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1965

SovietRxiv

Abstract

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CHEMISTRY

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On New Compounds of the Oxides of Rare-Earth Elements and Lithium

The problem of the amphoteric character of the oxides of rare-earth elements has been discussed in the literature for quite some time. Recently a number of works have been published devoted to the study of the interaction of the oxides of rare-earth elements (r.e.e.), Ln, with the oxides of elements of the first and second groups of the periodic system. Thus, as a result of the interaction of lithium oxide with the oxides of certain r.e.e., compounds of the type $LiLnO_2$ have been obtained [1–6].

In the literature there was no information on the interaction of praseodymium and terbium sesquioxides with lithium oxide. The aim of the present work was to obtain compounds of praseodymium and terbium oxides with lithium oxide.

For this purpose the oxides Pr_6O_{11} and Tb_4O_7 were first reduced with hydrogen at 600°. The completeness of reduction was monitored by X-ray phase analysis. A mixture of the sesquioxides Pr_2O_3 (or Tb_2O_3) and lithium carbonate was thoroughly ground for two hours with alcohol; then the alcohol was evaporated, and pellets were prepared from the powder. The ratio Ln : Li in the mixture was respectively 1 : 1, 1 : 2, 1 : 3. The samples were calcined in a stream of hydrogen in corundum crucibles at 500, 600,

Table 1

Results of indexing the X-ray pattern of $LiTbO_2$

I	hkl	$10^4/d^2$ exp.	$10^4/d^2$ calc.	I	hkl	$10^4/d^2$ exp.	$10^4/d^2$ calc.
6	110	432	440	1	310	3326	3320
1	120	674	680	3	002	3432	3440
5	130	1068	1082	3	250	3460	3445
4	021	1181	1181		320		3560
1	101	1239	1220	3	241	3560	3583
4	111	1278	1300	6	061	3718	3747
5	040	1298	1283	2	112	3901	3880
3	200	1436	1440	1	330	3966	3962
3	210	1499	1520		161		4107

I	hkl	$10^4/d^2$ exp.	$10^4/d^2$ calc.	I	hkl	$10^4/d^2$ exp.	$10^4/d^2$ calc.
3	121	1546	1541	4	301	4109	4100
1	140	1644	1643	4	311	4189	4180
4	131	1946	1942		470		4290
	041		2143	6	251	4278	4305
2	230	2157	2162		132		4523
	150		2365	6	340	4534	4523
2	211	2387	2380	3	042	4737	4723
2	141	2508	2503	3	202	4890	4880
7	221	2614	2601	2	080	5087	5130
8	240	2704	2723		261		5187
3	060	2878	2887	4	222	5191	5201
4	231	3019	3022		341		5383
	151		3225	4	270	5375	5370
8	160	3228	3247	1	180	5463	5493
				4	410	5836	5840
				4	351	6000	6100
				7	420	6084	6084
				7	242	6176	6163

700, 800°. The calcination time was 30 h. Powder photographs of the calcined samples were taken in an RKD camera. For recording X-ray patterns of preparations containing Pr_2O_3, Cu K_α radiation was used; for recording preparations containing terbium oxide, Co K_α radiation was used. The X-ray patterns of samples obtained at different calcination temperatures proved to be identical. The compound of lithium oxide with terbium oxide is isostructural with the previously described $LiGdO_2$ ([4,6]) and, consequently, has the formula

Table 2

Interplanar spacings for LiP_2O_2

I	d	I	d	I	d	I	d
4	4,148	1	1,878	3	1,471	1	1,204
5	3,611	3	1,849	1	1,444	5	1,197
5	3,093	4	1,788	1	1,432	2	1,177
2	2,804	2	1,749	3	1,405	1	1,164
2	2,673	3	1,677	3	1,376	2	1,162
5	2,526	2	1,643	3	1,332	2	1,143
1	2,304	5	1,612	1	1,316	3	1,126
1	2,157	2	1,597	2	1,287	1	1,118
1	2,108	1	1,543	3	1,271	3	1,107
5	2,057	3	1,526	1	1,243	1	1,087

I	d	I	d	I	d	I	d
4	1,909	3	1,506	1	1,219	5	1,076

$LiTbO_2$. Lithium terbate has a rhombic lattice. The lattice parameters of $LiTbO_2$ are: $a = 5.27$ Å; $b = 11.16$ Å; $c = 3.41$ Å. The results of calculating the X-ray pattern of $LiTbO_2$ are given in Table 1. The compound of lithium oxide and praseodymium oxide has a lattice different from that of $LiTbO_2$, which we were unable to index. Table 2 gives a set of interplanar distances

Table 3

Results of indexing the X-ray patterns of $LiLaO_2$

I	d	hkl	$10^4/d^2$ experiment	$10^4/d^2$ calc.	I	d	hkl	$10^4/d^2$ experiment	$10^4/d^2$ calc.
1	6,371	010	246	238	2	1,563	240	4099	4107
1	6,371	100	317	313	3	1,445	800	4796	4806
1	5,614	110	313	313	3	1,445	630	4796	4845
3	3,257	020	943	952	1	1,426	222	4918	4928
5	3,158	111	1000	991	3	1,344	332	5536	5529
2	2,802	220	1274	1252	1	1,322	820	5722	5758
	2,635	410	1440	1439	1	1,291	150	6000	6022
1	2,496	320	1606	1627	3	1,260	910	6299	6321
5	2,265	221	1949	1930	5	1,236	113	6546	6415
2	2,122	130	2221	2216	5	1,236	640	6546	6510
2	1,924	600	2701	2704					
2	1,924	002	2701	2712					
5	1,869	330	2863	2817					
2	1,820	112	3019	3025					
	1,727	430	3353	3343					
	1,727	601	3353	3382					
	1,687	331	3514	3495					
3	1,654	620	3655	3655					
2	1,621	040	3806	3806					
2	1,587	224	3971	3964					

characterizing the compound of Li_2O with Pr_2O_3. On the X-ray pattern of the sample in which the ratio $Pr : Li = 1 : 1$, several weak lines of Pr_2O_3 were present, evidently owing to the appreciable volatility of Li_2O under the synthesis conditions. Thus, it may be expected that the composition of the compound containing pra-

neodymium and lithium, can be expressed by the formula $LiPrO_2$. Under the same experimental conditions, a compound of lithium oxide with neodymium

oxide, isostructural with $LiPrO_2$, was obtained. Calcination of a mixture of lanthanum and lithium nitrates with the ratio La : Li = 1 : 2 in air at 800° for 10 h led to the formation of a new compound. The X-ray diffraction pattern of the sample was obtained in an RKV camera, Cu $K\alpha$ radiation. In contrast to the data of ([2]), the compound obtained crystallizes in the orthorhombic system and has an orthorhombically distorted cubic cell. The method of homology was used in indexing the X-ray diffraction pattern. Lattice parameters: $LiLaO_2$ $a = 11.540$ Å; $b = 6.482$ Å; $c = 3.840$ Å. Since the body-centered subcell must contain two heavy atoms, the true cell must contain six lanthanum atoms. The cell volume is 287 $Å^3$; thus, the volume per lanthanum atom is 47.8 $Å^3$, which is close to the half-sum of the volumes of lanthanum and lithium oxides (53.5 $Å^3$), i.e., $Z = 6$ for the composition of the compound $LiLaO_2$. The results of indexing the X-ray diffraction pattern of $LiLaO_2$ are given in Table 3.

By calcining ytterbium and lithium nitrates, the compound $LiYbO_2$ was obtained, crystallizing in the tetragonal system. The lattice parameters calculated for this compound coincided with the data of ([3]).

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Received
7 XII 1964

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