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Abstract

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HIGH-TEMPERATURE SYNTHESIS AND SOME PROPERTIES OF NORMAL TUNGSTATES OF YTTRIUM, LANTHANUM, AND LANTHANOIDS

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The first mentions of tungstates of rare-earth* elements (r.e.e.) date to 1876 (^1). However, even up to the present these compounds have been studied quite insufficiently. Reports have concerned only the formation of normal tungstates of r.e.e. of the cerium subgroup, precipitating as amorphous deposits when solutions of nitrates, chlorides, or sulfates of r.e.e. and sodium tungstate are mixed (^2-11).

Didier (^6) synthesized cerium tungstate by adding cerium oxide to a melt of sodium paratungstate. Direct synthesis of cerium tungstate by sintering CeO_2 with WO_3 was carried out by Tammann (^12), Nelson and McKeem (^13). For $Ce_2(WO_4)_3$, the type and parameters of the crystal lattice have been established, and the density and melting point have been determined ([7,8],^14). The high-temperature synthesis of normal tungstates of other r.e.e., as well as their properties, has not been described in the literature.

We have investigated the kinetics and conditions of formation of normal tungstates of r.e.e. during their high-temperature synthesis; on this basis we determined the optimal conditions for carrying it out and studied some properties of the tungstates obtained. As starting materials we used oxides or carbonates (in the case of Ce, Pr, Tb) of r.e.e., with a content of the principal substance in the product calcined at 900-950° of not less than 99.0-99.5%. The only impurities in the principal substance were oxides of accompanying r.e.e. The purity of tungsten trioxide was 99.95%. The bulk of the oxide particles consisted of grains smaller than 2-3 μ. Initially, the reacting starting substances were taken both according to the stoichiometric calculation for formation of normal tungstates of composition $Me_2O_3 \cdot 3WO_3$ and with an excess or deficiency of one of the reaction components relative to this composition. The molecular ratio $Me_2O_3 : WO_3$ was thereby varied from 4 : 1 to 1 : 4. Mixtures of specified molecular composition were mixed for ~20 min in an agate mortar and then fired for 4 h at a specified temperature (in the range 800-1000°), with threefold intermediate grinding of the sinter.

X-ray diffraction patterns

Figure 1: X-ray diffraction patterns

The sintering products were investigated by microscopic, X-ray, and the phase chemical analysis developed by us. Quantitative phase chemical analysis was based on selective dissolution of unreacted Me_2O_3 and the tungstates formed in a mixture of hydrochloric and phosphoric acids**. Transfer of the r.e.e. tungstates into solution was achieved as a result of their decomposition by hydrochloric acid according to the reaction:

$$Me_2O_3 \cdot xWO_3 + 6HCl + (x-3)H_2O \rightarrow 2MeCl_3 + xH_2WO_4$$

and simultaneous dissolution of the tungstic acid that separated in H_3PO_4 due to the formation of soluble heteropoly compounds of tungsten.

* In what follows, when considered together, the rare-earth elements will include yttrium, lanthanum, and the lanthanoids.

** Free WO_3 calcined at high temperatures in a mixture of these acids, during and under the conditions of the analysis, practically did not dissolve.

The possible formation of rare-earth orthophosphates did not threaten their precipitation, since the hydrates of the latter are readily soluble in mineral acids (15). The procedure for carrying out the analysis was as follows. A finely

Fig. 1. Character of the X-ray diffraction patterns of intermediate rare-earth tungstates (ion-exchange method).
a—from La to Ho; *b*—from Er to Lu and Y

ground sample of the sintering product, dried at 200° (~0.2 g), was treated with a mixture of acids containing 10 ml conc. HCl, 10 ml 88% H_3PO_4, and 10 ml H_2O, at a temperature of 100-120° (sand bath) for 2 hours, with a repeated addition of the same amount of solution after the first

hours of treatment. The residue was filtered, washed with water, and calcined at 800° to constant weight. From the amount of residue (unreacted WO_3) it was possible to judge both the limiting composition of the tungstate formed and the rate of interaction of the initial Me_2O_3 and WO_3 as a function of the synthesis conditions. The accuracy of the analytical method developed is ±0.5 (abs.)*. Preliminary experiments showed that, under the given temperature conditions of interaction (800-1000°), for mixtures of the initial Me_2O_3 and WO_3, the limiting compounds with respect to WO_3 content in the Me_2O_3–WO_3 series are the middle rare-earth tungstates of composition $Me_2O_3 \cdot 3WO_3$**. Therefore, further investigations were directed toward establishing the optimum synthesis conditions for these compounds. For this purpose, mixtures of Me_2O_3 and WO_3 with the molar ratio

$$Me_2O_3 : WO_3 = 1 : 3$$

were subjected to isothermal firing in the range 600-1000° (accuracy ±20°) for 15 to 480 min. The completeness of the reaction was monitored by phase chemical analysis. The interaction between Me_2O_3 and WO_3 was also studied by thermography and X-ray phase analysis. Intending to devote special attention to the kinetics of formation of the rare-earth tungstates elsewhere, we note here only the general features characteristic of the process of interaction of Me_2O_3 and WO_3. Reactions between them begin in the range 500-600° and, up to the temperature of the polymorphic transformation of WO_3 (750°), proceed relatively slowly. The rate of the process in this temperature region is limited by diffusion of the oxides through the layer of the reaction product being formed. Additional grinding of the sinter helps to increase the reaction rate. Upon reaching the temperature of the polymorphic transformation (750°), the mobility of the lattice elements of WO_3 increases as a result of its "loosening," and the rate of formation of the rare-earth tungstates rises considerably. At 900° the reactions between Me_2O_3 and WO_3 proceed practically to completion within a comparatively short interval of time. For the synthesis of about 10 g of a middle rare-earth tungstate, a mixture of Me_2O_3 and WO_3 is prepared in the stoichiometric ratio***, then mixed for 30-40 min in an agate mortar and subjected to 4-hour firing at 700-750° with three intermediate grindings of the sinter. Preliminary thermal treatment subsequently eliminates melting of the sinter due to the formation of a low-melting mixture of tungstate, Me_2O_3, and WO_3 (observed in the synthesis of tungstates of the cerium subgroup and of dysprosium). Final firing is carried out at 900° for 8 h with four intermediate grindings of the sinter. This yields middle rare-earth tungstates with a main-substance content of not less than 99-99.5%. The individuality of the synthesized compounds, in addition to phase chemical analysis, was confirmed by X-ray analysis. The rare-earth tungstates obtained under the indicated conditions are anisotropic fine-crystalline substances, insoluble in water, alcohol, and acetone. Some properties of the synthesized rare-earth tungstates are given in Table 1. X-ray analysis established that the structure of the middle rare-earth tungstates can be characterized by one of the two types of X-ray patterns presented in Fig. 1. The transition from one structural type to the other is characterized by a change in some properties of these compounds. The tungstates of yttrium and of the Er—Lu series, compared with the tungstates of the La—Ho series, possess a significantly greater adsorption capacity and lower stability toward the action of various chemical reagents. The transition from one structural type of middle rare-earth tungstates to another is confirmed—

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* The total error in kinetic investigations, owing to the influence of a number of technological factors (chiefly temperature fluctuations), may increase to ±2-3% (abs.).

** According to X-ray phase analysis data, in the Me_2O_3–WO_3 system one may expect the formation of basic rare-earth tungstates as well; refinement of their chemical composition requires additional investigations.

*** The volatility of WO_3 under the synthesis conditions does not exceed 0.1-0.2% of the initial amount.

is also accompanied by a disruption in the character of the change in the density of these compounds (see Table 1). The tungstates of Dy and Ho, being transitional from one series of tungstates to another, occupy an intermediate position in some of their properties. Thus, according to thermographic studies, they undergo a polymorphic transformation: $Dy_2O_3 \cdot 3WO_3$ at 960°, and $Ho_2O_3 \cdot 3WO_3$ at 935°. At the same time, for $Ho_2O_3 \cdot 3WO_3$, in contrast to $Dy_2O_3 \cdot 3WO_3$,

Table 1

Composition and some properties of the normal tungstates of yttrium, lanthanum, and lanthanoids

Compound	Found molar ratio $Me_2O_3 : WO_3$	Content of the main substance, % (phase chemical analysis)	Density, g/cm^3	Melting temp.,* °C	Color
$La_2O_3 \cdot 3WO_3$	1:3.09	99.43–99.47	6.506	1140	White
$Ce_2O_3 \cdot 3WO_3$	1:3.02	99.76–99.84	6.773	1100	Greenish-yellow
$Pr_2O_3 \cdot 3WO_3$	1:2.95	99.85–99.87	6.983	1140	Lettuce-green
$Nd_2O_3 \cdot 3WO_3$	1:3.01	99.65–99.72	7.065	1250	Pale lilac
$Sm_2O_3 \cdot 3WO_3$	1:2.92	99.40–99.64	7.229	1220	Pale yellow
$Eu_2O_3 \cdot 3WO_3$	1:3.05	99.70–99.79	7.357	1260	Pale pink, almost colorless
$Gd_2O_3 \cdot 3WO_3$	1:2.99	99.13–99.28	7.475	1290	White
$Tb_2O_3 \cdot 3WO_3$	1:2.97	99.55–99.63	7.624	1360	White

Compound	Found molar ratio $Me_2O_3 : WO_3$	Content of the main substance, % (phase chemical analysis)	Density, g/cm^3	Melting temp.,* °C	Color
$Dy_2O_3 \cdot 3WO_3$	1:2.93	98.00–98.50	7.686	1410	Pale green, almost colorless
$Ho_2O_3 \cdot 3WO_3$	1:3.06	99.00–99.20	7.948	1460	Pale yellow
$Er_2O_3 \cdot 3WO_3$	1:3.02	99.22–99.30	5.178	1500	Pink
$Tu_2O_3 \cdot 3WO_3$	1:3.08	99.02–99.10	5.225	1520	Pale green, almost colorless
$Yb_2O_3 \cdot 3WO_3$	1:2.98	99.80–99.90	5.323	1540	White
$Lu_2O_3 \cdot 3WO_3$	1:3.03	99.10–99.30	5.340	1580	White
$Y_2O_3 \cdot 3WO_3$	1:2.97	99.73–99.81	4.407	1470	White

* Determined with an optical micropyrometer (successive-approximation method) with an accuracy of ±20°.

this transition is irreversible. The X-ray diffraction patterns of the high-temperature forms of $Dy_2O_3 \cdot 3WO_3$ and $Ho_2O_3 \cdot 3WO_3$ have a general character similar to the X-ray diffraction patterns of yttrium tungstates and the Er–Lu series. Differential-thermal (up to 1050°) and X-ray phase (after melting) analyses of the other rare-earth tungstates did not reveal any transformations during their heat treatment. Phase chemical analysis of the molten tungstate samples established that, at least up to the melting temperatures, the normal rare-earth tungstates do not decompose.

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