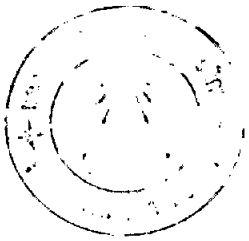
CHAPTER 1



INTRODUCTION

$CoWO_4$ is a member of the isomorphous series of tungstates of small cations which also includes $NiWO_4$, $MgWO_4$, $MnWO_4$, $FeWO_4$ and $ZnWO_4$. The structure of $MgWO_4$, with the exception of oxygen positions, was determined by Broch[1]. Keeling[2] determined the structure of $NiWO_4$ using the Fourier difference method to locate the oxygen atoms. The proposed structure of $NiWO_4$ is based on a distorted hexagonal close packing of oxygen atoms with Ni and W atoms each occupying one-fourth of the octahedral holes. The unit cell of $NiWO_4$ is monoclinic (space group P2/c; $a = 4.60 \pm 0.015$, $b = 5.66 \pm 0.02$, $c = 4.91 \pm 0.015$ Å and $\beta = 90^\circ\ 5' \pm 5'$) and contains two formula units. Atomic coordinates are:

$2Ni$ in (f) : $\pm(\frac{1}{2}, y_{Ni}, \frac{1}{4})$,

$2W$ in (e) : $\pm(0, y_W, \frac{1}{4})$,

$4O_I$ in (g) : $\pm(x_1, y_1, z_1; x_1, \bar{y}_1, z_1 + \frac{1}{2})$,

$4O_{II}$ in (g) : $\pm(x_2, y_2, z_2; x_2, \bar{y}_2, z_2 + \frac{1}{2})$,

with $y_{Ni} = 0.653$, $y_W = 0.180$, $x_1 = 0.22$, $y_1 = 0.11$, $z_1 = 0.96$, $x_2 = 0.26$, $y_2 = 0.38$ and $z_2 = 0.39$.

In this investigation, single crystals of $CoWO_4$ were grown from a melt of Na_2WO_4, WO_3 and CoO. Preliminary unit cell dimensions were obtained from oscillation, rotation, and Weissenberg photographs. Cell parameters were refined from diffraction data measured

on a Guinier-Hägg XDC-700 focusing powder camera calibrated with silicon. Intensity data were collected with the equi-inclination Weissenberg multiple film technique using MoKα radiation:h0l to h2l, $\bar{h}$0l to $\bar{h}$2l and hk0. The intensities were measured by a Nonius microdensitometer. The positions of W atoms were determined from Patterson function whereas those of Co atoms were revealed in the first F_o synthesis. The Fourier difference technique was applied to locate the oxygen atoms. The structure was refined by the full matrix least squares method.

There are five chapters in this thesis. A general information of the problem is given in the first chapter. Chapter two provides a background for the X-ray crystal structure determination. Chapter three describes the procedures for the experiments and the preliminary information about the crystal. Chapter four consists of the calculations for determining the crystal structure. The last chapter is concerned with conclusions and discussion of the results.