Synthesis and Characterization of Sodium–Titanium Phosphates, $Na_4(TiO)(PO_4)_2$, $Na(TiO)PO_4$, and $NaTi_2(PO_4)_3$*

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Experimental examination of part of the system Na_2O–TiO_2–P_2O_5 revealed the existence of two new sodium–titanium phosphates, $Na_4(TiO)(PO_4)_2$ and $Na(TiO)PO_4$. Their synthesis was accomplished by several different reactions and their identity was established by means of Raman spectroscopy and X-ray diffraction. Additionally, novel reactions for the synthesis of $NaTi_2(PO_4)_3$ have been demonstrated. © 1988 Academic Press, Inc.

Introduction

During the course of studies involving reactions of titanium phosphates with molten NaCN (*1*), the formation of $NaTi_2(PO_4)_3$ and of a new phase was detected. The latter contained sodium, exhibited a strong Raman peak at 687 cm^{-1}, and gave an X-ray diffraction (XRD) pattern different from any other reported sodium–titanium phosphate. In an attempt to identify this compound, the literature on sodium–titanium phosphates stable at high temperatures was reviewed. This literature is relatively sparse and indicates the existence of only a few compounds. $NaTi_2(PO_4)_3$ was prepared

by Wunder in 1871 (*2*) by melting together $NaPO_3$ and TiO_2. Almost 100 years later, Hagman and Kierkegaard (*3*) grew crystals of $NaTi_2(PO_4)_3$ at 1100°C from a $NaPO_3$-rich melt containing dissolved TiO_2 ($NaPO_3/$ $TiO_2 \simeq 13$); the XRD pattern of the compound was reported. The XRD pattern of $NaTi_2(PO_4)_3$ was also reported for crystals obtained from a 1:2:2 molar mixture of $NaH_2PO_4 \cdot H_2O$, $(NH_4)_2HPO_4$, and TiO_2 (anatase) heated to 1200°C (*4*). A compound with the stoichiometry $6Na_2O \cdot 3TiO_2 \cdot 4P_2O_5$, prepared by melting together TiO_2 with either Na_3PO_4 or $Na_4P_2O_7$, was reported by Ouvrard in 1890 (*5*). Clearfield and Frianeza (*6*) obtained $Ti(NaPO_4)_2$ by stepwise dehydration of the corresponding trihydrate (the anhydrous salt was obtained above 650°C) and reported its XRD pattern. Chernorukov *et al.* (*7*) have reported the dehydration of $TiHNa(PO_4)_2 \cdot$

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$2H_2O$ at 100°C and conversion of the anhydrous salt to a mixture of $NaTi_2(PO_4)_3$ and $NaPO_3$ at 400–438°C. Klement and Petz (8), starting with the same experimental conditions as Hagman and Kierkegaard but annealing their mixture at an undisclosed temperature, obtained crystals which, after analysis, were reported to be $Na_2(TiO)P_2O_7$; their XRD pattern was not reported. Finally, Delimarskii et al. (9) reported the formation of $Na_5(TiO)_5P_7O_{25}$ from TiO_2 dissolved in $NaPO_3$, kept at 900°C, followed by slow cooling to 720°C and rapidly to room temperature. The XRD pattern of the compound was also reported (9). Klement and Petz (8) disagree with the stoichiometry given by Delimarskii et al. (9) on the basis of the general equation for polyphosphoric acids $H_{n+2}P_nO_{3n+1}$ which would yield a heptaphosphate anion with stoichiometry $(P_7O_{22})^{9-}$.

Because we were unable to identify our unknown compound by comparison with the information available, we first attempted to synthesize $Na_2(TiO)P_2O_7$ according to (8) to see if it exhibited the 687 cm^{-1} Raman peak. This synthesis was unsuccessful; thus, we tried to obtain a compound with that stoichiometry by means of other reactions involving reagents containing Na, Ti, P, O_2, and H_2. Some of those reactions yielded products which exhibited the 687 cm^{-1} peak and therefore were studied further. During the course of this work, another new Raman peak (745 cm^{-1}) suggesting the presence of still another phase was occasionally detected. This was also investigated. Additionally, new methods were developed for synthesizing $NaTi_2(PO_4)_3$.

Experimental

The reagents TiO_2 (anatase), NaH_2PO_4, Na_2HPO_4, and Na_2CO_3 were all of "analytical-grade" purity; TiP_2O_7 and $(TiO)_2P_2O_7$ were synthesized by procedures reported

elsewhere (10). The reagents were mixed by dry grinding and heated in air at temperatures ranging from 630 to 1250°C, using platinum ware for containment. The heating schedule for exploratory tests generally consisted of two to three periods of 30 min each with grinding between heating. For the preparation of pure phases some of the mixtures of reagents were heated for a total period of 72 hr and were ground every 2 to 3 hr.

Routine XRD was performed using Guinier cameras of 11.4 cm diameter; more precise XRD data of the new phases were obtained using a Scintag diffractometer with a solid-state detector, fixed slit, and $CuK\alpha_1$ radiation with a wavelength of 1.54059 Å. The following conditions were used: accelerating potential, 45 kV; filament current, 40 ma; and scan rate, 0.2°/min. High temperature diffraction was done using a Scintag θ–θ goniometer with a Buehler high temperature attachment. The scan rate was 1°/min.

A Ramanor HG-2S spectrometer (Instruments SA) was used to obtain the Raman spectra. Data were accumulated with a Nicolet 1170 signal averager. Excitation was accomplished with the 514.5- or 488.0-nm lines of an argon-ion laser using incident power levels at the sample of 50–100 mW. Spike filters were used to reduce the plasma lines. Samples were powdered, sealed in melting point tubes, and their Raman spectra observed at an angle of 90° to the exciting laser light. The exciting laser light was polarized perpendicular to the plane formed by the exciting and observed light beams.
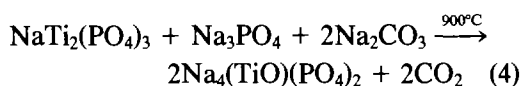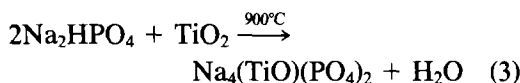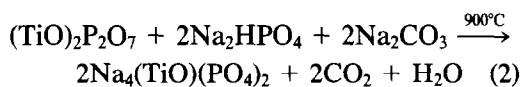
Results and Discussion

Exploratory tests were conducted in an attempt to synthesize $Na_2(TiO)P_2O_7$, a compound whose existence has been reported (8). The tests consisted of reacting TiP_2O_7 or $(TiO)_2P_2O_7$ at ~870°C with different amounts of Na_2CO_3, NaH_2PO_4, and

Na_2HPO_4 and recording the Raman spectra of the products while searching for the presence of a peak at 687 cm^{-1}, observed previously (*1*). Products from the reaction of TiP_2O_7 with widely differing amounts of Na_2CO_3 exhibited this peak among those of other products (e.g., $NaTi_2(PO_4)_3$, $Na_2Ti_6O_{13}$) and, therefore, this reaction was studied further. The reaction of TiP_2O_7 with $2Na_2CO_3$ at 900 and 950°C gave a product which exhibited a very strong 687 cm^{-1} Raman peak and several minor ones (Fig. 1a), none of which corresponded to the initial materials or other known compounds that could have formed. The XRD powder pattern (Table I) was also different from that of any of the known compounds. We deduced from these results that the reaction had proceeded as follows:

$$TiP_2O_7 + 2Na_2CO_3 \rightarrow$$
$$Na_4(TiO)(PO_4)_2 + 2CO_2. \quad (1)$$
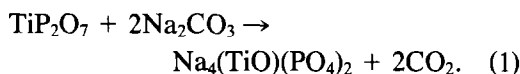
The stoichiometry of the new compound $Na_4(TiO)(PO_4)_2$ was thus chosen because no known compounds were detected by XRD and Raman spectroscopy in the product.

In order to confirm that $Na_4(TiO)(PO_4)_2$ was the actual product of Eq. (1), the following reactions were conceived and tested at 800 and 900°C for producing this compound:
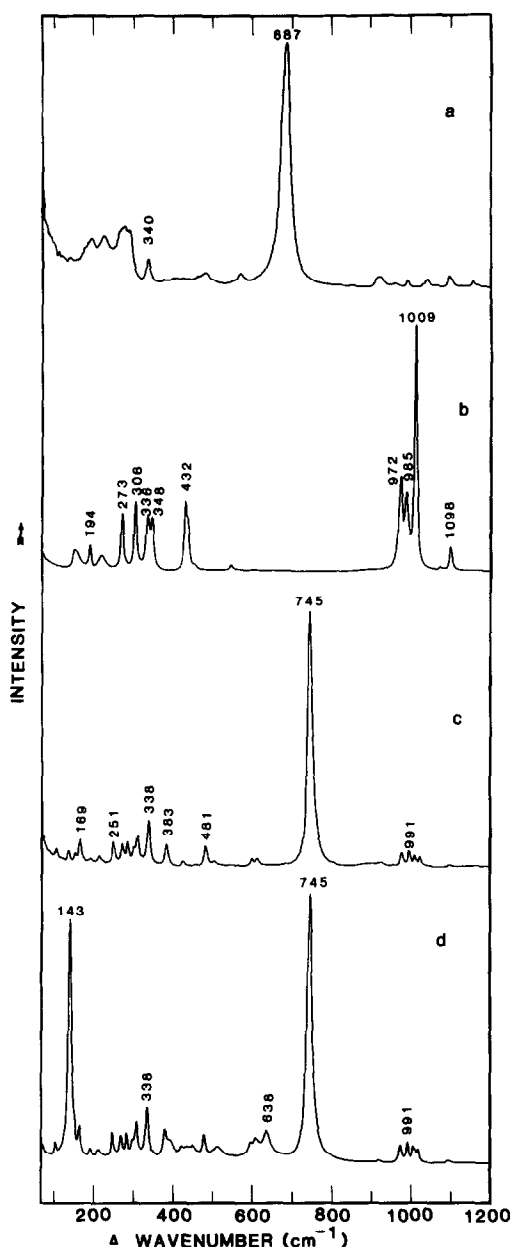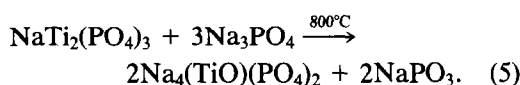
$$(TiO)_2P_2O_7 + 2Na_2HPO_4 + 2Na_2CO_3 \xrightarrow{900°C}$$
$$2Na_4(TiO)(PO_4)_2 + 2CO_2 + H_2O \quad (2)$$

$$2Na_2HPO_4 + TiO_2 \xrightarrow{900°C}$$
$$Na_4(TiO)(PO_4)_2 + H_2O \quad (3)$$

$$NaTi_2(PO_4)_3 + Na_3PO_4 + 2Na_2CO_3 \xrightarrow{900°C}$$
$$2Na_4(TiO)(PO_4)_2 + 2CO_2 \quad (4)$$

and

$$NaTi_2(PO_4)_3 + 3Na_3PO_4 \xrightarrow{800°C}$$
$$2Na_4(TiO)(PO_4)_2 + 2NaPO_3. \quad (5)$$

FIG. 1. Raman spectra, obtained with 514.5 nm excitation, of (a) $Na_4(TiO)(PO_4)_2$; (b) $NaTi_2(PO_4)_3$; (c) $Na(TiO)PO_4$; (d) $Na(TiO)PO_4$ with 10.3 wt% anatase.

The products from these reactions were characterized by Raman spectroscopy and yielded spectra identical to that of the product of reaction (1). All the weight losses

TABLE I

X-RAY DIFFRACTION DATA FOR
$Na_4(TiO)(PO_4)_2$[a]

d (Å)	I/I_0	d (Å)	I/I_0
7.737	47	2.601	17
7.569	37	2.573	61
5.402	14	2.132	5
4.926	32	2.118	7
4.848	14	2.052	7
4.384	6	1.984	5
3.694	16	1.938	30
3.650	5	1.918	6
3.601	28	1.899	14
3.447	37	1.888	5
3.397	30	1.879	6
3.208	11	1.801	10
3.188	23	1.769	5
3.163	14	1.760	7
3.058	11	1.568	19
2.914	6	1.544	5
2.840	5	1.538	8
2.816	6	1.530	8
2.795	5	1.520	7
2.702	100	1.492	5
2.652	29	1.326	5

[a] Many other weaker peaks also present.

recorded for reactions (1–4) agreed within 4% of the calculated values. Ratios of reactants different from those indicated in Eqs. (2–5) gave products, in addition to $Na_4(TiO)(PO_4)_2$, which were identifiable by XRD and Raman spectroscopy (e.g., $NaTi_2(PO_4)_3$ and $Na(TiO)PO_4$, described below). The reaction of TiP_2O_7 was also effected, at 850°C, with 1.96 and with 2.06 Na_2CO_3. The Raman spectrum of the resulting product from mixtures containing 1.96 Na_2CO_3 was similar to that obtained with $2Na_2CO_3$ but showed, in addition, the presence of a small amount of anatase. The spectrum of the product obtained with 2.06 Na_2CO_3 indicated the presence of the new compound as the major phase with, additionally, traces of what tentatively was
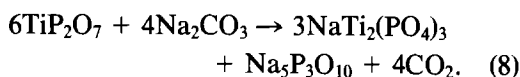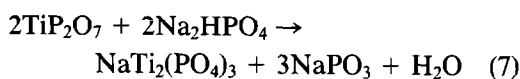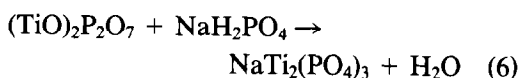
identified as a mixture of sodium titanates. The products of multiple preparations obtained from reactions depicted in Eqs. (1–5) performed at various temperatures between 840 and 1000°C were examined by XRD at room temperature; in all the cases the interplanar spacings were reproducible but the intensities of the strongest peaks occasionally varied. In order to decide whether the latter was due to some phase transformation, which could have been frozen in by rapid cooling or to the preferred orientation packing of the powders, a sample was examined at room temperature, 600°, 850°, 950°C, and again at room temperature. The only effects observed were a gradual increase of the interplanar spacings with temperature and the change of intensity of several peaks at 600° and 850°C. At 950°C the intensities of the peaks were similar to those at room temperature. The diffraction pattern from a sample after heating matched perfectly that obtained prior to the heating cycle. It was concluded that the variation of intensity was due to preferred orientation in samples examined at room temperature and that this effect was even present at the higher temperatures, probably caused by deflection of the platinum ribbon supporting the sample. A typical X-ray diffraction powder pattern obtained at room temperature is shown in Table I. Attempts to index the diffraction peaks were unsuccessful.

From the results described above we concluded that $Na_4(TiO)(PO_4)_2$ was actually the compound synthesized by means of reactions (1–5).

Tests performed on $Na_4(TiO)(PO_4)_2$ indicated that it was quite stable toward hydrolysis; several treatments with water at room temperature and at 90°C removed less than 1 wt%; the water remained neutral after separation by centrifugation. In regard to thermal stability the $Na_4(TiO)(PO_4)_2$ powder sintered without pressure at 950°C and was molten at 1000°C; on solidifying, its

Raman spectrum was the same as the initial material.

$NaTi_2(PO_4)_3$ was readily produced by reactions with molten NaCN (*1*), and by other reactions(*2–4, 7*). This compound was easily identified by XRD because its diffraction pattern had been reported (*4*). Its Raman spectrum is unique and quite characteristic of a phosphate, with a sharp peak at 1010 cm^{-1} (Fig. 1b), and did not overlap with that of $Na_4(TiO)(PO_4)_2$. Because of the ease of identifying $NaTi_2(PO_4)_3$ by XRD and Raman spectroscopy it was decided to see if we could devise alternative ways for its synthesis. The following reactions were performed at 900–1000°C, all successfully yielding $NaTi_2(PO_4)_3$:

$$(TiO)_2P_2O_7 + NaH_2PO_4 \rightarrow$$
$$NaTi_2(PO_4)_3 + H_2O \quad (6)$$

$$2TiP_2O_7 + 2Na_2HPO_4 \rightarrow$$
$$NaTi_2(PO_4)_3 + 3NaPO_3 + H_2O \quad (7)$$

$$6TiP_2O_7 + 4Na_2CO_3 \rightarrow 3NaTi_2(PO_4)_3$$
$$+ Na_5P_3O_{10} + 4CO_2. \quad (8)$$

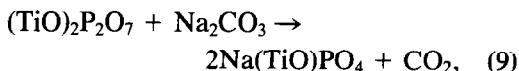The presence of $NaTi_2(PO_4)_3$ among the products of the reactions in Eqs. (6–8) was unequivocally determined by Raman spectroscopy; this method also showed the presence of $NaPO_3$ as the by-product of Eq. (7). The other sodium phosphate (Eq. (8)) was not seen and consequently its presence was inferred from material balance.

During exploratory work on the synthesis of $Na_4(TiO)(PO_4)_2$ another unidentified Raman peak at 745 cm^{-1} was occasionally observed in the products. It was speculated that this peak might arise from the compound reported by Delimarskii *et al.* (*9*) since attempts (above) to synthesize $Na_2(TiO)P_2O_7$ (*8*) had been unsuccessful. Because no exact temperature had been given in (*8*), and their experimental conditions may have been similar to those in (*9*), several preparations in which TiO_2 was dissolved at 1200°C in excess $NaPO_3$ and
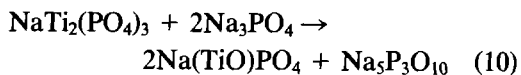
quenched into a clear glass were made and subsequently annealed for 18 hr at 630, 700, and 800°C. (Higher temperatures were not used because it had already been reported in (*3*) that $NaTi_2(PO_4)_3$ is obtained at 1100°C.) After dissolving the $NaPO_3$ in hot water, the residues obtained from annealing at the three temperatures were all identified as $NaTi_2(PO_4)_3$. The only noticeable difference was the size of the crystals which were larger at the highest annealing temperature, 800°C. Crystals of $NaTi_2(PO_4)_3$ were heated in air at increasing temperatures up to 1100°C and no melting occurred. All the above results concerned with the formation of $NaTi_2(PO_4)_3$ indicate that it probably is one of the most stable compounds in the system $Na_2O–TiO_2–P_2O_5$. Furthermore, a comparison of the XRD data reported in (*4*) and in (*9*) suggests that the compound reported by Delimarskii *et al.* (*9*) may contain $NaTi_2(PO_4)_3$ as its major phase. Since the reactions of TiO_2 with $NaPO_3$ did not yield a compound having a Raman peak at 745 cm^{-1}, such a compound was sought using synthetic methods similar to those used for $Na_4(TiO)(PO_4)_2$ since the 745 cm^{-1} peak was detected during some of its preparations. The unidentified peak at 745 cm^{-1} was found from the products of several reactions and was more intense in preparations stemming from mixtures of $(TiO)_2P_2O_7$ with Na_2CO_3 (1 : 1) and of $NaTi_2(PO_4)_3$ with Na_3PO_4 (1 : 1.7) both heated to 850°C. Other phases ($NaTi_2(PO_4)_3$, anatase, and rutile) were also present in these preparations and, consequently, conditions were sought which would produce the unknown compound in a pure state. The reaction of $NaTi_2(PO_4)_3$ with $2Na_3PO_4$ at 800°C yielded a product whose Raman spectrum contained the 745 cm^{-1} peak and did not show the presence of any known compound (Fig. 1c). If the overall composition of the reactants was written as $(TiO)_2P_2O_7 \cdot Na_3PO_4 \cdot Na_4P_2O_7$ it suggested that the reaction of a mixture of these compounds would lead to

the same product. The Raman spectrum of the product obtained when that mixture was heated to 800°C was the same as that obtained earlier. Examination under the microscope and by XRD revealed that the product of the reactions consisted of a mixture of crystalline and glass phases. Attempts to separate the phases by dissolution in water and in dilute HCl were not successful. Speculation that the crystalline phase was the compound, $Na_2(TiO)P_2O_7$, reported by Klement and Petz (8) was untenable because the by-product would have had to be Na_3PO_4 which is easily identifiable by XRD and Raman spectroscopy instead of the glass obtained.

Balancing the equations of the different reactions performed in which all the products, except that giving rise to the 745-cm^{-1} peak, had been identified by Raman spectroscopy suggested that the unknown compound may have the composition Na(TiO)PO$_4$. Such a composition, which was formulated by mixing $(TiO)_2P_2O_7$ with Na_2CO_3, was heated at 775°C for 4 hr. The product did not have a glass phase, gave the same Raman spectrum recorded previously from the product of reacting $NaTi_2(PO_4)_3$ with $2Na_3PO_4$ at 800°C, and did not show the presence of other compounds. Its XRD powder pattern was different from any known pattern (Table II) and was assumed to be that of a new phase. From this information we concluded that the following Eq. (9) represents the reaction that had taken place,

$$(TiO)_2P_2O_7 + Na_2CO_3 \rightarrow$$
$$2Na(TiO)PO_4 + CO_2, \quad (9)$$

and that the reactions tried before had been

$$NaTi_2(PO_4)_3 + 2Na_3PO_4 \rightarrow$$
$$2Na(TiO)PO_4 + Na_5P_3O_{10} \quad (10)$$

and

$$(TiO)_2P_2O_7 + Na_3PO_4 + Na_4P_2O_7 \rightarrow$$
$$2Na(TiO)PO_4 + Na_5P_3O_{10}. \quad (11)$$
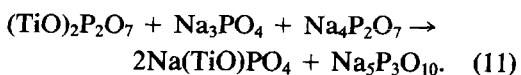
TABLE II

X-RAY DIFFRACTION DATA FOR
Na(TiO)PO$_4$[a]

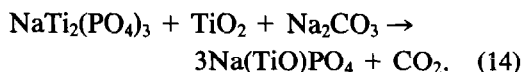| d (Å)	I/I_0	d (Å)	I/I_0
4.875	35	1.712	21
4.779	19	1.687	26
4.241	5	1.630	30
3.546	11	1.540	6
3.366	12	1.533	15
3.271	100	1.512	5
2.979	48	1.495	22
2.607	8	1.448	11
2.573	44	1.423	12
2.556	69	1.395	10
2.288	5	1.335	12
2.241	29	1.303	5
2.116	10	1.283	8
2.088	17	1.266	7
2.016	9	1.221	5
1.998	12	1.144	5
1.940	16	1.102	7
1.773	21	0.998	5
1.730	7		

[a] Many other weaker peaks also present.

The presumed identification of the compound as Na(TiO)PO$_4$ led us to an alternative synthesis method, described by Eq. (12):

$$TiO_2 + NaPO_3 \rightarrow Na(TiO)PO_4. \quad (12)$$
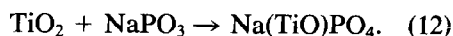
The reaction was performed at 870°C and was successful in that the spectral and XRD data of the product were similar to those obtained above. The reaction was monitored as a function of time by examining samples by Raman spectroscopy which is very sensitive to TiO$_2$ in the anatase form. It was concluded, from synthetic mixtures of Na(TiO)PO$_4$ and anatase, that 2 mole% anatase could have been easily detected (Fig. 1d). The following reactions were also tested at 870°C for synthesizing Na(TiO)PO$_4$:

$$Na_4(TiO)(PO_4)_2 + (TiO)_2P_2O_7$$
$$+ TiO_2 \rightarrow 4Na(TiO)PO_4 \quad (13)$$

and

$$NaTi_2(PO_4)_3 + TiO_2 + Na_2CO_3 \rightarrow$$
$$3Na(TiO)PO_4 + CO_2. \quad (14)$$
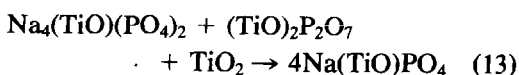
Washing repeatedly with water at 90°C had no effect on the compound. The spectral and XRD results were also similar to those obtained earlier. Although we were not able to index the diffraction pattern of Na(TiO)PO$_4$, the absence of any other identifiable phase, the uniqueness of its pattern and of its Raman spectrum, and the reactions used to synthesize it led us to conclude that Na(TiO)PO$_4$ represented the stoichiometry of the compound obtained from the reactions indicated by Eqs. (9), (12)–(14). It has been reported, from crystallographic and spectroscopic evidence that the titanyl (TiO^{2+}) group is present in only a few solid titanium(IV) oxocomplexes (11). The stretching frequency of the Ti=O was found to vary between 890 and 975 cm^{-1}, depending on the particular compound (11). Recently, the presence of Ti=O has also been confirmed in aqueous solutions using Raman spectroscopy (11) and O^{17} NMR spectroscopy (12). It is believed, however, that the characteristic frequency of the Ti=O bond stretching motion is not observed in the Raman spectra of many compounds containing Ti, O, and other elements because such motions remain strongly coupled in the ordered crystal structures. Furthermore, it is presently accepted that the titanium and oxygen atoms, in those compounds which do not show evidence for the presence of Ti=O, are present as –Ti–O–Ti–O– chains (13). Because the new compounds Na(TiO)PO$_4$ and Na$_4$(TiO)(PO$_4$)$_2$ each exhibit a strong Raman peak at, respectively, 745 and 687 cm^{-1} and because the Ti=O vibration is observed at higher (Figs. 1a and 1c) frequencies, we assign these peaks to the presence of –Ti–O–Ti–O– chains rather than to Ti=O discrete units. The same conclusion

can be drawn for (TiO)$_2$P$_2$O$_7$, ν = 719 cm^{-1}, reported earlier by us (10). The bands in the 1000-cm^{-1} region are due to the phosphate group; these bands are relatively very weak in compounds containing –Ti–O–Ti–O– chains but are the strongest in those in which the titanium atom is in a different environment, e.g., NaTi$_2$(PO$_4$)$_3$ (Fig. 1b).

A portion of Na(TiO)PO$_4$ was heated for 1 hr at each of the four temperatures 850°, 900°, 950°, and 1000°C; after each treatment a sample was removed and examined by Raman spectroscopy. The spectra revealed that total decomposition into TiO$_2$ (rutile) and NaTi$_2$(PO$_4$)$_3$ had occurred at 950°C, very likely according to the following equation:

$$6Na(TiO)PO_4 \rightarrow NaTi_2(PO_4)_3 + 4TiO_2$$
$$+ Na_5P_3O_{10}. \quad (15)$$
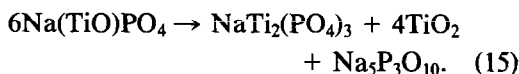
No effort was made to identify the sodium polyphosphate; its presence was inferred from a material balance. Heating the products of Eq. (15) at 870°C for 18 hr regenerated the Na(TiO)PO$_4$, demonstrating that the reaction is reversible.

The reaction of Na(TiO)PO$_4$ with Na$_3$PO$_4$ at 900°C was used as an alternate method for the preparation of Na$_4$(TiO)(PO$_4$)$_2$, i.e.,

$$Na(TiO)PO_4 + Na_3PO_4 \rightarrow$$
$$Na_4(TiO)(PO_4)_2. \quad (16)$$
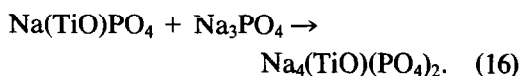
This reaction was confirmed by Raman spectrometry.

We also sought to duplicate the reaction of TiO$_2$ with Na$_3$PO$_4$ reported by Ouvrard (5) to yield a compound with stoichiometry 6Na$_2$O · 3TiO$_2$ · 4P$_2$O$_5$. We used here a 1 : 1 mixture of TiO$_2$ and Na$_3$PO$_4$ and heated it at increasing temperatures until a liquid appeared at 1100°C. Samples were taken after solidifying at room temperature and after subsequent annealing for 3 days at 800°C. The Raman spectra of both specimens were identical, showing the presence of only Na$_2$Ti$_6$O$_{13}$. The other by-product of the reaction

(possibly a sodium phosphate glass) was not observed because $Na_2Ti_6O_{13}$ exhibits the highest scattering factor among the sodium titanates (14) and higher than many other titanium-containing compounds. No indication of a sodium–titanium phosphate was observed, and the reaction of TiO_2 with Na_3PO_4 was not studied further.

The possibility that $Na(TiO)PO_4$ and $Na_4(TiO)(PO_4)_2$ exchange sodium for other alkali metal ions was cursorily tested by equilibrating the solids with neutral and acidic aqueous solutions containing ^{137}Cs at 23°C for up to 120 hr. The results were negative.

In order to measure the electrical resistivity of $Na_4(TiO)(PO_4)_2$, a portion of powder was isostatically pressed at 414 MPa (60,000 psi) into disks (4 mm height × 12.27 mm diameter) which were heated in air to 900°C for ca. 4 hr. The fired disks, with a density of 2.51 g/cm³, were cut with a diamond saw into parallelepipeds of 4 × 4 × 8 mm and gold electrodes attached to them. The resistivity, measured by ac impedance under vacuum at 250°C was 3.7×10^4 ohms cm.

Conclusions

Two new sodium–titanium phosphates $Na_4(TiO)(PO_4)_2$ and $Na(TiO)PO_4$ have been synthesized by various routes and characterized by XRD and Raman spectroscopy. The former compound melts above 950°C and the latter decomposes at ca. 900°C to $NaTi_2(PO_4)_3$, rutile TiO_2, and a sodium phosphate. New reactions, in addition to those reported in the literature, have been demonstrated for the synthesis of $NaTi_2(PO_4)_3$. No evidence was found in this work for the existence of $Na_2(TiO)P_2O_7$ or $Na_2Ti(PO_4)_2$.

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