The Preparation and Characterisation of the Compounds Na_4TiO_4 and Na_2ZrO_3

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Three preparations of the compounds Na_4TiO_4 and Na_2ZrO_3 are described and their formulae confirmed by thermogravimetric analysis. The *X*-ray diffraction pattern of Na_4TiO_4 is indexed as orthorhombic with cell dimensions a = 11·607, b = 13·610, and c = 9·693 Å, and the compound appears to be one member of an isostructural series of compounds.

We are interested in the corrosion of titanium and zirconium by liquid sodium containing oxygen, and have investigated the alkali-rich portion of the sodium oxide–titanium dioxide and sodium oxide–zirconium dioxide systems.

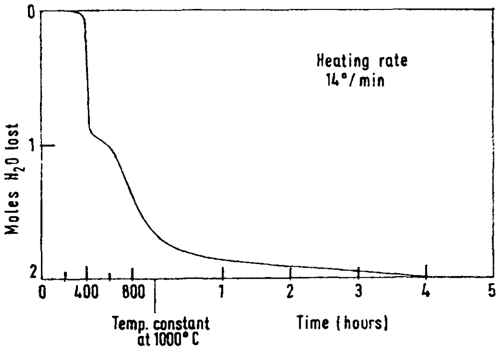
There is much contradictory evidence in the literature on the formation of sodium titanates, but little work has been reported on the only alkali-rich titanate, Na_4TiO_4. D'Ans and Loffler[1] claimed the formation of Na_4TiO_4 to have taken place upon the reaction of an 8NaOH : TiO_2 mixture at 800 °C for 5 h. However, a more recent attempt[2] to prepare the compound from a 4NaOH : TiO_2 mixture was not successful; reaction was not complete even in a fused mass at 900 °C. All the products contained excess of sodium hydroxide and the *X*-ray diffraction patterns obtained were not deemed reliable. It has been reported[3] that the compound Na_4TiO_4 is formed by the action of sodium peroxide on anatase, but the compound was characterised only by the apparent similarity of its i.r. spectrum to that of the sodium chromate Na_2CrO_4.

No analogous compound to Na_4TiO_4 has been observed in the sodium oxide–zirconium dioxide system. The only compound observed in this system is sodium metazirconate, Na_2ZrO_3; low- and high-temperature forms of this compound have been observed[4] with a transition temperature of 570 °C.

In this paper the preparations of the compounds Na_4TiO_4 and Na_2ZrO_3 by the reaction of both sodium oxide and hydroxide with the transition-metal dioxides, and sodium oxide with the metals themselves, are described. The formulae of the compounds were determined by thermogravimetric analysis, and high-temperature diffractometry is used to show that the *X*-ray diffraction pattern recorded for Na_4TiO_4 is that of a single phase. This pattern may be indexed as orthorhombic and is shown to be similar to previously reported[4] *X*-ray diffraction patterns for the compounds Na_4SnO_4 and Na_4PbO_4.

RESULTS AND DISCUSSION

Thermogravimetric Analysis.—Reactions of sodium hydroxide with titanium and zirconium dioxides. The reaction of a 4 : 1 molar mixture of sodium hydroxide and titanium dioxide proceeded in two distinct stages (Figure). Reaction commenced at 320 °C with a rapid initial weight loss of one mole of water corresponding to the formation of the compound Na_2TiO_3. A slower reaction then took place at higher temperatures, finally resulting in a total weight loss equivalent to two moles of water. The reaction was carried out under argon, a maximum temperature of 1000 °C being reached. The overall weight loss thus indicated the formation of the compound Na_4TiO_4, if a single product was formed. The *X*-ray diffraction pattern did not correspond to any previously identified titanate, and, being diffuse, could not be used for the accurate measurement of diffraction arcs.



Thermogravimetric analysis of 4 NaOH : 1 TiO_2 mixture

Batygin,[2] in a study of the same reaction, reported that at 900 °C reaction was incomplete since excess of sodium hydroxide was present in the final product. The *X*-ray diffraction pattern of the titanate formed in the reaction was not given by Batygin but it seems possible, from the present work, that prolonged heating at a higher temperature would have forced the reaction to go to completion.

The reaction of a 2 : 1 molar mixture of sodium hydroxide and zirconium dioxide gave a weight loss corresponding to the evolution of one mole of water. Reaction commenced at 320 °C and proceeded in a single stage with the formation of the low-temperature form of the metazirconate, α-Na_2ZrO_3 (the maximum temperature used in this reaction being 550 °C).

Reactions of sodium oxide with titanium and zirconium dioxides. 2 : 1 Molar mixtures of sodium oxide and titanium dioxide were heated at temperatures between

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[1] J. D'Ans and J. Loffler, *Ber.*, 1930, **63**, 1446.

[2] V. G. Batygin, *Russ. J. Inorg. Chem.*, 1967, **12**, 762.

[3] M. Viltange, *Compt. rend.*, 1954, **239**, 61.

[4] J. Claverie, C. Fouassier, and P. Hagenmuller, *Bull. Soc. chim. France*, 1966, 244.

500 and 850 °C for reaction times of 10 min to 2 h in an argon atmosphere. All mixtures gave products with *X*-ray diffraction patterns identical to that given by the reaction mixture of sodium hydroxide and titanium dioxide in the molar ratio 4 : 1, but the sharpness of the patterns indicated the samples to be of greater crystallinity than previously obtained. One of the samples from this series of reactions was heated in the high-temperature diffractometer, and no change in its *X*-ray diffraction pattern was detected at temperatures up to 1000 °C. When heated above 1000 °C the compound melted and fused with the silica sample holder. The stability of the compound up to a temperature of 1000 °C indicated the *X*-ray diffraction pattern to belong to a single phase, since if more than one phase were present there would almost certainly be a change in intensity, and relative position, of certain diffraction arcs in the pattern on heating.

The presence of a single phase in the reactions between sodium oxide and titanium dioxide in a molar ratio 2 : 1 (and sodium hydroxide and titanium dioxide in a molar ratio 4 : 1) indicates that the *X*-ray diffraction pattern obtained belongs to the compound Na_4TiO_4.

Reaction mixtures of sodium oxide and zirconium dioxide in the molar ratio 2 : 1 were heated at temperatures of 500—850 °C for reaction times of 30 min to 1 h in an argon atmosphere (Table 1). The products contained excess of sodium oxide with either α- or β-Na_2ZrO_3, depending on the reaction temperature used. No analogous compound to Na_4TiO_4 was found, substantiating previous results.[4]

TABLE 1

Reactions of sodium oxide with titanium and zirconium dioxides

Reactants	t/°C	Reaction time	Products
$Na_2O + TiO_2$	900	5 min	Na_2TiO_3
$Na_2O + TiO_2$	850	1 h	Na_2TiO_3
$2Na_2O + TiO_2$	500	1 h	Na_4TiO_4
$2Na_2O + TiO_2$	850	10 min	Na_4TiO_4
$2Na_2O + TiO_2$	850	1 h	Na_4TiO_4
$2Na_2O + TiO_2$	850	2 h	Na_4TiO_4
$2Na_2O + ZrO_2$	500	1 h	α-Na_2ZrO_3 + Na_2O
$2Na_2O + ZrO_2$	850	30 min	β-Na_2ZrO_3 + Na_2O
$2Na_2O + ZrO_2$	850	1 h	β-Na_2ZrO_3 + Na_2O

Reactions of sodium oxide with titanium and zirconium metals. Mixtures of sodium oxide and the transition metals were heated under vacuum. The reaction mixtures used and equilibrium products obtained are given in Table 2. To promote the rapid attainment of equilibrium, mixtures were used as well mixed powders, rather than as pellets. It was found to be considerably more difficult to attain equilibrium in these mixtures in comparison with those containing niobium and tantalum previously described.[5] The reaction mixtures had to be re-ground and re-heated at least three times before the reactions were complete. On heating, a small pressure change was observed at 340 °C for titanium, and 320 °C for zirconium, being immediately followed by the distillation of excess of sodium. Maximum temperatures reached were 400 °C for zirconium and 600 °C for titanium.

TABLE 2

Reaction of sodium oxide with titanium metal at 600 °C and zirconium metal at 400 °C

Reactants	Products
$Na_2O + Ti$	Ti + Na_4TiO_4
$2Na_2O + Ti$	Ti + Na_4TiO_4
$3Na_2O + Ti$	Na_4TiO_4 + Ti
$4Na_2O + Ti$	Na_4TiO_4
$Na_2O + Zr$	Zr + α-Na_2ZrO_3
$2Na_2O + Zr$	α-Na_2ZrO_3 + Zr
$3Na_2O + Zr$	α-Na_2ZrO_3
$4Na_2O + Zr$	α-Na_2ZrO_3 + Na_2O

In all reactions of sodium oxide with titanium the only ternary oxide formed was Na_4TiO_4; unchanged titanium metal was present in mixtures with molar ratios of less than 4 : 1. The expected formation of Na_2TiO_3 in mixtures with sodium oxide : titanium ratios of less than 4 : 1 did not occur. The reaction of sodium oxide and titanium appeared to stabilise the formation of Na_4TiO_4 relative to Na_2TiO_3, a result of significance when possible corrosion mechanisms of titanium in liquid sodium containing oxygen are considered.[6]

The reactions of sodium oxide and zirconium showed only the formation of α-Na_2ZrO_3; no compound analogous to Na_4TiO_4 was observed. Excess of sodium oxide was present in the product from the mixture with a sodium oxide : zirconium molar ratio of 4 : 1, and unchanged zirconium in the products from mixtures with molar ratios of less than 3 : 1.

I.r. and X-*Ray Powder Diffraction Studies on* Na_4TiO_4. —The reported i.r. spectrum [3] of the compound Na_4TiO_4 did not include data below 800 cm^{-1}, and some absorbance maxima were thought to be due to impurities. In the present study, the i.r. spectrum of Na_4TiO_4 over the range 2000—250 cm^{-1} was measured. The significant feature of this spectrum was a very strong, extremely broad, band with its maximum at *ca.* 700 cm^{-1}. Two smaller bands were observed at 390 and 360 cm^{-1}.

The *X*-ray powder diffraction pattern of Na_4TiO_4 was accurately measured and is presented in Table 3. The pattern was indexed as orthorhombic with cell constants $a = 11{\cdot}607$, $b = 13{\cdot}610$, and $c = 9{\cdot}693$ Å by use of the computer programme INDEX,[7] and refinement programme PARAM.[8] The theoretical values of interplanar spacings shown in Table 3 were computed from the unit-cell dimensions by the programme D.SPAC.[9] The density of Na_4TiO_4 was measured as 2·68 g cm^{-3} indicating the compound to contain 12 molecules per unit cell (theoretical density = 2·65 g cm^{-3}).

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[5] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 9.

[6] M. G. Barker and D. J. Wood, following paper.

[7] J. B. Goebel and A. S. Wilson, U.S.A.E.C. Report No. BNWL-22, 1965.

[8] Program PARAM, *X*-Ray 63 Series of Crystallographic Programmes.

[9] M. E. Pippy, N.R.C. Crystallographic Programme No. NRC-21, 1968.

The *X*-ray diffraction patterns of the compounds Na_4SnO_4 and Na_4PbO_4 have been reported[4] but it was concluded at the time that they were too complex to be indexed. However, a qualitative examination of the data for Na_4TiO_4, Na_4SnO_4, and Na_4PbO_4 showed their patterns to be very similar and lattice parameters for Na_4SnO_4 and Na_4PbO_4, comparable with those obtained for the compound Na_4TiO_4, were calculated by the indexing programme INDEX (Table 4). There is a very close agreement between the indexings and the compounds can be considered isostructural. The increased values for the lattice parameters of Na_4SnO_4 and Na_4PbO_4 can be directly related to the increased size of the M^{4+} ion,[10] as shown in Table 5.

TABLE 3

X-Ray powder diffraction pattern of Na_4TiO_4

d_{obs}/Å	d_{calc}/Å	I_{obs}	*h*	*k*	*l*
5·330	5·338	20	2	1	0
5·030	5·021	40	1	2	1
4·561	4·566	40	0	1	2
4·416	4·416	40	2	2	0
4·110	4·109	10	0	3	1
3·873	3·873	45	1	3	1
3·596	3·593	45	3	0	1
3·310	3·312	10	0	3	2
3·212	3·210	20	0	4	1
3·184	3·185	20	1	3	2
3·144	3·144	20	0	1	3
2·963	2·952	10	3	1	2
2·770	2·764	45	2	1	3
2·704	2·708	80	1	4	2
2·670	2·669	100	4	2	0
2·598	2·608	10	2	2	3
2·555	2·555	10	3	4	0
2·514	2·516	10	3	3	2
2·474	2·471	10	3	4	1
2·384	2·386	90	0	1	4
2·345	2·343	100	0	4	3
2·268	2·268	90	0	6	0
2·252	2·258	45	5	0	1
2·176	2·176	20	3	3	3
2·113	2·113	10	2	6	0
2·059	2·058	5	4	2	3
2·018	2·021	5	5	3	1
1·939	1·939	10	0	0	5
1·894	1·894	5	1	1	5
1·824	1·823	5	4	4	3
1·816	1·817	5	5	2	3
1·799	1·797	10	6	0	2
1·737	1·737	10	3	7	0
1·716	1·719	5	3	1	5
1·706	1·704	5	2	3	5
1·676	1·673	20	5	0	4
1·667	1·667	40	1	4	5
1·641	1·639	40	3 1	5 6	4 4
1·613	1·613	40	6	2	3
1·591	1·590	20	1	8	2

TABLE 4

Lattice parameters of Na_4TiO_4, Na_4SnO_4, and Na_4PbO_4

Compound	Structure type	*a*/Å	*b*/Å	*c*/Å
Na_4TiO_4	Orthorhombic	11·607	13·610	9·693
Na_4SnO_4	Orthorhombic	11·86	14·12	9·88
Na_4PbO_4	Orthorhombic	13·57	14·31	10·05

TABLE 5

Relation between unit-cell sizes and M^{4+} atomic radii, for Na_4TiO_4, Na_4SnO_4, and Na_4PbO_4

Compound	Atomic radii of M^{4+}/Å	Relative atomic radii	Relative atomic volumes *
Na_4TiO_4	0·68	1·00	1·00
Na_4SnO_4	0·71	1·04	1·08
Na_4PbO_4	0·84	1·24	1·24

* Calculated from values for the unit cells given in Table 4.

The data in Table 5 substantiate the postulate that these three compounds are isostructural. The recent preparations of the compounds Na_4CrO_4 and Na_4VO_4, and measurements of their *X*-ray diffraction patterns,[11] indicate that these compounds are also members of the same isostructural series.

EXPERIMENTAL

Reagents.—Sodium hydroxide was AnalaR and the purities of the transition metals and their dioxides were Ti, 99·5%; Zr, 99·7%; TiO_2, 99·5%; and ZrO_2, 99·8%. All reagents were dried to constant weight and stored in a dry argon atmosphere. Sodium oxide was prepared as described.[5]

The procedure for the preparation of reaction mixtures, together with descriptions of the thermogravimetric analysis apparatus and the *X*-ray diffractometer, have been given.[5,12] Density was measured by a method similar to that described by Barker and Martin,[13] but special precautions were taken because of the hygroscopic nature of the sample. I.r. spectra were obtained with a Perkin-Elmer 457 grating spectrophotometer.

High-temperature Diffractometer Attachment.—This was specially constructed to a design similar to that described by Baker *et al.*[14,15] All the *X*-ray diffraction patterns were obtained whilst dry helium was passed through the sample chamber. The temperature of the sample was measured with a chromel–alumel thermocouple located immediately below the silica sample holder, which was surrounded by a furnace of nichrome wire wound on a silica former. The *X*-rays entered and left the sample chamber through a $\frac{1}{2}$ in wide opening in the outer assembly that extended over an arc of 180°. This opening was sealed by a thin Mylar strip of low *X*-ray absorption to isolate the chamber from the atmosphere.

[2/1309 *Received, 9th June*, 1972]

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[11] M. G. Barker and A. J. Hooper, unpublished work.

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[13] I. Barker and G. Martin, *Analyt. Chem.*, 1963, **15**, 279.

[14] T. W. Baker, P. J. Baldock, and W. E. Spindler, U.K.A.E.A. Report A.E.R.E. M-1361, 1965.

[15] T. W. Baker, P. J. Baldock, and W. E. Spindler, *J. Sci. Instr.*, 1966, **43**, 803.