CHAPTER IV

EXPERIMENTAL DETAILS

4.1 PREPERATION OF PHOSPHORS :

The luminescent properties of a phosphor are usually sensitive to conditions during the synthesis. The preparation of inorganic crystalline phosphors require, in principle, first the maximum elimination of extraneous elements and then reintroduction of known elements in precise amounts. Certain impurities can affect the luminescence, if present in as small an amount as 10^{-4} % (78). Unfortunately, in spite of all precautions, it is usually very difficult to avoid some of the involuntarily added impurities completely. Necessary precautions were therefore taken against the misinterpretation of the experimental data that may be attributed to intrinsic luminescence.

In this section the nature of NaBr:Tl phosphors used in the present investigations have been discussed briefly. The starting material used was sodium bromide supplied by BDH. According to the manufacturer, the maximum probable impurities are : moisture 2 %, chloride (Cl) 6×10^{-1} % , sulphate (SO_4) 5×10^{-2} % , Arsenic (As) 1×10^{-4} % , Iron (Fe) 1×10^{-3} % , Lead (Pb)

5×10^{-4} % . Microcrystalline samples were prepared by the usual method of crystallization from aqueous solution. Regarding the cleanliness and purity while preparing and handling the samples, extreme care has been taken. All the surfaces which were to come in contact with the phosphor were cleaned by washing soda and thoroughly washed with water. Afterwards the surfaces were kept in contact with freshly prepared aqua regia for 24 hours to remove contamination and stray elements. Finally the surfaces were kept in contact with boiling distilled water for nearly two hours to remove the traces of aqua regia left behind and then were dried in an oven.

The impurity was introduced in the host material by the usual method of crystallization from aqueous solution. In the present investigations the main impurity concerned is thallium used in the form of a salt, namely, thallous bromide (TlBr) which was supplied by BDH . The weighed quantity of sodium bromide was dissolved in double distilled deminerlized water. The weight of the impurity, as determined by the molar calculation, was added to this solution .

The solution was then heated slowly on a hot plate with constant stirring until all the water evaporated. The microcrystalline powder thus obtained was dried in an oven. The microcrystals formed were collected, dried at about 60°C, powdered and mixed homogeneously. The samples thus received were designated 'as-received' samples. Because NaBr is highly hygroscopic, special care has been taken in examining the sample only in dry atmosphere.

The concentration of thallium in different specimens was determined by spectrophotometric analysis. The 214 nm absorption band of Tl^+ in water solution was used for this purpose. Thallium concentration in these samples varied in the range of 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} m.f. . The samples were studied in 'as-received' condition and after various thermal and mechanical pretreatments. Thermal treatment was given to the samples in three different ways :

(i) Heat treatment of the specimens, 'as-received' from solution, involved their annealing at 500°C for four hours in evacuated and sealed tubes

(vacuum $\sim 10^{-3}$ mm of Hg) made of pyrex glass and their rapid quenching to room temperature by exposure to a blast of cold air. The rate of quenching of the specimen was of the order of 100°C/minute. The samples received in this way were termed "annealed and quenched in vacuum".

(ii) A second representative lot, enclosed in another evacuated and sealed pyrex glass tubes was kept in the furnace maintained at 500°C for 4 hours and then cooled very slowly to room temperature by reducing the current through the furnace by means of a gear mechanism. The rate of cooling in this case was of the order of 1°C/minute. These samples were designed as "annealed and slowly cooled" samples.

(iii) The "as-received" samples were kept in a silica crucible instead of evacuated sealed tubes and the same procedure, as that for "annealed and quenched" samples, was repeated. These samples were called "annealed and quenched in air".

The 'as-received' and variously heat treated samples were also studied after subjecting them to

pressure treatment. For this purpose, a requisite amount of the sample was introduced in a steel press and was compressed in a mechanical vice to form a tablet of about 1 cm in diameter and 0.1 cm thick. The average pressure under which the specimens were compressed was of the order of 2000 kg/cm^2 .

The solid phosphors examined also included specimens prepared by quenching the TlBr - melt, to which NaBr was added as an impurity, to room temperature. NaBr powder of known weight as determined by the molar calculation, was placed at the bottom of porcelain crucible and the requisite amount of TlBr - powder was placed on its top. The porcelain crucible was then kept in the furnace whose temperature was maintained little above the melting point of TlBr ($\sim$ 500°C) . The TlBr melt formed in the crucible was subsequently quenched to room temperature by withdrawing the crucible from the furnace and exposing it to the blast of cold air. The specimen thus obtained was crushed to form homogeneous powder. The activator (Na) concentration was of the order of 0.3 and 0.5 m.f.

Measurements were also made on the excitation and emission spectra of aqueous TlBr - solution of various concentrations and of NaBr - solution with varying amount of TlBr dissolved in it.

4.2 INSTRUMENTATION :

A) PRINCIPLES OF OPERATION :

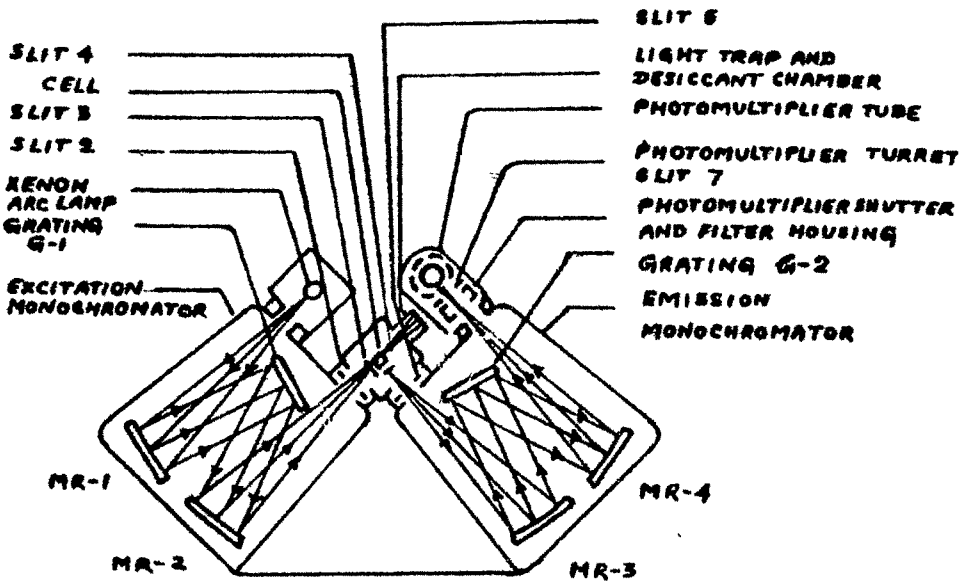
The fundamental principles of fluorescence measurement are as follows :

The desired narrow band of wavelengths of exciting radiation is selected by the excitation monochromater placed between the radiation source and the sample. The wavelength of fluorescence radiant energy to be measured is selected by a similar emission monochromator placed between the sample and a photo-detector located at a 90° angle from the incident optical path. The output of the photodetector, a current that is proportional to the intensity of the fluorescent energy, is amplified to give a reading on a meter or a recorder.

B) EXPERIMENTAL SYSTEM :

The instrument used for examining the excitation and emission spectra was Aminco-Bowman spectrophotofluorometer supplied by American Instrument Co., Inc., which is one of the most popular spectrofluorometer. It consists of an optical unit, photomultiplier, microphotometer and a power supply. The optical unit includes an electrical panel, Xenon lamp with housing and blower, two monochromators, two slit holders (installed in monochromators) sample compartment, photomultiplier housing with manually operated rotary slit turret and filter holder with shutter control. The Xenon - lamp power is supplied from D. C. power supply, and the sweep power circuit is energized by a mercury battery contained within the optical unit.

The components of the Aminco - Bowman spectrophotofluorometer are as in diagram presented in Fig. I.



OPTICAL UNIT SHOWING POSITION OF SLITS

FIG. I

(i) OPTICAL UNIT :

Light from the Xenon lamp is dispersed by the excitation monochromator (grating type) into monochromatic radiation incident on the sample. The light emitted from the sample is dispersed by the emission monochromator into monochromatic radiation incident on the photomultiplier. The light is then transformed into a weak electrical signal and fed to the photometer where it is amplified. The photometer output is indicated on the self contained meter. This output signal is connected to a strip-chart recorder. The gratings are oscillated by motor-driven cams. For visual observations and adjustment of wavelength, graduated discs are coupled to these gratings. Provision is also made to adjust the wavelength manually. Spring loaded arms follow the continuous cam rotation and oscillate the gratings. The maximum and minimum angular positions of the gratings correspond to the high and low points of the cams and to the maximum and minimum wavelengths of the monochromators, namely, 800 and 200 nm respectively. Properties of the mounting of grating monochromators are discussed fully in two

articles by W. G. Fastie[122]. It incorporates two grating monochromators of the basic type first described by Ebert[123].

Both the monochromators are optically identical except for a difference in "blaze" wavelength between the two gratings. The excitation grating is blazed at 300 nm (1st order) to strengthen the output from the Xenon lamp which decreases below 400 nm. The emission grating is blazed at 500 nm (1st order) to improve the response to the emission at wavelength from 400 - 600 nm.

At the focus of the spherical mirror, MR - 1 (Fig. I) is situated the Xenon arc lamp. It produces a continuous spectrum peaking at 400 nm and again at 900 nm (beyond by the range of the instrument). Light from the Xenon lamp, indicated by the three rays, strikes MR - 1 which renders it parallel and directs it to the planegrating Dispersed light from the grating is redirected to the second mirror MR - 2 (identical with MR - 1) which focuses a monochromatic image of the lamp on the centre of the sample holder. The magnification of the system is unity resulting in an

image equal in size to the Xenon-arc (1.8 mm wide by 3.5 mm high). Emitted light from the sample is similarly dispersed by the emission monochromator and imaged on the photomultiplier slit. Five slit positions are provided in the optical unit. Slits 2 and 3 determine the band - width and the resolution for excitation spectra whereas slits 5 and 4 decide the band - width and the resolution in the case of emission spectra. Photomultiplier slit turret (7) controls the intensity. A convenient arrangements of the slits was found out by trial and this arrangement remained unchanged throughout all the measurements, thereby keeping the band - width and resolution constant.

A dessicant chamber mounted on the sample housing of the spectrophotofluorometer performs two functions, (i) serves as a light trap for the excitation wavelength and (ii) prevents condensation on the cell window or sample, especially under conditions of high humidity. For liquid sample, cells made of fused quartz are used. Care is taken not to touch the sides

of the cell. The solid sample is fixed on the sample holder with the help of a non-fluorescent grease, and placed diagonally in the sample compartment such that the sample faces the excitation and emission monochromater slits. The position is adjusted in such a way that it gives maximum emission. The sample holder is made of ebonite whose surface was covered with black paper which did not show any excitation or emission peaks without the phosphor.

ii) PHOTOMULTIPLIER AND MICROPHOTOMETER :

This assembly essentially consists of a light sensitive photomultiplier tube with associated circuitry and an amplifier which responds to the small current produced by the photomultiplier tube and registers the amplified current on a microphotometer. The photometer sensitivity is controlled by the meter-multiplier switch and sensitivity knob. Coarse adjustments are made with meter - multiplier switch which reduces the meter readings in steps of 1, 3, 10, 30, 100, 300, 1000. Fine adjustments are made with the sensitivity knob

which continuously adjusts the recorder output signal, together with the meter readings over a range of 3.5 to 1. The photomultiplier tube used in this set up is IP21 with S_4 spectral response.

c) PROCEDURE FOR OBTAINING EXCITATION AND EMISSION SPECTRA :

Whenever the instrument was switched on for measurement, a warm up period of about half an hour was given for stability. The sample under study was inserted in the sample chamber and the photomultiplier shutter was opened. With the help of slow-fast control, the emission monochromator wavelength disc was allowed to rotate slowly. The photometer was set for high sensitivity. Subsequently, the excitation wavelength disc was changed manually in steps of 20 nm at the completion of each emission scan until a maximum was indicated on the photometer. When the excitation wavelength was located the emission scan was stopped and the emission wavelength was adjusted for maximum emission indicated on the meter. The excitation wavelength disc was again adjusted until

a new maximum on-scale meter reading was obtained. Knowing the excitation peak wavelength, the emission monochromator wavelength disc was kept at the above value, and excitation spectrum was recorded. During the above procedure the sensitivity was adjusted with the help of meter-multiplier, so that the photometer reading was within the range of the meter.

The excitation and emission spectra were recorded immediately one after another to avoid the effect of voltage fluctuations. These fluctuations were kept to a minimum with the help of a voltage stabilizer. The speed of the chart recorder was kept at 5 sec./inch for recording the excitation and emission spectra just for the sake of convenience. The recorder could be started or stopped at any desired wavelength reading on the graduated scale. As the motor - driven cam moves with uniform speed, the intermediate wavelength values between two extreme readings on the chart could be determined by equally dividing the linear distance between two end points into the number of wavelengths involved in the

corresponding range. The peak position of an excitation or an emission peak read from the chart was found to be coinciding with the position of the corresponding peak as observed by the manual operation of the graduated disc.

A certain amount of scatter is always present in varying degree in any optical instrument. This is especially true for instruments which measure fluorescence. In the design of the equipment presently being used, though the scatter has been reduced to a practical minimum, a certain amount of scatter exists. Thus one observes scatter or reflection peaks whenever the excitation and emission wavelengths are equal. Due to unlimited second order light from the gratings a noticeable amount of apparently spurious signal will frequently be present at high wavelengths. For example, if emission is maximum at 300 nm , there will be some indication at 600 nm . This spurious indication should be ignored, since it would usually not interfere with the shape of the peaks (both excitation and emission spectra). It can be eliminated with the use of suitable optical filters. Thus whether a given peak is genuine or not can be verified by the use of appropriate optical filters.