

การศึกษาโครงสร้างของผลึกทังสเตนวาเนเดียมออกไซด์ $W_3V_5O_{20}$

โดยการเลี้ยวเบนรังสีเอ็กซ์



นางสาวอารีย์ หาญประสพวัฒน์

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ศูนย์วิทยทรัพยากร

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X-RAY DIFFRACTION STUDY OF
THE CRYSTAL STRUCTURE OF
TUNGSTEN VANADIUM OXIDE $W_3V_5O_{20}$



Miss Aree Hanprasopwattana

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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By Miss Aree Hanprasopwattana
Department Chemistry
Thesis Advisor Associate Professor Supanich Pramatus
Thesis Co-advisor Associate Professor Salag Dhabanandana, Ph.D.



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partial fulfillment of the requirements for the Master's degree.

..... *S. Bhisal*
(Associate Professor Sorachai Bhisalbutra, Ph.D.)
Acting Associate Dean for Academic Affairs for
Acting Dean of the Graduate School

Thesis Committee

..... *Padet Sidisunthorn* Chairman
(Professor Padet Sidisunthorn, Ph.D.)

..... *Supanich Pramatus* Advisor
(Associate Professor Supanich Pramatus)

..... *Salag Dhabanandana* Co-advisor
(Associate Professor Salag Dhabanandana, Ph.D.)

..... *Phathana Phavanantha* Member
(Associate Professor Phathana Phavanantha, Ph.D.)

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หัวข้อวิทยานิพนธ์	การศึกษาโครงสร้างของผลึกทังสเตนวาเนเดียมออกไซด์ $W_3V_5O_{20}$ โดยการเลี้ยวเบนรังสีเอ็กซ์
ชื่อ	นางสาวอารีย์ ทำญประสพวัฒน์
อาจารย์ที่ปรึกษา	รองศาสตราจารย์ สุทธิจ พราหมทัศ
อาจารย์ที่ปรึกษาร่วม	รองศาสตราจารย์ ดร.ศลักษณ์ ทวรรณันท์
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บทคัดย่อ

วิธีที่ใช้เตรียมผลึกเดี่ยวทังสเตนวาเนเดียมออกไซด์ในงานนี้ได้ใช้ 3 วิธี คือวิธีหลอมโดยตรงและแอนนัล วิธีหลอมด้วยไซเดียมทังสเตนและวิธีเทคนิคของบริคแมนแบบปรับปรุงวิธีที่สาม เป็นวิธีเตรียมผลึกเดี่ยวทังสเตนวาเนเดียมออกไซด์ ที่ได้ผลึกเดี่ยวที่ดีที่สุด

การทำโครงสร้างของทังสเตนวาเนเดียมออกไซด์ โดยการเลี้ยวเบนรังสีเอ็กซ์ ใช้วิธีฟูเรียร์และอะตอมหนัก หาค่าแห่งออกซิเจน โดยการสังเคราะห์แผนภาพความหนาแน่นอิเล็กตรอนหารปรับค่าอย่างละเอียดของตำแหน่งและพารามิเตอร์ เนื่องจากความร้อนแบบไอโซโทรปิกของอะตอมต่าง ๆ ใช้วิธีกำลังสองน้อยที่สุดแบบเมทริกซ์เต็มชุด ซึ่งให้ค่า $R=0.113$ สำหรับจุดสะท้อนอิสระ 469 จุด

ทังสเตนวาเนเดียมออกไซด์ตกผลึกในระบบโมโนคลินิก โดยมีค่ามิติของเซลล์ $a=24.412(2)$, $b=7.4479(8)$, $c=3.9506(3)$ Å, $\beta=91.028(7)^\circ$, ปริมาตรของเซลล์ $= 718.19$ Å³ ค่าความหนาแน่น $D_m=5.10(3)$ กรัมต่อลูกบาศก์เซนติเมตร ที่อุณหภูมิ 25 องศาเซลเซียส $D_x=5.21$ กรัมต่อลูกบาศก์เซนติเมตร หมู่สมมาตรสามมิติ $C2/m$ และ $Z=2$

จากการทดลองพบว่า โครงสร้างของทังสเตนวาเนเดียมออกไซด์มีการจัดตัวแบบ $R-Nb_2O_5$ ซึ่งประกอบด้วยออกตาฮีดราที่มีบิดเบี้ยวไป โดยออกตาฮีดราเหล่านี้จะมีสันและมุมร่วมกันในทิศ b และอะตอมโลหะข้างในออกตาฮีดราเลื่อนจากจุดศูนย์กลางไปข้าง การจัดตัวของออกตาฮีดราในระนาบ bc เป็นแผ่นแบบ ReO_3 ซึ่งประกอบด้วยออกตาฮีดรา 2 ระดับ

ออกตาฮีดราที่บรรจุทั้งสเดนสลักับวาเนเดียมอยู่ที่ระดับหนึ่งและออกตาฮีดราอีกระดับหนึ่งบรรจุด้วย ($W_{1/2} V_{3/4}$) แบบการจัดกระจายความไม่ เป็นระเบียบของโครงสร้างนี้อยู่ที่ตำแหน่งของโลหะที่มีโอกาสจะเป็นทั้งสเดนหนึ่งในสี่และวาเนเดียมสามในสี่.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Thesis Title X-ray Diffraction Study of the Crystal
Structure of Tungsten Vanadium Oxide $W_3V_5O_{20}$

Name Miss Aree Hanprasopwattana

Thesis Advisor Associate Professor Supanich Pramatus

Thesis Co-advisor Associate Professor Salag Dhabanandana, Ph.D.

Department Chemistry

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ABSTRACT

Single crystals of tungsten vanadium oxide were prepared by three different methods. They are direct melt-and-anneal technique, Na_2WO_4 melt and modified Bridgeman technique. Of the three methods, the third method gave the best single crystals.

The structure had been determined by X-ray diffraction using Fourier and heavy atom methods. The F_0 synthesis was used to locate the oxygen atoms. Positional and isotropic thermal parameters were refined by the full matrix least squares method to a final R index of 0.113 for 469 independent observed reflections.

Tungsten-vanadium-oxide, $W_3V_5O_{20}$ crystallizes in the monoclinic system with cell dimensions $a = 24.412(2)$, $b = 7.4479(8)$, $c = 3.9506(3)$ Å, $\beta = 91.028(7)^\circ$, $V = 718.19$ Å³, $D_m = 5.10(3)$ g.cm.⁻³ at 25°C, $D_x = 5.21$ g.cm.⁻³, space group C2/m and $Z = 2$.

The structure of $W_3V_5O_{20}$ which is the same type as $R-Nb_2O_5$ is based on distorted octahedra, sharing edges and corners in "b" direction with a different off-centre of the metal atoms inside the octahedra. The arrangement of octahedra in "bc" plane is considered as ReO_3 type slabs, consisting of two levels of octahedra. The octahedra at one level are filled alternately with "W" and "V" while the octahedra at the other level are filled with $(W\frac{1}{2}V\frac{1}{2})$ in random distribution. The disorder is described as structure with one position occupied by both "W" and "V". The probability of "V" in this position is $\frac{3}{4}$ and of "W" $\frac{1}{4}$.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



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 จุฬาลงกรณ์มหาวิทยาลัย

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย