CANADA

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by

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THE COMPOUND CaO.Ti$_2$O$_3$[1]

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ABSTRACT

By electrolyzing baths of molten CaCl$_2$ containing perovskite (CaO.TiO$_2$), a compound within the ternary Ca–Ti–O system, namely CaO.Ti$_2$O$_3$, has been obtained. The compound has been identified by chemical analysis, and its crystallographic data have been determined by X-ray means. Attempts to synthesize the compound apart from the electrolytic cell have, so far, failed.

INTRODUCTION

The only publications of work dealing with compounds within the ternary system Ca–Ti–O in which the titanium is in any state of valency other than the tetravalent are those of Bertaut and Blum (1, 2). In their work, the crystallography of a compound, to which is assigned the formula CaTi$_2$O$_4$, is described. The system CaO–TiO$_2$ has been studied by von Wartenberg, Reusch, and Saran (3), and their work did not indicate the existence of any compound between CaO.TiO$_2$ and TiO$_2$, but merely of a eutectic having a melting point of approximately 1450° C.; further, there was no indication in their work of any compound containing a lower proportion of oxygen.

In the course of work on the electrochemistry of the production of titanium, a material was encountered which forms the subject of this paper. The material was examined by chemical, X-ray diffraction, and spectrographic means and has been shown to be CaTi$_2$O$_4$ (or CaO.Ti$_2$O$_3$); some of its properties have been determined. This work was done independently and without the knowledge of the work of Bertaut and Blum. Their work was entirely crystallographic, whereas, as mentioned above, the present work includes chemical data.

EXPERIMENTAL

(a) Preparation of the Compound

When a bath composed of 300 g. of calcium chloride and containing 60 g. of calcium titanate, CaO.TiO$_2$, which is slightly soluble in the molten chloride, was electrolyzed under an inert atmosphere for 70 minutes at a current of 14 amp. at 850° C. and allowed to cool, some black, lustrous, well-formed crystals were observed close to the cathode.

(b) Chemical Examination of the Compound

Examination of the crystals under a low-power microscope showed them to be prismatic in form and very well developed. No difficulty was experienced in selecting suitable specimens for detailed X-ray crystallographic examination.

The examination of the material by semiquantitative spectrographic analysis showed that Ca and Ti were the only detectable major metallic constituents.

About 60 mg. of the material was available for chemical analysis, and the determinations shown in Table I were made.

The methods used for analysis were as follows:

Calcium.—Determined with a Perkin–Elmer flame photometer at 6200 Å, after

TABLE I

Element	% by weight
Ca	20.3 ± 0.2
Ti	47.0 ± 0.1 (all trivalent)
Fe	1.05 ± 0.05 (mean of two determinations)
C	0.07 ± 0.02
F	None detectable

removal of iron and titanium as "cupferrides", aluminum as 8-hydroxyquinolate, and after removal of excess organic reagents.

Iron.—Determined in the chloroform solution of the "cupferride" by colorimetric means with o-phenanthroline, using a Coleman MK.14 spectrophotometer at $\lambda = 500\ \mu\mu$.

Titanium.—Determined in the chloroform solution of the "cupferride" by colorimetric means with hydrogen peroxide, using a Coleman MK.14 spectrophotometer at $\lambda = 410\ \mu\mu$. This gives the total titanium. The trivalent titanium was determined by dissolving the sample in aqueous sulphuric acid, and titrating against standard ferric alum, all under an argon atmosphere.

Carbon.—Determined by a standard combustion procedure.

Fluorine.—HF steam-distilled off at $135°$–$140°$ C. from an aqueous perchloric acid suspension of the sample. Fluoride estimated amperometrically at pH = 7.0 using thorium nitrate solution previously standardized against NaF.

The unestimated material, approximately 31.6%, is presumably oxygen since no major constituent other than calcium and titanium was detectable spectrographically.

An X-ray powder diffraction pattern of the crushed material was taken using CoK_α radiation and a 57.3 mm. diameter Debye-Scherrer camera. The pattern was well defined, but could not be identified by reference to either the A.S.T.M. Card Index of X-Ray Diffraction Patterns or any other source of data available to the authors.

The material showed slight signs of ferromagnetism, and certain weak lines in the X-ray diffraction pattern could be interpreted as being due to the presence of a small amount of metallic iron. It was considered, therefore, that the iron in the above chemical analysis is probably due to the presence of a small quantity of free metallic iron and that the main compound is essentially a calcium–titanium–oxygen compound. On this basis, the observed and theoretical compositions and atomic ratios of the relevant compounds are as follows:

	Ca	Ti	O
Observed	$20.3\pm0.2\%$	$47.0\pm0.1\%$	$31.6\pm0.3\%$ (by difference)
Atomic ratios	1.000	1.937 ± 0.015	3.900 ± 0.075
Calculated for $CaTi_2O_4$	20.1%	47.9%	32.0%
Calculated for $CaTi_2O_5$	18.6%	44.4%	37.0%

It thus seems reasonable to conclude that the compound represented by our data is, in fact, $CaO.Ti_2O_3$. It must, however, be borne in mind that the above chemical analyses were made on very small quantities of material and, in any case, the analytical procedures were not simple.

The limits of error quoted in Table I are merely those of the final stage of each estimation; with the very small quantities of material available for investigation there was no

TABLE II

Data	Present work	Data of Bertaut and Blum
Crystal system	Orthorhombic	Orthorhombic
Cell dimensions, Å	$a_0 = 9.73$	9.727
	$b_0 = 9.99$	9.976
	$c_0 = 3.14_7$	3.136
Z	4	4
Space group	$Bbmm - D_{2h}^{17}(V_h^{17})$	$Bbmm - (D_{2h}^{17})$

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR $CaO.Ti_2O_3$

Intensities assessed visually with strongest line as 100. Calculated d-spacings based on orthorhombic unit cell having dimensions $a = 9.73$, $b = 9.99$, $c = 3.14_7$ Å

Int.	d (meas.)	d (calc.)	(hkl)	Int.	d (meas.)	d (calc.)	(hkl)
20	4.96	4.99	020	10	1.610	1.621	600
		4.86	200	10	1.594	1.600	610
20	2.985	2.994	101			1.575	260
30	2.858	2.868	111	70	1.569	1.574	002
100	2.742	2.747	230			1.571	521
30	2.556	2.568	121	10	1.531	1.544	450
10	2.489	2.498	040			1.542	620
20	2.418	2.431	400			1.501	022
10	2.379	2.362	410	30	1.493	1.497	202
30	2.244	2.258	301			1.496	351
20	2.213	2.222	240	20	1.478	1.482	531
90	2.196	2.202	311			1.481	212
10	2.166	2.186	420	30	1.458	1.457	630
80	2.052	2.058	321			1.455	161
10	1.947	1.964	430	10	1.428	1.434	222
30	1.906	1.918	141	—	—	1.379	541
20	1.869	1.869	331	—	—	1.374	460
20	1.837	1.848	250			1.369	270
10	1.742	1.742	440	40	1.370	1.365	232
10	1.681	1.675	341		1.362	1.360	640
80	1.658	1.665	060	10	1.345	1.340	361
		1.662	151	20	1.321	1.331	042
		1.654	501			1.321	402
20	1.632	1.632	511	10	1.305	1.310	412

ready means of assessing the errors of the various stages of separation involved in these analyses; hence it is possible that the estimations, considered as a whole, may be subject to somewhat larger errors than those quoted. This being the case, a molecular formula of $CaO.2TiO_2$ (i.e., $CaTi_2O_5$) is regarded as very unlikely but not entirely impossible. Such a formula would be analogous to that of magnesium dititanate, $MgO.2TiO_2$, which is a well-established compound. This supposition is, however, in conflict with the work of von Wartenberg et al. (3).

Several attempts were made to synthesize both $CaO.Ti_2O_3$ and $CaO.2TiO_2$ by sintering suitable mixtures of the constituent oxides at high temperature under appropriate atmospheric conditions. In neither case was any success achieved, and all the results obtained confirmed the work of von Wartenberg et al.

In general, however, it may be said that the chemical evidence supports the formula $CaO.Ti_2O_3$ for the material which forms the subject of the present study, rather than the formula $CaO.2TiO_2$.

(c) Crystallographic Studies of the Compound

The following morphological data were obtained as the average of observations on two well-formed crystals, using a standard two-circle optical goniometer:

Crystal class: orthorhombic.

Axial ratio: $a:b:c = 0.916:1:0.308$.

The single crystal X-ray work included rotation photographs, zero-layer and first-layer Weissenberg photographs, and cone-axis, zero-level, and first-level precession photographs. The Weissenberg photographs were made using CoK_α radiation, with rotation about the prismatic axis, and the precession photographs were made using MoK_α radiation, with the prismatic axis as the dial axis. The cell edges were determined from these photographs; from the systematic extinctions, the space group was obtained. The results of these examinations are given in Table II.

The space group quoted is the same as for the mineral pseudobrookite, $Fe_2O_3.TiO_2$ (i.e. $TiFe_2O_5$), and for the isomorphous compound magnesium dititanate, $MgO.2TiO_2$ (i.e. $MgTi_2O_5$), referred to earlier.

The powder diffraction pattern was indexed according to our cell dimensions, as shown in Table III, and the agreement between the observed and calculated spacings is quite good; also, the axial ratios determined by optical goniometry agree well with those determined by X-ray diffraction.

DISCUSSION OF RESULTS

It has thus been possible to describe the crystallography of this compound, to which is assigned the formula $CaO.Ti_2O_3$, in a reasonably complete fashion, and to provide a chemical analysis of sufficient accuracy to indicate the molecular formula with virtual certainty, even though it was not found possible to synthesize it apart from the electrolytic method in which it was first prepared. In the work of Bertaut and Blum, the material was obtained by the electrolysis of TiO_2 in molten $CaCl_2$. Their formula is based entirely on X-ray crystallographic evidence. There is good agreement between their X-ray results and those obtained in the course of the present work. The formula, $CaTi_2O_4$, quoted by them is also in good accord with our chemical data. The fact that the titanium is in the trivalent condition, as shown by the chemical analysis, indicates that this compound is best represented by the formula $CaO.Ti_2O_3$. Thus, the present work gives additional data on the electrolytic conditions of preparation of this compound and on its chemical composition, while providing good confirmation of the X-ray crystallographic work of Bertaut and Blum.

ACKNOWLEDGMENTS

REFERENCES

1. BERTAUT, E. F. and BLUM, P. J. phys. radium, 17, 17S (1956).
2. BERTAUT, E. F. and BLUM, P. Acta Cryst. 9, 121 (1956).
3. VON WARTENBERG, H., REUSCH, H. J., and SARAN, E. Z. anorg. Chem. 230, 257 (1937).