The Lanthanum–Titanium–Oxygen System

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The preparation of $LaTiO_3$, a compound with the perovskite structure, was described in a previous publication.[1] A lanthanum titanium oxide having the composition $La_{2/3}TiO_3$ has been reported.[2] According to G. H. Jonker,[3] the formation of a phase approximating this composition is facilitated by the presence of a small amount of an alkaline earth ion in the stoichiometric mixture of lanthanum sesquioxide and titanium dioxide. The structure is said to be a deformed perovskite type.

It occurred to us that a phase with the perovskite structure should exist with a composition range $La_{(2/3\,+\,x)}TiO_3$ where x could have values from 0 to $^1/_3$. Such a phase would be analogous to the sodium tungsten bronzes. The assumption appeared more reasonable since it has been shown that a similar phase ($Sr_{(0.5\,+\,x)}NbO_3$) exists in the strontium–niobium–oxygen system.[4] This paper describes the preparation and properties of the lanthanum titanium analog.

Experimental

The preparation of phases as indicated by the formula $La_{(2/3+x)}Ti^{III}_{3x}Ti^{IV}_{(1-3x)}O_3$ was attempted by heating stoichiometric mixtures of the reactants in evacuated silica capsules. The mixtures used contained lanthanum(III) oxide, titanium(IV) oxide and (a) lanthanum metal, (b) titanium metal, (c) titanium(III) oxide. Because of reaction with the containers, the mixtures containing lanthanum metal gave only impure products. Cubic perovskite phases were obtained from the mixtures containing metallic titanium, but complete reaction was not obtained even with prolonged heating at 1200°. Changes in lattice constant were observed in the products, however, when mixtures containing different proportions of titanium metal were used.

The most satisfactory procedure was to prepare mixtures according to the equation

$$(1/3 + x/2)La_2O_3 + (3/2x)Ti_2O_3 + (1 - 3x)TiO_2 = La_{(2/3+x)}TiO_3$$

The lanthanum oxide was ignited at 1100° just before weighing and mixing with the titanium oxides. The titanium(III) oxide was prepared by the method of Friedel and Guerin.[5] The mixture was thoroughly ground in an agate mortar and pressed into pellet form. The sample was heated in an evacuated, sealed, silica capsule at 1150° for 24 hours and finally at 1250° for 48 hours, with regrinding every 24 hours. For samples over 1 g., the second heating process had to be extended for five days to ensure complete reaction.

Phases which appeared homogeneous under microscopic and X-ray examination were obtained for values of x from 0.03 to 0.33. The phases with lanthanum content above $x = 0.09$ are black, but, with lower lanthanum content the phases gradually lighten in color. Qualitative tests indicate that they are fairly good conductors of electricity. The products are impervious to attack by cold hydrochloric acid, nitric acid, perchloric acid, hot, dilute nitric acid and boiling perchloric acid. They are slowly attacked by aqua regia.

For analysis, the samples were brought into solution by fusing with potassium bisulfate containing a few drops of sulfuric acid and taking up the melt in 1 *M* sulfuric acid solution. The titanium was precipitated with cupferron, and the lanthanum was precipitated as the oxalate at *p*H 4. The percentage of titanium(III) was determined as described previously.[1] The results of analysis are given in Table I.

TABLE I

COMPOSITION AND LATTICE CONSTANTS OF PURE PHASES OBTAINED BY INTERACTION OF La_2O_3, Ti_2O_3 AND TiO_2[a]

x	La, %	Ti(III), %	Ti(total), %	Lattice constant[b] (Å.)
0.33	58.95	20.58	19.75	3.926
	(59.16)	(20.40)	(20.40)	
.25	56.73	15.84	21.01	3.918
	(57.13)	(16.06)	(21.41)	
.15	...	...	...	3.904
	(54.29)	(10.27)	(22.83)	
.09	51.93	6.25	23.95	3.896
	(52.40)	(6.42)	(23.77)	
.03	49.95	2.11	25.02	3.888
	(50.35)	(2.14)	(24.80)	

[a] The values given in parentheses are calculated from the quantities of oxides used in making the mixtures. [b] Precision of determination ±0.002 Å. Weighted value for the wave length of CuKα used was 1.5418 Å.

The structure of the phases was determined from X-ray powder diffraction patterns using copper Kα radiation with a camera of 57.3 mm. radius. All of the phases listed in Table I have the cubic perovskite structure.

The Straumanis method was used in calculating the $\sin^2\theta$ values. The lattice constants were obtained by extrapolation of a_0 *versus* $^1/_2$ $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ to $\theta = 90°$. The unit cell was found to vary from 3.887 to 3.926 (±0.002 Å.) with increasing lanthanum content. The cell constants are given in Table I. The density as determined pycnometrically indicates one formula weight of $La_{(2/3+x)}TiO_3$ per unit cell.

The plot of the lattice constant as a function of x (Fig. 1) shows a Vegard's law dependence. A mixture corresponding to $x = 0.02$ gave a product having a complex X-ray diffraction pattern which, however, contained the lines of the cubic perovskite. Extrapolation to the lattice constant given by the latter ($a_0 = 3.887 \pm 0.002$ Å.) suggests that the lower limit of composition of the cubic phase is near $La_{0.70}TiO_3$. This point appears as a full circle in Fig. 1. The half circle represents a phase for which no analyses were performed. The white product obtained with the mixtures corresponding to $x = 0$ gave a very complex diffraction pattern which has not, as yet, been interpreted.

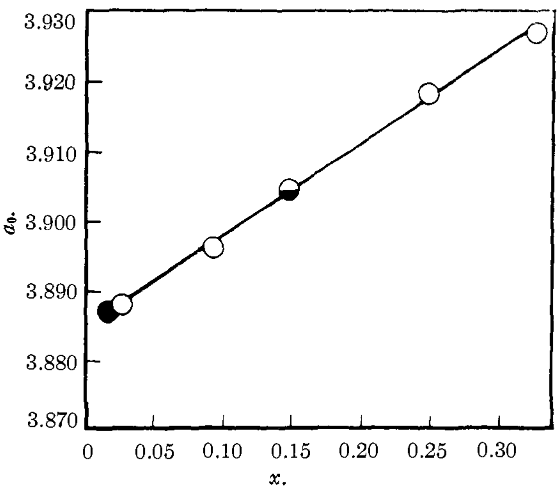

Fig. 1.—The variation of lattice constant with composition in the cubic phases of composition $La_{(2/3\,+\,x)}TiO_3$.

It is interesting to note that the presence of a very small amount of titanium(III) is capable of stabilizing the cubic perovskite structure leading to a relatively wide range of homogeneity. The properties of the phases throughout this

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[1] M. Kestigian and R. Ward, THIS JOURNAL, **76**, 6027 (1954).

[2] English Patent 574,577 (1946).

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

[4] D. Ridgley and R. Ward, THIS JOURNAL, **77**, 6132 (1955).

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

range are reminiscent of the tungsten bronzes except for the more restricted range of color.

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The Osmotic and Activity Coefficients of Aqueous Solutions of Thorium Chloride at 25°

BY R. A. ROBINSON

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Isopiestic vapor pressure measurements have been made on solutions of thorium chloride at 25°. The results are not claimed to be of high accuracy but they are of some interest in that they add to our very meager knowledge of 1:4 and 4:1 electrolytes, thorium nitrate and potassium ferrocyanide being the only two electrolytes already studied.

Thorium chloride was prepared by crystallization of a commercial sample which analysis showed to be considerably basic and to which therefore was added slightly more than the requisite amount of hydrochloric acid to give the correct Th:Cl ratio. After three recrystallizations the solution gave the correct Th:Cl ratio on analysis. Table I gives the results of the isopiestic measurements, using sodium chloride as reference salt. Table II gives the calculated osmotic and activity coefficients, the latter being expressed relative to the arbitrary value of 0.350 at 0.05 *M*.

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS OF THORIUM CHLORIDE AND SODIUM CHLORIDE

$ThCl_4$	NaCl	$ThCl_4$	NaCl
0.05252	0.1029	0.7864	2.356
.1286	.2584	.8805	2.755
.1584	.3241	.9983	3.249
.2137	.4551	1.112	3.752
.3009	.6833	1.223	4.199
.3699	.8813	1.368	4.803
.5025	1.288	5.372	1.495
.6152	1.682	5.818	1.590
.6712	1.892	6.156	1.663

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF THORIUM CHLORIDE AT 25°

m	φ	γ	m	φ	γ
0.05	0.731	(0.350)	0.7	1.129	0.327
.1	.736	.292	.8	1.214	.364
.2	.776	.257	.9	1.302	.409
.3	.840	.253	1.0	1.390	.463
.4	.906	.261	1.2	1.536	.583
.5	.974	.275	1.4	1.665	.729
.6	1.048	.297	1.6	1.847	.966

I suspect that, as in the case of uranyl nitrate,[1] the osmotic coefficient is very sensitive to any departure from the exact Th:Cl ratio. Moreover, there is a possibility of this being promoted by loss of hydrogen chloride, formed by hydrolysis, during the evacuation of the desiccator. Thus, in an attempt to extend the range of measurement beyond 1.6 *M* $ThCl_4$, using sulfuric acid as reference electrolyte, I failed to get any consistent results at these high concentrations. For this reason, I do not claim high accuracy for the data in Table II. I think, however, that they are accurate enough to show that thorium chloride has higher osmotic coefficients than thorium nitrate, as has been found with the chlorides and nitrates of lower valency metals.

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(1) R. A. Robinson and C. K. Lim, *J. Chem. Soc.*, 1840 (1951).

Solid Solutions Treatment of Calorimetric Purity Data

BY S. V. R. MASTRANGELO AND R. W. DORNTE

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The application of calorimetry to the absolute determination of purity, in the absence of solid solution formation, is well established.[1-4] Although methods are available[4,5] for detecting solid solutions, no quantitative treatment for these data exists. We have derived a solid solutions treatment for calorimetric melting point data which provides a method for calculating T_0, the melting point of pure major component, and X_2, the total mole fraction of minor component. This treatment is based on analysis of the curvature of the plot of the equilibrium temperature, T_γ, *vs.* $1/\gamma$, the reciprocal of the fraction melted. The occurrence of solid solutions, although rare at low temperatures, is relatively great at high temperatures.

The Lewis and Randall[6] differential equation for solid solutions

$$\frac{dT}{dX_2} = \left(\frac{k}{k'} - 1\right)\frac{RT^2}{H_1 - H'} \qquad (1)$$

on integration yields

$$T_0 - T_M = \frac{RT_0^2}{\Delta H_F} X_2''(1 - K) \qquad (2)$$

where T_0 is the melting point of pure major component, T_M is the melting point of a sample containing a total mole fraction X_2'' of minor component whose distribution equilibrium between the solid and liquid phases is expressed by $K = k/k'$, the Henry's law constant, ΔH_F is the heat of fusion of pure major component, and R is the gas constant.

Let X_2' and X_2 be the instantaneous mole fraction of minor component dissolved in the solid and liquid phases, respectively, at any equilibrium temperature, T_γ, corresponding to a fraction of sample, γ, melted in the calorimeter, and let n_2', n_2 and n_0 be

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(1) H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929).

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(3) A. C. Werner and S. V. R. Mastrangelo, THIS JOURNAL, **75**, 5244 (1953).

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(6) G. N. Lewis and M. Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 238.