complex, further investigations are necessary in order to establish the existence of a tridentate linkage.

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The Preparation of Lanthanum Titanium Oxide, $LaTiO_3$[1]

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Ternary oxides of the general formula $LaMO_3$ have been described for all of the 1st Period transition elements from vanadium to cobalt, inclusive. These compounds all have the perowskite-type structure.[2-5]

The manganese compound always contains some tetravalent manganese which suggests that some of the lanthanum positions in the lattice are vacant.[3]

Prior investigations of the lanthanum–titanium system appear to have been confined to tetravalent titanium. Among a number of solid phases which have been reported is $La_{2/3}TiO_3$ which is said to have a defect perowskite structure with one third of the lanthanum positions vacant.[3,6] It was an obvious possibility that the compound $LaTiO_3$ should be formed under the proper experimental conditions. This paper deals with the synthesis of the compound and its characterization.

Experimental

Products which gave X-ray diffraction patterns containing the lines of a cubic perowskite were obtained by heating the mixture of composition La_2O_3:$2TiO_2$ at 1200° for prolonged periods in a hydrogen atmosphere. The samples, however, were not homogeneous under the microscope but consisted of a white and black phase. The same phase with the perowskite structure was prepared by heating stoichiometric mixtures ($La_2O_3 + 3TiO_2 + La$) of lanthanum oxide, titanium dioxide and lanthanum metal *in vacuo* in a sealed silica capsule at 1150°. These products were always contaminated with silicon due to the reaction of the lanthanum metal with the container. A similar procedure using titanium metal as reducing agent gave products which always contained some unreacted titanium metal. The same results were obtained using either lanthanum hydride or titanium hydride as a reducing agent.

The purest products were prepared by the reaction

$$La_2O_3 + Ti_2O_3 \longrightarrow 2LaTiO_3$$

The titanium sesquioxide was prepared according to the method of Friedel and Guerin.[7] C.P. titanium dioxide and freshly prepared titanium tetrachloride were used. Analysis of the preparation by the method of MacCardle and Scheffer[8] gave 66.86% Ti^{+3} compared with the theoretical 66.63% Ti^{+3}. Because of the rapid hydrolysis of lanthanum oxide, it was ignited at 1000° just prior to weighing and mixing with the titanium sesquioxide. The sample was pressed into a pellet and heated in an evacuated silica capsule for 24 hr. at 1180°. The surface of the pellet was removed and the remaining sample reground and reheated at 1220° for 48 hr. in the same manner. The product was homogeneous under the microscope and consisted of small, black, slightly iridescent crystals. The same product was obtained using a slight excess of lanthanum oxide which was removed after the final heating by extraction with 2 N hydrochloric acid.

The products were analyzed for titanium and lanthanum by subjecting a sample to fusion with potassium bisulfate containing a few drops of concd. sulfuric acid. The colorless melt obtained in this way was dissolved in 1 M sulfuric acid solution from which the titanium was precipitated with cupferron. The lanthanum was precipitated as the oxalate from the solution at pH 4. These analyses gave 19.75% Ti and 58.95% La compared with 20.40% Ti and 59.16% La for $LaTiO_3$. The percentage of titanium in the black product was also determined by a modification of the procedure of MacCardle and Scheffer.[8] The use of hydrofluoric acid had to be abandoned because of the precipitation of lanthanum fluoride. The reaction was carried out by heating the sample with 50 ml. of 18 N sulfuric acid containing an excess of vanadium(V). The excess vanadium was titrated with standardized Mohr salt solution. These analyses gave 20.58% Ti.

The structure as determined from the X-ray diffraction powder pattern using a camera of radius 107.8 mm. with Cu K_α radiation is the cubic perowskite (a_0 = 3.92 ± 0.01 Å.). The X-ray data are listed in Table I. With short exposures of 3 hr., only the perowskite lines were observed, but with prolonged exposures up to 60 hr. additional weak lines appeared. All of these were identified with the stronger lines of the white product which is formed by heating the black product in air. It is possible that the oxidation may occur during the exposure to X-rays. The density, determined pycnometrically is 6.26 g./cm.^{3} corresponding to 0.97 molecule of $LaTiO_3$ per unit cell.

TABLE I

DETERMINATION OF CELL CONSTANT

I	d/n	hkl	$h^2 + k^2 + l^2$	a_0 (Å.)
W+	3.92	100	1	3.92
S+	2.78	110	2	3.93
M+	2.27	111	3	3.93
S	1.967	200	4	3.93
W	1.756	210	5	3.93
S	1.603	211	6	3.93
M	1.388	220	8	3.93
W−	1.309	300	9	3.93
M	1.241	310	10	3.92
W−	1.183	311	11	3.92
W	1.134	222	12	3.93
M−	1.040	321	14	3.92
W−	0.979	400	16	3.92
W−	0.948	322, 410	17	3.91
M+ diffuse	0.921	411	18	3.91
M diffuse	0.873	420	20	3.91
M diffuse	0.833	332	22	3.91

Average cell constant 3.92 ± 0.01 Å.

These results show conclusively that the compound corresponds closely to the normal perowskite type. In view of the reported defect structure of the compound $La_{2/3}TiO_3$, we are planning to investigate the range of composition between this and the compound $LaTiO_3$.

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[1] Abstracted from the Master's Thesis of Michael Kestigian, June, 1954.

[2] $LaVO_3$ and $LaCrO_3$: A. Wold and R. Ward, THIS JOURNAL, **76**, 1029 (1954).

[3] $LaMnO_3$: G. H. Jonker and J. H. van Santen, *Physica*, **16**, 337 (1950).

[4] $LaFeO_3$: S. Náray-Szabó, *Naturwissenschaften*, **31**, 203 (1943).

[5] $LaCoO_3$: F. Askham, I. Fankuchen and R. Ward, THIS JOURNAL, **72**, 3799 (1950).

[6] Private communication from G. H. Jonker, N. V. Philips' Gloielampenfabriken, Eindhoven, Holland.

[7] C. Friedel and J. Guerin, *Ann. chim.*, **8**, 38 (1876).

[8] L. E. MacCardle and E. R. Scheffer, *Anal. Chem.*, **23**, 1169 (1951).