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NEW LANTHANUM OXYTUNGSTATE $2La_2O_3 \cdot 3WO_3$

(Presented by Academician N. V. Belov, 25 VII 1968)

Oxy tungstates of rare-earth elements have been obtained mainly in the form of sinters in the study of systems of the type TR_2O_3—WO_3 ([1–6]). Only recently have some of them, for Ce, Nd, Pr with TR_2O_3/WO_3 ratios equal to 1 : 2, 1 : 1, 2 : 3, become known also in the form of single crystals ([7]). From the crystallochemical standpoint, oxy tungstates have been almost unstudied, and only for some of them have the unit-cell parameters and Fedorov groups been established ([2,7]).

Oxy tungstates with a La_2O_3/WO_3 ratio equal to 2 : 3 were not found in the study of the La_2O_3—WO_3 system, but this compound was obtained by us in the ternary system La_2O_3—WO_3—NaCl over a wide range of temperatures and concentrations of sodium chloride. The starting charge was a mixture of La_2O_3 and WO_3 oxides in the ratio 1 : 3. Crystals of lanthanum oxy tungstate grow under isothermal conditions due to evaporation of sodium chloride and, in part, WO_3; the largest ones (up to 3–4 mm in elongation) were obtained at 1000–1400° and solvent concentrations from 50 to 80 wt. %. The yield of crystals and their size depend on the rate and magnitude of evaporation; their habit varies from short prismatic to strongly elongated, almost needle-like. The crystals are colorless, water-transparent, optically uniaxial, positive, and have high refractive indices (> 2.0).

Chemical analysis of crystals from several experiments, on recalculation, gives the stable formula $2La_2O_3 \cdot 3WO_3$ (La_2O_3 48.90%, WO_3 51.52%; theoretical composition: La_2O_3 48.37%, WO_3 51.63%). The melting temperature is $\sim$ 1560°, but with decomposition.

Goniometric measurements revealed symmetry $4/mmm$. The morphology of the crystals is simple: a combination of the tetragonal prism {110} and the tetragonal dipyramid {101} (Table 1). The relative parameters from the goniometric data are $a = 1$, $c = 1.26$. The interplanar spacings (Table 2), calculated

from diffraction patterns (URS 50-IM, Cu K_α radiation, Ni filter), differ from those for previously known compounds of similar chemical composition.

Table 1

Results of the goniometric study of crystals of $2La_2O_3 \cdot 3WO_3$

Symbol	ρ_{meas}, deg.	φ_{meas}, deg.	Symbol	ρ_{meas}, deg.	φ_{meas}, deg.
{110}	90	45	{101}	51.38	0
{110}	90	135	{101}	51.38	90
{110}	90	225	{101}	51.38	180
{110}	90	315	{101}	51.38	270

For the X-ray goniometric study, a crystal measuring $0.4 \times 0.2 \times 0.2$ mm was selected. The symmetry $4mm$ of the Laue pattern, taken in the camera

RCP along the elongation axis (Mo radiation) confirms the tetragonal symmetry of the crystal (diffraction class $4mmmP-/n-c$). The parameters of the tetragonal cell, determined from rotation radiographs in the same camera, are $a = 10.06 \pm 0.03$ Å, $c = 12.63 \pm 0.06$ Å. At a density $d_{meas} = 7.16$ g/cm^3 (hydrostatic weighing in CCl_4), there are 4 formula units per cell. To determine the space group, 0- and 1-layer line Weissenberg photographs along the b axis were used

Table 2

Diffraction data for crystals of $2La_2O_3 \cdot 3WO_3$

d, Å	I/I_1	hkl	d, Å	I/I_1	hkl	d, Å	I/I_1	hkl
5.2958	3	–	2.4947	25	040	1.1736	16	440
4.6707	7	–	2.4397	3	{040 < br > 041 < br > 015	1.6980	14	442
4.1986	2	121	2.2012	3	332	1.6650	8	154
3.8567	4	013	2.0077	8	035	1.5986	5	–
3.2045	7	{023 < br > 031	1.9665	8	–	1.5861	8	353
3.1317	27	004	1.9529	27	044	1.5655	5	{336 < br > 055
3.0644	100	222	1.9333	6	{026 < br > 151	1.5418	5	155

d, Å	I/I_1	hkl	d, Å	I/I_1	hkl	d, Å	I/I_1	hkl
2.9308	5	032	1.9202	4	144	1.5302	11	{262 163
2.7015	3	231	1.8647	9	–	1.4479	5	362
2.5636	6	124	1.8358	4	251	1.4154	5	–
2.5177	8	133	1.8019	19	{343 053	1.3367	5	272

(Weissenberg RCP; Mo K_α radiation). Analysis of the extinctions made it possible to determine the space group quite unambiguously as $D_{4h}^{15} = P4_2/nmc$. The infrared spectrum of lanthanum oxytungstate (I. I. Plyusnina) is characterized by absorption bands in the regions 810–860, 740, 620, and 440 cm^{-1}.

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named after M. V. Lomonosov

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