# Gmelin Handbook of Inorganic Chemistry

8th Edition

# Gmelin Handbook of Inorganic Chemistry

8th Edition

---

# W
# Tungsten

**Supplement Volume B 5**

Tungstates of Group IIIA and IIIB Metals

With 100 illustrations


AUTHORS Dieter Gras, Friedrich Schröder, Susanne Waschk

EDITORS Lieselotte Berg, Hartmut Katscher, Friedrich Schröder

CHIEF EDITOR Hartmut Katscher



**System Number 60**

Springer-Verlag Berlin · Heidelberg · New York · Tokyo 1984

LITERATURE CLOSING DATE: 1981
IN MANY CASES MORE RECENT DATA HAVE BEEN CONSIDERED

Library of Congress Catalog Card Number: Agr 25-1383

ISBN 3-540-93492-8 Springer-Verlag, Berlin · Heidelberg · New York · Tokyo
ISBN 0-387-93492-8 Springer-Verlag, New York · Heidelberg · Berlin · Tokyo


Printed in Germany

Typesetting, printing, and bookbinding: LN-Druck Lübeck

## Volumes published on "Tungsten" (Syst. No. 54)

**Tungsten**
Main Volume – 1933

**Tungsten Suppl. Vol. A 1**
Metal, Technology – 1979

**Tungsten Suppl. Vol. B 1**
Systems with Noble Gases, Hydrogen, and Oxygen – 1978

**Tungsten Suppl. Vol. B 2**
Oxides – 1979

**Tungsten Suppl. Vol. B 3**
Compounds of Tungsten with Oxygen and Antimony, Bismuth; Alkali Tungstates – 1979

**Tungsten Suppl. Vol. B 4**
Tungstates of Group IIA and IIB Metals – 1980

**Tungsten Suppl. Vol. B 5**
Tungstates of Group IIIA and IIIB Metals – 1984 (present volume)

## Preface

The supplement volume "Tungsten" B 5 continues the description of the anhydrous tungstates which was started in "Wolfram" Erg.-Bd. B 3. Volume B 5 covers the tungstates with main and subgroup 3 metals, i.e. with Al to Tl, Sc, Y, and La to Lu (system Nos. 35 to 39). Most of the compounds are tungstates(VI), but in addition some bronzes of the $M_xWO_3$ type are known. The tungstates with Al to Tl have not been investigated very much and occupy only a small part of the volume. In contrast the rare earth tungstates have been investigated very intensively and thus occupy the main part of the volume. Comparative data for the various types of rare earth tungstates are given in separate sections to facilitate an overview before covering the individual compounds. $M_6WO_{12}$ and $M_2(WO_4)_3$ type tungstates are known for all rare earth metals Sc to Lu and $M_2WO_6$ tungstates for Y to Lu. Tungstates with other metals in addition to the rare earth metals show a still larger variety of types. $AM(WO_4)_2$ tungstates are known for all alkali metals A and Tl and M = Sc to Lu, except $CsCe(WO_4)_2$. These tungstates show an intricate manifold of polymorphic transitions. The optical properties in particular of the double tungstates, especially those doped with alkali or alkaline earth metals, have been investigated in substantial detail.

Frankfurt am Main, October 1983 Hartmut Katscher

# Table of Contents


Page

**3 Tungsten and Oxygen** ..... 1

**3.3 Anhydrous Compounds of Tungsten with Oxygen and Other Metals** ..... 1

**3.3.7 Tungstates with Main Group 3 Metals** ..... 1

Aluminium Tungstates ..... 1

The $Al_2O_3$-$WO_2$ System ..... 1

$AlWO_4$ ..... 2

Aluminium Tungsten Oxide Bronzes $Al_xWO_3$ ..... 4

The $Al_2O_3$-$WO_3$ System ..... 5

$Al_2WO_6$ ..... 6

$Al_2(WO_4)_3$ ..... 6

Formation, Preparation ..... 6

Crystallographic Properties ..... 8

Other Physical Properties ..... 9

Chemical Reactions ..... 11

Aluminium Metal Tungstates ..... 11

$Bi_2Al_{4.6}W_{2.9}O_7$ ..... 11

The $Al_2(WO_4)_3$-$Li_2WO_4$ System ..... 12

$LiAl(WO_4)_2$ ..... 12

The $Al_2O_3$-$Na_2O$-$WO_3$ System ..... 13

$Na_3Al(WO_4)_3$ ..... 13

$NaAl(WO_4)_2$ ..... 13

$KAl(WO_4)_2$ ..... 14

$K_{3x}Al_xW_{2-x}O_6$ Phases ..... 14

$Rb_{3x}Al_xW_{2-x}O_6$ Phases ..... 16

$Cs_{3x}Al_xW_{2-x}O_6$ Phases ..... 17

$Ca_6[Al_{12}O_{24}](WO_4)_2$ ..... 19

The $Al_2O_3$-SrO-$WO_3$ System ..... 20

$Sr_6[Al_{12}O_{24}](WO_4)_2$ ..... 20

$Sr_5(MgAl_2W_2)O_{15}$ ..... 20

$Ba_5(MgAl_2W_2)O_{15}$ ..... 21

Gallium Tungstates ..... 21

Gallium Tungsten Oxide Bronzes $Ga_xWO_3$ ..... 21

The $Ga_2O_3$-$WO_3$ System ..... 21

$Ga_2WO_6$ ..... 21

$Ga_2(WO_4)_3$ ..... 21

Gallium Metal Tungstates ..... 22

$LiGa(WO_4)_2$ ..... 22

$NaGa(WO_4)_2$ ..... 23

$K_{3x}Ga_xW_{2-x}O_6$ Phases ..... 24

$Rb_{3x}Ga_xW_{2-x}O_6$ Phases ..... 25

$Cs_{3x}Ga_xW_{2-x}O_6$ Phases ..... 26

Indium Tungstates ..... 26

Indium Tungsten Oxide Bronzes $In_xWO_3$ ..... 26

The $In_2O_3$-$WO_3$ System ..... 29

$In_6WO_{12}$ ..... 29

$In_2(WO_4)_3$ ..... 31

| | Page |
|---|---|
| Indium Metal Tungstates | 32 |
| The $In_2(WO_4)_3$-$Li_2WO_4$ System | 32 |
| $LiIn(WO_4)_2$ | 32 |
| The $In_2(WO_4)_3$-$Na_2WO_4$ System | 33 |
| $NaIn(WO_4)_2$ | 33 |
| The $In_2(WO_4)_3$-$K_2WO_4$ System | 36 |
| $K_5In(WO_4)_4$ | 37 |
| $K_3In(WO_4)_3$ | 37 |
| $KIn(WO_4)_2$ | 38 |
| The $In_2(WO_4)_3$-$Rb_2WO_4$ System | 40 |
| $Rb_5In(WO_4)_4$ | 40 |
| $Rb_3In(WO_4)_3$ | 40 |
| $RbIn(WO_4)_2$ | 41 |
| $Rb_{0.66}In_{0.22}W_{1.78}O_6$ | 43 |
| $CsIn(WO_4)_2$ | 43 |
| $Cs_{0.66}In_{0.22}W_{1.78}O_6$ | 43 |
| The $NaIn(WO_4)_2$-$MgWO_4$ System | 43 |
| The $NaIn(WO_4)_2$-$CaWO_4$ System | 44 |
| $SrIn_{0.67}W_{0.33}O_3$ | 44 |
| $Sr_2In_{0.5}Li_{0.5}WO_6$ | 44 |
| $Sr_2In_{0.5}Na_{0.5}WO_6$ | 45 |
| $BaIn_{0.67}W_{0.33}O_3$ | 45 |
| $Ba_2In_{0.5}Li_{0.5}WO_6$ | 45 |
| $Ba_2In_{0.5}Na_{0.5}WO_6$ | 45 |
| The $NaIn(WO_4)_2$-$ZnWO_4$ System | 45 |
| The $In_2(WO_4)_3$-$CdWO_4$ System | 46 |
| The $NaIn(WO_4)_2$-$CdWO_4$ System | 46 |
| Thallium Tungstates | 47 |
| Thallium Tungsten Oxide Bronzes $Tl_xWO_3$ | 47 |
| $Tl_2WO_4$ | 51 |
| $Tl_2W_2O_7$ | 54 |
| $Tl_2W_3O_{10}$ | 54 |
| $Tl_2W_4O_{13}$ | 54 |
| Thallium Peroxotungstates $Tl_2WO_5$, $Tl_2WO_6$, and $Tl_2WO_8$ | 55 |
| Thallium Metal Tungstates | 56 |
| $TlSbWO_6$ | 56 |
| The $Tl_2WO_4$-$Li_2WO_4$ System, $TlLiWO_4$ | 56 |
| The $Tl_2WO_4$-$Na_2WO_4$ System | 56 |
| $TlNa_{0.2}W_{0.6}O_3$? | 56 |
| The $Tl_2WO_4$-$K_2WO_4$ System | 57 |
| The $Tl_2WO_4$-$Rb_2WO_4$ System | 57 |
| The $Tl_2WO_4$-$Cs_2WO_4$ System | 58 |
| $TlMg_{0.25}W_{0.75}O_3$? | 58 |
| $TlCd_{0.25}W_{0.75}O_3$? | 58 |
| $TlGa_{0.33}W_{1.67}O_6$ | 58 |
| The $Tl_2WO_4$-$In_2(WO_4)_3$ System | 59 |
| $Tl_3In(WO_4)_3$ | 60 |
| $TlIn(WO_4)_2$ | 60 |

Page

3.3.8 Tungstates with Subgroup 3 Elements ..... 61

Rare Earth Tungstates ..... 61
Systems ..... 61
The Y-W-O System ..... 61
The $La_2O_3$-$WO_3$-W System ..... 61
The $Ce_2O_3$-$WO_3$-W System ..... 62
The $Pr_2O_3$-W-$O_2$ System ..... 62
The $Nd_2O_3$-$WO_3$-W System ..... 63
The $Sm_2O_3$-$WO_3$-W System ..... 64
The Eu-W-O System ..... 65
The $Er_2O_3$-$WO_3$-W System ..... 68

Tungsten Oxide Bronzes $M_xWO_3$ ..... 68
Review ..... 68
Homogeneity Ranges ..... 69
Preparation ..... 69
Crystallographic Properties ..... 70
Other Physical Properties ..... 72
Electrochemical Behavior and Chemical Reactions ..... 75

Tungsten Oxide Bronzes with Several Rare Earth Elements ..... 75

Rare Earth Tungstates(VI). Comparative Data ..... 76
$M_6WO_{12}$ ..... 76
$M_{10}W_2O_{21}$ ..... 80
$M_{14}W_4O_{33}$ ..... 81
$M_2WO_6$ ..... 81
$M_4W_3O_{15}$ ..... 88
$M_2W_2O_9$ ..... 88
$M_2(WO_4)_3$ ..... 89

Scandium Tungstates(VI) ..... 99
The $Sc_2O_3$-$WO_3$ System ..... 99
$Sc_6WO_{12}$ ..... 99
$Sc_2W_2O_9$ ..... 100
$Sc_2(WO_4)_3$ ..... 100

Yttrium Tungstates(VI) ..... 104
The $Y_2O_3$-$WO_3$ System ..... 104
$Y_6WO_{12}$ ..... 107
$Y_{10}W_2O_{21}$ ..... 111
$Y_{14}W_4O_{33}$ ..... 112
$Y_2WO_6$ ..... 113
$Y_2W_2O_9$ ..... 116
$Y_2(WO_4)_3$ ..... 117

Lanthanum Tungstates(VI) ..... 118
The $La_2O_3$-$WO_3$ System ..... 118
$La_6WO_{12}$ ..... 120
$La_{10}W_2O_{21}$ ..... 121
$La_4WO_9$ ..... 122
$La_6W_2O_{15}$ ..... 123
$La_2WO_6$ ..... 124
$La_{14}W_8O_{45}$ ..... 125
$La_4W_3O_{15}$ ..... 126

| | Page |
|---|---|
| $La_2W_2O_9$ | 126 |
| $La_2(WO_4)_3$ | 127 |
| $La_2W_4O_{15}$ | 128 |
| $La_{10}W_{22}O_{81}$ | 128 |
| Cerium Tungstates(VI) | 129 |
| The $Ce_2O_3$-$WO_3$, $Ce_2O_3$-$CeO_2$-$WO_3$, and $CeO_2$-$WO_3$ Systems | 129 |
| $Ce_6WO_{12}$ | 130 |
| $Ce_6W_2O_{15}$ | 130 |
| $Ce_2WO_6$ | 130 |
| $Ce_2W_2O_9$ | 131 |
| $Ce_2(WO_4)_3$ | 131 |
| $Ce_{10}W_{22}O_{81}$ | 133 |
| $Ce(WO_4)_2$ | 133 |
| Praseodymium Tungstates(VI) | 134 |
| The $Pr_2O_3$-$WO_3$ System | 134 |
| $Pr_6WO_{12}$ | 135 |
| $Pr_6W_2O_{15}$ | 135 |
| $Pr_2WO_6$ | 135 |
| $Pr_6W_5O_{27}$ | 136 |
| $Pr_4W_3O_{15}$ | 136 |
| $Pr_2W_2O_9$ | 136 |
| $Pr_2(WO_4)_3$ | 139 |
| $Pr_2W_4O_{15}$ | 139 |
| $Pr_{10}W_{22}O_{81}$ | 139 |
| Neodymium Tungstates(VI) | 139 |
| The $Nd_2O_3$-$WO_3$ System | 139 |
| $Nd_6WO_{12}$ | 141 |
| $Nd_{10}W_2O_{21}$ | 142 |
| $Nd_4WO_9$ | 142 |
| $Nd_{14}W_4O_{33}$ | 142 |
| $Nd_6W_2O_{15}$ | 142 |
| $Nd_2WO_6$ | 142 |
| $Nd_4W_3O_{15}$ | 145 |
| $Nd_2W_2O_9$ | 146 |
| $Nd_2(WO_4)_3$ | 147 |
| $Nd_2W_4O_{15}$ | 149 |
| $Nd_{10}W_{22}O_{81}$ | 149 |
| Promethium Tungstates(VI) | 150 |
| The $Pm_2O_3$-$WO_3$ System | 150 |
| $Pm_2(WO_4)_3$ | 150 |
| Samarium Tungstates(VI) | 151 |
| The $Sm_2O_3$-$WO_3$ System | 151 |
| $Sm_6WO_{12}$ | 152 |
| $Sm_{10}W_2O_{21}$ | 153 |
| $Sm_{14}W_4O_{33}$ | 153 |
| $Sm_2WO_6$ | 153 |
| $Sm_2W_2O_9$ | 155 |
| $Sm_2(WO_4)_3$ | 155 |

Page

Europium Tungstates(VI) ..... 156
The $EuWO_4$-$Eu_2(WO_4)_3$ System $Eu_xWO_4$ ..... 156
$Eu^{II}WO_4$ ..... 157
$Eu_6WO_{12}$ ..... 159
$Eu_{10}W_2O_{21}$ ..... 160
$Eu_{14}W_4O_{33}$ ..... 160
$Eu_2WO_6$ ..... 160
$Eu_2W_2O_9$ ..... 160
$Eu_2(WO_4)_3$ ..... 161

Gadolinium Tungstates(VI) ..... 165
$Gd_6WO_{12}$ ..... 165
$Gd_{10}W_2O_{21}$ and $Gd_{14}W_4O_{33}$ ..... 165
$Gd_2WO_6$ ..... 166
$Gd_2W_2O_9$ ..... 166
$Gd_2(WO_4)_3$ ..... 166

Terbium Tungstates(VI) ..... 168
$Tb_6WO_{12}$ ..... 168
$Tb_{10}W_2O_{21}$ ..... 168
$Tb_2WO_6$ ..... 168
$Tb_2(WO_4)_3$ ..... 168

Dysprosium Tungstates(VI) ..... 169
The $Dy_2O_3$-$WO_3$ System ..... 169
$Dy_6WO_{12}$ ..... 170
$Dy_{10}W_2O_{21}$ ..... 170
$Dy_{14}W_4O_{33}$ ..... 171
$Dy_2WO_6$ ..... 171
$Dy_2(WO_4)_3$ ..... 171

Holmium Tungstates(VI) ..... 172
$Ho_6WO_{12}$ ..... 172
$Ho_{10}W_2O_{21}$ ..... 172
$Ho_{14}W_4O_{33}$ ..... 173
$Ho_2WO_6$ ..... 173
$Ho_2(WO_4)_3$ ..... 173

Erbium Tungstates(VI) ..... 174
The $Er_2O_3$-$WO_3$ System ..... 174
$Er_6WO_{12}$ ..... 174
$Er_{10}W_2O_{21}$ ..... 175
$Er_{14}W_4O_{33}$ ..... 175
$Er_{22}W_6O_{51}$ ..... 175
$Er_2WO_6$ ..... 175
$Er_2W_2O_9$ ..... 176
$Er_2(WO_4)_3$ ..... 176

Thulium Tungstates(VI) ..... 178
$Tm_6WO_{12}$ ..... 178
$Tm_{14}W_4O_{33}$ ..... 178
$Tm_2WO_6$ ..... 178
$Tm_2(WO_4)_3$ ..... 178

Page

Ytterbium Tungstates(VI) ... 178
$Yb_6WO_{12}$ ... 178
$Yb_{14}W_4O_{33}$ ... 178
$Yb_2WO_6$ ... 178
$Yb_2(WO_4)_3$ ... 179
Lutetium Tungstates(VI) ... 179
$Lu_6WO_{12}$ ... 179
$Lu_{14}W_4O_{33}$ ... 179
$Lu_2WO_6$ ... 180
$Lu_2(WO_4)_3$ ... 180
Tungstates with More Than One Rare Earth Element ... 180
The $CeO_2$-$La_6WO_{12}$ System ... 180
$La_{3x}Sm_{6-3x}WO_{12}$ ... 181
$(M,M')_2WO_6$ ... 182
$(M,M')_2(WO_4)_3$ ... 182

Tungstates with Rare Earth and Other Metals ... 184
Bismuth Rare Earth Tungstates ... 184
$Bi_2Sc_{4/3}W_{2/3}O_7$ ... 184
The $Bi_2WO_6$-$M_2WO_6$ Systems ... 184
$Bi_{2-x}M_xWO_6$ Solid Solutions ... 184
Alkali Rare Earth Tungstates ... 188
$Li_3M_3W_2O_{12}$ ... 188
The $Li_2WO_4$-$M_2(WO_4)_3$ and $LiM(WO_4)_2$-$M_2(WO_4)_3$ Systems ... 188
$Li_2WO_4$-$Sc_2(WO_4)_3$ ... 188
$Li_2WO_4$-$Y_2(WO_4)_3$ ... 188
$LiLa(WO_4)_2$-$La_2(WO_4)_3$ ... 189
$LiNd(WO_4)_2$-$Nd_2(WO_4)_3$ ... 189
$LiSm(WO_4)_2$-$Sm_2(WO_4)_3$ ... 190
$Li_2WO_4$-$Tb_2(WO_4)_3$ ... 190
$Li_2WO_4$-$Dy_2(WO_4)_3$ ... 190
$Li_2WO_4$-$Er_2(WO_4)_3$ ... 190
$Li_2WO_4$-$Yb_2(WO_4)_3$ ... 191
$LiM(WO_4)_2$ ... 191
Preparation ... 191
Crystallographic Properties ... 193
Other Physical Properties ... 199
Chemical Reactions ... 201
$LiM_3(WO_4)_5$ and $Li_{1.12}Tb_{2.95}(WO_4)_5$ ... 202
$LiM_5(WO_4)_8$ ... 203
Sodium Rare Earth Tungsten Oxide Bronzes $Na_yM_xWO_3$ ... 203
The $Na_2WO_4$-$M_2(WO_4)_3$ Systems ... 204
$Na_2WO_4$-$Sc_2(WO_4)_3$ ... 204
$Na_2WO_4$-$Y_2(WO_4)_3$ ... 204
$Na_2WO_4$-$Nd_2(WO_4)_3$ ... 204
$Na_2WO_4$-$M_2(WO_4)_3$, M = Sm, Gd, Dy, Ho, Er, Yb ... 205
$Na_9Sc(WO_4)_6$ ... 208
$Na_5M(WO_4)_4$ ... 208

Page

$NaM(WO_4)_2$ ... 214
Preparation and Formation ... 214
Crystallographic Properties ... 216
Other Physical Properties ... 219
Chemical Reactions ... 223
$Na_2M_4(WO_4)_7$ ... 223
$NaM_3(WO_4)_5$ ... 224
The $K_2WO_4$-$M_2(WO_4)_3$ Systems ... 225
$K_2WO_4$-$Sc_2(WO_4)_3$ ... 225
$K_2WO_4$-$Pr_2(WO_4)_3$ ... 226
$K_2WO_4$-$Nd_2(WO_4)_3$ ... 226
$K_2WO_4$-$Tb_2(WO_4)_3$ ... 227
$K_2WO_4$-$Er_2(WO_4)_3$ ... 227
$K_5M(WO_4)_4$ ... 227
$K_3Sc(WO_4)_3$ ... 228
$KM(WO_4)_2$ ... 228
Preparation ... 228
Crystallographic Properties ... 230
Polymorphism ... 230
Habit ... 233
Crystal Structures ... 234
Other Physical Properties ... 240
$K_{1-3x}M_{1+x}(WO_4)_2$ ... 243
$KM_3(WO_4)_5$ ... 245
The $Rb_2WO_4$-$M_2(WO_4)_3$ Systems ... 245
$Rb_5La(WO_4)_4$ ... 246
$Rb_3Sc(WO_4)_3$ ... 247
$RbM(WO_4)_2$ ... 247
Preparation. Formation ... 247
Crystallographic Properties ... 248
Polymorphism ... 248
Crystal Structures ... 251
High-Pressure Modifications ... 254
Other Physical Properties ... 255
$Rb_{0.66}Sc_{0.22}W_{1.78}O_6$ ... 258
$RbM_3(WO_4)_5$ ... 258
The $Cs_2WO_4$-$M_2(WO_4)_3$ Systems ... 258
$Cs_3Sc(WO_4)_3$ ... 259
$CsM(WO_4)_2$ ... 260
Preparation ... 260
Crystallographic Properties ... 261
Other Physical Properties ... 263
Chemical Reactions ... 265
$Cs_{0.66}Sc_{0.22}W_{1.78}O_6$ ... 266
$CsM_3(WO_4)_5$ ... 266
$A_5(M,M')(WO_4)_4$ ... 266
$A(M,M')(WO_4)_2$ ... 268

Page

Alkaline Earth – Rare Earth Tungstates ... 271
$La_{1.33}MgWO_6$ ... 271
$Eu_2MgWO_6$ ... 272
The $CaWO_4$-$M_2(WO_4)_3$ Systems ... 272
$Eu_2CaWO_6$ ... 275
$Ca_xM_y(WO_4)_7$ and $Ca_{0.5}La_3(WO_4)_5$ ... 275
The $SrWO_4$-$M_2(WO_4)_3$ Systems ... 276
$Eu_2SrWO_6$ ... 277
$Sr_3Y_2WO_9$ ... 277
$SrM_4(WO_4)_7$, $Sr_{0.5}M(WO_4)_2$, and $Sr_{0.5}M_3(WO_4)_5$ ... 277
$Ba_2MWO_6$ ... 279
$Ba_3M_2WO_9$ ... 279
$Ba_2M_{0.67}WO_6$ ... 280
$Ba_2(Nd_{1-x}Y_x)_{0.67}WO_6$ ... 284
$Ba_3LaM(WO_6)_2$ ... 285
The $BaWO_4$-$La_2(WO_4)_3$ System ... 285
$BaLa_4(WO_4)_7$ ... 285
The $CaWO_4$-$NaM(WO_4)_2$ Systems ... 286
$Ca_{1-2x}M_xA_xWO_4$ Solid Solutions ... 287
$Sr_{1+x}La_{1-x}Li_{1-0.2x}W_{1+2x}O_6$ and $Sr_2M_{0.5}A_{0.5}WO_6$ ... 289
$Sr_{1-x}Ca_xLa_{0.5}Na_{0.5}WO_6$ ... 290
The $Na_2WO_4$-$SrWO_4$-$Nd_2(WO_4)_3$ System, $Sr_{1-2x}Nd_xNa_xWO_4$ Solid Solutions ... 291
$BaLaAWO_6$ and $Ba_2(M,A,W)O_6$ ... 291
$Ba_{1.5}Ca_{0.5}La_{0.5}Na_{0.5}WO_6$ and $Ba_{1-x}Sr_xLa_{0.5}Na_{0.5}WO_6$ ... 292
$SrMgLaWO_6$ ... 293
$Sr_xMg_yM_zWO_6$ ... 293
$Ba_2Mg_{1-x}Y_{0.67x}WO_6$ and $Ba_2Ca_{1-x}Y_{0.67x}WO_6$ ... 294
$Ba_2MgLa_2(WO_6)_2$ ... 297

Tungstates of Rare Earth and Subgroup 2 Elements ... 297
The $ZnWO_4$-$Nd_2(WO_4)_3$ System ... 297
$Ba_2ZnLa_2(WO_6)_2$ ... 297
The $CdO$-$Nd_2O_3$-$WO_3$ System ... 298
$CdNd_2(WO_4)_4$ ... 299
$Cd_2M_2(WO_4)_5$ ... 299

Tungstates of Rare Earth and Main Group 3 Metals ... 300
The $Al_2O_3$-$Y_2O_3$-$WO_3$ System ... 300
$Ba_3LaIn(WO_6)_2$ ... 300
$TlM_{1/3}W_{2/3}O_3$ and $TlCe_{0.5}W_{0.5}O_3$ ... 301
The $Tl_2WO_4$-$Sc_2(WO_4)_3$ System ... 302
$TlM(WO_4)_2$ ... 303

**Table of Conversion Factors** ... 305

# 3 Tungsten and Oxygen (continued)

Chapter 3.1 "The W-O System" can be found in the volume "Wolfram" Erg.-Bd. B 1, 1978, pp. 89/172 and Chapter 3.2 "The Tungsten Oxides" in "Wolfram" Erg.-Bd. B 2, 1979.

## 3.3 Anhydrous Compounds of Tungsten with Oxygen and Other Metals (continued)

Sections 3.3.1 to 3.3.4 can be found in the volume "Wolfram" Erg.-Bd. B 3, 1979. They cover the compounds of tungsten with oxygen and the main group 5 metals, the tungsten oxide bronzes, the tungstate ions, and the alkali tungstates. Sections 3.3.5 and 3.3.6 are contained in "Wolfram" Erg.-Bd. B 4, 1980. They cover the tungstates of the alkaline earth and those of the subgroup 2 metals.

### 3.3.7 Tungstates with Main Group 3 Metals

#### 3.3.7.1 Aluminium Tungstates

Older data are given in "Wolfram", 1933, p. 313.

##### 3.3.7.1.1 The $Al_2O_3$-$WO_2$ System

The phase compositions of the products of the reactions between $Al_2O_3$ and $WO_2$ formed in vacuum at 900°C and different roasting times, identified by X-ray phase analysis, are listed in the following table:

| pressure in $10^{-6}$ Torr | time in h | phases observed |
|---|---|---|
| ~3 | 25 | $\alpha$-$Al_2O_3$, $WO_2$, $AlWO_4$ (traces) |
| ~3 | 65 | $\alpha$-$Al_2O_3$, $WO_2$ (traces), $AlWO_4$ (traces) |
| ~1 | 120 | $\alpha$-$Al_2O_3$, $WO_2$, W, $AlWO_4$ |
| ~50 | 500 | $\alpha$-$Al_2O_3$ (little), W, $AlWO_4$ |

During the reaction $WO_2$ possibly disproportionates with formation of metallic W and its higher oxides with compositions similar to $WO_3$. The aluminium tungstate is formed by $2Al_2O_3 + 5WO_2 \rightarrow 4AlWO_4 + W$. The composition has been established by direct synthesis according to $Al_2O_3 + WO_2 + WO_3 \rightarrow 2AlWO_4$.

V. A. Levitskii, V. N. Chentsov, A. F. Kozlova, V. V. Makagon, T. D. Nevzorova (Izv. Akad. Nauk SSSR Neorgan. Materialy **12** [1976] 61/5; Inorg. Materials [USSR] **12** [1976] 48/51), V. A. Levitskii, V. N. Chentsov, A. N. Klimenko, V. P. Marin, Yu. V. Men'shenin, A. A. Gugnin (Izv. Akad. Nauk SSSR Neorgan. Materialy **13** [1977] 699/702; Inorg. Materials [USSR] **13** [1977] 569/72).

### 3.3.7.1.2 $AlWO_4$ (= $Al_2O_3 \cdot$ "$W_2O_5$")

**Preparation. Formation.** The brown-black compound is prepared by heating stoichiometric mixtures of $Al_2O_3$, $WO_2$, and $WO_3$ at 850°C for 20 to 30 min under a 40 kbar pressure [1, 2]. The synthesis can also be carried out in an evacuated quartz ampule (about $10^{-6}$ Torr) at 900°C (340 h) [3, 4].

Heating $Al_2O_3$ and W in a moist hydrogen atmosphere (900 to 1500°C) gives $AlWO_4$. The reaction obviously takes place via the intermediately formed $WO_2$ [3, 4]. For the reaction of $WO_2$ with $Al_2O_3$ see p. 1. $AlWO_4$ also forms from $Al_2O_3$ and $WO_3$. An equimolar mixture of the finely powdered oxides is pelletized with addition of a 5% aqueous solution of dextrin as a binder. Annealing the pellets at successively increasing temperatures (1000 → 1100 → 1200°C) in an Ar atmosphere (1.2 to 1.4 atm) yields $AlWO_4$ [5, 6].

Anthracite-colored single crystals are obtained by cathodic reduction of mixtures of $WO_3$ and $Na_2WO_4$ in an aluminium crucible [2] or from a molten mixture of $Al_2O_3$, $WO_3$, and $Na_2WO_4$, both at 900°C [1].

In the concentration cell $Pt|Al_2O_3, W, AlWO_4|O^{2-}|Fe_{0.95}O, Fe|Pt$ the current-forming reaction at 1000 to 1250 K is $0.5\,Al_2O_3 + W + 2.5\,Fe_{0.95}O \rightarrow AlWO_4 + 2.375\,Fe$. The Gibbs free energy $\Delta G°$ (in cal/mol) of this reaction in the temperature range investigated is represented by $\Delta G°_f(\pm 60) = 800(\pm 440) - 1.04(\pm 0.40)T$. For the reaction (1) $0.5\,Al_2O_3 + W + 1.25\,O_2 \rightarrow AlWO_4$ in the same temperature range the Gibbs free energy of formation can be calculated by the relation $\Delta G°_f(\pm 120) = -157000(\pm 780) + 38.35\,(\pm 0.62)T$. Some thermodynamic data ($\Delta H°$ and $\Delta G°$ in kcal/mol, $\Delta S°$ in cal·mol$^{-1}$·K$^{-1}$) are given by [4] for reaction (1) and reaction (2) $2\,Al_2O_3 + 5\,WO_2 \rightarrow 4\,AlWO_4 + W$:

| reaction | $\Delta H°_{1200}$ | $\Delta S°_{1200}$ | $\Delta G°_{1050}$ | $\Delta G°_{1150}$ | $\Delta G°_{1200}$ | $\Delta G°_{1250}$ |
|---|---|---|---|---|---|---|
| (1) | $-157.4 \pm 0.8$ | $-38.35 \pm 0.6$ | $-117.1 \pm 0.1$ | $-113.3 \pm 0.1$ | $-111.4$ | $-109.5 \pm 0.1$ |
| (2) | $+41.4$ | $+37.35$ | $+2.2$ | $-1.5$ | $-3.4$ | $-5.3$ |

**Crystallographic Properties.** $AlWO_4$ forms acicular crystals [5] or twinned polyhedra (slight angular deviation between (201) and (20$\bar{1}$)) [2]. No transition occurs on heating it up to 1100°C [1].

Single crystal investigations showed $AlWO_4$ to be monoclinic [2]. Later orthorhombic symmetry was derived from powder patterns [3, 5]. However, the published d values [2, 3, 5] are practically the same. In all three cases the crystal structure has been derived from the rutile ($TiO_2$) type [2, 3, 5]. Single crystal investigations show $CrWO_4$ to be isomorphous with monoclinic $AlWO_4$.

The lattice parameters of the monoclinic $AlWO_4$ are $a = 9.069 \pm 0.005$, $b = 5.705 \pm 0.006$, $c = 4.541 \pm 0.005$ Å, $\beta = 92.29° \pm 0.01°$; $Z = 4$. Space group $C2/m$-$C^3_{2h}$ (No. 12). Atom parameters ($R = 0.055$ after final refinement with anisotropic temperature parameters):

| atom | position | x | y | z |
|---|---|---|---|---|
| Al | 4i | 0.2590(4) | 0 | 0.4858(9) |
| W | 4g | 0 | 0.7716(1) | 0 |
| O(1) | 8j | 0.1504(7) | 0.2449(6) | 0.3012(8) |
| O(2) | 4i | 0.1141(5) | 0 | 0.7791(8) |
| O(3) | 4i | 0.4023(5) | 0 | 0.1975(9) |

The following table shows some atomic distances (in Å):

| atoms | distance | atoms | distance | atoms | distance |
|---|---|---|---|---|---|
| Al-Al | 2.868(2) | Al-O(1) (2×) | 1.891(3) | W-O(1) (2×) | 1.898(2) |
| W-W | 2.613(2) | Al-O(1) (2×) | 1.919(3) | W-O(2) (2×) | 1.968(2) |
| W-W | 3.108(1) | Al-O(2) | 1.910(3) | W-O(3) (2×) | 2.018(2) |
| | | Al-O(3) | 1.883(3) | W-O | 1.961 |
| | | Al-O | 1.901 | | |

A table with the O-Al-O and O-W-O angles is given in the paper [2].

The Al and W atoms are nearly octahedrally coordinated by O atoms and form chains along [010] by edge sharing, see **Fig. 1**. The W atoms are not located in the centers of the $WO_6$ octahedra but have alternating distances along [010], the shorter of which (2.613 Å) is smaller than in metallic W (2.65 Å). It is assumed that the $W^V$ is stabilized by these W-W pairs. The Al atoms, however, are equidistant along [010] in spite of slight antiparallel displacements along [100] and [001] [2]. One O-O distance is relatively short (2.56 Å), a phenomenon which is also observed in the crystal structure of $CrWO_4$. Such a structure is also realized in $Cr_{0.024}V_{0.976}O_2$ [7]. In addition, there are some relationships to the crystal structure of $WO_2$ (see "Wolfram" Erg.-Bd. B 2, 1979, pp. 26/8) [2]. A short preliminary description of the $AlWO_4$ structure is given in [1].

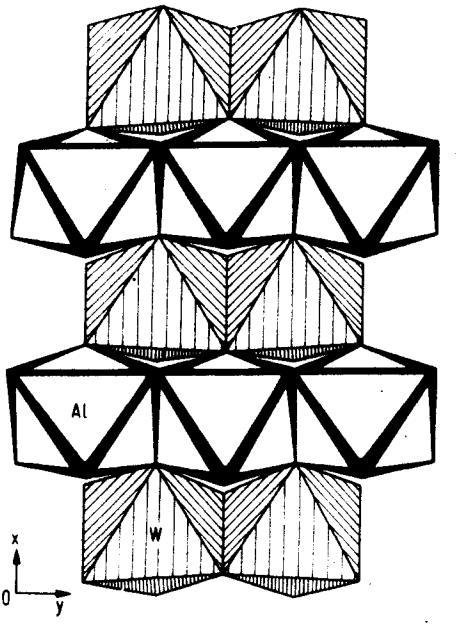


Fig. 1. Linkage of the $AlO_6$ and $WO_6$ octahedra along [010] in the crystal structure of $AlWO_4$ [2].

The orthorhombic interpretation gives the lattice parameters a = 6.57, b = 6.32, c = 2.85 Å [3] and a = 6.578 ± 0.003, b = 6.319 ± 0.002, c = 2.874 ± 0.001 Å [5]; Z = 2. In the space group Cmmm-$D_{2h}^{19}$ (No. 65) the atoms occupy the following positions: Al on 2c (0.5, 0, 0.5, etc.), W on 2a (0, 0, 0, etc.), O(1) on 4g (x, 0, 0, etc.) with x ≈ 0.3, and O(2) on 4j (0, y, 0.5, etc.) with y ≈ 0.3 [3].

The possible band structure has been discussed and compared with those of rutile-type dioxides and $WO_2$ [1, 2].

**Other Physical Properties.** The measured density, $D_m = 7.69 \pm 0.01$ g/cm³, agrees well with the calculated value. $D_x = 7.69$ g/cm³ [1, 2].

Measurements of the electrical conductivity of a single crystal between 300 und 1050 K show $AlWO_4$ to be a semiconductor. At about 300 K the electrical conductivity is around $10^{-3}\ \Omega^{-1} \cdot cm^{-1}$. The activation energy $E = 0.35$ eV is derived from the temperature dependence over the investigated temperature range [1, 2].

Measurements of the magnetic susceptibility between 300 and 1000 K show that $AlWO_4$ is diamagnetic; $\chi_{mol} = -40 \times 10^{-6}$ cm³/mol [1, 2].

The crystals show straight extinction, with pleochroism from pink($n_\alpha$) to reddish brown or dark brown ($n_\gamma$) and high birefringence: $n_\alpha = 2.09 \pm 0.05$, $n_\gamma > 2.40$ [5].

**Chemical Reactions.** To check the volatility $AlWO_4$ was placed in one end of a double evacuated quartz tube and heated at 1100 to 1150°C while the other end of the tube was kept at room temperature. After 200 h the specimen had sublimed to the cold end of the tube without leaving a residue. X-ray phase analysis of the condensate revealed $Al_2O_3$, oxides of tungsten, and $AlWO_4$ [4].

**References:**

[1] J. P. Doumerc, M. Vlasse, G. Demazeau, M. Pouchard (Compt. Rend. C **279** [1974] 201/3). – [2] J. P. Doumerc, M. Vlasse, M. Pouchard, P. Hagenmuller (J. Solid State Chem. **14** [1975] 144/51). – [3] V. A. Levitskii, V. N. Chentsov, A. F. Kozlova, V. V. Makagon, T. D. Nevzorova (Izv. Akad. Nauk SSSR Neorgan. Materialy **12** [1976] 61/5; Inorg. Materials [USSR] **12** [1976] 48/51). – [4] V. A. Levitskii, V. N. Chentsov, A. N. Klimenko, V. P. Marin, Yu. V. Men'shenin, A. A. Gugnin (Izv. Akad. Nauk SSSR Neorgan. Materialy **13** [1977] 699/702; Inorg. Materials [USSR] **13** [1977] 569/72). – [5] I. I. Vishnevskii, A. M. Gavrish, N. V. Gul'ko, G. G. Eliseeva, N. D. Tal'yanskaya (Zh. Neorgan. Khim. **23** [1978] 217/20; Russ. J. Inorg. Chem. **23** [1978] 121/3).

[6] I. I. Vishnevskii, N. D. Tal'yanskaya (Dokl. Akad. Nauk SSSR **234** [1977] 1144/7; Dokl. Chem. Technol. Proc. Acad. Sci. USSR **232/237** [1977] 106/9). – [7] M. Marezio, D. B. McWhan, J. P. Remeika, P. D. Dernier (Phys. Rev. [3] B **5** [1972] 2541/51).

### 3.3.7.1.3 Aluminium Tungsten Oxide Bronzes $Al_xWO_3$, $x < 0.010$ to 0.36

The Al-W bronzes $Al_xWO_3$ with $x < 0.010$ to $< 0.135$ have been prepared from Al powder and $WO_3$ at 1000°C. For $x < 0.10$ the reaction was carried out at 800°C in Vycor ampules [2], in two stages [1]: $0.10\,Al + WO_3 \rightarrow Al_{0.10}WO_3$ and $10x\,Al_{0.10}WO_3 + (1-10x)\,WO_3 \rightarrow Al_xWO_3$. For $Al_{0.120}WO_3$ a mixture of $WO_3$ and Al powder was fired for 48 h at 1000°C in a sealed Vycor tube or in an $Al_2O_3$ boat in vacuum [3]. A deep blue bronze $Al_{0.36}WO_3$ was obtained when pressed samples of 1:3:1 mole ratio $Al_2O_3 \cdot 3H_2O$, $WO_3 \cdot H_2O$, and W plus some water were heated in a sealed Pt tube at 600°C and an external pressure of 2995 atm water vapor [4].

The following phases have been found after preparation at 1000°C, both on slow cooling and by quenching to room temperature [1]:

**Monoclinic Phase** ($0 < x < 0.010$). This phase is isomorphous with monoclinic $WO_3$. It is considered to be a solid solution that arises by insertion of $Al^{3+}$ ions into the $WO_3$ lattice, which leads to an average oxidation state for W of $6-3x$. The distortion of the monoclinic lattice decreases with increasing x. At $x = 0.010$, $\beta = 90°$ [1], see also [2].

**Orthorhombic Phase** ($0.010 \leqq x < 0.020$). This phase is isomorphous with orthorhombic $WO_3$. The lattice parameters of $Al_{0.015}WO_3$ are $a = 7.368 \pm 0.004$, $b = 7.476 \pm 0.004$, and $c = 3.850 \pm 0.002$ Å. With increasing x, a increases and b drops. The extrapolated identical values at $x \approx 0.24$ were, however, not achieved experimentally [2], see also [1].