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Single-Crystal Synthesis and Investigation of the Double Tungstates $NaR^{3+}(WO_4)_2$, where R^{3+} = Fe, Sc, Ga, and In

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Single crystals of the $NaR^{3+}(WO_4)_2$ tungstates for R^{3+} = Fe, Sc, Ga and In have been obtained by the flux method and have been investigated by optical goniometry, X-ray analysis, and DTA. The compounds are isostructural with each other. The $NaIn(WO_4)_2$ crystal structure has been studied in detail. It is similar to the structure of the natural wolframite, but sodium and indium constitute distinct files parallel to the *c* axis. Space group is $P2/c$.

1. Introduction

There is information on preparation of some sodium trivalent metal tungstates of the formula $NaR(WO_4)_2$ in a single crystal form. Double sodium tungstates of bismuth, yttrium and almost of all rare-earth elements were prepared and found to crystallize into a scheelite type structure (*1*, *2*). Some tungstates have interesting fluorescent properties (*3*) and laser action has been shown in $NaGd(WO_4)_2$: Nd^{3+} (*4*).

In the present study the tungstates $NaR(WO_4)_2$ of the iron, scandium, gallium, and indium have been crystallized and their crystallographic properties and thermal stability have been investigated. These compounds have lately been prepared by firing the mixtures of constituents in proper proportions (*5*, *6*). But it seems that very few single-crystal studies on these compounds have yet been made (*7*).

2. Experimental

The preparation of single crystals of these tungstates by the flux method is similar to that for potassium rare-earth tungstates (*8*). A charge consisting of 25% (mole) of the desired crystal composition and 75% of Na_2WO_4 used as solvent is melted at 1150–1200°C in a platinum crucible. Then the charge is cooled at a rate of 3–5°C/hr to 700–600°C. The crystals can be removed by leaching in boiling water. The runs have yielded crystals of the size and quality suitable for morphological measurements and X-ray study.

For the purposes of the identification of the crystals stoichiometric tungstates $NaR(WO_4)_2$ were prepared by a solid state reaction of the mixture of oxides of R^{3+}, W^{6+}, and Na^+. The mixture of the starting materials was heated at temperatures within the range from 700 to 900°C until the X-ray pattern of the reaction product did not change on further heating. The X-ray powder diffraction patterns of the sintered samples and the crystals were obtained using nickel-filtered $CuK\alpha$ radiation. Their patterns were found to be identical.

The $NaFe(WO_4)_2$ crystals are green; the tungstates of In, Ga, and Sc are colourless with a light brownish tint.

The thermal stability of $NaR(WO_4)_2$ prepared herein was studied using a differential thermal analysis (DTA) unit (*8*). The DTA was conducted at a heating rate of 10°/min. The accuracy of the temperature measurements is believed to be within ±20°C.

3. Results and Discussion

3.1. Crystal Growth Forms

The visual observation shows that the single-crystal habits of all tungstates synthesized are alike. The crystals are tabular and elongated. The goniometrical study was carried out with the crystals of $NaFe(WO_4)_2$. The measurement data have been marked on the stereographic projection (Fig. 1), from the consideration of which symmetry elements are found to be L_2, P, and C. The crystals are

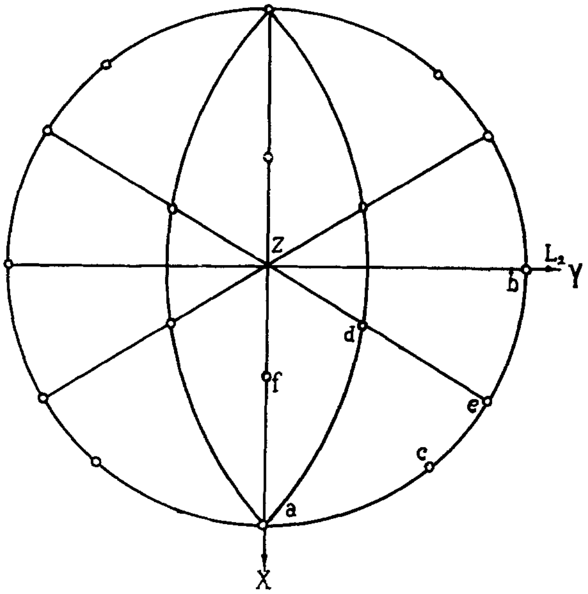

FIG. 1. Stereographic projection of the $NaFe(WO_4)_2$ single crystals.

monoclinic, class $2/m$. The angle β is close to 90°. The elongation of the crystals is always by extension of the {100} pinacoid in the [001] direction. This simple form is the most developed. The crystals are tabular on it. Other crystallographic forms arranged in the decreasing order of the observed morphological importance (frequency of occurrence and relative size) are *c* {210}, *b*{010}, *d*{111}, *e*{110},and *f*{201}. The latter forms (*e* and *f*) are usually small and of little consequence in controlling habit. The axial ratio calculated from the positional coordinates of the (111) face is $a:b:c = 1.72:1:0.87$. The crystals display an eminent cleavage on the (010) plane.

Twins are observed among the crystals. Twinning on *b*{010} is characteristic and appears to be common. In this case the axis *c* is a twin one.

3.2. X-Ray Crystal Data

The $NaR(WO_4)_2$ tungstates for R = Fe, Sc, Ga, or In are isostructural with each other. X-Ray powder diffraction data of $NaFe(WO_4)_2$ (CuKα radiation, a diffractometer URS-50I) are given in Table I. Originally the lattice constants of the unit cell of $NaFe(WO_4)_2$ have been measured during a preliminary X-ray examination of single crystals and then refined using the powder diffraction data. Calibration of diffraction angle was made with the silicon as a standard.

The unit cell parameters of the compounds and

TABLE I

INDEXED X-RAY DIFFRACTION DATA OF THE COMPOUND $NaFe(WO_4)_2$[a]

hkl	*d*,Å	I/I_0	*hkl*	*d*,Å	I/I_0
100	9.88	31	610 013	1.581	4
010	5.73	11	$11\bar{3}$	1.565	2
200 110	4.94	100	113	1.562	2
210 011	3.748	53	$50\bar{2}$ $52\bar{1}$	1.549	4
300	3,293	2	521 502	1.538	2
$21\bar{1}$	2.993	49	$61\bar{1}$ $21\bar{3}$ 430 032	1.511	18
211	2.974	48	611 213	1.503	15
020 310	2.862	13	$42\bar{2}$	1.4966	9
120	2,750	2	$23\bar{2}$	1.4504	4
$31\bar{1}$ 220 021 400 002	2.469	53	232	1.4423	4
$12\bar{1}$	2.410	2	$31\bar{3}$ 040	1.4304	5
121	2.396	2	620 023	1.4275	5
410 012	2.266	7	123 700	1.4100	2
$20\bar{2}$ $22\bar{1}$	2.225	8	$60\bar{2}$ $62\bar{1}$ $22\bar{3}$ $33\bar{2}$ 041	1.3740	7
221 202	2.208	13	612 413 $24\bar{1}$	1.3249	8
$41\bar{1}$ $21\bar{2}$	2.065	9	711	1.3158	2
411 212	2.055	14	630	1.2560	5
$30\bar{2}$ 500	1.975	5	800 004	1.2350	7
030	1.909	3	622 423	1.2305	5
$31\bar{2}$ 130	1.873	15	$71\bar{2}$ $44\bar{1}$ $24\bar{2}$	1.2023	5
420 022	1.869	18	$20\bar{4}$ 441	1.2003	5
230	1.778	14	$81\bar{1}$ $21\bar{4}$	1.1745	2
$40\bar{2}$ $42\bar{1}$ $22\bar{2}$	1.754	17	811	1.1703	2
421 222	1.744	18			
402	1.741	19			
$41\bar{2}$ $23\bar{1}$	1.677	3			
330 600	1.647	6			
520	1.626	2			

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[a] For indexing the X-ray powder lines the reflexion intensities on Weissenberg photographs were taken into consideration.

TABLE II

UNIT CELL PARAMETERS, DENSITIES, AND MELTING POINTS OF $NaR(WO_4)_2$

R	a, ±0.02 Å	b, ±0.01 Å	c, ±0.02 Å	d_x, gcm^{-3}	d_m, gcm^{-3}	T°C
In	10.08	5.81	5.03	7.16	7.13	1010
Sc	10.05	5.75	5.00	6.50	—	840
Fe	9.88	5.72	4.94	6.85	6.83	900
Ga	9.83	5.69	4.93	7.11	—	835

densities calculated and measured picnometrically at 298°K (maximum values) are summarized in Table II. The angle $\beta = 90 \pm 0.5°$ for all compounds. Two $NaR(WO_4)_2$ formula units are contained in the unit cells.

In this series the unit cell parameters are in the relative accordance with the values of the R^{3+} cation radius (In, 0.92; Sc, 0.83; Fe, 0.67, and Ga, 0.62 Å (*9*)). The axial ratio for $NaFe(WO_4)_2$ calculated from the X-ray data is $a:b:c = 1.73:1:0.86$ and agrees very well with the morphological one. The unit cell parameters obtained in this study support the data recently published (*5*, *6*).

Single-crystal diffraction methods have been used to study the peculiarities of the crystal structure of these compounds. For the measurement of intensities a small crystal of $NaIn(WO_4)_2$ of approximate dimensions 0.25 × 0.25 × 0.80 mm was selected. Equi-inclination Weissenberg photographs of the layers $l = 0 \div 6$ and $h0l$ were taken with MoKα radiation. A total of about 800 nonzero independent reflexions were measured. The only systematic absences among the reflexions are in $h0l$ for $l = 2n + 1$. The space group is hence $P2/c$ or Pc. The test for piezoelectricity was negative. This and the morphological data described indicate the presence of an inversion centre. The final and convincing evidence that the space group is indeed $P2/c$ is given by the refinement of the structure.

3.3. On Crystal Structure

Diffracted intensities were visually estimated by comparison with a calibrated film strip. The intensities were corrected for Lorentz and polarization factors but absorption was neglected. The positional coordinates of the heavy atoms W and In were determined from two-dimensional Patterson functions $P(xy)$ and $P(xz)$. The sodium and oxygen atoms could be located unambiguously in the electron-density distribution, $\rho(xy)$ and $\rho(xz)$. Refinement has been performed by the method of least squares assuming isotropic temperature factors for all atoms. Brusentsev's program was used (*10*). The atomic scattering factors for neutral W, In, Na, and O were taken from the "International Tables for X-ray Crystallography" (*11*). About 650 independent structure factors were used in the analysis within a reciprocal lattice hemisphere of radius $(\sin\theta)/\lambda = 0.9$ Å^{-1}. The agreement factor between measured and calculated structure factors at this stage is 13.5%. The resulting positional and thermal parameters are listed in Table III. The positional coordinates together with the lattice

TABLE III

POSITION ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR $NaIn(WO_4)_2$

Atom	x	y	z	β
W	0.2432 ± 3	0.1785 ± 3	0.2468 ± 5	−0.13 ± 4
In	0	0.6856 ± 11	0.25	0.42 ± 7
Na	0.50	0.655 ± 11	0.25	2.3 ± 9
O_I	0.120 ± 4	0.626 ± 7	0.598 ± 10	0.3 ± 4
O_{II}	0.357 ± 6	0.374 ± 10	0.365 ± 13	1.1 ± 6
O_{III}	0.337 ± 4	0.095 ± 8	0.939 ± 10	0.3 ± 5
O_{IV}	0.131 ± 5	0.101 ± 9	0.536 ± 12	0.7 ± 6

TABLE IV

NEAREST-NEIGHBOUR INTERATOMIC DISTANCES IN $NaIn(WO_4)_2$, IN ANGSTROMS[a]

W Octahedron	In Octahedron	Na Octahedron
$W\text{-}O_I = 1.84$	$In\text{-}O_I = 2.16$ (2)	$Na\text{-}O_{II} = 2.25$ (2)
$W\text{-}O_{II} = 1.72$	$In\text{-}O'_I = 2.31$ (2)	$Na\text{-}O'_{II} = 2.42$ (2)
$W\text{-}O_{III} = 1.88$	$In\text{-}O_{IV} = 2.11$ (2)	$Na\text{-}O'_{III} = 2.39$ (2)
$W\text{-}O_{IV} = 1.90$		
$W\text{-}O'_{III} = 2.09$		
$W\text{-}O'_{IV} = 2.24$		
O–O = 2.42–2.91	O–O = 2.86–3.41	O–O = 2.90–3.80
W–W = 3.26	In–In = 3.31	Na–Na = 3.07

[a] The value in parenthesis is the number of equivalent distances.

constants were used to derive the interatomic distances in Table IV.

The crystal structure projected on the (010) plane is represented in Fig. 2. The W atoms are surrounded by oxygen octahedra. Relatively small distance W–W = 3.26 Å indicates that sharing oxygen edges by two neighbour W octahedra is most likely to be found in this structure (*12*). As can be seen each W octahedron shares the edges $O_{III}\text{–}O_{IV} = 2.42$ Å with two other W octahedra. The W octahedra form zigzag chains extended infinitely along the [001] direction.

The In and Na atoms have also six O atoms as nearest neighbours which form rather distorted octahedra. The In and Na atoms are located on twofold axes. The arrangements and environments of the In and Na octahedra in the structure are similar to those for the W octahedra. The infinite chains of octahedral groups of oxygen atoms around the In and Na cations follow the [001] direction and are formed by either In octahedra or Na octahedra only (Fig. 3). The W octahedral chains are linked to the In and Na octahedral chains through sharing O corners.

The lattice constants of $NaR(WO_4)_2$ and the crystal structure described are similar to that of the natural wolframite $(Fe, Mn)WO_4$, but with a doubled *a* parameter (cf. for $FeWO_4$ $a = 4.730$ Å, $b = 5.703$ Å, and $c = 4.952$ Å, $\beta = 90°$ (*13*)). The wolframite structure can be considered as a slightly deformed hexagonal closepacked lattice of oxygen atoms in which one-half of the octahedral holes is occupied by the Me^{2+} and W^{6+} ions. There are two layers of the octahedral holes parallel to (100) along the *a* axis. The W^{6+} ions occupy the octahedral holes in the first layer ($x = 0$), the M^{2+} ions in the second layer ($x = 0.5$).

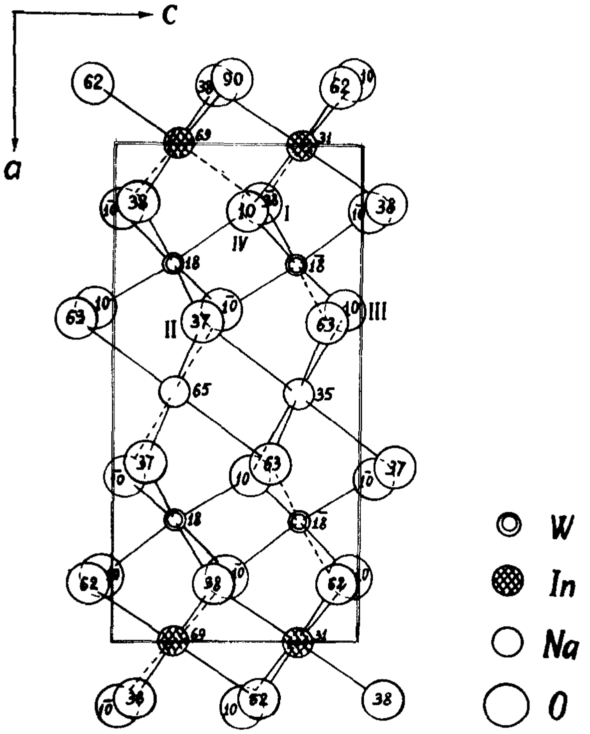

FIG. 2. The $NaIn(WO_4)_2$ structure viewed along the *b* axis. The letters I–IV refer to oxygen atoms as identified in Tables III and IV.

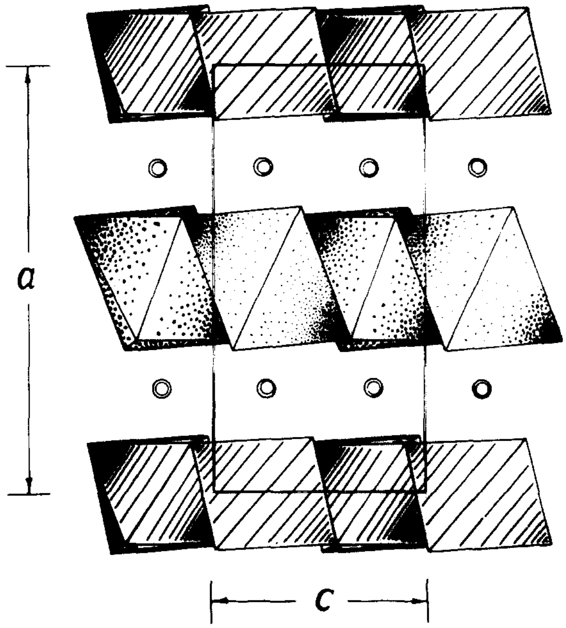

FIG. 3. View of the In($x = 0$) and Na($x = 0.5$) octahedral chains in the $NaIn(WO_4)_2$ structure along the *b* axis.

But there are four layers of similar octahedral holes along the *a* parameter in the crystal structure of $NaR(WO_4)_2$ (Fig. 3), two layers of which at $x = 0.25$ and $x = 0.75$ are occupied by the W^{6+} ions, the layers at $x = 0$ and $x = 0.5$ belong to the R^{3+} and the Na^+ ions, respectively. The W layers are related to each other with the glide translation in the wolframites and with twofold axes in the double tungstates. In the wolframite structure both cations (M^{2+} and W^{6+}) are located on twofold axes, so that all octahedra display a twofold symmetry. In the double tungstate structure the Na^+ and R^{3+} cations are located only on twofold axes, each distributing in the individual layers of the octahedral holes. These features make the unit cell parameter *a* twice as long in $NaR(WO_4)_2$ than in the wolframites and keep the *b* and *c* parameters invariable.

This crystal structure corresponds to the first kind of the isomorphous substitutions $2M^{2+} \rightarrow M^+ + R^{3+}$ in the wolframite structure (a variant with an inversion centre) studied by Le Flemm et al. (*6*). Second substitution kind, when each M^{2+} octahedra chain contains both the M^+ and R^{3+} cations, is realized in the low-temperature form of the double tungstates of lithium and of rare earths from terbium to lutetium and yttrium (*14*). The crystal structure investigation was accomplished for the lithium ytterbium tungstate $LiYb(WO_4)_2$ (*15*). The space group P2/n was assumed in this case. The $LiR(WO_4)_2$ tungstates for R = Fe, Cr, Sc crystallize in a third wolframite-like structure in which two unit cell parameters, *a* and *b*, are doubled according to Le Flemm et al. (*6*). The crystal structure of $LiFe(WO_4)_2$ has been solved in the centric space group C2/c [16].

3.4. Thermal Stability

The wolframite-like structure of $NaR(WO_4)_2$ for R = Fe, Sc, Ga, and In is stable in the air atmosphere up to the melting point (melting point values are given in Table II). The tungstates yield on the DTA curves only one endothermal effect caused by melting. This effect and the X-ray powder pattern of samples of the NaIn and NaSc tungstates melted and then solidified are reversible. The X-ray powder pattern for the NaFe tungstate sample held in the molten state for about 5 hr contains additional lines indicating a dissociation.

The sodium gallium tungstate undergoes thermal dissociation after melting. Several phases were found by the X-ray powder pattern analysis. Together with $NaGa(WO_4)_2$ the tetratungstate $Na_2W_4O_{13}$ ($Na_2O \cdot 4WO_2$) (*17*) and the gallium oxide ϵ-Ga_2O_3 (*18*) have been identified. The decomposition corresponds to $2NaGa(WO_4)_2 \rightarrow Na_2W_4O_{13} + Ga_2O_3$. The molten sodium tetratungstate is also instable and decomposes into the bitungstate $Na_2W_2O_7$ and WO_3. This results from the DTA curves and the X-ray powder patterns.

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