

Room-Temperature-Initiated Routes to Titanium and Vanadium Pnictides

Andrew L. Hector and Ivan P. Parkin*

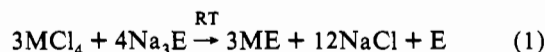
Department of Chemistry, Christopher Ingold Laboratories,
University College London, 20 Gordon Street,
London WC1H 0AJ, U.K.

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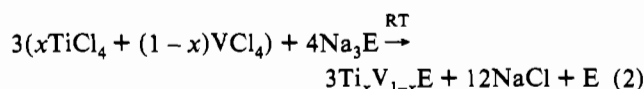
Metal phosphides, arsenides, antimonides, and bismuthides are ceramic materials used for a variety of industrial processes, for instance, as catalysts, semiconductors, and phosphorescence devices.¹ They are conventionally made by combination of the elements at high temperature (600–1400 °C), by reactions of EH_3 ($\text{E} = \text{P, As, Sb, Bi}$) and the metal, by electrochemical synthesis, or by molecular precursor routes.² Recently Bonneau *et al.*³ have developed solid-state metathesis routes to layered transition metal dichalcogenides, refractory materials, and group III–V semiconductors. This represents an extension of the self-propagating high-temperature synthesis methods originally developed by Russian researchers.⁴ We have reported the metathetical syntheses of a number of materials including oxides, nitrides, and phosphides.⁵ From these studies it is evident that “solid-state” metathesis reactions proceed rapidly when one of the precursors undergoes a phase change.^{3c,5e} The extension of these methods to reactions of titanium and vanadium tetrachlorides with sodium pnictides is interesting as this is a rare example of a solid–liquid heterogeneous metathesis reaction (solution phase metathesis reactions are well-known⁶). Further, no heating is required in these reactions to induce a phase change to stimulate the reaction as VCl_4 and TiCl_4 are both liquids at room temperature. The ease with which the liquid metal chlorides can be mixed allows for the facile synthesis of completely mixed metal pnictides at low initiation temperature. Mixed-metal pnictides are conventionally made by alloying the metals and then reacting with pnictogens at elevated temperatures for extensive time periods.¹

Addition of Na_3E ($\text{E} = \text{P, As, Sb, Bi}$; 0.3–0.5 g) to stirred MCl_4 ($\text{M} = \text{Ti, V}$; ratio of $\text{Na}:\text{Cl} = 1:1$) results in a solid–liquid metathesis reaction.⁷ The reaction self-initiates immediately and is accompanied by a red–white flash and a sublimed solid (NaCl and E).⁸ Voracity of reactions visibly decreases from phosphide to bismuthide. The scale of the reaction is important because at less than *ca.* 0.1 g of Na_3E the reaction often failed to initiate at room temperature and required heating. The main product

from the reaction, ME_n ($n = 1, 2$), is contained in a partly fused black mass, which showed a smooth morphology (from SEM⁹ studies) and the presence of sodium, chlorine, and to a lesser extent metal and pnictogen by EDXA.⁹ Trituration of the black mass with water or methanol removed the NaCl coating to leave a porous surface (from SEM studies) and only metal and pnictogen by EDXA. The powder XRD¹⁰ data of the triturerated metal pnictides are summarized in Table 1. In general the binary metal pnictides detected by XRD were of stoichiometry ME .¹¹ This was confirmed by EDXA results. The pnictogen formed in the reaction does not appear in the fused mass but is cosublimed with NaCl , eq 1. The Scherrer equation¹⁰ gives average crystallite sizes of 300–350 Å for the pnictide powders. FT-IR analysis reveals no bands from 4000–300 cm^{-1} .

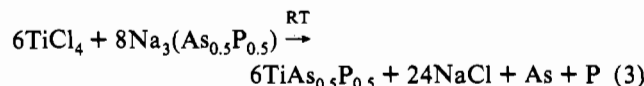


Initiation of a mixture of TiCl_4 , VCl_4 , and Na_3E ($\text{E} = \text{P, As}$) produces the mixed-metal pnictides $\text{Ti}_x\text{V}_{1-x}\text{E}$ in a stoichiometrically controlled fashion, eq 2. The XRD pattern of $\text{Ti}_x\text{V}_{1-x}\text{E}$



after methanol trituration showed a phase intermediate between the TiE and VE patterns, Figure 1. For $\text{Ti}_x\text{V}_{1-x}\text{As}$ ($x = 0, 0.25, 0.5, 0.75, 1$), lattice parameters closely matched reported^{11c} values. However, for $\text{Ti}_{0.75}\text{V}_{0.25}\text{As}$, the patterns were weak and the lattice parameters, indexed by the TREOR program, were determined using a Vegard's law relation between lattice parameter and composition for values between $x = 0.6$ and 0.8 . The previous work^{11c} describes these compositions as a “nonequilibrium” region and the powder patterns as complex and made up of fairly sharp and rather diffuse reflections. These nonequilibrium mixtures may represent nonuniform distributions of V and Ti over essentially MnP type sublattices.

Step EDXA of $\text{Ti}_x\text{V}_{1-x}\text{E}$ showed constant ratios for Ti/V across the surface. The triturerated metal pnictides had satisfactory quantitative EDXA with levels of sodium and chlorine incorporation less than the limit of detection (estimated at ~0.5%). Reaction of TiCl_4 with $\text{Na}_3\text{As}_{0.5}\text{P}_{0.5}$ formed the phase $\text{TiAs}_{0.5}\text{P}_{0.5}$, indicating that mixed pnictide materials could also be made, eq 3. The XRD pattern from the products of the reaction between



MCl_4 and Na_3Sb showed primarily Sb but also some MSb_2 and MSb . With Na_3Bi only Bi is observed. Thus formation of ME

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- (7) All reactions were carried out under a nitrogen atmosphere either in a glovebox or using Schlenk line techniques. TiCl_4 and VCl_4 were added in the appropriate stoichiometric ratios and stirred to form an intimately mixed solution before the addition of Na_3E .
- (8) *Caution! This reaction is spontaneous and very exothermic. Na_3E was produced by the thermolysis (550 °C, 10 h) of sodium and pnictogen in a sealed, evacuated glass ampule. Sodium was purchased from BDH; pnictogens and metal tetrachlorides were purchased from Aldrich Chemical Co. Yields were typically 70–80%.

- (9) Scanning electron microscopy (SEM) was performed with a Jeol JSM820 instrument. Energy-dispersive X-ray analysis (EDXA) was obtained with Kevex Delta 4 quantum detector and Quantex 6.2 software.
- (10) Powder X-ray diffraction (XRD) measurements were performed on a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ ($\gamma = 1.5418 \text{ \AA}$) radiation, at ambient temperature. An external NBS 6100 silicon standard was used for calibration with resolution better than 0.02°.
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Table 1. Powder XRD Data for the Products of the Reactions of MCl_4 ($M = Ti, V$) with Na_3E ($E = P, As, Sb, Bi$)

reagents	phase detected by XRD	cryst system	lattice params (lit. ¹¹ values)
$TiCl_4 + Na_3P$	TiP	hexagonal (TiAs)	$a = 3.50$ (3.49), $c = 11.68$ (11.65)
$TiCl_4 + VCl_4 + Na_3P$	$Ti_{0.5}V_{0.5}P$	hexagonal ^a	
$VCl_4 + Na_3P$	VP	hexagonal (NiAs)	$a = 3.17$ (3.18), $c = 6.22$ (6.22)
$TiCl_4 + Na_3As$	TiAs	hexagonal (TiAs)	$a = 3.64$ (3.64), $c = 12.01$ (12.06)
$TiCl_4 + VCl_4 + Na_3As$	$Ti_{0.25}V_{0.75}As$	hexagonal (NiAs)	$a = 3.60$ (3.62), $c = 6.12$ (6.12)
$TiCl_4 + VCl_4 + Na_3As$	$Ti_{0.5}V_{0.5}As$	hexagonal (NiAs)	$a = 3.59$ (3.55), $c = 6.15$ (6.14)
$TiCl_4 + VCl_4 + Na_3As$	$Ti_{0.75}V_{0.25}As$	orthorhombic (MnP)	$a = 6.48$ (~6.32), $b = 5.86$ (~5.93), $c = 3.17$ (~3.42)
$VCl_4 + Na_3As$	VAs	orthorhombic (CoAs)	$a = 6.29$ (6.32), $b = 5.84$ (5.89), $c = 3.36$ (3.33)
$TiCl_4 + Na_3As_{0.5}P_{0.5}$	$TiAs_{0.5}P_{0.5}$	hexagonal (TiAs)	$a = 3.51$ (3.56), $c = 11.72$ (11.84)
$TiCl_4 + Na_3Sb$	Sb [TiSb ₂ , TiSb]	hexagonal (As)	$a = 4.31$ (4.31), $c = 11.27$ (11.27)
$VCl_4 + Na_3Sb$	Sb [VSb ₂]	hexagonal (As)	$a = 4.31$ (4.31), $c = 11.27$ (11.27)
$TiCl_4 + Na_3Bi$	Bi	hexagonal (As)	$a = 4.55$ (4.55), $c = 11.90$ (11.86)
$VCl_4 + Na_3Bi$	Bi	hexagonal (As)	$a = 4.55$ (4.55), $c = 11.90$ (11.86)

^a Compositional confirmed by EDXA. We can find no literature reference to this phase, but preliminary XRD work indicates a hexagonal lattice.

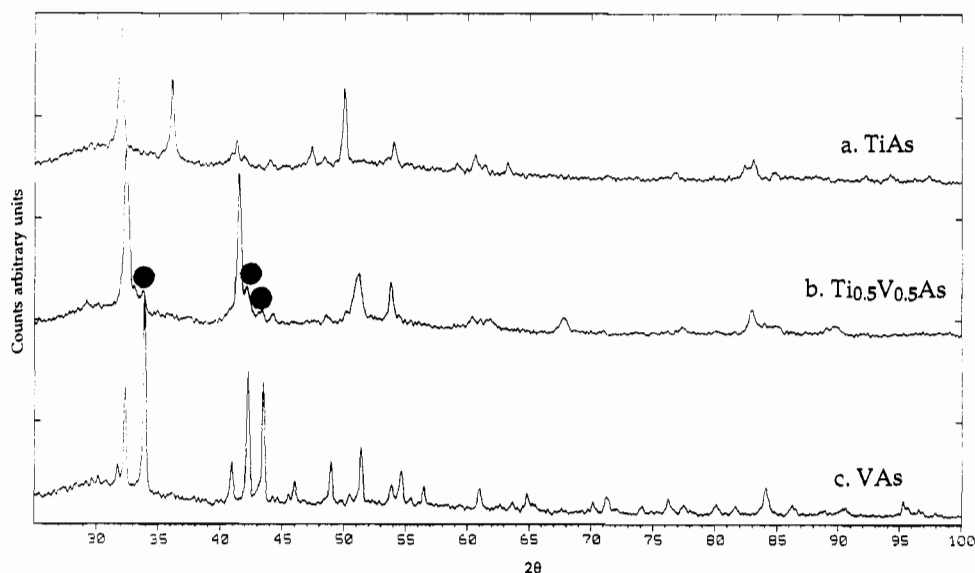


Figure 1. (a) X-ray powder diffraction pattern of TiAs formed from reaction of $TiCl_4$ and Na_3As . (b) X-ray powder diffraction pattern from reaction of equimolar amounts of $TiCl_4$ and VCl_4 with Na_3As (● = VAs). (c) X-ray powder diffraction pattern of VAs formed from reaction of VCl_4 and Na_3As .

in the reaction is disfavored down the pnictogen group. This could be due to the lower reduction potentials of the pnictide ions down the group, resulting in a greater tendency for elements to form. Presumably elemental Ti and V are not observed by XRD because the reaction temperature is not maintained for long enough to substantially anneal these products. EDXA shows that they are present.

The reactions of Na_3E with MCl_4 are exothermic (as evidenced by sublimed NaCl, thermal flash, and product crystallinity) typically with $\Delta H_f = -600$ kJ mol⁻¹ as assessed from Hess' law calculations.¹¹ The room-temperature initiation is probably due to the good solid-liquid contact between the reagents as compared to analogous solid-state reactions which often require heating (400–600 °C) to overcome the solid-state diffusion barrier to reaction.⁴

The ease of separation of the metal pnictide from the coproduced NaCl and the rapid reaction, room-temperature initiation, and ease of formation of ternary materials illustrate the utility of solid-liquid metathesis reactions to form metal-pnictide ceramics. Reactions are successful for phosphide and arsenide formation, but for $E = Sb$ and Bi elemental pnictogen is observed. Formation of antimonides or bismuthides would require high-temperature annealing of the elemental mixtures which are yielded by these reactions.

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