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Abstract

Full Text

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CHEMISTRY

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STUDY OF THE INTERACTION BETWEEN OXIDES OF RARE-EARTH AND ALKALINE-EARTH METALS

As is known, in the series of rare-earth elements from lanthanum to lutetium and from lanthanum to scandium there is a noticeable weakening of the basic properties. This leads to the fact that scandium ([1,2]), and apparently lutetium and ytterbium ([3]), exhibit amphoteric properties. Thus, sodium lutetiate and ytterbiate of composition $Na_3[Lu(OH)_6]$ and $Na_3[Yb(OH)_6]$ ([3]) have been described. Recently the compound $SrEu_2O_4$ was obtained, which proved to be isostructural with calcium ferrite $CaFe_2O_4$ ([4]).

It was of interest to establish in what cases amphotericity would be manifested by the oxides of rare-earth elements and what influence the sizes of the ions would have in this process. For this purpose the interaction of strontium oxide with a group of oxides of rare-earth elements, whose ionic radii differ appreciably, was studied: La^{3+} (1.06), Sm^{3+} (0.96), Dy^{3+} (0.91), Yb^{3+} (0.85). To check the influence of the size of the alkaline-earth-element ion, the reactions of Sm_2O_3 with BaO and CaO, and also of Yb_2O_3 with CaO, were studied.

Carefully ground oxides of rare-earth elements and oxalates, carbonates, or nitrates of alkaline-earth elements, taken in calculated amounts, were calcined in corundum crucibles in air. In some cases the mixture of oxides was treated with nitric acid and the mixture of nitrates was calcined. The resulting preparations were examined by X-ray phase analysis (RKD-57 camera, Cu K_α radiation, Ni filter).

The results of the X-ray phase analysis are given in Table 1.

Table 1

Composition of initial mixture	Calcination conditions: temp., °C	Calcination conditions: duration, h	Results of X-ray phase analysis
$CaCO_3 + Sm_2O_3$	1000	5	Sm_2O_3**
$3CaCO_3 + Sm_2O_3$	1100	5	Sm_2O_3**
$SrCO_3 + Sm_2O_3$	1000	5	$SrSm_2O_3$
$SrCO_3 + Dy_2O_3$	1000	5	$SrDy_2O_4$

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Composition of initial mixture	Calcination conditions: temp., °C	Calcination conditions: duration, h	Results of X-ray phase analysis	Composition of initial mixture	Calcination conditions: temp., °C	Calcination conditions: duration, h	Results of X-ray phase analysis
$CaCO_3 + 3Sm_2O_3$	1100*	5	Sm_2O_3**	$SrCO_3 + Yb_2O_3$	1000	6, 12	$SrYb_2O_4$
$CaCO_3 + Yb_2O_3$	1000	5	Yb_2O_3**	$Ba(NO_3)_2 + Sm_2O_3$	1100	6	$BaSm_2O_4$
$Sr(NO_3)_2 + La_2O_3$	1100*	5	La_2O_3**				

* The same results were obtained with oxalates and nitrates.
** The oxides of alkaline-earth metals are apparently obtained in the amorphous state or are poorly crystallized; therefore, only the lines of the rare-earth-element oxide are present on the X-ray patterns.
*** The same with nitrates.

As is clear from the data of Table 1, calcium oxide does not react with ytterbium and samarium oxides and, apparently, does not dissolve in them. In the case of ytterbium oxide, this is indicated by the constancy of the lattice parameter. For monoclinic samarium oxide the lattice parameters cannot be calculated with sufficient accuracy, but the absence of a noticeable shift of the samarium oxide lines at large θ shows that the parameters practically do not change.

Table 2

Results of indexing the X-ray diffraction pattern of $SrSm_2O_4$

$SrSm_2O_4$	$CaFe_2O_4$ (5)					
I	*hkl*	*d*	$1/d^2$ found	$1/d^2$ calc.	*I*	*hkl*
–	–	–	–	–	20	120200
–	–	–	–	–	5	220
Med.	040320	3.0012.934	0.11100.1162	0.10960.1158	100	040220
Br.	121140	2.897	0.1192	0.11880.1196	65	121201
Weak	201	2.878	0.1207	0.1208		
V. v. weak	211	2.791	0.1285	0.1277		
V. weak	131	2.544	0.1545	0.1530	20	131
V. v. weak	311	2.378	0.1760	0.1768	25	311420
V. v. weak	420150231	2.345	0.1820	0.18460.1812	15	0.1825 311420
V. v. weak	141	2.231	0.2010	0.2010	15	141

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$SrSm_2O_4$	$CaFe_2O_4$ (5)					
Br.	241331	2.078	0.2316	0.23040.2316	40	241401
Med. br.	401	2.047	0.2387	0.2388	40	241401
V. v. weak	260	1.862	0.2883	0.2859	151020	411051520260
V. v. weak	251	1.855	0.2906	0.2921		
V. v. weak	530	1.796	0.3100	0.3072		
Med.	002450	1.751	0.3262	0.32620.3284		
Br.	360511	1.727	0.3355	0.33500.3342	20	360
Br.	161351	1.717	0.3393	0.33800.3412		
Med.	441170	1.696	0.3479	0.34830.3452	30	600161
Med. br.	600521022	1.681	0.3339	0.35360.3542	250.3536	441002521
Weak	202261	1.651	0.3671	0.36540.3674	15	261
V. weak	531	1.603	0.3894	0.3887	8	630460
V. v. weak	469451361	1.565	0.4083	0.40380.40990.4142		361
Weak	042601080541516		0.4351	0.43610.4352	20.43840.4367	40
Br.	322611	1.507	0.4403	0.44200.4420	10	180
Med.	621640	1.468	0.4640	0.46260.4632	25	382042
V. v. weak	280152	1.446	0.4786	0.47770.5062		
V. v. weak	720152371	1.404	0.5073	0.50860.5072	20.5056	720461371
V. v. weak	181	1.372	0.5316	0.5298	8	422
V. v. weak	432641730	1.356	0.5440	0.54500.5442	20.5429	181

(continued)

$SrSm_2O_4$	$CaFe_2O_4$ (*)						
I	hkl	d	$1/d^2$ found	$1/d^2$ calc.		I	hkl
Tr.	281	1.337	0.5592	0.5592		2	711
Tr.	471512561	1.317	0.5765	0.57440.5784	0.5737		
Tr.	740721442	1.301	0.5906	0.59090.5902	0.5931	10	281740561721

Strontium oxide reacts with the oxides of ytterbium, dysprosium, and samarium, forming isotypic compounds $Me^{II}Me_2{}^{III}O_4$, which are isostructural with calcium

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ferrite and crystallize in the rhombic system. The same compound is formed as a result of the reaction of Sm_2O_3 with BaO. Table 2 gives the results of indexing the Debye pattern of $SrSm_2O_4$ (the radiographs of $SrYb_2O_4$, $SrDy_2O_4$, and $BaSm_2O_4$ are indexed analogously). Comparison of the line intensities of the X-ray patterns of $SrSm_2O_4$ and $CaFe_2O_4$ makes it possible to assign $SrSm_2O_4$ unambiguously to the structural type of calcium ferrite (space group *Pnam*). The numerous coincidences of lines with different indices in the Debye patterns of the compounds studied do not make it possible to refine the arrangement of atoms in the lattice. Table 3 gives the values of the lattice parameters of the compounds we obtained.

Table 3

Lattice parameters of $SrSm_2O_4$, $SrDy_2O_4$, $SrYb_2O_4$, $BaSm_2O_4$ (in angstroms)

Compound	*a*	*b*	*c*
$SrSm_2O_4$	10.29	12.08	3.50
$SrDy_2O_4$	10.11	12.00	3.44
$SrYb_2O_4$	9.97	11.71	3.34
$BaSm_2O_4$	10.04	12.34	3.53

Thus, strontium oxide apparently forms compounds with the oxides of most rare-earth elements (from samarium to ytterbium); analogous compounds should probably also be formed in the case of BaO, since the latter reacts with samarium oxide (the samarium ion has the largest radius in this group of elements). A further increase in the radius of the rare-earth element (the transition from Sm to La) leads to the disappearance of amphoteric properties (strontium oxide does not react with lanthanum oxide).

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References Cited

1. I. Sterba-Böhm, C. Melichar, *Coll. Czechoslov. Chem. Commun.*, **7**, 131 (1955).

2. W. I. Spitzen, L. N. Komissarova et al., *Zs. Chem.*, **1**, 328 (1961).

3. B. N. Ivanov-Emin, E. A. Ostroumova, *ZhNKh*, **5**, 1921 (1960).

4. H. Bärnighausen, G. Brauer, *Acta Crystallogr.*, **15**, 1059 (1962).

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5. B. E. Decker, J. S. Kasper, *Acta Crystallogr.*, **10**, 332 (1957).

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