Chapter 1

INTRODUCTION

Tungsten-vanadium-oxygen compounds which are ternary phases can be used in several ways such as semiconductors, catalysts and cathodes of nonaqueous batteries. Studies of the structures of these compounds, therefore, are very interesting. X-ray, neutron and electron diffraction methods are normally used for determining the structures of molecules and crystals. The difference between these methods are such that they supplement one another to a remarkable degree, each giving a particular kind of information which the others are incapable of supplying.[1]

The existence of two intermediate phases in W-V-O system was firstly reported by Freundlich[2] in 1965. One of these phases, with a composition close to $WV_2O_{7.5}$, was obtained below 800°C and was found to posses tetragonal symmetry. The second phase, stable up to 1000°C, was reported to be monoclinic and to have the composition WV_2O_{8-x} with a homogeneity range $0.9 < x \leq 1.1$. Since then, there have been some more publications reported on structures of W-V-O compounds. Three new phases in the W-V-O system are reported by Launay-Mondet and Susanne[3] (1971). They are V_2WO_7 (monoclinic, space group C_2, "a" = 24.4, "c" = 3.95 Å, $\beta \simeq 90°$, $V_2WO_{7.5}$ (tetragonal, space group I4/mmm, "a" = 19.50, "c" = 3.70 Å, $V_2WO_{7.5-\delta}$ (tetragonal, space group I4/mmm, "a" = 14, "c" = 3.7 Å). These results were obtained by X-ray diffraction method. The compound of $V_{16}W_9O_{65}$ by Heurung, G. and Gruehn, R. (1984)[4],

was prepared by chemical transport reactions. The space group of this compound was I4/mmm, with "a" = 25.074, "c" = 3.714 Å determined by the X-ray powder method. The electron microscope study directly reveals the block structure of the $V_{16}W_9O_{65}$ compound. The work on monoclinic ternary phase in W-V-O system was also reported by Kihlborg et al. (1970)[5] but instead of a composition V_2WO_7, it was pointed out that the composition should be $W_3V_5O_{20}$. The $W_3V_5O_{20}$ crystals by Kihlborg were prepared by heating mixture of reagent-grade WO_3, V_2O_5 and V_2O_3 in evacuated sealed silica or platinum tubes for several days. The sesquioxide had been prepared by reducing V_2O_5 in a stream of hydrogen. By X-ray diffraction study it was found to be monoclinic, space group C2/m with "a" = 24.41 Å, "b" = 7.446 Å, "c" = 3.95 Å, "β" = 91.03°. In this work, monoclinic ternary phase in W-V-O system has been studied by X-ray diffraction. The preparation of the single crystals reported here, however is simpler and slightly different. The method used here is modified from Bridgeman method[6]. The single crystals are found to have composition $W_3V_5O_{20}$ which confirm the result from Kihlborg. The $W_3V_5O_{20}$ compound in this work were obtained by heating mixtures of equimolar mixture of WO_3 and V_2O_5 in evacuated quartz and pulling out the ampule from step-freeze furnace. Unit cell dimensions were obtained from oscillation, rotation, Weissenberg photographs. Cell parameters were refined from powder diffraction data obtained from a Guinier-Hägg photograph with silicon as internal calibration standard. Intensity data were collected with the Weissenberg multiple film technique using MoK_α radiation. The intensities were estimated by visual comparison with an intensity calibrated scale. The position of M_1 atom ($W_{1/4}V_{3/4}$) was determined from Patterson function whereas those of M_2 (W), M_3 (V)

and oxygen were revealed in F_o syntheses. The structure was refined by the full matrix least squares method.

There are six 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. Introduction to defects in crystals and diffuse X-ray reflections is written in chapter three. Chapter four describes the procedures for the experiments and the preliminary information about the crystal. Chapter five consists of the calculation for determining the crystal structure. The last chapter is concerned with conclusion and discussion of the results.