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Abstract

Full Text

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ON THE POLYMORPHISM OF LANTHANUM OXIDE

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According to Goldschmidt ([1]), lanthanum oxide La_2O_3 crystallizes in the hexagonal structure (*A*-form). In 1935 Loberg ([1]) reported the preparation of cubic lanthanum oxide (*C*-form La_2O_3) by decomposition of the double ammonium-lanthanum nitrate salt when it was heated for 20 hours at 450°. The X-ray diffraction pattern of this preparation was, however, very indistinct, so that only 4 lines could be indexed. After repeated heatings of the oxide

Fig. 1. X-ray diffraction patterns of the decomposition products of lanthanum nitrate *(a)* and lanthanum oxalate *(b)*: 1—480°, 4 hours; 2—450°, 6 hours; 3—450°, 3 hours; 4—400°, 3 hours; 5—700°, 2 hours; 6—570°, 20 hours; 7—450°, 16 hours.

with additions of mineralizers, in order to obtain a better-crystallized product, no lanthanum oxide lines at all were found on the X-ray diffraction patterns. Only at a temperature of 650° did lines belonging to the *A*-form of La_2O_3 appear. Yandelli ([3]), who investigated the polymorphism of rare-earth oxides, mentions the appearance, at a temperature of 350–500°, in the X-ray pattern of the *A*-form of La_2O_3 of some additional lines, which he attributed to the *C*-form of the oxide. Shafer and Roy ([4]) concluded that it is impossible to obtain the *C*-form at temperatures above 500°. In a recently published work, Roth and Schneider (1960) ([5]) repeated Loberg' s experiments, but the *C*-form of La_2O_3 was not detected. They made an attempt to obtain the *C*-form of La_2O_3 by decomposing the hydroxide at low temperatures. However, upon decomposition of the hydroxide, as also of lanthanum nitrate, basic salts were formed as intermediate products; these are stable at least up to 500°, a temperature too high for obtaining the *C*-form of La_2O_3. Roth and Schneider did not succeed in obtaining pure lanthanum oxide at temperatures below 500°.

In our previous work we studied the decomposition of various lanthanum salts and its hydroxide during slow heating in air.

Fig. 2. X-ray diffraction patterns of C- and A-La2O3

Figure 2: Fig. 2. X-ray diffraction patterns of C- and A-La2O3

Fig. 3. X-ray diffraction patterns of lanthanum oxide calcined at temperatures: a—500°, 4 hours; b—550°, 2 hours; v—600°, 30 min.; g—700°, 30 min.

Figure 3: Fig. 3. X-ray diffraction patterns of lanthanum oxide calcined at temperatures: a—500°, 4 hours; b—550°, 2 hours; v—600°, 30 min.; g—700°, 30 min.

The results we obtained coincided with the data of Roth, Schneider, Wendland, and others ([5,7]). Thus it was shown that it is impossible to obtain the low-temperature form C-La_2O_3 by decomposition of salts and the hydroxide upon heating them in air. It was of interest to study the decomposition of lanthanum salts in vacuum, since lowering the pressure could reduce the temperature for obtaining the pure oxide to the stability temperature of the C-form of La_2O_3. However, the first experiments at a pressure of 1 mm Hg did not lead to the desired results. In all cases, upon decomposition of the basic salts, the A-form of La_2O_3 was immediately formed.

Fig. 2. X-ray diffraction patterns of C- and A-La_2O_3

Experiments at a lower pressure of the gas phase in the reaction volume were carried out in a vacuum furnace with a molybdenum heater. The substance under study (lanthanum salt or hydroxide) was placed in a platinum ampoule in the furnace and slowly heated to the required temperature. The temperature in the furnace was measured with a standard platinum thermocouple; the accuracy of maintaining the temperature was $\pm 5^\circ$. The rate of heating of the substance was such that the pressure during the entire experiment did not rise above $1 \cdot 10^{-3}$ mm Hg. After the required temperature had been reached, the samples were held at it for several hours. The products obtained after calcination were analyzed by X-ray and chemical analyses.

The decomposition of lanthanum carbonate, oxalate, hydrate, and nitrate was studied in vacuum $1 \cdot 10^{-3}$—$1 \cdot 10^{-4}$ mm Hg. The results obtained are summarized in Table 1. As an example, Fig. 1 gives some X-ray diffraction patterns of products obtained in the decomposition of lanthanum nitrate and oxalate.

Fig. 3. X-ray diffraction patterns of lanthanum oxide calcined at temperatures: a—500°, 4 hours; b—550°, 2 hours; v—600°, 30 min.; g—700°, 30 min.

Thus, upon decomposition of lanthanum oxalate and carbonate in vacuum, an amorphous product was formed containing a significant amount of carbon. The presence of carbon both in the basic salt and in the oxide impeded their crystallization up to a temperature of 570°, when weak lines of A-La_2O_3 appeared. Upon decomposition of the hydrate, an amorph-

Table 1

Temp., °C	Duration, h	Color	Phase composition	Structure
20	—	White	$La_2(C_2O_4)_3 \cdot 7H_2O$	Cryst.
300	13	”	$La_2(C_2O_4)_3$	Amorph.
350	110	Brown	$La_2O_3 + xCO_2 + yC$	”
400	50	Black	$La_2O_3 + xCO_2 + yC$	”
450	16	”	$La_2O_3 + C$	”
500	4	”	$La_2O_3 + C$	”
570	20	”	$La_2O_3 + C$	Traces of lines, A-La_2O_3
700	2	”	$La_2O_3 + C$	A-La_2O_3
100	3	White	$La_2(CO_3)_3$	Amorph.
350	110	Gray	$La_2O_3 + xCO_2 + yC$	”
450	16	”	$La_2O_3 + xCO_2 + yC$	$LaO(CO_3)_3/_2$
570	20	”	$La_2O_3 + C$	A-La_2O_3
20	—	White	$La(NO_3)_3 \cdot 6H_2O$	Cryst.
320	9	”	$LaONO_3$	$LaONO_3$
400	50	”	$LaONO_3$	$LaONO_3$
450	6	”	$La_2O_3 + LaONO_3$	C-La_2O_3 + $LaONO_3$
470	4	”	$La_2O_3 + (LaONO_3)$	C-La_2O_3 + $LaONO_3$
550	20	”	La_2O_3	C-La_2O_3
570	2	”	La_2O_3	C-La_2O_3 + (A-La_2O_3)
200	2	”	$La(OH)_3$	Amorph.
390	4	”	$LaO(OH)$	”
450	6	”	La_2O_3	”
470	14	”	La_2O_3	Traces of C-La_2O_3
500	6	”	La_2O_3	C-La_2O_3
550	6	”	La_2O_3	C-La_2O_3, traces of A-La_2O_3
600	6	”	La_2O_3	A-La_2O_3

···product which at a temperature of about 470° crystallizes in the cubic struc-

ture (C-form La_2O_3). However, already at 550° C-La_2O_3 begins slowly to transform into the A-form. The best-crystallized C-form of La_2O_3 is formed upon decomposition of lanthanum nitrate in vacuum.

Table 2

C-La_2O_3: d/n exp.	C-La_2O_3: I/I_0	C-La_2O_3: hkl	C-La_2O_3: d/n calc.	A-La_2O_3: d/n exp.	A-La_2O_3: I/I_0	A-La_2O_3: d/n	A-La_2O_3: I/I	A-La_2O_3: hkl (*)
3,258	100	222	3,279	3,396	25	3,41	34	100
2,840	32	400	2,840	3,058	45	3,063	31	002
2,426	9	332	2,422	2,968	100	2,980	100	101
2,232	11	510	2,228	2,269	53	2,278	58	102
2,004	49	440	2,008	1,958	53	2,968	63	110
1,841	5	611	1,842	1,743	70	1,753	52	103
1,741	40	622	1,712	1,702	8	1,705	4	200
1,637	8	444	1,639	1,653	60	1,656	24	112
1,424	6	800	1,420	1,642	45	1,642	17	201
1,305	14	662	1,303	1,569	15	1,532	3	004
1,271	9	840	1,270	1,487	17	1,490	5	202
				1,394	14	1,398	2	104
				1,308	28	1,309	7	203
				1,287	7	1,289	2	210
				1,260	33	1,261	12	211
				1,209	29	1,209	6	114
				1,188	15	1,188	4	212
				1,154	28	1,1538	4	105
				1,137	16	1,1367	4	300
				1,0902	30	1,0901	7	213
				1,0660	17	1,0658	4	302

Figure 2 presents the X-ray diffraction patterns (Cu K_α radiation), and Table 2 gives the interplanar spacings and intensities of the *C*- and *A*-forms of La_2O_3. As a result of indexing the X-ray diffraction patterns, the following values were obtained for the unit-cell parameters: the low-temperature *C*-form—body-centered fluorite-type lattice, $a_0 = (11.36 \pm 0.02)$ Å; the high-temperature *A*-form—hexagonal, $a_0 = 3.937$ Å, $c_0 = 6.130$ Å, $c/a = 1.56$.

When heated in air, *C*-La_2O_3 at a temperature of about 300° absorbs carbon dioxide and water vapor from the air and is converted into a basic salt; upon further heating to 650–700°, the product obtained decomposes, again forming the oxide, but now the *A*-form of La_2O_3. When heated in vacuum or in dry oxygen, *C*-La_2O_3 slowly transforms into *A*-La_2O_3 at temperatures above 550° (Fig. 3).

The C-form of lanthanum oxide, first obtained by us in pure form, is a metastable form of lanthanum oxide which, upon heating, like C-Nd_2O_3, transforms into the hexagonal form, the only stable form for these oxides. For the C-form of La_2O_3, the lattice constant and the temperature interval of its transition to the A-form of La_2O_3 have been measured.

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