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Abstract

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ON NEW COMPOUNDS OF OXIDES OF RARE-EARTH ELEMENTS, STRONTIUM, AND BARIUM

We have already reported ([1]) on the synthesis of compounds of the type $SrLn_2O_4$ (where Ln = Sm, Dy, and Yb), having the $CaFe_2O_4$ structure ([2]). In the present work the results are given of a study of the interaction of strontium oxide with oxides of the remaining rare-earth elements, and also of barium oxide with oxides of certain rare-earth elements.

The synthesis of the compounds was carried out by calcining mixtures of oxides or salts—carbonates, nitrates, oxalates—at a temperature of 1100-1300°. Usually the mixtures, containing the interacting components in various

Table 1

Results of phase analysis

Composition of initial mixture	Calcination conditions, *t*-ra, °C	Calcination conditions, duration, hr	Phase composition	Composition of initial mixture	Calcination conditions, *t*-ra, °C	Calcination conditions, duration, hr	Phase composition
SrO—La_2O_3	1100	12	La_2O_3	4SrO—6Sm_2O_3	1700	0.12	$SrSm_2O_4$—Sm_2O_3 (solid solution)
SrO—Pr_2O_3	1100*	12	Pr_2O_3	3SrO—7Sm_2O_3	1700	0.12	Sm_2O_3 (solid solution)
2SrO—Pr_2O_3	1100*	12	Pr_2O_3	2SrO—8Sm_2O_3	1700	0.12	Sm_2O_3 (“”)
$SrPrO_3$	1100*	12	Pr_2O_3	1SrO—9Sm_2O_3	1700	0.12	Sm_2O_3 (“”)
SrO—Nd_2O_3	1100	6	$SrNd_2O_4$	SrO—Eu_2O_3	1100	36	$SrEu_2O_4$
SrO—Nd_2O_3	1100	14	$SrNd_2O_4$	SrO—Gd_2O_3	1100	36	$SrGd_2O_4$

Composition of initial mixture	Calcination conditions, t-ra, °C	Calcination conditions, duration, hr	Phase composition	Composition of initial mixture	Calcination conditions, t-ra, °C	Calcination conditions, duration, hr	Phase composition
SrO—Nd_2O_3	1100	36	$SrNd_2O_4$	SrO—Tb_2O_3	1100*	28	$SrTb_2O_4$
SrO—Nd_2O_3	1300	16	$SrNd_2O_4$	SrO—Dy_2O_3	1100	36	$SrDy_2O_4$
9SrO—1Sm_2O_3	1200	36	$SrSm_2O_4$ + SrO** (a = 5.157± 0.001 Å)	SrO—Ho_2O_3	1100	36	$SrHo_2O_4$
8SrO—2Sm_2O_3	1200	36	$SrSm_2O_4$ + SrO	SrO—Er_2O_3	1100	36	$SrEr_2O_4$
7SrO—3Sm_2O_3	1200	36	$SrSm_2O_4$ + SrO	SrO—Tu_2O_3	1100	36	$SrTu_2O_4$
6SrO—4Sm_2O_3	1200	36	$SrSm_2O_4$ + SrO	SrO—Yb_2O_3	1100	36	$SrYb_2O_4$
5SrO—5Sm_2O_3	1200	36	$SrSm_2O_4$ + SrO	SrO—Lu_2O_3	1100	36	$SrLu_2O_4$
4SrO—6Sm_2O_3	1200	36	$SrSm_2O_4$ + $BaSm_2O_4$	BaO—La_2O_3	1250	36	La_2O_3—BaO_2
3SrO—7Sm_2O_3	1200	36	$SrSm_2O_4$ + $BaSm_2O_4$	2BaO—La_2O_3	1250	36	La_2O_3—BaO_2
2SrO—8Sm_2O_3	1200	6	$SrSm_2O_4$ + $BaSm_2O_4$	BaO—Pr_2O_3	1200*	10	$BaPr_2O_4$
1SrO—9Sm_2O_3	1200	6	$SrSm_2O_4$ + $BaSm_2O_4$	BaO—Pr_2O_3	1200*	10	$BaPr_2O_4$—Pr_2O_3
7SrO—3Sm_2O_3	1700	0.12	$SrSm_2O_4$ + SrO (a = 5.156± 0.002)	BaO—CeO_2	1200*	20	$BaCeO_3$—Ce_2O_3
5SrO—5Sm_2O_3	1700	0.12	$SrSm_2O_4$	2BaO—CeO_2	1200*	20	$BaCeO_3$
				BaO—Sm_2O_3	1000	10	$BaSm_2O_4$
				BaO—Yb_2O_3	1000	10	$BaYb_2O_4$

* The samples were calcined in a stream of hydrogen.
** For pure SrO, $a = 5.1588 \pm 0.0005$ Å was found.

ratios, were calcined in the form of pressed pellets. For the SrO—Sm_2O_3 system, annealing of samples at 1700° with subsequent quenching was also carried out. Mixtures containing praseodymium oxide and terbium oxide were calcined in a stream of hydrogen. X-ray diffraction patterns of the resulting preparations were recorded in RKD-57 and RKU-86 cameras; radiation FeK (Sm), CoK_α (Eu, Gd, Dy, Tb), and CuK_α (La, Ce, Pr, Nd, Ho, Er, Tu, Yb, Lu) was used. In several cases the recording was carried out in a focusing camera–monochromator ([3]).

The results of phase analysis, presented in Table 1, show that at 1100° the rare-earth oxides do not dissolve noticeable amounts of strontium and barium oxides and do not dissolve in them (the lattice parameter of SrO is practically

does not change after calcination in the presence of Sm_2O_3). Strontium oxide reacts with rare-earth oxides in the series from neodymium to lutetium, forming compounds $SrLn_2O_4$. In this case the rate of interaction drops sharply with increasing ionic radius of the rare-earth element. Thus, in the case of the Nd_2O_3

–SrO mixture, the reaction is completed at 1300° in 16 h, and at 1100° only in 36 h, whereas for complete

Table 2

Lattice parameters of the compounds (Sr,Ba)Ln_2O_4

Compounds	a, Å	b, Å	c, Å	V, Å^3	Compounds	a, Å	b, Å	c, Å	V, Å^3
$SrNd_2O_4$	10,28	12,19	3,568	446,7	$SrEr_2O_4$	10,02	11,87	3,406	405,0
$SrSm_2O_4$	10,11	12,11	3,510	429,6	$SrTu_2O_4$	10,00	11,77	3,373	397,0
$SrEu_2O_4$	10,15	12,11	3,506	430,6	$SrYb_2O_4$	9,99	11,74	3,348	392,5
$SrGd_2O_4$	10,12	12,04	3,468	422,4	$SrLu_2O_4$	9,97	11,75	3,337	390,6
$SrTb_2O_4$	10,09	11,93	3,440	414,0	$BaPr_2O_4$	10,60	12,50	3,618	479,2
$SrDy_2O_4$	10,11	12,03	3,448	419,2	$BaSm_2O_4$	10,45	12,36	3,541	457,5
$SrHo_2O_4$	10,04	11,89	3,412	407,4					

interaction of the reagents in other cases, calcination at 1100° for 16 h is sufficient.

Barium oxide reacts with rare-earth oxides in the series from praseodymium to lutetium, i.e., the formation of $BaLn_2O_4$ compounds is possible for rare-earth elements with larger ionic radii than in the case of analogous strontium compounds. An attempt to synthesize the compounds $SrPr_2O_4$ and $BaCe_2O_4$ by reducing the corresponding tetravalent rare-earth compounds $SrPrO_3$ and $BaCeO_3$ with hydrogen at 1200° was unsuccessful. Under these conditions cerium is not reduced from $BaCeO_3$, while the compound $SrPrO_3$ decomposes, apparently with the formation of a mixture of Pr_2O_3 and SrO. By contrast, reduction of $BaPrO_3$ under these conditions leads to the formation of $BaPr_2O_4$.

Table 3

Results of indexing the Debye diagram of $BaYb_2O_4$

Intensity	hkl	d, Å	$1/d^2$ found	$1/d^2$ calculated	Intensity	hkl	d, Å	$1/d^2$ found	$1/d^2$ calculated
Very very bright	110	3,021	0,1096	0,1102	Medium	202	1,466	0,4654	0,4656
Very very bright	101	2,930	0,1165	0,1166	Very bright	311	1,339	0,5576	0,5568
Very bright	201	2,099	0,2269	0,2265	Bright	212	1,318	0,5760	0,5757
Weak	—	2,031	0,2424	—	Bright	401	1,220	0,6714	0,6669

Intensity	hkl	d, Å	$1/d^2$ found	$1/d^2$ calculated	Intensity	hkl	d, Å	$1/d^2$ found	$1/d^2$ calculated
Bright	300	1,738	0,3311	0,3303	Very bright	410	1,140	0,7692	0,7707
Very very bright	211	1,722	0,3373	0,3365	Very bright	321	1,133	0,7786	0,7770
Very weak	—	1,703	0,3448	—	Medium	312	1,119	0,7983	0,7959
Weak	102	1,676	0,3560	0,3555	Very very weak	113	1,098	0,8290	0,8291
Very bright	220	1,507	0,4403	0,4404	Very very weak	—	1,070	0,8732	—
Weak	—	1,483	0,4549	—	Bright	402	1,050	0,9072	0,9060

Almost all the synthesized compounds crystallize in the rhombic system (structure of the $CaFe_2O_4$ type, like $SrSm_2O_4$ ([1]) and $SrEu_2O_4$ ([4])). The lattice parameters are given in Table 2. Comparison of the lattice parameters and the intensities of the lines on the X-ray diagrams of the compounds obtained clearly shows that these substances are isostructural with calcium ferrite.

The barium oxide compound with ytterbium oxide has a structure of another type—it apparently crystallizes in the hexagonal system. All the intense lines of the X-ray diagram are indexed (Table 3) assuming a hexagonal cell with a volume equal to 111,9, which is very close to the value of the sum of the volumes of BaO and Yb_2O_3 per one formula unit (113 Å^3). The X-ray diagram contains only lines with indices satisfying the condition $h-k\pm l = 3n$, i.e., the coordinates of the heavy atoms are 000, $1/3, 2/3, 1/3$, and $2/3, 1/3, 2/3$. Ordered

the arrangement of the heavy atoms leads to the appearance of a superstructure. It was not possible to determine the parameters of the true cell; the parameters of the subcell are: $a = 6.038$ Å, $c = 3.545$ Å, $V = 111.9$ Å^3.

As indicated above, strontium and samarium oxides at 1100° practically do not dissolve in one another. In the case of samples quenched from 1700°, however, considerable solubility of strontium oxide in samarium oxide was found (up to 30 mol.% SrO). Conversely, Sm_2O_3 is practically insoluble in SrO. The change in the lattice parameters of the solid solution of SrO in Sm_2O_3 as a function of the composition of the mixtures is shown in Table 4. These data present

Table 4

Lattice parameters of the solid solution of SrO in Sm_2O_3

Composition	a, Å	b, Å	c, Å	β°	V, Å^3
Sm_2O_3	14.18	3.633	8.847	99.97	448.8
90% Sm_2O_3 + 10% SrO	14.19	3.628	8.846	99.97	448.7
80% Sm_2O_3 + 20% SrO	14.10	3.676	8.895	101.09	452.4
70% Sm_2O_3 + 30% SrO	14.02	3.716	8.922	101.72	455.1

great interest in connection with the presumed existence of a region of homogeneity in Sm_2O_3 (the β-form) ([5]). Our data confirm the possibility of the existence of a considerable region of homogeneity in Sm_2O_3, since we have shown that the oxide of a divalent metal (SrO in the present case) dissolves in Sm_2O_3 at high temperatures.

The interaction of rare-earth-element oxides with strontium and barium oxides and the formation of compounds of the type $(Sr, Ba)Ln_2O_4$ may be regarded as a manifestation of amphoteric properties by the rare-earth oxides, since the atoms of the divalent and trivalent metals in the $CaFe_2O_4$ structure differ substantially in the type of coordination. The absence of interaction in systems with La_2O_3 and CeO_3 (and also Pr_2O_3 in the case of strontium oxide) can be explained by crystallographic features of the $CaFe_2O_4$ structure. Indeed, the rare-earth atom in a compound of the $CaFe_2O_4$ type has sixfold coordination—an octahedron. Such a type of coordination polyhedron is observed in metastable modifications of the oxides of neodymium, samarium, and other rare-earth elements having a smaller ionic radius, but is not characteristic of lanthanum and cerium.

We studied the stability of the synthesized compounds toward the action of water vapor, moist and dry CO_2, at room temperature. In all three cases no formation of a new phase was detected. For the $SrYb_2O_4$ preparation, kept in a stream of moist CO_2 for 20 h, a gain in weight amounting to 0.02% of the weight of the initial preparation was observed. Thus, partial decomposition nevertheless did occur.

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