Chapter II

Experimental
This chapter describes the experimental techniques employed in the present work. The method of preparation of glass samples and the instrumentation of ESR spectrometer and UV-VIS-NIR spectrophotometer are described briefly. The method of preparation of phosphors is explained in their respective Chapters (VI & VII).

The luminescence emission and excitation spectra (Shimadzu spectrofluorophotometer, model RF 510 with a 150 W Xenon lamp) and the FT-IR spectrum (Perkin – Elmer FT-IR Spectrophotometer using KBr pellet technique) of the phosphors were recorded at room temperature at Indian Institute of Science, Bangalore, India. Hence the description of these instruments is not presented here.

1. Glass preparation

All the glass systems studied in the present work were prepared by the melt-quenching technique. The starting materials used for the preparation of the glass systems are of high purity. The chemicals were weighed accurately using an electrical balance, mixed thoroughly and ground to fine powder. The batches were melted in porcelain crucibles by placing them in an electrical furnace at their respective melting temperatures. The melts were then poured on a polished brass plate and pressed quickly with another brass plate. The glasses thus obtained were transparent. The colour of the glass samples depends on the nature of the dopant. About 100 mg of powdered glass samples were used to record EPR spectra. The polycrystalline diphenyl picryl hydrazyl (DPPH) is used as a standard field marker. The optical absorption spectra were recorded for the polished glass samples having uniform thickness.
2. ESR spectrometer

In the present work, the EPR measurements were carried out on a JEOL FEIX ESR spectrometer operating in the X-band frequency (8.8 to 9.6 GHz) with a field modulation of 100 kHz. A photograph of JEOL FEIX ESR spectrometer is shown in Fig. 1. The block diagram of ESR spectrometer is shown in Fig. 2. The block diagram of the JEOL FEIX ESR spectrometer is shown in Fig. 3 [1].

The JEOL FEIX ESR spectrometer operates at 100 V / 260 VA. It consists of the following parts.

(a) Microwave unit (b) Cavity resonator (c) Electromagnet and its excitation power supply and (d) Detectors.

(a) Microwave unit

The microwave unit along with a pre-amplifier, an Automatic frequency control (AFC) circuit and a Gunn diode oscillator power supply form the heart of the instrument. The microwave power supply provides approximately +10 V to the Gunn diode oscillator and +25 V to the varactor diode. They will be mounted in the middle of the cavity. The Gunn diode oscillator generates microwaves over a frequency range of 8.8 GHz to 9.6 GHz (i.e. in X-band) at a power, which can be varied from 0.1 μW to 200 mW. The frequency of oscillation can be varied mechanically by varying the cavity resonant frequency. The AFC circuit measures the frequency stability so that the frequency of the Gunn diode oscillator matches the resonant frequency of the sample cavity resonator.
Fig. 1. A photograph of JEOL FE1X ESR spectrometer.
Fig. 2. The block diagram of ESR spectrometer.
Fig. 3. The block diagram of JEOI-FEIIX ESR spectrometer.
The microwaves then pass through the isolator, which minimises the perturbations in microwave frequency that may occur due to significant background reflections from the rest of the system. The directional coupler divides microwaves into reference line and signal line. The signal line can be attenuated to the required power level. It finally enters the cavity resonator. The coupling of the cavity resonator is adjusted for critical coupling so that the microwaves do not reflect from the cavity resonator. When EPR is excited, the microwaves reflect from the cavity resonator and enter the balance mixer, which is made up from the magic T and the crystal mount. The microwaves are then detected and amplified by the preamplifier. In this, the reference line is adjusted to be in same phase as that of the signal by the phase shifter.

(b) Cavity resonator

The cavity resonator is equipped with an ultraviolet ray irradiation aperture, a cooling device, a 100 kHz modulation coil, bayonet connectors for connecting variable temperature attachments, a nitrogen gas inlet port, etc. The cavity resonator is cylindrical in shape and operated in TE_{011} mode. The sample tube, held by the sample tube holder is inserted into the sample insertion port located on the upper wall of the cavity.

(c) Electromagnet and excitation power supply

Each pole of the electromagnet will be 54 cm wide and the poles are separated by 60 mm. The electromagnet operates at 200 V, 2 kVA. The excitation power supply provides a highly stabilized excitation current to the electromagnet. Its magnetic field can be varied from 0 to 600 mT with a maximum field sweep of ± 250 mT. The field can be swept in different times
from 0.5 min/360 mm to 128 min/360 mm. The Hall element provides A.C. voltage to the magnetic field control unit, which is proportional to the field and hence the field is swept linearly. Modulating coils modulate the field at 100 kHz. It has a linear field sweep whose detection employs a Hall element. The electromagnet is provided with a cooling system, which circulates water with a pressure of 0.5 kg/cm² or over and at a flow rate of 4 l/min.

First, the sample is placed in the cavity resonator so that it lies at the middle of the poles of the electromagnet, where the magnetic field is B. Then the sample is subjected to a microwave magnetic field of constant frequency, which is perpendicular to B. By varying the excitation current of the electromagnet, the magnitude of B is changed. When the resonance condition is fulfilled, a part of the microwave energy is absorbed by the sample. As a result, the Q-value of the cavity resonator changes. This variation in Q-value is detected, amplified and recorded.

When the magnetic field is varied at a constant frequency, an absorption signal is observed. In addition to this field, an alternating magnetic field having the same direction as B and amplitude smaller than the width of the absorption signal is also applied. Now if B is varied, the detector output at each point on the absorption signal will form a sinusoidal wave having the same period as the alternating field and amplitude in proportion to the gradient of the absorption line. Thus, a derivative of the absorption curve is obtained. This sinusoidal derivative curve is amplified by a selective amplifier and phase detected throughout the absorption signal width. However, the EPR spectrum can be recorded as either first or second derivative of the absorption signal.
The instrument has a high magnetic field homogeneity and stability. It has a very high sensitivity ($2 \times 10^9 - 3 \times 10^9$ spins/mT) and high resolution ($1 \times 10^5$) with a frequency stability of $1 \times 10^{-6}$. While recording the signal with the recorder, the horizontal axis is expandable from 360 mm to 1080 mm.

EPR spectra at different temperatures can be recorded by using a JES-VT-3A2 variable temperature controller capable of regulating the temperature from 103 K to 523 K. A temperature stability of $\pm 1$ K can be easily obtained by waiting for 30 minutes before recording the spectra.

(d) Detectors

After detection by the crystal diode detector, the signal undergoes narrow band amplification. By using the phase sensitive detector, the noise in the amplified signal is reduced. Finally, the EPR signal is recorded by the D-Y T recorder, which records the signal on a chart of width 250 $\times$ 360 mm. Before recording the EPR signal, it can be observed on the oscilloscope screen (133 mm) for mode check, malfunction check, etc.

3. Optical absorption studies

Optical absorption spectra were recorded using a double beam JASCO V-570 UV-VIS-NIR spectrophotometer. A photograph of the JASCO V-570 UV-VIS-NIR spectrophotometer is shown in Fig. 4. The optical alignment of this spectrophotometer is shown in Fig. 5.

This spectrophotometer measures the absorption spectra in the wavelength range 190 - 2500 nm. It uses a deuterium ($D_2$) lamp in the UV region (190 to 350 nm) and a tungsten iodine (WI) lamp in the VIS-NIR region (340 to 2500 nm) as light source. The light from the source is reflected into the
Fig. 4. A photograph of the JASCO V-570 UV-VIS-NIR spectrophotometer.
Fig. 5. Optical alignment of the JASCO V-570 UV-VIS-NIR spectrophotometer.
monochromator. In the monochromator, the grating disperses the light and allows monochromatic light to pass through the exit slit. This light is split into two beams by a sector mirror. One beam passes through the sample and the other passes through the reference sample such as undoped sample, solvent, etc. These beams, after passing through the sample and the reference sample incident on the photomultiplier tube or the PbS photoconducting cell and get converted into an electrical signal. After being synchronously rectified, this signal is converted into a digital signal and is processed by the computer. The computer displays the output in the form of absorption spectrum. The absorption spectrum gives the optical density (arbitrary units) versus wavelength in UV-VIS-NIR region. Light source changeover, wavelength drive, slit drive, filter drive, etc., are controlled by the computer.

In the present work, the optical absorption spectra of the glass samples were recorded in absorbance mode. The wavelengths of the observed bands were converted into corresponding wavenumbers by using Table of Wavenumbers, published by National Bureau of Standards [3].
References

