure 3.8** Traps level in a crystal.

In Thermoluminescence (TL) study,  $\text{Co}^{60}$  source was used to perform  $\gamma$  irradiations over  $\text{ZnO}(20\%)\text{-SrAl}_2\text{O}_4$  composite calcined at  $700\text{ }^\circ\text{C}$  and  $1200\text{ }^\circ\text{C}$ . The small pieces of sample were exposed to  $\gamma$  rays using  $5\text{ Gy/min}$  dose rate at room temperature. TL measurements were carried out using a heating rate of  $5\text{ }^\circ\text{C/s}$ . TL glow curves were recorded for each sample using a Harshow TLD reader (Model 3500) fitted with a 931B photo multiplier tube (PMT).

### 3.4.13 SQUID Magnetometer

SQUID uses a Superconducting Quantum Interference Device (SQUID) magnetometer to monitor very small changes in magnetic flux that explores the magnetic properties of the samples. The SQUID detects and measures the magnetic moment of the sample. From this, the magnetization, magnetic susceptibility can be determined.

In the present case, the magnetic measurements were carried out for Mg and Co codoped ZnO with a magnetic property measurement system (MPMS - XL) from Quantum Design, USA with reciprocating sample option (RSO) mode. Few limitations of the instrument are given bellow.

- **Maximum Sample Size:** 9 mm
- **Field Uniformity:** 0.01% over 4 cm
- **Temperature Range:** 1.9 – 400 K