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Abstract

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SYNTHESIS AND SOME PROPERTIES OF THE LOWER CRYSTALLINE HYDRATES OF YTTRIUM, LANTHANUM, AND LANTHANIDE PERRHENATES

(Presented by Academician I. V. Tananaev, January 23, 1963)

Yttrium, lanthanum, and lanthanide perrhenates* have up to the present time not been studied, possibly because, until quite recently, pure rhenium compounds and especially compounds of the rare-earth elements (r.e.e.) were very scarce. There have been reports only on the formation of lanthanum, cerium [1], and neodymium [2] perrhenates in the process of dissolving freshly precipitated lanthanum and neodymium hydroxides or cerium carbonate in perrhenic acid, followed by evaporation of the solutions and crystallization of the salts at room temperature. To the crystalline hydrates of lanthanum perrhenate, without proof, compositions corresponding to the formulas $La(ReO_4)_3 \cdot 2H_2O$ and $La(ReO_4)_3 \cdot 3H_2O$ were assigned. Their stability was not studied. The existence of anhydrous perrhenates of definite composition was not established.

We have developed a method for obtaining anhydrous r.e.e. perrhenates by dehydration of their lower crystalline hydrates, which thus proved to be intermediate products of the synthesis.** None of these crystalline hydrates had previously been described, and below the conditions for their preparation and some of their properties are considered.

As starting materials for the synthesis of crystalline hydrates of r.e.e. perrhenates, r.e.e. oxides were used, containing not less than 98.0% of the principal substance (Nd, Lu); 99.0% (Ce, Pr, Dy, Tu) and 99.5% (La, Sm, Eu, Gd, Tb, Ho, Er, Yb, Y); the impurities to the principal substance were only oxides of other r.e.e. The source of rhenium was ammonium perrhenate with the following content (wt.%): 0.01 Mg, 0.00014 Ca, 0.0005 Al, 0.006 Si, and 0.0005 Fe. Ammonium perrhenate was reduced in a tubular furnace with hydrogen at 300–350°, and the rhenium powder was pressed in a hydraulic press (under a pressure of 4.5 t/cm^2) into rods, which were subjected to high-temperature sintering in a laboratory vacuum direct-heating electric furnace [3] at 2600–2700°; in this process the indicated impurities were removed. The refined rods were dissolved in conc. chemically pure HNO_3, and the perrhenic acid formed was evaporated on a water bath until complete removal of HNO_3 (checked by the greening of

Fig. 1. Crystalline forms of lower crystalline hydrates of rare-earth perrhenates (40×): a—La and Ce, b—from Pr to Dy, c—from Ho to Lu and Y

Figure 1: Fig. 1. Crystalline forms of lower crystalline hydrates of rare-earth perrhenates (40×): a—La and Ce, b—from Pr to Dy, c—from Ho to Lu and Y

the precipitate as a result of the formation of a mixture of lower rhenium oxides; to convert the latter into Re_2O_7, H_2O_2 was added to the precipitate). Then the pure Re_2O_7 was dissolved in distilled water to obtain an $HReO_4$ solution with a concentration of 240 g/l. The NO_3^- content (reaction with diphenylamine) did not exceed 0.0002%.

Since $HReO_4$ belongs to the strong acids [4], it could be assumed that preparation of crystalline hydrates of r.e.e. perrhenates is feasible on the basis of r.e.e. oxides. The use of r.e.e. oxides has considerable advantages over the use of hydroxides. Although dissolution of the latter in $HReO_4$ proceeds even at ordinary temperature, their use is inconvenient and impractical. First of all, r.e.e. hydroxides are [5] very good adsorbents and are difficult to wash free of the ions introduced during their precipitation; moreover, they filter poorly and slowly, and in the finished form (as

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* Hereafter, when yttrium, lanthanum, and the lanthanides are considered together, they will be referred to as rare-earth elements.

** Direct high-temperature synthesis of r.e.e. perrhenates from oxides (Me_2O_3 and Re_2O_7) was excluded because of the high volatility of Re_2O_7 (boils at 363°).

and carbonates of the rare-earth elements are usually not manufactured. In addition, the oxides of the rare-earth elements make it possible to obtain more concentrated solutions of rare-earth perrhenates. It is true that in some cases dissolution of the rare-earth oxides in $HReO_4$ proceeds slowly, but the reaction is readily accelerated by adding H_2O_2. The differing stability of rare-earth oxides with respect to $HReO_4$ is apparently connected with their prior history (temperature and duration of calcination), and also with the decrease in basicity in the lanthanum-lutetium series.

Fig. 1. Crystalline forms of lower crystalline hydrates of rare-earth perrhenates (40×):
a —La and Ce, *b* —from Pr to Dy, *c* —from Ho to Lu and Y

Initially, the starting reactants were taken both from the calculation for the formation of normal perrhenates of composition $Me(ReO_4)_3$ and with an excess or deficiency of rare-earth oxides relative to the amount required by the equation:

$$Me_2O_3 + 6HReO_4 = 2Me(ReO_4)_3 + 3H_2O.$$

With an excess of $HReO_4$, during evaporation of the solution on a water bath at 75-80° the crystals of the salt of the precipitated perrhenate became coated with a blue film of a mixture of lower rhenium oxides; with an excess of Me_2O_3 it, after neutralization of $HReO_4$, remained in the perrhenate solution as an insoluble precipitate. Preliminary experiments thus showed that, in the series Me_2O_3 –Re_2O_7, under the given synthesis conditions only one chemical compound is formed with respect to the ratio of Me_2O_3 and Re_2O_7. Therefore, in subsequent work the synthesis was carried out with an excess of Me_2O_3, which ensured complete neutralization of $HReO_4$ in a sufficiently short time (the precipitate is readily filtered off). To prepare ~5 g of rare-earth perrhenate, 1.2-1.4 g of rare-earth oxide (corresponding to a ~20% excess of Me_2O_3) is transferred to a beaker containing 35 ml of $HReO_4$ solution (240 g/l), and the mixture is heated on a water bath to dissolve Me_2O_3. Completion of the reaction is monitored with methyl red: the change from crimson color (at pH 6.2) to yellow indicates the end of the reaction. If it is necessary to accelerate the course of the reaction, H_2O_2 is added to the solution (in this case, after decomposition of H_2O_2, the indicator should be added again, since H_2O_2 destroys it). The resulting solution is filtered from the excess Me_2O_3 and then evaporated on a water bath at 75-80° to dryness.

In the course of the synthesis it was established that all rare-earth perrhenates dissolve in water in considerable amounts. In this connection, the described synthesis scheme makes it possible to use the starting materials most efficiently, with a yield of not less than 95%. Perrhenates with a minimally constant content of water of crystallization are thereby obtained.

Perrhenates of rare-earth elements obtained at 75-80° are nonhygroscopic, finely crystalline substances, readily soluble in water, alcohol, and acetone. Their color is determined by the Me^{3+} ion. A microcrystalloscopic study established that crystals of rare-earth perrhenates belong to one of the three types shown in Fig. 1. The transition from one crystal type to another is also noticeable from the character of the change in the refractive indices (see Table 1).

Table 1

Composition and some properties of the lower crystalline hydrates of the perrhenates of yttrium, lanthanum, and lanthanoids

Compound	Found molar ratio	Density*, g/cm^3	N_p	N_g	N_m
$La(ReO_4)_3 \cdot H_2O$	3,06 : 1,00	5,139	1,671	1,680	
$Ce(ReO_4)_3 \cdot H_2O$	2,94 : 1,01	5,160	1,680	1,690	
$Pr(ReO_4)_3 \cdot H_2O$	2,99 : 1,01	5,262	1,668	1,675	

Compound	Found molar ratio	Density*, g/cm^3	N_p	N_g	N_m
$Nd(ReO_4)_3 \cdot H_2O$	2,96 : 0,97	5,285	1,668	1,675	
$Sm(ReO_4)_3 \cdot H_2O$	2,96 : 1,08	5,331	1,675	1,684	
$Eu(ReO_4)_3 \cdot H_2O$	2,96 : 1,01	5,337	1,679	1,684	
$Gd(ReO_4)_3 \cdot H_2O$	2,96 : 1,01	5,391	1,679	1,684	
$Tb(ReO_4)_3 \cdot 2H_2O$	3,06 : 1,99	5,160	1,684	1,691	
$Dy(ReO_4)_3 \cdot 2H_2O$	2,94 : 2,00	5,210	1,684	1,691	
$Ho(ReO_4)_3 \cdot 2H_2O$	3,00 : 1,99	5,218	1,651	1,686	1,670
$Er(ReO_4)_3 \cdot 2H_2O$	3,00 : 2,02	5,232	1,651	1,686	1,670
$Tu(ReO_4)_3 \cdot 2H_2O$	3,06 : 2,07	5,244	1,651	1,686	1,670
$Yb(ReO_4)_3 \cdot 2H_2O$	2,95 : 2,00	5,254	1,654	1,688	1,672
$Lu(ReO_4)_3 \cdot 2H_2O$	3,03 : 1,99	5,263	1,654	1,688	1,672
$Y(ReO_4)_3 \cdot 2H_2O$	2,95 : 1,97	4,765	1,644	1,680	1,661

* Accuracy of determination ±0,005.
** Accuracy of determination ±0,003.

The synthesized rare-earth perrhenates were analyzed for the contents of Me_2O_3 and Re_2O_7. For the analysis, a sample weighing ~ 1 g was dissolved in 100 ml of water, and 20 ml was taken for the determination of Me_2O_3, adding a 2 *M* solution of NH_4NO_3 and precipitating $Me(OH)_3$ with ammonia solution. After washing the $Me(OH)_3$ with a 2% solution of NH_4NO_3, the precipitate was ignited to constant weight at 900° and weighed as Me_2O_3. For the determination of rhenium, 10 ml of the solution was taken, diluted to a volume of 50 ml, acidified with CH_3COOH, and rhenium was precipitated with a 5% aqueous solution of nitron acetate. The mixture was then cooled to 6-8° and held for 2 h, after which it was filtered through a No. 3 filter with a porous bottom, washed with a dilute solution of nitron acetate, and dried at 110°, obtaining the weight of nitron perrhenate, from which the Re_2O_7 content was calculated. As is evident from Table 1, the composition of the synthesized perrhenates with respect to the ratio of Me_2O_3 to Re_2O_7 corresponds to 1 : 3. The water content was determined by difference, and was also estimated from the results of studying

the thermal stability of the compounds during their isothermal dehydration. For this purpose, a sample of the compound weighing 0.2-0.3 g was placed in a drying oven (in the range 80-200°; accuracy ±1°) or a furnace (in the range 200-650°; accuracy ±20°) and kept at the specified temperature to constant weight; the temperature was then raised to the next step. The crystalline hydrates of rare-earth perrhenates were also studied by thermography (Kurnakov pyrometer) and thermogravimetry (continuous-weighing balances).

Intending to devote special attention to the question of the thermal stability of the crystalline hydrates of rare-earth perrhenates, we shall indicate here only that the dehydration behavior of individual representatives of this series of compounds has certain individual features; however, all are characterized by loss of water of crystallization up to complete dehydration without

of decomposition of perrhenates and without the formation of other intermediate stable crystal hydrates. The individual character of these compounds is confirmed by X-ray analysis.

From the results of isothermal drying it was definitively established that the REE perrhenates obtained by crystallization from hot solutions or by their evaporation crystallize with one (in the La—Gd series) or two (in the Tb—Lu series and yttrium perrhenate) molecules of water. The transition from monohydrates to dihydrates of REE perrhenates (Gd—Tb) is confirmed by the discontinuity in the character of the change in the density of the compounds (see Table 1).

The loss of water of crystallization in perrhenates of the elements of the cerium subgroup (all of them monohydrates) occurs mainly in the interval 140-160°, begins at a temperature not below 120°, and ends at a temperature not above 180°. The perrhenates of the elements of the yttrium subgroup and yttrium perrhenate (dihydrates) are less stable*; they lose most of the water in the interval 100-110°, and the remainder at 140-160°. In this connection we note that gadolinium perrhenate occupies an intermediate position between the perrhenates of the elements of the cerium and yttrium subgroups: it is the last in the series of monohydrates, but in its lower stability it is closer to the dihydrates, since it begins to lose water at 110°. It is characteristic that the decrease in stability of REE perrhenates on going from their mono- to dihydrates is especially pronounced in the compounds of terbium and dysprosium (the first in the series of dihydrates), which already in the interval 100-110° lose both molecules of water of crystallization**.

After removal of the water of crystallization, further heating of all anhydrous REE perrhenates to 500-550° does not lead to loss of weight.

The formation of anhydrous REE perrhenates, stable over a considerable temperature interval (200-550°), and their individual character were confirmed by chemical and X-ray phase analysis of samples of the corresponding crystal hydrates dried to constant weight at 250°. Only on calcination above 550° do the anhydrous REE perrhenates decompose according to the equation:

$$2Me(ReO_4)_3 = Me_2O_3 + 3Re_2O_7.$$

The decomposition proceeds slowly. Thus, a sample (~0.3 g) of one of the least stable, $Yb(ReO_4)_3$, lost 78.4% of its weight in a week at 650°, i.e., decomposed completely (the theoretical content of Re_2O_7 in $Yb(ReO_4)_3$ is 78.7%); X-ray phase analysis showed that only Yb_2O_3 was present in the decomposition residue, and it did not dissolve, whereas anhydrous REE perrhenates dissolve excellently in water. Yttrium perrhenate under the indicated conditions lost ~50% of its weight, while neodymium perrhenate lost only a few percent.

Thus, at present we have a reproducible method for synthesizing the lower crystal hydrates of the rare-earth elements and the corresponding sufficiently stable anhydrous compounds; consideration of their properties will be the subject of a separate communication.

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* However, the crystal hydrates of all REE are stable over $CaCl_2$, and none of them is dehydrated even partially at a temperature below 100°.

** This is evidently not accidental, since the compounds of terbium and dysprosium differ in structure from the following compounds of the series, which is reflected in the optical characteristics.

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