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Abstract

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SYNTHESIS AND CRYSTALLOGRAPHIC STUDY OF OXYTUNGSTATE CHLORIDES OF COMPOSITION

$Ln_3WO_6Cl_3$ (Ln = Ce, Pr, Nd)

(Presented by Academician N. V. Belov, May 20, 1969)

A study of the conditions for the hydrothermal synthesis of crystals of alkali-rare-earth tungstates and rare-earth oxytungstates, carried out by us in aqueous solutions of alkali-metal and ammonium chlorides, as well as a detailed study of synthesis in certain chloride systems containing praseodymium and tungsten oxides ([1]), led to the preparation of a new group of compounds, which, in addition to rare-earth elements and tungsten, contain chlorine anions. At present, two types of crystalline tungstate chlorides can already be distinguished in this group:

1. $LnWO_4Cl$ for La, Ce, Pr, and Nd.

2. Ln_3WO_6Cl ($Ln_2WO_6 \cdot LnCl_3$) for Ce, Pr, and Nd.

The first type of these compounds was described by us in paper ([2]). The present communication is devoted to compounds of composition $Ln_3WO_6Cl_3$.

Experiments on hydrothermal crystallization were carried out in standard stainless-steel autoclaves with self-sealing closures. Titanium liners were used as reaction vessels. The charge was loaded in the form of mixtures $Ln_2O_3 : WO_3 = 1 : 1,\ 2 : 1,\ 3 : 1$ (molar ratios) or their sinters. The charge : solvent ratio was 1 : 5 and 1 : 10 (weight ratios).

Compounds $Ln_2WO_6Cl_3$ for praseodymium and neodymium are formed in 5% ammonium chloride and in mixed solutions of 20% LiCl + 10% NH_4Cl and 20% KCl + 5% NH_4Cl over a wide temperature range: 500–600° in the first two cases and 450–600° in the last (the filling of the autoclaves, depending on temperature, varied from 70 to 40%). In addition, oxytungstate chlorides for cerium and neodymium were obtained in solutions of alkaline-earth-metal chlorides (20–35% $MgCl_2$ and 20% $CaCl_2$) at a temperature of 550° and an autoclave filling of 60%.

Fig. 1. Heating curves of differential thermal and thermogravimetric analysis of $Nd_3WO_6Cl_3$ crystals

Figure 1: Fig. 1. Heating curves of differential thermal and thermogravimetric analysis of $Nd_3WO_6Cl_3$ crystals

Experiments carried out on crystallization of these compounds from solution in a melt showed that oxytungstate chlorides can crystallize not only in closed aqueous systems at elevated temperatures and pressures, but also at atmospheric pressure and in the absence of water. Anhydrous lithium chloride was used as the solvent in this case,

Table 1

Face	+x	+y	+u	+z	Number of faces	*hkil*	Growth form
1	30	90	150	90	6	$10\bar{1}0$	Hexagonal prism
2	0	120	120	90	6	$2\bar{1}\bar{1}0$	» »
3	61	90	119	33	12	$10\bar{1}1$	Hexagonal dipyramid

The charge consisted of melts of medium tungstates of composition $Ln_2(WO_4)_3$, where $Ln = Pr, Nd$. The maximum temperature, at which the experiment was held for about 10 h, was 800°; the cooling rate was 3° per hour in the interval 800-600° and below this 10° per hour. The charge : solvent ratio in molar fractions was $\sim 1 : 50$.

Single crystals of $Ln_3WO_6Cl_3$ have the form either of elongated hexagonal prisms or of thin hexagonal plates. The size of the single crystals is up to 1-2 mm. More often, the oxywolframate chlorides crystallize as intergrowths of needle-prismatic crystals or plates, the size of the intergrowths being 2-5 mm. Optical goniometric measurements of the single crystals showed that they belong to the class L_6PC. The growth forms of $Pr_3WO_6Cl_3$ crystals are given in Table 1. The most strongly developed faces are those of the hexagonal prism $\{10\bar{1}0\}$. The ratio of the unit-cell parameters is $c/a = 0.57$.

Fig. 1. Heating curves of differential thermal and thermogravimetric analysis of $Nd_3WO_6Cl_3$ crystals

The chemical formula of the compound $Ln_3WO_6Cl_3$ was established on the basis of chemical analysis and determination of its crystal structure (3). Tungsten, rare-earth element, and chlorine were found in the compound. Results of analysis of neodymium oxywolframate chloride: Nd 51.9% (calculated 52.7%), W 23.4% (calculated 22.5%), Cl 12.3% (calculated 13.0%). Quantitative analysis for alkali metals established that they do not enter the compound. According to IR spectroscopy data, the compound contains no water.

From the Debye patterns the isostructural character of the compounds $Ln_3WO_6Cl_3$ for cerium, praseodymium, and neodymium was established.

Table 2 gives the results of calculation of the powder X-ray pattern for $Pr_3WO_6Cl_3$, recorded on a URS-50 diffractometer with Cu K_α radiation. The unit-cell parameters of this compound, obtained from oscillation and rotation X-ray patterns and refined on a computer from the powder diffractogram data according to program (4), are $a = 9.314$, $c = 5.369$ Å.

The character of the displacement of lines on the powder diffractograms of the investigated compounds $Ln_3WO_6Cl_3$ indicates an increase in the unit-cell parameters–

Table 2

X-ray diffraction data for $Pr_3WO_6Cl_3$

hkl	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0	*hkl*	*d*, Å	I/I_0
100	8.10	25	400}	2.015	40	213	1.542	15
110	4.61	4	212}	2.015	40	420	1.522	
101	4.46	5	302}	1.896	16	322		5
200	4.05	10	401}	1.896	16	303	1.488	4
111	3.524	40	230	1.848	11	412	1.468	12
201	3.230	43	410}	1.758	27	421	1.465	13
210	3.050	39	222}	1.758	27	510	1.446	7
300}	2.683	38	231}	1.758	27	511}	1.393	11
002}	2.683	38	103	1.743	33	313}	1.393	11
211	2.645	100	312	1.713	7	004}	1.339	4
301	2.403	4	113	1.669	8	403}	1.339	4
310	2.232	20	203	1.635	8	422}	1.322	4
221	2.136	4	500}	1.604	7	104}	1.322	4
311	2.059	5	402}	1.604	7			

of the unit cell in the series from Nd to Cl, in accordance with the increase in the ionic radius of Ln^{3+}.

The behavior of the compounds $Ln_3WO_6Cl_3$ upon heating in air was studied on a derivatograph. It was shown that they are rather stable substances, unlike $LnWO_4Cl$: their decomposition begins only at 1000° (whereas $LnWO_4Cl$ begins at 570°) and proceeds rather slowly; moreover, on the thermal curve the effect is very weak and is detected mainly by analogy with the weight-loss curve (Fig. 1). Complete decomposition of the compound is achieved as a result of calcining it for 5 h at 1100°. The proposed decomposition scheme for the compounds

$$Nd_3WO_6Cl_3 + {}^3/_4O_2 \rightarrow Nd_2WO_6 + {}^1/_2Nd_2O_3 + {}^3/_2Cl_2 \uparrow$$

is confirmed by X-ray diffraction data for the substance after calcination at 1100°: all lines in the diffraction pattern belong to Nd_2WO_6 (the predominant

phase) and Nd_2O_3. The weight loss calculated from the reaction upon calcination is 10.1%; experimentally, after 5 h of calcination, 9.9% was obtained.

Thus, it may be considered that the two rare-earth oxywolframate chlorides indicated above are derivatives of 1 : 2 oxywolframate $Ln_2W_2O_9$ (Ln, WO_4Cl) and 1 : 1 oxywolframate $Ln_2WO_6 \cdot (Ln_3WO_6Cl_3)$.

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