CRYSTALLINE TUNGSTATE CHLORIDE

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Fig. 1

Figure 1: Fig. 1

Abstract

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CRYSTALLOGRAPHY

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CRYSTALLINE TUNGSTATE CHLORIDE

$LnWO_4Cl$ (Ln = Ce, Pr, Nd)

(Presented by Academician N. V. Belov, 16 XII 1966)

It is known that the intermediate or normal tungstates of rare-earth elements, $Ln_2(WO_4)_3$, are unstable in aqueous solutions of chloride salts both under ordinary conditions ([1]) and under hydrothermal conditions (at high pressures and temperatures). Under hydrothermal conditions, in solutions of alkali-metal chlorides ($M^+ = Li, Na, K$), crystals of double tungstates $M^+Ln(WO_4)_2$ ([2]), forming solid solutions with $Ln_2(WO_4)_3$, as well as oxytungstates $Ln_2W_2O_9$ ($Ln = Ce, Pr, Nd$) ([3]), were synthesized from intermediate tungstates.

The composition of the solid phases formed during the decomposition of the intermediate tungstate of rare-earth elements depends on the medium and on the thermodynamic parameters. Identification and study of them contribute to an understanding of the phase equilibria and chemical transformations in the hydrothermal systems under investigation. In the present communication we give the results of studying one of these phases—the tungstate chloride of rare-earth elements $LnWO_4Cl$ ($Ln = Ce, Pr, Nd$).

Fig. 1

Crystalline tungstate chloride of composition $LnWO_4Cl$ was obtained in the study of hydrothermal crystallization in the systems $Ln_2(WO_4)_3 - NH_4Cl - H_2O$. It is also formed during the crystallization of oxytungstates $Ln_2W_2O_9$ in certain mixed solvents consisting of ammonium chloride (5–15%) and alkali-metal chlorides (Li, Na).

The experiments were carried out under isothermal conditions in stainless-steel autoclaves with a self-sealing closure. Direct synthesis is carried out in "floating" titanium liners.

The tungstate chloride for the given rare-earth elements is formed in ammonium

chloride solutions (2.5–10%) in the temperature range 450–500° at a filling coefficient of 75–50%, respectively. Evidently, it is a product of decomposition of the intermediate tungstate as a result of chemical interaction with dissolved ammonium chloride,

$$Ln_2(WO_4)_3 + 2NH_4Cl \rightarrow Ln_2(WO_4)_2Cl_2 + (NH_4)_2WO_4.$$

Crystals of $LnWO_4Cl$ have a plate-like habit; the base of the plate is a rhombus. In most cases the crystals are defective. They form twinned intergrowths along the plane of the plate. On the surface of the plates, funnel-shaped, layered-step depressions– "rhombic" pyramids–are often observed. The size of the crystals is up to 1 mm.

Crystals of cerium tungstate chloride have a light-yellow color, those of praseodymium–green, and those of neodymium–lilac.

The behavior of $NdWO_4Cl$ upon heating in air was studied on a derivatograph. The curves of differential thermal and thermogravimetric analysis recorded on the instrument are reproduced in Fig. 1. They indicate that the compound $NdWO_4Cl$ decomposes at a temperature of 575° with loss in weight.

Powder X-ray diffraction patterns showed that the product of the thermal decomposition is the 1 : 2 oxy tungstate $Nd_2W_2O_9$ (3). Consequently, in air thermal decomposition proceeds according to the reaction

$$2NdWO_4Cl + \tfrac{1}{2}O_2 \rightarrow Nd_2O(WO_4)_2 + Cl_2 \uparrow$$

The loss on ignition calculated from this is 8.1 wt. %. Experimentally, l.o.i. was found to be 7.9%.

Chemical analysis of neodymium tungstate chloride for neodymium and tungsten gave the following results: Nd 32.5%, W 43.1% (calculated from the formula $NdWO_4Cl$: Nd 33.6%, W 43.4%). Semiquantitative analysis for chlorine on an X-ray microanalyzer showed that chlorine is present in this compound in a considerable amount. Among other elements, only neodymium and tungsten were found qualitatively. According to IR spectroscopy, water is absent from the compound. From comparison of the infrared spectra of $Nd_2(WO_4)_3$ and $NdWO_4Cl$ it may be assumed that the tetrahedral coordination of tungsten is retained in the tungstate chloride.

Powder X-ray diffraction patterns of $LnWO_4Cl$ for Ce, Pr, and Nd are analogous and indicate isostructurality of these three compounds. The table gives the results of calculating the X-ray diffraction pattern for $NdWO_4Cl$, recorded on a URS-50I instrument in filtered copper radiation. In indexing the powder X-ray diffraction pattern, the intensities of reflections in single-crystal X-ray photographs were taken into account.

Table 1

X-ray data for $NdWO_4Cl$

hkl	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0
002	9,53	5	145	1,641	1,5
004	4,76	10	046	1,641	1,5
104	3,697	9	1.2.10	1,638	2
120	3,215	7	324	1,638	2
006	4,178	6	240	1,604	1,5
122	3,040	4,5	241	1,599	1,5
024	2,983	6	2.0.10	1,599	1,5
200	2,939	4	0.0.12	1,587	2
202	2,792	5	146	1,579	1
106	2,792	5	0.2.11	1,579	1
124	2,663	4	047	1,571	1
125	2,447	2	229	1,571	1
026	2,447	2	308	1,512	1,5
108	2,205	7	2.2.10	1,476	3
224	2,092	4	400	1,463	1
028	2,023	4	402	1,450	2
040	1,919	2,5	148	1,450	2
302	1,919	2,5	328	1,406	1
041	1,905	3,5	2.0.12	1,398	1
0.0.10	1,905	3,5	247	1,382	1
042	1,881	4,5	149	1,382	1
226	1,881	4,5	3.0.10	1,352	2
1.0.10	1,811	5	0.0.14	1,352	2
304	1,811	5	248	1,331	1
044	1,781	1	406	1,331	1
143	1,746	1	1.4.10	1,317	1,5
320	1,739	1	424	1,314	1,5
321	1,739	1	344	1,314	1,5
045	1,714	1	063	1,253	4
322	1,714	1	1.2.14	1,253	4
0.2.10	1,705	4	160	1,253	4
144	1,705	4	161	1,244	1
228	1,665	1,5	064	1,236	1
305	1,665	1,5	2.0.14	1,236	1

From the symmetry of the latter, the belonging of $LnWO_4Cl$ crystals to the orthorhombic system was established. The parameters of the unit cell of $NdWO_4Cl$, obtained from rotation and Weissenberg photographs and then refined on an electronic computer from the powder diffraction pattern (4), are as follows: $a = 5.86$, $b = 7.67$, and $c = 19.05$ Å. With the measured density $d_{\text{meas}} = 6.53$ g/cm^3, the unit cell contains 8 formula units of $NdWO_4Cl$.

The 0-, 1-, 2-, 3-, and 4-layer-line rotation photographs about the axes a and b (Mo radiation) were taken. Systematic extinctions observed in them occur in the $h0l$ zone for reflections with $l = 2n + 1$ and in the $0kl$ zone with $k = 2n + 1$.

It follows that the probable space groups are $D_{2h}^{11} = Pbcm$ and $C_{2v}^{5} = Pbc2_1$. The absence of a piezoelectric effect in the crystals makes the choice of the first group preferable. However, owing to the presence in the structure of a strong pseudoperiod $b' = b/2$, it remains unclear whether the extinctions of reflections in the $0kl$ zone with $k = 2n + 1$ are systematic. Therefore another centrosymmetric space group, $D_{2h}^{5} = Pmcm$, is also possible.

The X-ray data are given in Table 1.

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