JOURNAL OF SOLID STATE CHEMISTRY **13**, 131–135 (1975)

New $A^{III}B^{III}O_3$ Interlanthanide Perovskite Compounds

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Received March 13, 1974

The new interlanthanide perovskites $LaHoO_3$, $CeLuO_3$, $CeYbO_3$, $CeTmO_3$, $PrLuO_3$, $PrYbO_3$, and $NdLuO_3$ have been prepared by solid state reactions. $PrYbO_3$ and $NdLuO_3$ are metastable at high temperatures and cannot be prepared by heating up the mechanically mixed binary oxides. The thermal stability of the $A^{III}B^{III}O_3$ perovskites decreases with increasing ionic radius of B(III), the dissociation temperatures of $LaHoO_3$ and $LaYO_3$ being 1300°C and 1470°C, respectively. No perovskites with $A = Pu$ and Am have been obtained, therefore the existence of $A^{III}B^{III}O_3$ lanthanide–actinide and of interactinide perovskites can be excluded. Lattice constants, detailed preparation methods, and the phase diagrams of the systems $LaO_{1.5}$–$HoO_{1.5}$, $LaO_{1.5}$–$YO_{1.5}$, and $LaO_{1.5}$–$SmO_{1.5}$–$YbO_{1.5}$ are reported.

I. Introduction

Interlanthanide $A^{III}B^{III}O_3$ ternary oxides with the perovskite structure have only been described for $A = La$ and $B = Lu$, Yb, Tm, Er, and Y (*1–6*). The authors of (*4*) have suggested that compositions of the type $LaHoO_3$, $LaDyO_3$, $CeLuO_3$, and $NdLuO_3$ would also crystallize in the perovskite structure when prepared at high temperatures. The possible existence of $CeLuO_3$-perovskite has earlier been suggested (*1*). A single crystal structure determination of $LaYbO_3$ is given in (*4*) which proved the proposed orthorhombic structure (space group (C_{2v}^{9}–$Pna2_1$). According to (*5*) $LaYbO_3$ is stable only at temperatures below 1860°C. As concerns the phase width of $LaYbO_3$, in (*3*) a phase width between 38 and 55 m/o $YbO_{1.5}$ is reported for 1650°C, whereas in (*5*) the phase width extends to the $YbO_{1.5}$-richer side, ranging, e.g., from 47 to 62 m/o $YbO_{1.5}$ at 1400°C and from 45 to 63 m/o $YbO_{1.5}$ at 1800°C.

Detailed studies in the interlanthanide, interactinide, and lanthanide/actinide sesquioxide systems have shown that no other A^{III}-$B^{III}O_3$ perovskite compounds than previously described can be prepared by common solid state techniques (with the exception of $A = Ac(III)$) (*7*).

II. Methods of Investigations

The following types of reactions have been used for the preparation.

a. Solid state reaction of finely powdered mixtures of $AO_{1.5}$ and $BO_{1.5}$ at 1250–1550°C.
b. Solid state reaction of coprecipitated $A(OH)_3$–$B(OH)_3$ mixed hydroxides at 1250°C.
c. Solid state reaction of finely powdered mixtures of separated precipitated $A(OH)_3$ and $B(OH)_3$ at 1250°C.
d. Hydrothermal reaction of coprecipitated mixed hydroxides at 210°C for 10 days.

The solid state reactions have been carried out in air at temperatures up to 1550°C and up to 14 days. For $A = Ce$, Pu, and Am, the dioxides (or hydrated dioxides) have been used as the starting materials. These reactions have been carried out in extremely purified hydrogen —and in a glove box, if $A = Pu$ and Am. The crucibles were made of Pt (for reactions in air) or Ir (for reactions in hydrogen).

The starting lanthanides and actinides had a purity of 99.9% the ^{241}Am and the Pu (≈90% ^{239}Pu, ≈8% ^{240}Pu, ≈2% ^{241}Pu) were specially purified by common ion exchange and extraction techniques.

The lattice constants have been calculated by using a computer program (*8*).

III. Results and Discussions

By using method IIb the new perovskites $LaHoO_3$, $CeLuO_3$, $CeYbO_3$, $CeTmO_3$, $PrLuO_3$, $PrYbO_3$ and $NdLuO_3$ have been prepared, the lattice constants of which are summarized in Table I together with own values for the known $LaBO_3$ (B = Lu–Er) compounds, these values, however, not differing much from published lattice constants. The *d*-values of the diffraction powder patterns ($Cu_{K\alpha}$-radiation, Ni-filtered, Au as an internal standard) of the new compounds are given in Table II.

Even by using method IIa, $LaHoO_3$, $CeLuO_3$, $CeYbO_3$, $CeTmO_3$ and $PrLuO_3$ can be prepared in pure form. The kinetics of the $AO_{1.5} + BO_{1.5}$-reaction shows, however, that the preparation of pure substances needs the more reaction time, the more similar the ionic radii of the metal ions are. When mixed precipitations of $A(OH)_3 + B(OH)_3$ are used as the starting materials a reaction time of about 2 days at 1250°C is sufficient for complete reactions. By using method IIa. for the preparation of $LaErO_3$ the reaction product at 1250°C/8 days is mainly C–(La, Er)$O_{1.5}$ plus only a small quantity of $LaErO_3$.

TABLE I

LATTICE CONSTANTS OF $A^{III}B^{III}O_3$ INTERLANTHANIDE PEROVSKITE COMPOUNDS (±0.003 Å)

B=/A=		La	Ce	Pr	Nd
Lu	*a* [Å]	5.832	5.793	5.768	5.737
	b [Å]	6.013	5.997	5.991	5.974
	c [Å]	8.387	8.344	8.340	8.311
	$3(V)^{1/2}$	6.650	6.618	6.605	6.579
Yb	*a* [Å]	5.843	5.806	5.776	
	b [Å]	6.033	6.009	5.995	
	c [Å]	8.432	8.373	8.368	
	$3(V)^{1/2}$	6.674	6.635	6.617	
Tm	*a* [Å]	5.859	5.828		
	b [Å]	6.047	6.035		
	c [Å]	8.453	8.405		
	$3(V)^{1/2}$	6.690	6.661		
Er	*a* [Å]	5.870			
	b [Å]	6.073			
	c [Å]	8.465			
	$3(V)^{1/2}$	6.708			
Ho	*a* [Å]	5.884			
	b [Å]	6.094			
	c [Å]	8.508			
	$3(V)^{1/2}$	6.732			
Y	*a* [Å]	5.877			
	b [Å]	6.199			
	c [Å]	8.538			
	$3(V)^{1/2}$	6.776			

Neither $PrYbO_3$ nor $NdLuO_3$ could be prepared in the pure form. The best preparations after method IIb. only contained about 50% of the perovskite, the rest being a mixture of monoclinic B–(A, B)$O_{1.5}$ and cubic C–(B, A)-$O_{1.5}$. Attempts to prepare these compounds by methods IIa and IIc at temperatures up to 1550°C failed, the products only were mixtures of B–(A, B)$O_{1.5}$ and C–(B, A)$O_{1.5}$. This means that $PrYbO_3$ and $NdLuO_3$ are no thermodynamic stable constituents of the $PrO_{1.5}$–$TmO_{1.5}$ and $NdO_{1.5}$–$LuO_{1.5}$ systems. No perovskite compounds at all have been obtained by hydrothermal reactions (method IId).

The greenish Ce-perovskites contain Ce^{3+}. This has been proved by the oxidation of the $CeBO_3$–compounds to Ce(IV)–B(III)–fluorite phases with oxygen by using a Mettler thermomicrobalance and registration of the weight changes which correspond to the formula $CeLuO_{2.97}$, $CeYbO_{3.00}$ and $CeTmO_{3.00}$ of the compounds before oxidation.

Only up to 1300°C is $LaHoO_3$ stable, at which temperature transformation to B–(La, Ho)$O_{1.5}$ occurs. $LaYO_3$ dissociates into a mixture of B–(La, Y)$O_{1.5(ss)}$ and C–(Y, La)-$O_{1.5(ss)}$ at 1470 ± 30°C. This shows that the new perovskites are stable at low and medium temperatures and not at very high temperatures as has been stated in (*3*).

Figure 1 shows the phase relationships of the pseudobinary $LaO_{1.5}$–$HoO_{1.5}$ and $LaO_{1.5}$–$YO_{1.5}$ systems between 1250 and 1550°C. The phase diagram of the pseudoternary system $LaO_{1.5}$–$YbO_{1.5}$–$SmO_{1.5}$ at 1400°C (Fig. 2) demonstrates that in $LaYbO_3$ up to about 13 m/o $LaO_{1.5}$ can be substituted by $SmO_{1.5}$.

TABLE II

d-VALUES AND RELATIVE INTENSITIES FOR $LaHoO_3$, $CeLuO_3$, $CeYbO_3$, $CeTmO_3$, $PrLuO_3$, $PrYbO_3$, AND $NdLuO_3$ (Ni-FILTERED, CuK_α-RADIATION, ROOM TEMPERATURE 25 ± 2°C)

I	hkl	$LaHoO_3$		$CeLuO_3$		$CeYbO_3$		$CeTmO_3$		$PrLuO_3$		$PrYbO_3$		$NdLuO_3$	
		d obsd	d calcd	d obsd	d calcd	d obsd	d calcd	d obsd	d calcd	d obsd	d calcd	d obsd	d calcd	d obsd	d calcd
2	020	3.0476	3.0455	2.9995	2.9955	3.0074	3.0014	3.0193	3.0153	2.9916	2.9935	3.0014	2.9955	2.9857	2.9838
10	112	2.9975	2.9975	2.9473	2.9454	2.9587	2.9530	2.9722	2.9664	2.9359	2.9416	2.9511	2.9473	2.9303	2.9303
2.5	200	2.9435	2.9397	2.8969	2.8932	2.9042	2.9005	2.9190	2.9116	2.8787	2.8823	2.8878	2.8859	2.8678	2.8660
0.3	021	2.8696	2.8660	2.8202	2.8202	2.8307	2.8254	2.8411	2.8376	2.8167	2.8167				
0.2	113			2.3121	2.3109	2.3212	2.3189	2.3317	2.3270	2.3064	2.3086	2.3189	2.3143		
3	220	2.1147	2.1136	2.0823	2.0814	2.0869	2.0860	2.0952	2.0942	2.0759	2.0759	2.0777	2.0777	2.0669	2.0669
0.4	221			2.0196	2.0196	2.0256	2.0239			2.0136	2.0145			2.0068	2.0060
0.5	131	1.8710	1.8717	1.8412	1.8419	1.8447	1.8454	1.8531	1.8531	1.8391	1.8391	1.8405	1.8405		
1.5	132	1.7489	1.7489	1.7202	1.7202	1.7232	1.7238	1.7305	1.7311	1.7184	1.7178	1.7184	1.7196		
1	024	1.7434	1.7427	1.7119	1.7113	1.7161	1.7161	1.7226	1.7226	1.7101	1.7095	1.7155	1.7143		
1	204	1.7220	1.7220	1.6908	1.6914	1.6960	1.6966	1.7025	1.7031	1.6885	1.6885	1.6908	1.6925		
2	312	1.7083	1.7083	1.6805	1.6805	1.6840	1.6845	1.6902	1.6908	1.6760	1.6748	1.6783	1.6777		

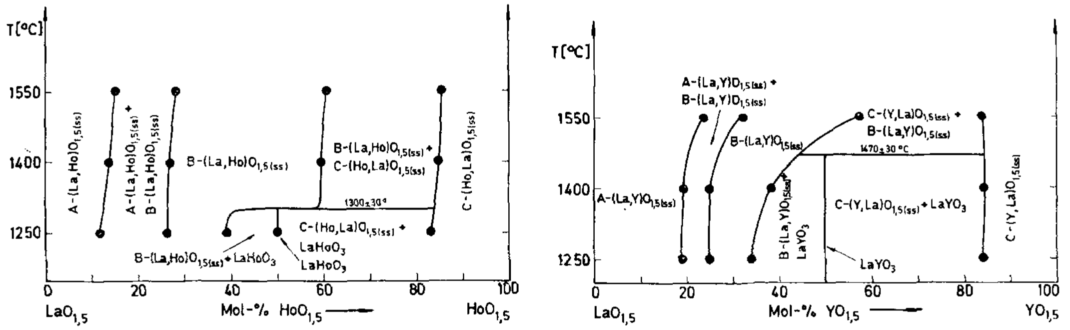

FIG. 1. Phase diagrams of the pseudobinary systems $LaO_{1.5}$–$HoO_{1.5}$ and $LaO_{1.5}$–$YO_{1.5}$ between 1250 and 1550°C.

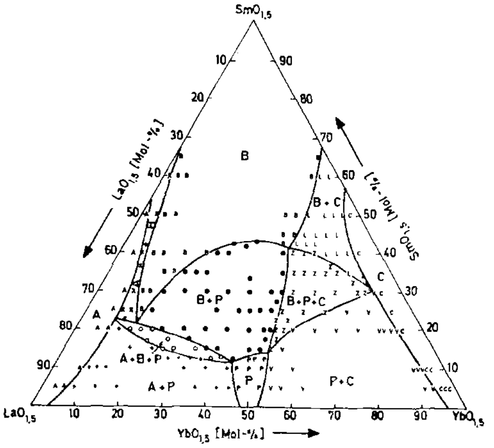

FIG. 2. Phase diagram of the pseudoternary system $LaO_{1.5}$–$SmO_{1.5}$–$YbO_{1.5}$ at 1400°C.

Figure 2 further shows that the phase width of $LaYbO_3$ seems to be much smaller than reported in (*3*, *5*), but extending when substitution of La^{3+} by Sm^{3+} occurs. The phase diagram also shows that hexagonal A–(La, Sm)-$O_{1.5}$ and cubic C–(Yb, Sm)$O_{1.5}$ have only small solubilities for $YbO_{1.5}$, or $LaO_{1.5}$ respectively, whereas a homogeneous monoclinic B–(Sm, La, Yb)$O_{1.5}$ phase of large extension occurs in the $LaO_{1.5}$–$SmO_{1.5}$–$YbO_{1.5}$ system. Between 1100 and 1550°C, the solubility of $YbO_{1.5}$ in A–$LaO_{1.5}$ increases from 1.5 mole % at 1100°C up to 5.0 m/o at 1550°C, whereas there seems to be no temperature dependence of the solubility of $LaO_{1.5}$ in C–$YbO_{1.5}$ (3.8 ± 0.4 m/o at all temperatures). The mutual solubilities of $LaO_{1.5}$ and $YO_{1.5}$ are more pronounced, ranging up to 23.5 m/o $YO_{1.5}$ in A–$LaO_{1.5}$ and up to 16.3 m/o $LaO_{1.5}$ in C–$YO_{1.5}$ at 1550°C.

Attempts to prepare perovskite compounds in other interlanthanide oxide systems by thermal and hydrothermal methods failed.

Therefore, we believe that no other interlanthanide perovskite compounds occur. Furthermore, no perovskite compounds could be found in reaction mixtures of the systems $PuO_{1.5}$–$LuO_{1.5}$ ($TmO_{1.5}$) and $AmO_{1.5}$–$LuO_{1.5}$ ($TmO_{1.5}$). In the latter case, only B–(Am, Lu)$O_{1.5}$ and B–(Am, Tm)$O_{1.5}$ have been obtained, thus stabilizing the nonexisting B–$^{241}AmO_{1.5}$ when using very pure ^{241}Am (*9*). Therefore, it may be assumed that $A^{III}B^{III}O_3$ perovskite compounds in the actinide–lanthanide oxide systems can only be prepared with Ac^{3+} and—because no weighable amounts of transfermium elements are obtainable (*10*)—a preparation of interactinide $A^{III}B^{III}O_3$ perovskites is not possible. The occurrence, however, of $A^{II}B^{IV}O_3$ actinide–lanthanide perovskites, e.g., $Eu^{II}ThO_3$, can not be excluded.

Acknowledgment

We thank the Fonds der Chemischen Industrie and the Deutschen Forschungsgemeinschaft for financial support.

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