3. EXPERIMENTAL WORK

3.1 SYNTHESIS OF MOLYBDATE AND TUNGSTATE BASED PHOSPHORS

This chapter presents the depiction of materials and method used for synthesizing phosphor materials for various lighting applications. It also deals with the various instruments used for characterization of the synthesized phosphors.

3.1.1 Materials

\( \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \) (Merck), \( \text{CaCl}_2 \) (Merck), \( \text{EuCl}_3 \) (Himedia), \( \text{TbCl}_3 \) (Himedia), \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \) (Merck), \( \text{SrCl}_2 \) (Merck), \( \text{LiCl} \) (Merck), \( \text{BaCl}_2 \) (Merck), \( \text{GdCl}_3 \) (Merck), \( \text{PrCl}_3 \) (Himedia) and \( \text{SmCl}_3 \) (Himedia) are the various chemicals used for the synthesis of the phosphor materials discussed in this thesis.

Keeping in mind that even a small amount of impurity lowers the luminescent intensity of the light emitting materials, all the chemicals used for the synthesis of the phosphors were of high purity i.e. >99%.

3.1.2 Mechanochemically (ball mill) assisted solid state metathesis route

The origin of the word metathesis had come from the phrase “move out of my sun” spoken by Diogenes to Alexander the great [125]. Metathesis thus means moving from one place to another. It is reported that micro/nano structured materials such as nanotubes, nanocrystals, and high-surface-area materials can be produced by this simple and economical route. The principle behind these reactions is to use the exothermicity of formation of a salt to produce a compound rapidly. If the appropriate starting materials are chosen, a highly exothermic reaction can be devised. Metathesis reactions have been used successfully in the preparation of several crystalline materials such as vanadates, molybdates, tungstates, etc.
The room temperature mechanochemically assisted solid-state metathesis (SSM) reaction has the following advantages as shown in Figure 3.1.

**Figure. 3.1:** Advantages of room temperature solid state metathesis route.

SSM reactions can be initiated by flame, furnace, heated filament, ball mill (to be used in our experimentation) and microwave. The phase produced is often determined by the rate of the reaction. Similarly, the reaction rate can be tuned to control the crystallite size of the products formed.

Different types of milling equipments (SPEX shaker mill, Attritor mill, commercial mill, planetary ball mill (to be used in our experimentation (Figure. 3.2))) are used to produce mechanically alloyed powders. They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating, etc.

Planetary ball mills are used wherever the highest degree of fineness is required. Apart from the classical mixing and size reduction processes, the mills also meet all the technical requirements for colloidal grinding and have the energy input necessary for mechanical alloying processes. The planetary
ball mill owes its name due to planet-like movement of its vials and can mill about 10±20 g of the powder at a time.

Figure 3.2: Planetary ball mill

The extremely high centrifugal forces of the planetary ball mill result very high pulverization energy and therefore short grinding times. Since the rotation directions of the bowl and turn disc are opposite, the centrifugal forces are alternately synchronized. Thus, friction resulted from the hardened milling balls and the powder mixture being ground alternately rolling on the inner wall of the bowl and striking the opposite wall. The impact energy of the milling balls in the normal direction attains a value of up to 40 times higher than that due to gravitational acceleration. Hence, the planetary ball mill can be used for high-speed milling.

Together with the “comfort” grinding jars, the planetary ball mills offer the highest possible degree of performance, safety and reliability. Planetary ball mills pulverize and mix soft, medium-hard to extremely hard, brittle and fibrous materials. Dry and wet grinding can be carried out. Planetary ball mills are used successfully in virtually all industry and research sectors, in particular wherever the highest demands are placed on purity, quickness, fineness and reproducibility.
Various factors influencing the milling process for obtaining best possible product phase is shown in figure. 3.3 and are considered in the following texts.

(i) Milling media and container

The composite of the milling container is crucial as materials may dislocate from the inner wall owing to the impact of milling. Cross contamination might be avoided by using the same material for the grinding container and for the grinding medium. The inner wall of the grinding medium ought to be thick and high as much as necessary to allow the ball to create high impact force on the grinding material. Different types of materials, such as hardened steel, tempered steel, stainless steel, chromium, tungsten carbide lined etc. are generally used for the milling container.

(ii) Milling Speed

It is one of the parameters, which has to be optimised to produce homogenous distribution of phosphor materials. In ball mill, increasing the rotation speed of the ball may jam the ball, applying no effects on the materials. Therefore, the milling speeds should be optimised in order to keep the ball moving. In addition to that, high milling speed produces high temperature that might contaminate the materials in the container.

(iii) Milling time

To obtain good results, materials should be milled for an optimal time. If the powder is milled longer than the required time, unwanted contamination and phase transformation might take place. The required milling time for a particular sample can be found based on the parameter such as type of mill, ball to powder ratio, temperature of milling and intensity of milling.
(iv) Ball to powder weight ratio

The ball to powder weight ratio (BPR) or charge ratio is one of the important variables for the milling operation. It plays significant effects on time required to obtain a fine particle from powder. The higher the BPR the shorter the time required. Different researchers have used the BPR as low as 1:1 to as high as 220:1.

(v) Extent of filling the milling vial

To produce a fine powder particles, milling vial should be 50% filled and 50% empty to allow the free moving of the milling ball and the powder particles around the chamber. If the quantity of the ball and powder particles is large, there will be not enough space for balls to move. This would produce less impact on powder particles. Thus, special care has to be taken during the filling of milling machine with ball and powder.

(vi) Milling atmosphere

The milling atmosphere is one of the factors responsible for contaminating the milling powder. Generally, the milling chamber is evacuated or filled with inert gas such as argon or helium to avoid this contamination. Different atmospheres can be used in the milling media if particular effects are desired.
(vii) Temperature effects

The temperature of the milling container depends on the characteristics of the milling powder, milling vessels and the kinetic energy of the milling ball. The arising temperature induces diffusion and defects in the milling powder followed by particle phase transformation.

3.1.3 Preparation of Phosphors

The various molybdate and tungstate based phosphors were prepared by mechanochemically assisted SSM route at room temperature by using AR grade chemicals as the starting materials without any further purification. The flowchart for the synthesis of phosphor powder by mechanochemically assisted SSM reaction route at room temperature is shown in figure 3.4.

![Flowchart for the synthesis of phosphor powder by mechanochemically assisted SSM reaction route at room temperature.](image)

**Figure. 3.4:** The flowchart for the synthesis of phosphor powder by mechanochemically assisted SSM reaction route at room temperature.
The appropriate stoichiometric mixtures of starting materials were mixed and were milled for a period of one hour in a planetary ball mill Pulverisette 7 (FRITSCH) by fixing the parameters as given in table 3.1.

**Table. 3.1:** The parameters used in mechanical milling with a planetary ball mill (Pulverisette-7 (Monomill))

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding Bowl Volume</td>
<td>15 ccm</td>
</tr>
<tr>
<td>Material</td>
<td>Tungsten Carbide</td>
</tr>
<tr>
<td>Ball-To-Powder Weight Ratio</td>
<td>1:1</td>
</tr>
<tr>
<td>Ball Diameter</td>
<td>12 mm</td>
</tr>
<tr>
<td>Ball And Vial Material</td>
<td>Hardened Tungsten Carbide</td>
</tr>
<tr>
<td>Rotation Speed (optimised)</td>
<td>300 Rpm</td>
</tr>
<tr>
<td>Milling Time (optimised)</td>
<td>1 Hour</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Air</td>
</tr>
<tr>
<td>Interruption Time</td>
<td>Nil</td>
</tr>
</tbody>
</table>

Milling was carried out in two grinding vials of 15 ccm volume containing ball with a diameter of 12 mm. Both the container and balls were made of tungsten carbide material. The number of milling balls and the rotation speed of the planetary system of milling device were optimized and kept constant.

The resultant powder was washed with distilled water to remove sodium chloride that was the by-product of the reaction and then dried at 80 °C for 3h in a muffle furnace in air and sieved. At long last, the productive red and green phosphor materials were obtained.
3.2 Synthesis of CaMoO$_4$:xEu$^{3+}$ and CaMoO$_4$:xTb$^{3+}$ phosphor

The red phosphors of CaMoO$_4$:xEu$^{3+}$ (x = 0.02, 0.04, 0.06, 0.08, 0.10) and green phosphors of CaMoO$_4$:x Tb$^{3+}$ (x = 0.02, 0.04, 0.06, 0.08 and 0.10 mol) were prepared by mechanochemically assisted SSM route at room temperature by using AR grade Na$_2$MoO$_4$.2H$_2$O, CaCl$_2$, EuCl$_3$ (99.9%) and TbCl$_3$ (99.9%) as the starting materials without any further purification. The phosphor materials of different rare earth doping concentrations were prepared as described in section 3.1.3.

\[
\text{CaCl}_2 + \text{Na}_2\text{MoO}_4.2\text{H}_2\text{O} \rightarrow \text{CaMoO}_4 + \text{NaCl} \quad (B = \text{Mo, W})
\]

3.3 Synthesis of AWO$_4$:Tb$^{3+}$ (A=Ca, Sr) phosphor

The green phosphors of Ca$_{1-x}$WO$_4$:xTb$^{3+}$ (x = 0.02, 0.04, 0.06, 0.08 and 0.1 mol) and Sr$_{1-x}$WO$_4$:xTb$^{3+}$ (x = 0.02, 0.04, 0.06, 0.08 and 0.1 mol) were prepared by mechanochemically assisted SSM route at room temperature by using AR grade Na$_2$WO$_4$.2H$_2$O, CaCl$_2$, SrCl$_2$ and TbCl$_3$ (99.9%) as the starting materials. All the chemicals were utilized without any further refinement. The green phosphors are synthesised as described in section 3.1.3.

\[
\text{ACl}_2 + \text{Na}_2\text{WO}_4.2\text{H}_2\text{O} \rightarrow \text{AWO}_4 + \text{NaCl} \quad [A= \text{Ca, Sr}]
\]

3.4 Synthesis of Li$_3$Ba$_2$Gd$_3$(MoO$_4$)$_8$:RE$^{3+}$ (Eu$^{3+}$/ Tb$^{3+}$/ Pr$^{3+}$/ Sm$^{3+}$) phosphor

The red phosphors of Li$_3$Ba$_2$Gd$_{3-x}$(MoO$_4$)$_8$:xRE$^{3+}$ (x = 0.01, 0.03, 0.05, 0.07 and 0.09 mol) were prepared by mechanochemically assisted SSM route at room temperature by using AR grade LiCl, BaCl$_2$, GdCl$_3$, Na$_2$MoO$_4$.2H$_2$O, PrCl$_3$ (99.9%), SmCl$_3$ (99.9%) and EuCl$_3$ (99.9%) as the starting materials and used without any further purification. The efficient red phosphors were prepared as described in section 3.1.3. The synthesized system may be as follows:

\[
3\text{LiCl} + 2\text{BaCl}_2 + 3\text{GdCl}_3 + 8\text{Na}_2\text{MoO}_4 \rightarrow \text{Li}_3\text{Ba}_2\text{Gd}_3\text{(MoO}_4)_8 + 16\text{NaCl}
\]
3.5 CHARACTERIZATIONS

3.5.1 X-Ray Diffraction (XRD) Analysis

X rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X rays (hard X rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of X rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X rays can penetrate deep into the materials and provide information about the bulk structure. Powder diffraction data are usually presented as a diffractogram in which the diffracted intensity is shown as function either of the scattering angle, 2θ or interplanar spacing, d. The diffractogram data can be analysed for phase identification and for calculation of lattice parameters, extent of crystallinity, crystallite size and strain present in the lattice. For the structural characterization of phosphor materials, here PAN analytical X’pert PRO Xray diffractometer is used. The instrumental parameters are summarized in Table 3.2.

**Table. 3.2:** Instrumental parameters of PAN analytical X’pert PRO X ray diffractometer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goniometer radius</td>
<td>240 mm</td>
</tr>
<tr>
<td>Scan Type</td>
<td>Continuous</td>
</tr>
<tr>
<td>Divergence slit type</td>
<td>Fixed</td>
</tr>
<tr>
<td>Divergence slit width</td>
<td>0.5°</td>
</tr>
<tr>
<td>Specimen length</td>
<td>10 mm</td>
</tr>
<tr>
<td>Anode material</td>
<td>Cu</td>
</tr>
</tbody>
</table>
3.5.2 Scanning Electron Microscope (SEM)

For structural analysis using SEM, non-conductive solid specimens should be coated with a layer of conductive material except when observed with Variable Vacuum or Environmental SEM. Such coatings are made on the surface of non-conductive samples using gold or palladium (Goldstein J. I et al 1981). The micro structural analysis of the as prepared phosphors was carried out by SEM Philips XL30 scanning electron microscope. The details of the instrumental settings are summarized in Table 3.3.

<table>
<thead>
<tr>
<th>Table 3.3: Instrumental parameters of SEM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
</tr>
<tr>
<td>Accelerating Voltage</td>
</tr>
<tr>
<td>Working depth</td>
</tr>
<tr>
<td>Magnification</td>
</tr>
<tr>
<td>Probe Current</td>
</tr>
<tr>
<td>Filament</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Specimen Holder</td>
</tr>
</tbody>
</table>

3.5.3 Vibrational spectroscopy

Vibrational spectroscopic techniques are extensively used to identify the nature of different linkages present in the material. These methods also provide valuable information regarding the symmetry of different vibrational units. Two types of vibrational techniques, namely IR and Raman spectroscopy are used in the present study for selected samples and the principle is briefly described below.
(i) IR spectroscopy

Vibrations of bonds and groups, which involve a change in the dipole moment results in the absorption of infrared radiation, which forms the basis of IR spectroscopy. Modern IR instruments are based on Fourier transformation method to improve the signal to noise ratio. Unlike conventional IR instrument, in FTIR instrument, all the frequencies are used simultaneously to excite all the vibrational modes of different types of bonds/linkages present in the sample. This reduces the experimental time considerably.

In the present study, Fourier Transform Infrared spectroscopy (FTIR) measurements were carried out in the wavelength range of 400–4000 cm\(^{-1}\) with a Nicolet 6700 FTIR equipped with a deuterated triglycine sulfate detector.

(ii) Raman spectroscopy

Raman spectroscopy is a very convenient technique for identification of crystalline or molecular phases, for obtaining structural information. Backscattering geometries allow films, coatings and surfaces to be easily analyzed. Ambient atmosphere can be used and no special sample preparation is needed for analyzing samples by this technique.

Raman spectra were monitored by a RFS/100/S Bruker FT-Raman spectrometer with an Nd doped yttrium aluminium garnet laser providing excitation light at 1064 nm at the frequency range of 150 - 1000 cm\(^{-1}\). The spectra were collected using a grating with 1200 groves/mm with a slit width of \(~50\) micron (yielding a resolution of \(~1\) cm\(^{-1}\)), along with Peltier cooled CCD and a Razor edge filter.
3.5.4 Luminescence Spectroscopy

It is the study of luminescence, which arises due to spin-forbidden transitions in phosphorescence and spin-allowed transitions in fluorescence, their stimulation and subsequent relaxation. It provides information about the electronic structure, and how energy may be dissipated into other modes of molecular motions. The photoluminescence spectra are obtained by plotting the relationship between the wavelength and the intensity of the emitted light from a sample excited by an appropriate excitation source of constant energy. The emission mostly occurs from the lowest electronically excited state with the lowest vibrational state to the electronic ground state at different vibrational levels. Consequently, often the spectrum of the fluorescent light is independent of the excitation wavelength. The excitation source can be light, electron beam, heat, X-rays or radiation from radioactive materials. The spectra are obtained using a monochromator equipped with an appropriate light detector.

In general, Photoluminescence (PL) spectra are taken for phosphors in the powder form only. The powder is placed in a cleaned quartz cuvetts. PL spectra are taken by exciting the samples with a particular wavelength of light (usually the wavelength of peak absorption). The light source is a xenon arch lamp with broad-spectrum emission. In the case of an excitation spectrum, on the other hand, the relationship is obtained by observing change in the emitted light intensity at a set wavelength while varying the excitation energy. When the excitation source is light, single-frequency light produced by a monochromator on the sample and the emitted light intensity is recorded as the excitation wavelength is varies. In spectra, light intensity at a given wavelength is expressed along the ordinate and the wavelength along the abscissa. Both the excitation and emission spectra are recorded by fixing the excitation and emission monochromator slit widths at 0.5 and 1 nm respectively.