HYDROTHERMAL SYNTHESIS AND SYMMETRY OF CRYSTALS OF OXYTUNGSTATES $\mathrm{Ln}_2\mathrm{W}_2\m ($\mathrm{Ln} = \mathrm{Ce}, \mathrm{Pr}, \mathrm{Nd}$)

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HYDROTHERMAL SYNTHESIS AND SYMMETRY OF CRYSTALS OF OXYTUNGSTATES $Ln_2W_2O_9$ (Ln = Ce, Pr, Nd)

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In recent years a considerable number of works have appeared on the synthesis and crystallization of medium rare-earth tungstates of composition $Ln_2(WO_4)_3$. However, up to now comparatively little information has been given on the investigation of binary oxide systems of the type Ln_2O_3—WO_3 and of new phases in these systems.

Recently Rode and Karpovym ([1]), in studying the system Nd_2O_3—WO_3 by the pyrosynthesis method, in addition to the previously known phases with molar ratio $Nd_2O_3 : WO_3 = 1 : 3$ and $1 : 1$ ([2]), obtained a new compound of composition $Nd_2W_2O_9$ with molar ratio $Nd_2O_3 : WO_3 = 1 : 2$. According to the authors' data, on heating this compound exhibits two polymorphic transformations at 438 and 1248° and melts incongruently at 1354°.

In studying the hydrothermal crystallization of rare-earth tungstates in aqueous solutions of alkali-metal chlorides, we synthesized, for cerium, praseodymium, and neodymium, crystals of compounds with a molar ratio of the oxides of the rare-earth elements and tungsten equal to $1 : 2$.

These compounds proved stable in a wide range of solvents (individual and mixed chlorides of lithium, sodium, potassium, and ammonium) in the temperature range 450–550° and at pressures of the order of 500–1700 atm. The optimum conditions for the synthesis of $Pr_2W_2O_9$: a) mixed solvent NaCl 20% + NH_4Cl 5%, charge $Pr_2(WO_4)_3$, temperature 550°, filling coefficient 60%; b) concentrated LiCl, charge $LiPr(WO_4)_2$, filling 60%, temperature 550°; for $Nd_2W_2O_9$ and $Ce_2W_2O_9$—concentrated LiCl solutions (35% and above) at 525–550°; charges $Nd_2(WO_4)_3$ and $Ce_2(WO_4)_3$, respectively, filling coefficient 50–60%.

The color of the crystals of praseodymium oxytungstate is green, of neodymium oxytungstate—lilac, and of cerium oxytungstate—yellow.

Fig. 1. Four possible variants for choosing the unit cell of $Pr_2W_2O_9$

Figure 1: Fig. 1. Four possible variants for choosing the unit cell of $Pr_2W_2O_9$

Single crystals of $Pr_2W_2O_9$ were obtained in the form of elongated, flattened prisms up to 0.3–0.4 mm in size. However, in most cases, both for $Pr_2W_2O_9$ and for $Nd_2W_2O_9$, weakly faceted intergrowths were obtained, having the form of "combs," irregular plates, and isometric pieces. The size of the intergrowths was up to 1 mm.

The symmetry of the obtained $Pr_2W_2O_9$ crystals was investigated by methods of optical and X-ray goniometry. For optical-goniometric measurements, well-formed crystals with all-sided faceting were used. In analysis of the stereographic projection it was found that the crystals belong to the monoclinic system, class L_2PC. The symmetry axis L_2 passes along the length of the crystal. The most highly developed faces are those of the pinacoid $(10\bar{1})$, giving the crystals a platy habit. In the plane xz, in addition to the z axis, the axes x_1 and x_2 of other, most developed zones of faces lie at angles $\beta_1 = 107^\circ$ and $\beta_2 = 133^\circ$. In this case the plane yx_2 coincides with the plane of the plate.

The results of measurements on the optical goniometer are presented in Table 1.

The indices of the growth forms are given in the setting x, z with the monoclinic angle $\beta = 107^\circ$. A unit face was not observed on the crystals. Its coordinates were calculated on the basis of X-ray data.

To determine the parameters of the unit cell and the space group, X-ray photographs were taken on an RKOPe camera (Cu radiation), as well as zero-, first-, and second-layer rotation photographs about the b axis (Ag radiation). The symmetry of the Laue patterns and rotation photographs, in agreement with the optical goniometry data, corresponds to monoclinic symmetry.

From the Weissenberg photograph $h0l$, the angles β were determined for different choices of the x and z axes, and from oscillation photographs the corresponding parameters a and c. The above-mentioned monoclinic angles $\beta = 107^\circ$ and 133° correspond to four possible choices of the base of the unit cell ac, which are shown in Fig. 1 (in this case the parameter c is constant, while the corresponding z axis in some variants changes direction to the opposite one). In variants 1 and 2 the cells have similar angles β (106.5 and 107.5°, respectively), while in variants 3 and 4 they are $\sim 133^\circ$. However, cells 2 and 4 are characterized by a body-centered basis B.

Fig. 1. Four possible variants for choosing the unit cell of $Pr_2W_2O_9$

For the intended subsequent X-ray structural investigations and in indexing the powder diffractogram (Table 2), we chose the first setting.

Table 1

Growth forms of $Pr_2W_2O_9$ crystals

hkl	ρ, deg	φ, deg	Angle with $+x$	Angle with $+y$	Angle with $+z$	Simple growth form
$10\bar{1}$	90	133	30	90	136	Pinacoid
100	90	0	16	90	90	»
010	0	0	90	0	90	»
001	90	74	90	90	16	»
$20\bar{1}$	90	157	7	90	113	»
111	–	–	57	64.7	63	Rhombic prism
110	55	0	39	55	90	» »
$11\bar{2}$	72	47	64	72	47	» »
$1\bar{1}2$	66	119	60	66	151	» »

The parameters of the unit cell, refined by the least-squares method from the diffractogram data ([3]), are as follows: $a = 7.70$ Å, $b = 9.84$ Å, $c = 9.27$ Å, and $\beta = 106.5^\circ$.

Chemical analysis found a content of Pr 36.0%, W 46.6%, which, on recalculation to a formula, gives the compound $Pr_2W_2O_9$ (calculated data for this compound: Pr 35.5%, W 46.0%).

From these data the density of an ideal $Pr_2W_2O_9$ crystal was calculated as $d_x = 7.82$ g/cm^3 (for 4 formula units in the unit cell). The mean density value measured by the pycnometric method is $d_{meas} = 7.69$ g/cm^3.

The space group $C_{2h}^5 = P2_1/c$ was determined unambiguously from the extinctions: in the $h0l$ zone reflections are present only with $l = 2n$, in the zone

$0k0$—with $k = 2n$ (from the $hk0$ scan); for reflections of general type, no extinctions are observed.

The crystals of neodymium and cerium oxytungstates were identified by comparing powder X-ray diffraction patterns. The compounds $Nd_2W_2O_9$ and $Ce_2W_2O_9$ are isostructural with $Pr_2W_2O_9$. Their powder X-ray diffraction patterns are very close

Table 2

X-ray data for $Pr_2W_2O_9$

hkl	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0
011	6.647	5	202	2.513	5	[[unclear: hkl]]			224	1.604	7

hkl	d, Å	I/I_0	hkl	d, Å	I/I_0	hkl	d, Å	I/I_0	hkl	d, Å	I/I_0
110	5.845	2	040	2.458	40	241	1.906	31	115	1.604	7
111	5.485	3	311	2.458	40	051	1.906	31	253	1.604	7
020	4.920	5	302	2.432	9	143	1.906	31	325	1.582	17
120	4.010	5	223	2.354	37	302	1.892	18	235	1.582	17
012	4.010	5	132	2.354	37	314	1.892	18	323	1.574	7
112	4.010	5	232	2.333	7	150	1.892	18	243	1.561	4
121	3.945	9	140	2.333	7	043	1.886	20	035	1.561	4
200	3.677	4	104	2.309	3	134	1.886	20	351	1.548	4
211	3.514	6	141	2.296	3	151	1.862	23	153	1.548	4
121	3.514	6	114	2.296	3	223	1.862	23	352	1.530	32
102	3.329	100	321	2.241	26	234	1.821	15	350	1.530	32
202	3.269	98	231	2.241	26	243	1.821	15	342	1.508	34
022	3.269	98	141	2.203	20	115	1.821	15	234	1.508	34
122	3.223	33	033	2.203	20	324	1.810	15	154	1.498	23
112	3.193	32	204	2.182	20	052	1.810	15	335	1.498	23
212	3.159	89	322	2.182	20	152	1.810	15	333	1.475	15
031	3.077	23	014	2.163	8	322	1.778	28	145	1.475	15
221	2.990	72	313	2.148	8	215	1.778	28	054	1.472	12
130	2.990	72	042	2.148	8	341	1.769	35	353	1.472	12
211	2.990	72	142	2.148	8	152	1.708	20	254	1.461	17
131	2.913	87	124	2.092	9	225	1.708	20	351	1.461	17
220	2.913	87	233	2.072	4	204	1.695	35	245	1.452	12
113	2.913	87	241	2.061	3	252	1.695	35	135	1.452	12
013	2.855	14	240	2.030	11	134	1.695	35	045	1.443	20
122	2.804	11	331	2.005	31	025	1.671	46	314	1.433	7
222	2.764	21	224	2.005	31	334	1.671	46	253	1.417	7
131	2.723	6	321	2.005	31	251	1.651	26	324	1.383	28
032	2.622	37	213	1.981	61	315	1.651	26	345	1.383	28
132	2.622	37	133	1.981	61	153	1.651	26	225	1.383	28
221	2.622	37	142	1.981	61	332	1.651	26	352	1.370	5
023	2.588	6	232	1.971	69	044	1.642	43	155	1.345	5
213	2.588	6	242	1.971	69	343	1.642	43	255	1.333	14
123	2.588	6	332	1.954	26	135	1.609	3			
023	2.548	3	330	1.954	26						

to one another. For $Nd_2W_2O_9$, the values of d_{hkl}, and consequently also the unit-cell parameters, are smaller than the corresponding values for $Pr_2W_2O_9$ only by a few units in the second decimal place.

Differential thermographic analysis up to 1000° for $Nd_2W_2O_9$ showed that this compound undergoes a reversible polymorphic transition in the region 410–420°.

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Note: Figure translations are in progress. See original paper for figures.