CHAPTER III

EXPERIMENTAL TECHNIQUE EMPLOYED FOR X-RAY POWDER DIFFRACTION STUDY OF CaS : Zr PHOSPHORS
Introduction

The study of polycrystalline aggregate of materials by X-rays was discovered by Debye and Scherrer (1) in Germany and by Hull (2) in the United States. Fine powders and crystalline aggregates of all kinds may be analysed for ultimate crystalline structure in a most satisfactory way by this method. The method is particularly suitable for the study of metals, as they cannot easily be obtained in form of large single crystals. The method requires the conversion of such substances into fine powders before they can be examined by X-Rays and hence the name powder method. The development of X-ray diffractometer with Geiger counter has greatly facilitated the work of powder analysis. By means of automatic recorders, integrating/Geiger counts at continuously varying angle, the powder pattern appears as a series of peaks on a continuous background, each corresponding in position to a line on a photographed crystal spectrum and each providing a direct measure of intensity from peak height. Geiger counter eliminates film entirely. However, for a discovery of a phenomenon the photographic pattern is almost a necessity (3).

There are three methods of powder diffraction studies:

(1) **Debye-Scherrer Method:**

In this method the specimen is rotated along the axis of the cylinder and the film is placed along the surface of a cylinder.
(ii) **Pin hole Method:**

The film is flat and is placed at a convenient distance from the specimen and perpendicular to the X-ray beam.

(iii) **Focussing Method:**

Surface of the cylinder contains the film, the specimen and the X-ray source.

Only the first method will be described here.

**Debye-Scherrer Method:**

In this method any polycrystalline material filled in a Lindemann glass capillary or the same held together by a proper binder can act as specimen for this type of X-ray examination. Powder diffraction camera consists of cylindrical chamber covered with round lid by friction fit and is light proof. Two diametrically opposite holes are provided in this cylinder for inserting the collimator and exit port assembly. The collimator consists of an internal nozzle shaped tube pointed towards the specimen. Two lead discs having central holes are mounted inside the tube. The hole towards the X-ray source is the limiting pin hole. The nozzle of the cone apart from limiting the aperture of the cone originating from pin hole, focusses the diverted X-ray beam on the specimen and removes the X-rays diffracted from pin holes. Air scattering is also reduced. The exit port assembly is another nozzle shaped tube, the hole of which is closed with three different materials (i) a black paper to make camera light proof, (ii) a fluorescent screen facing outwards for centring the beam and specimen at any time (iii) a lead glass to protect the observer. The
nozzle of the tube extends nearly to the specimen so that air scattering is reduced to a minimum and diffraction pattern is recorded right up to film holes. The specimen holder is mounted at the centre of a small drum, which can be made eccentric within a small radius. The holder is at the centre of the base of the cylindrical camera and is made to rotate exactly along the axis of the cylinder containing the film. By means of a spring, the drum can be held at any position in the central area of the base of the cylindrical camera. The drum can be pushed downwards by means of a pusher working against a spring.

Specimen should be placed perpendicular to the base of the cylinder and then viewed through the collimator by means of a simple microscopic lens. It is aligned along the axis of the camera by manually rotating the sample and pushing it each time it goes above the centre of the view through the microscope.

The film is expanded directly against the metal cylinder of the camera by means of fingers one at each end of the film. One of the fingers is fixed to the camera, while the other can slide along the circumference of the camera. It can be clamped from outside in any position. When put into tangential compression by means of the movable finger the film expands radially against the camera wall. Film arrangement provided in the above type of camera is called the asymmetric method, and was first described by Straumanis and Levins (4). The diffraction record is complete without any missing region near either zero or 180°. The position of zero and 180° can be determined
accurately by noting the mid position of number of corresponding lines at low and high angle side of the film. Each photograph is self calibrating (5) and effective camera diameter and the film shrinkage can be determined for each film. Moreover double back reflection record is always available for precision measurement by the method of Cohen (6) or by the modification of the method of Bradley and Jay (7).

**Specimen:**

Specimen should be powdered in a clean dry mortar and passed through 240 mesh screen in order to give smooth continuous lines. Sample should be ground repeatedly and the whole sample should pass through the screen, otherwise the sample will not be fully representative of the original sample as some of the less brittle phases will be present in the material remaining on the sieve.

Excessive grinding results in broad diffraction lines. On the other hand crystal of lower symmetry will give generally a spotty appearance in spite of fine grinding. There are devices developed by Barrett and Guy (8), Straumanis and Aka (9) and others in which translational motion is super imposed on the usual rotational motion of Debye-Scherrer specimen. This exposes large number of particles to the X-ray beam and reduces the spotty appearance of the pattern.

**Choice of Radiation:**

In the present investigation since calcium sulphide formed the main bulk of phosphor material, copper Kα radiation filtered by Ni filter was found to be most useful. Filtering cuts off the Kβ radiation as well as a good portion of the continuous
background. One of the considerations for not using Mo Kα is that the wavelength of Cu Kα is twice that of Mo Kα and therefore the powder diffraction diagram would be more crowded on the low angle site, although absorption error would be reduced if Mo Kα is used. Also Mo Kα would have given larger scattering and fogged the film.

**Diffraction Apparatus (P.W. 11704):**

X-ray diffraction photographs were recorded with Phillips X-ray diffraction unit type No. 11704. It consists of high tension generator, a tube shield, and a desk with control panel built together to form a compact unit. A circular table is mounted around the tube shield, thus permitting the use of special cameras and auxiliary instruments. The high tension generator is situated in the lower part of the apparatus. The X-ray diffraction tube is fed by H.T. transformer. The tube voltage is adjustable from 20-60 KV in ten steps. The tube current is continuously variable from 0-40 ma.

The X-ray tube has four windows permitting the use of both, two window and four window X-ray diffraction tubes. Filter slides can be placed in front of the windows in vertical slots to eliminate the Kβ radiations. The camera bracket can be attached to four sides of the shield top by fitting screws, fitting in threaded holes. X-ray tube type No. 25293/32 with copper target has been used in this unit for diffraction.

**The Present Investigation:**

The Debye-Scherrer camera used in the present investigation is similar to that of Buerger (10), improved by Parrish and
Cisney (11). The diameter of the camera used in the present investigation was 114.33 mm so that one millimeter on the film corresponds to half degree of Bragg angle \( \theta \) when the film has been developed and fully stretched. The pin hole diameter is one millimeter for X-ray studies of all phosphors. The phosphor powder (240 mesh) prepared according to specification given above has been filled in the Lindemann glass capillary of 0.5 mm diameter. Exposure of four hours was found most suitable.

For recording the X-ray powder diagram high contrast double coated X-ray film (Ilford Industrial 0.35x 355 mm) was used in the asymmetric position. All powder diffraction diagrams were taken at 30KV and 10 ma. The powder photographs were taken continuously and room temperature did not vary more than 1°C either ways. The temperature was 25°C ± 1°C throughout. I.D. 19 developer was used. The developing time for all the films was one minute.

Powder diagrams were measured by means of vernier microscope No. 14, supplied by Precision Tool Manufacturing Co. Ltd., Thornton Heath, Surrey, England. This instrument fitted with low power eye piece was capable of measuring upto 0.002 mm. The cross wire was set at the position of maximum intensity as judged by visual estimation after removing the parallax.

Diameters were measured between two corresponding lines on either side of exit and entrance holes respectively. Position of centre of two holes was found out from the measurement
of diameters of a few corresponding lines around entrance and exit holes. Theoretically distance between the two centres should be 180 mm. Error due to the shrinkage of the film was found out and corresponding correction applied. $\theta$ Values corresponding to each line were then calculated. Bragg's spacing corresponding to $\theta$ values were found from tables given by Gunier (12).

For accurate determination of lattice parameter of CaS cubic lattice back reflection lines were used. The parameter 'a' corresponding to these lines was calculated and graphs were drawn between this parameter and $\cos^2 \theta$. The graphs were extrapolated to $\cos 90^\circ = 0$ (13). Bragg's spacing was tabulated for every photograph.
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