

Reactions of the alkaline earth metal pyro- and ortho-vanadates with ammonia

H.-Zh. Li, L.-M. Liu, K.P. Reis and A.J. Jacobson*

Department of Chemistry and Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5641 (USA)

(Received June 18, 1993)

Abstract

Reactions of the alkaline earth metal vanadates $A_2V_2O_7$ and $A_3V_2O_8$ ($A \equiv Ca, Sr, Ba$) with hydrogen and ammonia have been investigated by thermogravimetric analysis and in a flow reactor. Reactions in ammonia do not lead to the formation of oxynitride phases, in contrast with the formation of $LaVO_{3-x}N_x$ from $LaVO_4$ under similar conditions. Both hydrogen reduction and ammonia reactions of the $A_2V_2O_7$ compounds are dominated by the formation of the corresponding $A_3V_2O_8$ phases. $Ba_3V_2O_8$ and $Sr_3V_2O_8$ do not react easily in ammonia at temperatures below 1000 °C and $Ca_3V_2O_8$ converts to CaO and VN or to CaO, VN and $CaVO_3$.

1. Introduction

Mixed metal oxynitrides with the perovskite and related structures have previously been reported for several early transition metals. Most of the known phases are insulators, e.g. $ATaO_2N$ ($A \equiv Ca, Sr, Ba$), $ANbO_2N$ ($A \equiv Sr, Ba$), $ATiO_2N$ ($A \equiv La-Yb$), $ABON_2$ ($A \equiv Ln$; $B \equiv Nb, Ta$), A_2TaO_3N ($A \equiv Ca, Sr, Ba$) and the pyrochlore $Ln_2Ti_2O_{5.5}$ ($Ln \equiv Y, Dy, Sm$) [1–4]. Some compositions have been found to be semiconductors with mixed valence cations and a range of nitrogen contents, e.g. $LaWO_xN_{3-x}$ ($x = 0.6-0.8$) and $LaVO_{3-x}N_x$ ($x \leq 0.9$) [5–7]. Metallic conductivity is known to occur in ternary nitrides [8] and has recently been reported in $AMo_{3-x}N_x$ ($A \equiv Sr, Ba$) [9].

Mixed metal oxides containing vanadium(IV) with perovskite-related structures have recently been of interest as early transition metal analogs of the cuprate superconductors. Specifically, the phases $SrVO_3$, $Sr_4V_3O_{10}$, $Sr_3V_2O_7$ and Sr_2VO_4 have been synthesized and their electronic properties investigated [10–17]. All these compounds with the exception of Sr_2VO_4 are reported to be metallic conductors but do not show superconductivity. It is of interest to further modify the properties of these perovskite-related structures by replacing some oxygen atoms in the structure by nitrogen atoms, thereby increasing the average formal vanadium oxidation state and the degree of band filling. For this reason we have investigated the reaction of ammonia with the compounds $A_2V_2O_7$ and $A_3V_2O_8$ ($A \equiv Ca, Sr,$

Ba) as a potential route to synthesis of oxynitride phases with hypothetical compositions $AVO_{3-x}N_x$ and $A_3V_2O_{7-x}N_x$. Syntheses of the oxynitride phases reported previously have typically been carried out by reaction of an appropriate ternary oxide with ammonia gas at high temperature. For example, $LaVO_4$ was converted to $LaVO_{3-x}N_x$ with $0 \leq x \leq 0.9$ by reaction in ammonia at temperatures in the range 650–850 °C [6]. In the case of the alkaline earth metal vanadates, however, we find that ternary oxynitride phases are not formed owing to competitive side reactions. The details of reaction pathways of $A_2V_2O_7$ and $A_3V_2O_8$ in both NH_3 and H_2 have been determined and are described in this paper.

2. Experimental details

2.1. Synthesis of precursors

The $A_2V_2O_7$ and the $A_3V_2O_8$ ($A \equiv Ca, Sr, Ba$) starting materials were prepared by reaction of the corresponding alkaline earth metal carbonate MCO_3 with V_2O_5 in the appropriate stoichiometric ratios. The reactants used were: V_2O_5 (99.6+%, Aldrich), $CaCO_3$ (99+% ACS reagent, Aldrich), $SrCO_3$ (98+% ACS reagent, Aldrich) and $BaCO_3$ (98+% ACS reagent, Aldrich). The calcium-containing phases $Ca_2V_2O_7$ and $Ca_3V_2O_8$ were prepared from stoichiometric mixtures of $CaCO_3$ and V_2O_5 . The reactants were ground and fired at 600 °C for 2 days and then at 700–900 °C for an additional 2 days with several intermediate re-grinds to ensure homogeneity. The procedure used to synthesize $Sr_2V_2O_7$,

*Author to whom correspondence should be addressed.

Ba₂V₂O₇ and Sr₃V₂O₈ was essentially the same, except that the final firing temperature was raised to 1000 °C. The phase purity of the products was verified by X-ray powder diffraction.

2.2. Reactions in hydrogen and ammonia

Reactions of the vanadate starting materials in ammonia and hydrogen were carried out both thermogravimetrically and, on a larger scale, in a flow reactor. The thermogravimetric analyses (TGA) were made using a Du Pont Instruments 951 thermobalance. The samples typically were heated at a rate of 5 °C min⁻¹ to the final temperature or held at a constant temperature for 3 h. The reactant gases used were 5% hydrogen in nitrogen or 33% ammonia in nitrogen. Flow rates were controlled by Tylan RO-28 mass flowmeters. A platinum boat was used for hydrogen reduction experiments, but a quartz boat was preferred for ammonia reactions. Blank runs using the same temperature program and flow rates were made to correct small weight changes due to buoyancy.

Larger-scale reactions in ammonia or hydrogen were carried out in an ATS 3210 tube furnace (Applied Test Systems, Inc.) fitted with an alumina tube, sealed with stainless steel end covers and connected to a stainless steel gas distribution system. The partial pressure of the NH₃ and the flow rate of the reactant gas were controlled by two flowmeters located in front of the inlet end of the furnace. In all experiments the NH₃ partial pressure P_{NH_3} , the flow rate of the purging gas and the temperature ramp were $\frac{1}{3}$ atm, 50 ml min⁻¹ and 10 °C min⁻¹ respectively. Samples of the starting oxides (typically 0.5–1 g) were contained in alumina boats. Reaction times at the final temperature were either 8 or 16 h. Reaction products were furnace cooled and identified by X-ray powder diffraction.

A sample of LaVO_{3-x}N_x was prepared for reference by reaction of tetragonal LaVO₄ in ammonia (75 ml min⁻¹, $P_{\text{NH}_3} = \frac{1}{3}$ atm) at 750 °C for 5 h.

2.3. Nitrogen content determination

The micro-Kjeldahl method has been most commonly used for the chemical determination of nitrogen in nitrides [18]. In this method the sample is first digested in concentrated sulfuric acid or an aqueous oxidant to bring the nitrogen into the solution as an ammonium salt. An excess of strong base is then added to the solution and the mixture heated to expel the ammonia. The ammonia is quantitatively absorbed by an excess of a standardized dilute acid and the excess acid is determined either by titration or colorimetrically using Nessler's reagent [19]. Accurate nitrogen analysis in refractory metal nitride or oxynitride systems using this method, however, is difficult owing to incomplete solubility in aqueous reagents.

An alternative approach for the analysis of oxynitrides which overcomes the solubility problem has been used by Marchand's group [6, 7, 20]. The nitrogen contents of a series of ternary oxynitrides were determined by fusion in potassium hydroxide following a procedure described by Guyader *et al.* [21]. The ammonia expelled was analyzed by the usual Kjeldahl method. A similar technique has been described in a Japanese patent [22].

In this work two modifications to the Marchand method have been used. The sample to be analyzed together with the solid alkali hydroxide were contained in an alumina boat placed in an alumina tube fitted with gas tight end covers. An equimolar mixture of KOH and NaOH was employed to decrease the melting point from 360 °C to less than 200 °C [23]. In a typical experiment a mixture of 2 g KOH, 2 g NaOH and 0.1 g sample was used. The alumina tube was sealed and heated by heating tape. Nitrogen was passed through the system at 20–25 ml min⁻¹. The temperature was held at 350 °C for 2 h and at 500–530 °C for a further 2 h. The ammonia expelled was absorbed in 50 ml of 0.01–0.02 M HCl and the excess acid was titrated with 0.1 M sodium hydroxide. The method was developed using ammonium sulfate, titanium nitride, vanadium nitride (all supplied by Aldrich) and ammonium vanadate (Fisher) as standards. A sample of the ternary oxynitride LaVO_{3-x}N_x was also analyzed. The results from the analysis of the standard samples are given in Table 1. Each measured value represents the average of three determinations.

The analytical results for the ammonium compounds are in very good agreement. The measured nitrogen contents of the binary nitrides are found to be slightly lower than the theoretical values, but the exact compositions of these materials as supplied are known with less certainty. The results obtained for LaVO_{3-x}N_x are in the range of values previously reported [6].

2.4. Characterization

Phase identification was carried out by powder X-ray diffraction using a Scintag XDS 2000 machine, Cu K α radiation and a solid state detector. Magnetic susceptibility measurements were made from 2 to 10 K using a Quantum Design SQUID (superconducting

TABLE 1. Nitrogen determinations

Standard	Theoretical N%	Measured N%
(NH ₄) ₂ SO ₄	21.20	20.90
NH ₄ VO ₃	11.97	11.75
TiN	22.66	21.99
VN	21.57	20.33
LaVO _{3-x} N _x	–	2.89 (x=0.49)

quantum interference device) magnetometer. Measurements were made at 8 Oe.

3. Results and discussion

3.1. Reduction of A₂V₂O₇ and A₃V₂O₈ phases in hydrogen

For comparison with the corresponding reactions in ammonia, the reduction reactions of the A₂V₂O₇ and A₃V₂O₈ phases in 5% H₂ in nitrogen were investigated by thermogravimetric analysis (TGA). The expectation from at least some literature reports was that the reduction reactions would lead straightforwardly to the formation of either perovskite phases of general composition AVO_{3-x} or to the Ruddlesden and Popper phases A₃V₂O₇. The reactions are more complex, however, and ambiguities exist in the published literature. Our results resolve some of these discrepancies and provide insight into the reactions of the same phases with ammonia.

TGA data for the A₂V₂O₇ phases in hydrogen are compared in Fig. 1. The results for A≡Ca are the simplest. Thermogravimetric reduction of Ca₂V₂O₇ in 5% H₂ gives an overall weight loss of 6.67% at 1038 °C, corresponding to the loss of 1.23 oxygen atoms per formula unit (1.23O). The X-ray diffraction data of the residue from the thermogravimetric analysis show that the phase formed is CaVO_{3-x} with a distorted perovskite structure and lattice parameters very similar to those reported for a CaVO₃ phase prepared at high pressure [24]. The observed weight loss corresponds to the formula CaVO_{2.89}. In the reduction of Ca₂V₂O₇ at lower temperature (600 °C for 8 h), Ca₃V₂O₈ is observed as an intermediate.

Thermogravimetric reduction of Ca₃V₂O₈ (5 °C min⁻¹ to 986 °C, 3 h at 986 °C) gave a weight loss of 5.41%

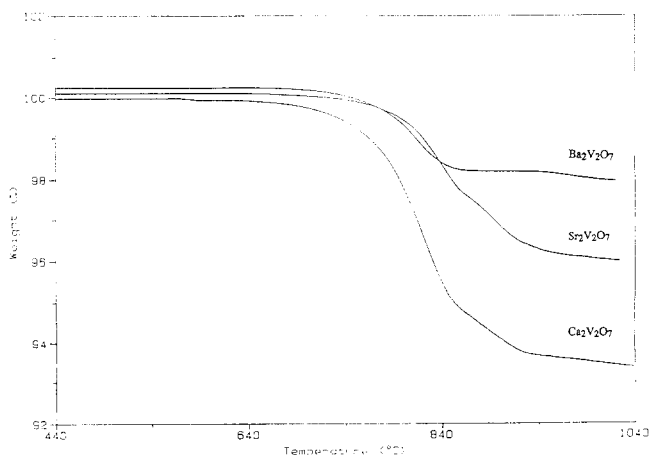


Fig. 1. Thermogravimetric reduction of A₂V₂O₇ (A≡Ca, Sr, Ba) phases in 5% H₂ at 5 °C min⁻¹. The curves for A≡Sr, Ba have been offset by 0.2% for clarity.

(1.18O) and the X-ray diffraction pattern of the residue showed the presence of CaO in addition to CaVO_{3-x}. The weight loss indicates a composition for the perovskite phase of CaVO_{2.91}, similar to that observed in the Ca₂V₂O₇ reduction.

The behavior of the strontium system is more complex and literature reports disagree significantly. Chamberland and Danielson synthesized SrVO₃ by reaction of SrO and VO₂ under pressure in a sealed system at 1000 °C and reported the formation of a metallic cubic perovskite phase with $a = 3.8424 \text{ \AA}$ [24]. Reduction in hydrogen of Sr₂V₂O₇, however, apparently gave different results. Reduction in 100% H₂ at 800 °C [25] gave a phase with composition SrVO₃ but with additional lines in the diffraction pattern which could not be indexed on the simple cubic cell previously reported [24]. In a parallel study the reduction of Sr₂V₂O₇ was measured thermogravimetrically also in 100% H₂ [26]. An intermediate phase with composition Sr₆V₆O₁₉ to Sr₈V₈O₂₅ was observed between 580 and 630 °C in the reduction reaction. The final product above 820 °C was SrVO₃. The intermediate phase has lattice constants closely related to those of Sr₃V₂O₈. In a more recent study the thermogravimetric results [26] were closely reproduced [17]. A cubic SrVO_{2.88} phase was observed after reduction in 100% H₂ for 24 h but the nature of the intermediate phase was not discussed. However, it was noted that reduction of Sr₂V₂O₇ in H₂ at 1000 °C for shorter times (1 h) gave a product containing Sr₃V₂O₈ in addition to SrVO_{2.88}. In other recent studies, SrVO₃ with $a = 3.842 \text{ \AA}$ was synthesized by reduction in a sealed tube at 1050 °C using a reduced titanium oxide to abstract oxygen [11] and pure cubic SrVO_{2.84} with a cell constant of 3.849 Å was prepared by reduction in hydrogen at 1300 °C [12].

Our experiments in 5% H₂ are consistent with those of Rey *et al.* [17]. Thermogravimetric reduction at a heating rate of 5 °C min⁻¹ shows an inflection in the weight loss curve at 832 °C (Fig. 1) rather than a plateau, presumably owing to the higher reduction temperature required in 5% than in 100% H₂. The overall weight loss at 1014 °C is 4.21% as expected for the formation of SrVO₃. However, the X-ray diffraction pattern of the residue clearly shows the presence of Sr₃V₂O₈ in addition to SrVO₃. The additional vanadium phase which must also be present could not be identified. In a thermogravimetric experiment in which the temperature was raised to 680 °C and then maintained for 5 h, the weight loss was 2.68% and the products were identified by X-ray diffraction as V₂O₃ and Sr₃V₂O₈ (the theoretical weight loss for this reaction is 2.74%). Further experiments in a flow reactor at 1000 °C initially for 20 h and then for a further 28 h showed a decrease in the amount of Sr₃V₂O₈ and a corresponding increase in the amount of SrVO₃ with increasing reaction time. However, even after 48 h the strong diffraction peaks

TABLE 2. Reactions of A₂V₂O₇ and A₃V₂O₈ phases with ammonia^a

Starting oxide	Reaction temperature (°C)	Reaction time ^b (h)	Weight loss (%)	Nitrogen content (%)	Experimental method	Phase(s) observed
Ca ₂ V ₂ O ₇	550	8	3.92	0.87	Flow	Ca ₃ V ₂ O ₈
	650	8	5.52	4.01	Flow	CaO, VN, Ca ₃ V ₂ O ₈ , CaVO ₃
	750	8	13.26	9.09	Flow	CaO, VN, Ca ₃ V ₂ O ₈ , CaVO ₃
	750	16	16.15	–	Flow	CaO, VN
	900	8	10.92	5.69	Flow	CaO, VN, CaVO ₃
	900	16	Pellet	–	Flow	CaO, VN, CaVO ₃
	1027	5 °C min ⁻¹	12.96	6.3	TGA	CaO, VN, CaVO ₃
Sr ₂ V ₂ O ₇	550	8	2.8	0.96	Flow	Sr ₃ V ₂ O ₈ , VN
	722	5 °C min ⁻¹ , 3	3.82	1.90	TGA	Sr ₃ V ₂ O ₈ , VN
	800	8	4.39	2.9	Flow	Sr ₃ V ₂ O ₈ , VN
	900	8	5.0	2.3	Flow	Sr ₃ V ₂ O ₈ , VN, SrVO ₃
	900	16	Pellet*	2.2	Flow	Sr ₃ V ₂ O ₈ , VN, SrVO ₃
	913	5 °C min ⁻¹ , 3	4.39	1.91	TGA	Sr ₃ V ₂ O ₈ , VN
	900 ^c	5 °C min ⁻¹ , 3	4.42	1.90	TGA	Sr ₃ V ₂ O ₈ , VN
Ba ₂ V ₂ O ₇	800	8	3.26	2.11	Flow	Ba ₃ V ₂ O ₈ , VN
	900	8	–	2.10	Flow	Ba ₃ V ₂ O ₈ , VN
	900	16	Pellet*	2.07	Flow	Ba ₃ V ₂ O ₈ , VN
	1019	5 °C min ⁻¹	3.54	2.03	TGA	Ba ₃ V ₂ O ₈ , VN
	1126 ^c	5 °C min ⁻¹	3.51	2.27	TGA	Ba ₃ V ₂ O ₈ , VN
Ca ₃ V ₂ O ₈	750	8	2.70	2.14	Flow	CaO, VN, unreduced oxides
	900	8	11.06	6.19	Flow	CaO, VN, CaVO ₃
Sr ₃ V ₂ O ₈	900	8	0.33	~0	Flow	Sr ₃ V ₂ O ₈
	1000	8	0.36	~0	Flow	Sr ₃ V ₂ O ₈
	1000	16	2.59	1.77	Flow	Sr ₃ V ₂ O ₈ , SrO, VN

^aHeating rate 10 °C min⁻¹, P_{NH₃} = ½ atm; ^bIn TGA experiments the heating rate to and the time held at the final temperatures are reported; ^cSample reduced in hydrogen for 3 h at 900 °C prior to reaction with NH₃* see text.

of Sr₃V₂O₈ were still visible. The results indicate that the reduction of Sr₂V₂O₇ in H₂ proceeds via initial formation of Sr₃V₂O₈ and V₂O₃. With increasing temperature, further reduction and reaction occur ultimately leading to the formation of SrVO_{3-x}. The overall reaction is slow presumably because recombination of two separate phases is required. In a separate experiment, thermogravimetric reduction of Sr₃V₂O₈ in 5% H₂ gave only a very small weight loss (0.2% or less).

The results for the reduction of Ba₂V₂O₇ are generally similar to the Sr₂V₂O₇ data. The weight loss observed by thermogravimetric analysis at 1010 °C is 2.43%, to be compared with the theoretical weight loss of 2.18% for formation of Ba₃V₂O₈ and V₂O₃. Above 919 °C further reduction of V₂O₃ occurs (see Fig. 1). Previous results reporting the formation of BaVO₃ by hydrogen reduction also appear to have led to the formation of Ba₃V₂O₈ [25]. BaVO₃ with a hexagonal perovskite-related (14H) polytype structure rather than the cubic perovskite structure was synthesized by high pressure reaction of BaO and VO₂ [24].

It is interesting to note that catalytic studies of the oxidative dehydrogenation of butane using MgO–V₂O₅ catalysts show that Mg₃V₂O₈ does not reduce at 600 °C [27].

3.2. Reaction of A₂V₂O₇ and A₃V₂O₈ phases with ammonia

Reactions of ammonia with the compounds A₂V₂O₇ (A ≡ Ca, Sr, Ba) and A₃V₂O₈ (A ≡ Ca, Sr) were investigated by thermogravimetric analysis and in a flow reactor. Reaction conditions, products, weight losses and nitrogen contents determined by chemical analysis are summarized in Table 2. A comparison of the reactivity of A₂V₂O₇ (A ≡ Ca, Sr, Ba) is shown in Fig. 2.

3.2.1. Ca₂V₂O₇ and Ca₃V₂O₈

Two distinct reaction pathways were observed in the reaction of Ca₂V₂O₇ with ammonia. When the temperature was raised to above 900 °C at 5 or 10 °C min⁻¹, the reaction proceeded in two steps. The first step corresponds to the formation of Ca₃V₂O₈ and VN and the second to the conversion of Ca₃V₂O₈ to CaVO_{3-x} and CaO. The final products of the reactions carried out in TGA experiments or by reaction at 900 °C in a flow reactor are CaO, VN and CaVO_{3-x}. The observed nitrogen contents and weight losses (Table 2) are close to the values calculated for the formation of an equimolar mixture of CaO, VN and CaVO₃ (5.38% N content and 11.60% weight loss).

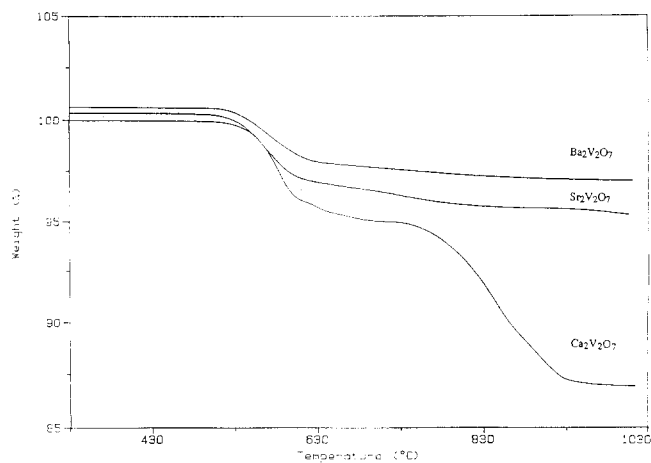


Fig. 2. Thermogravimetric reduction of $A_2V_2O_7$ ($A \equiv Ca, Sr, Ba$) phases in NH_3 at $5\text{ }^\circ\text{C min}^{-1}$. The curves for $A \equiv Sr, Ba$ have been offset by 0.2% for clarity.

Reactions carried out at lower temperatures (below $750\text{ }^\circ\text{C}$) apparently follow a different pathway. Examination of the diffraction patterns of the products formed in the flow reactor at temperatures below $750\text{ }^\circ\text{C}$ and under isothermal conditions in the thermogravimetric analyzer shows that $Ca_3V_2O_8$ is formed initially but that complete conversion to CaO and VN can occur. Reactions in the flow reactor at 550 and $650\text{ }^\circ\text{C}$ and in the thermogravimetric analyzer at $535\text{ }^\circ\text{C}$ clearly show the presence of VN and $Ca_3V_2O_8$ together with other products. At $750\text{ }^\circ\text{C}$ after 8 h of reaction the products are $VN, CaO, CaVO_3$ and $Ca_3V_2O_8$. After reaction at the same temperature for 16 h the X-ray diffraction data indicate complete conversion to CaO and VN . The analytical data suggest that a small amount of unreacted oxide remains. Diffraction patterns of the products of the two different pathways are shown in Fig. 3.

Reactions of $Ca_3V_2O_8$ at 750 and $900\text{ }^\circ\text{C}$ result in the formation of the phases anticipated from the data for $Ca_2V_2O_7$ (see Table 2).

3.2.2. $Sr_2V_2O_7$ and $Sr_3V_2O_8$

Thermogravimetric data for the reaction of $Sr_2V_2O_7$ in ammonia are shown in Fig. 2. The onset temperature for reduction is found to be comparable with that observed for the reactions of the other two alkaline earth metal vanadates. After reaction at $800\text{ }^\circ\text{C}$ for 8 h the only products detected by X-ray diffraction were $Sr_3V_2O_8$ and VN . The observed weight loss (4.39%) and the nitrogen content (2.9%) are close to the theoretical values for this reaction (4.45% weight loss and 2.5% nitrogen content). The X-ray diffraction pattern of the product is shown in Fig. 4(a). In reactions at lower temperatures, however, both the weight losses and the nitrogen contents of the products are lower

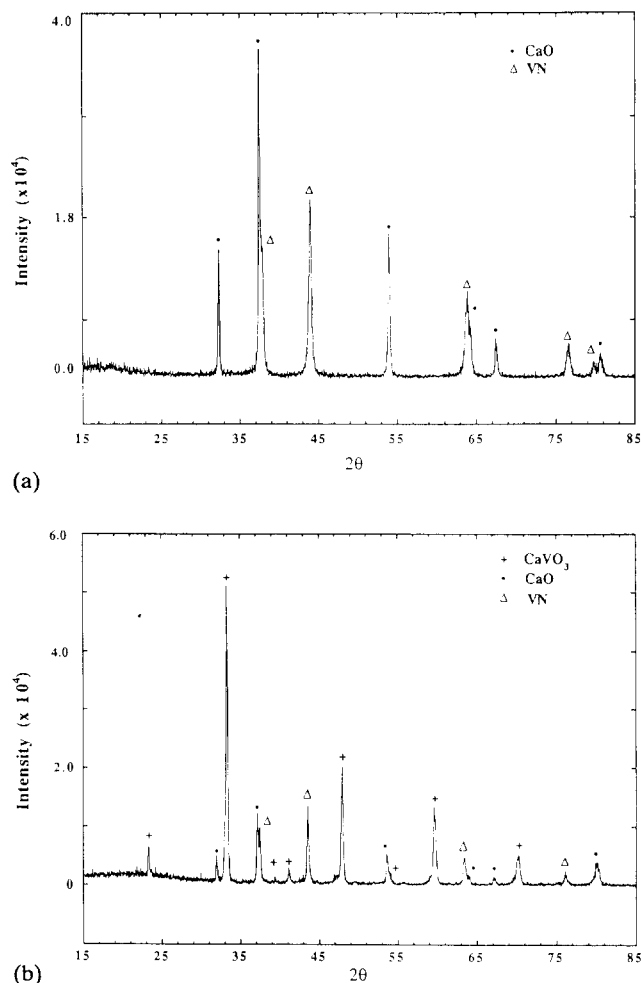


Fig. 3. Powder X-ray diffraction patterns of products of reactions of $Ca_2V_2O_7$ with ammonia at (a) $750\text{ }^\circ\text{C}$, 16 h and (b) $900\text{ }^\circ\text{C}$, 8 h.

than the theoretical values, presumably owing to the presence of a reduced vanadium oxide phase not detected by X-ray diffraction.

At $900\text{ }^\circ\text{C}$ for short reaction times (3 h, TGA) the weight losses are close to theoretical but the nitrogen contents are lower, again suggesting the presence of a reduced but not nitrated vanadium oxide phase. Longer reaction times give higher nitrogen contents but also indicate the formation of $SrVO_3$ (Fig. 4(b)). At higher temperatures the overall reaction represents a combination of hydrogen reduction and the nitridation reaction, presumably as a consequence of the higher degree of ammonia dissociation [28].

Reduction of $Sr_2V_2O_7$ in 5% H_2 at $1000\text{ }^\circ\text{C}$ to give a mixture of $Sr_3V_2O_8$ and $SrVO_3$ followed by reaction in ammonia as a second step was also studied. The final products were the same as those observed in the direct reactions at similar temperatures, *i.e.* $Sr_3V_2O_8$ and VN at about $800\text{ }^\circ\text{C}$ and $Sr_3V_2O_8, SrVO_3$ and VN at $900\text{ }^\circ\text{C}$. This result suggests that at lower temperatures

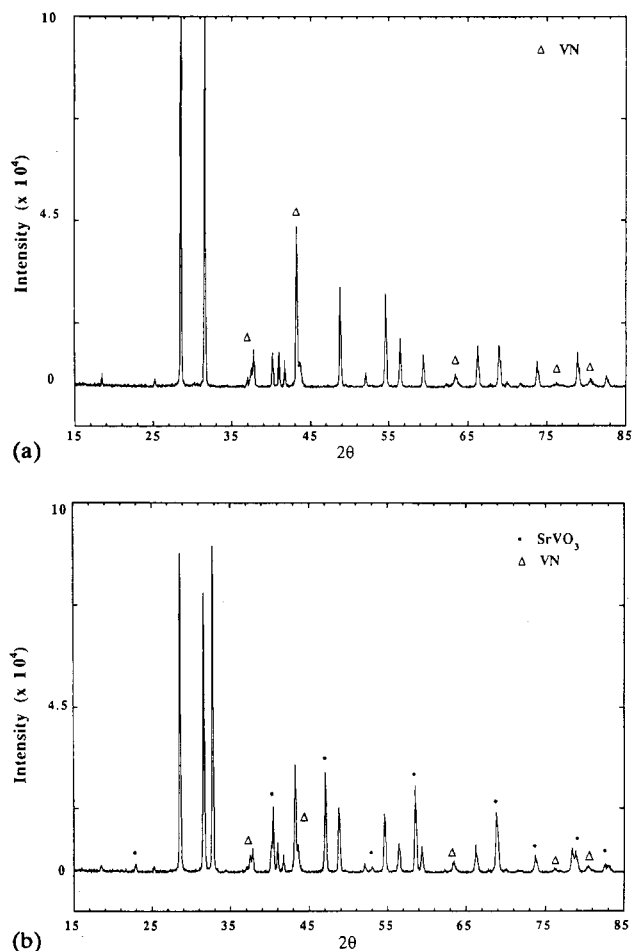


Fig. 4. Powder X-ray diffraction patterns of products of reactions of $\text{Sr}_2\text{V}_2\text{O}_7$ with ammonia at (a) 800 °C, 8 h and (b) 900 °C, 16 h. All unlabelled peaks correspond to $\text{Sr}_3\text{V}_2\text{O}_8$.

SrVO_3 also reacts with ammonia to give $\text{Sr}_3\text{V}_2\text{O}_8$ and VN.

As anticipated, $\text{Sr}_3\text{V}_2\text{O}_8$ is significantly more stable than $\text{Sr}_2\text{V}_2\text{O}_7$ in ammonia. A small amount of reduction is observed by weight change after 8 h in ammonia at 900 °C but there is no apparent change in the X-ray powder pattern. At 1000 °C after 8 h some small changes appear in the diffraction pattern, but after 16 h partial decomposition into SrO and VN is clearly observed.

3.2.3. $\text{Ba}_2\text{V}_2\text{O}_7$

The reaction of $\text{Ba}_2\text{V}_2\text{O}_7$ with NH_3 is generally similar to that of $\text{Sr}_2\text{V}_2\text{O}_7$. The weight changes and the nitrogen contents are very similar for all samples prepared in the flow reactor or thermogravimetrically. The reaction products are VN and $\text{Ba}_3\text{V}_2\text{O}_8$ in all cases (Fig. 5). Reduction of $\text{Ba}_2\text{V}_2\text{O}_7$ in H_2 followed by reaction in ammonia gives identical products. No evidence is observed for the formation of BaVO_3 with the 14H hexagonal structure [24]. Reactions of $\text{Ba}_3\text{V}_2\text{O}_8$ were

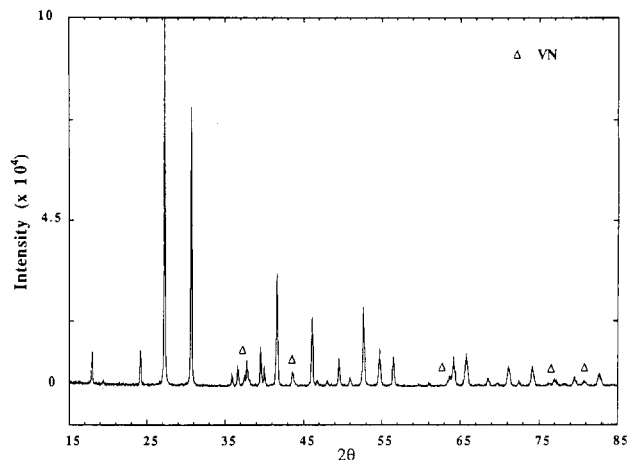


Fig. 5. Powder X-ray diffraction patterns of products of reaction of $\text{Ba}_2\text{V}_2\text{O}_7$ with ammonia at 900 °C, 16 h. All unlabelled peaks correspond to $\text{Ba}_3\text{V}_2\text{O}_8$.

not studied because of the anticipated greater difficulty of reduction relative to $\text{Sr}_3\text{V}_2\text{O}_8$.

Magnetic susceptibility measurements were made on samples prepared by reacting pressed pellets of $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Ba}_2\text{V}_2\text{O}_7$ at 900 °C for 16 h in ammonia (marked by * in Table 2). The magnetic data show the presence of the same superconducting phase in each sample. The measured T_c in both cases is 7.5 K, which is the value previously reported for vanadium nitride with the composition $\text{VN}_{0.97}$ [29]. The results confirm the existence of $\text{VN}_{0.97}$ in both products, in agreement with the X-ray results.

4. Conclusions

Reduction and nitriding reactions of all the $\text{A}_2\text{V}_2\text{O}_7$ phases proceed through the formation of an intermediate $\text{A}_3\text{V}_2\text{O}_8$ phase. The specific details depend on the ease with which the $\text{A}_3\text{V}_2\text{O}_8$ phases are converted thereafter to other product phases. In the case where $\text{A} \equiv \text{Ba}$ the reactions are particularly simple, because $\text{Ba}_3\text{V}_2\text{O}_8$ is very difficult either to reduce or to convert to a nitride-containing phase. The products observed are $\text{Ba}_3\text{V}_2\text{O}_8$ and VN or VO_x in the case of reactions in ammonia or hydrogen respectively. In contrast, reactions of $\text{Ca}_2\text{V}_2\text{O}_7$ are more complex, because $\text{Ca}_2\text{V}_2\text{O}_8$ when formed readily converts to other phases. In hydrogen CaVO_{3-x} is formed, whereas in ammonia the products are either CaO and VN or CaO, VN and CaVO_{3-x} depending on the conditions. Reactions of $\text{Sr}_2\text{V}_2\text{O}_7$ are as expected intermediate. In hydrogen the formation of cubic SrVO_{3-x} is slow and it is difficult to completely eliminate traces of $\text{Sr}_3\text{V}_2\text{O}_8$ in 5% H_2 at 1000 °C. In ammonia the reaction products are

similar to those formed by Ca₂V₂O₇ products, *i.e.* Sr₃V₂O₈ and VN below 800 °C, and SrO, VN and SrVO_{3-x} at 900 °C. The A₃V₂O₈ (A ≡ Sr, Ba) phases are very stable in both H₂ and NH₃; Ca₃V₂O₈ is less stable and converts to CaVO₃ and CaO in H₂. In ammonia CaO, CaVO₃ and VN are the reaction products at temperatures above 900 °C, whereas CaO and VN are formed at lower temperatures.

In conclusion, in contrast with rare earth vanadates, reactions of the alkaline earth metal vanadates with ammonia do not lead to the formation of oxynitride phases with perovskite-related structures.

Acknowledgments

This work was supported in part by the Robert A. Welch Foundation (Grant E-1207) and the Texas Center for Superconductivity at the University of Houston. One of us (H.-Zh. Li) thanks the CATIC Foundation for providing a visiting fellowship. The magnetic susceptibility data were provided by P.-H. Hor and H.-H. Feng.

References

- 1 R. Marchand, F. Pors and Y. Laurent, *Rev. Int. Hautes Temp. Refract. Fr.*, **23** (1986) 11.
- 2 R. Marchand, F. Pors and Y. Laurent, *Ann. Chim. Fr.*, **16** (1991) 553.
- 3 F. Pors, R. Marchand and Y. Laurent, *Ann. Chim. Fr.*, **16** (1991) 547.
- 4 V.A. Dolgikh and E.A. Lavut, *Russ. J. Inorg. Chem.*, **36** (1991) 1389.
- 5 P. Antoine, R. Marchand, Y. Laurent, C. Michel and B. Raveau, *Mater. Res. Bull.*, **23** (1988) 953.
- 6 P. Antoine, R. Assabaa, P. L'Haridon, R. Marchand, Y. Laurent, C. Michel and B. Raveau, *Mater. Sci. Eng. B*, **5** (1989) 43.
- 7 P. Bacher, P. Antoine, R. Marchand, P. L'Haridon, Y. Laurent and G. Rault, *J. Solid State Chem.*, **77** (1988) 67.
- 8 S.H. Elder, L.H. Doerr, F.J. DiSalvo, J.B. Parise, D. Guyomard and J.M. Tarascon, *Chem. Mater.*, **4** (1992) 928.
- 9 G. Liu, X. Zhao and H.A. Eick, *J. Alloys Comp.*, **187** (1992) 145.
- 10 M. Cyrot, B. Lambert-Andron, J.L. Soubeyroux, M.J. Rey, Ph. Dehaut, F. Cyrot-Lackmann, G. Fourcaudot, J. Beille and J.L. Tholence, *J. Solid State Chem.*, **85** (1990) 321.
- 11 A. Nozaki, H. Yoshikawa, T. Wada, H. Yamauchi and S. Tanaka, *Phys. Rev. B*, **43** (1991) 181.
- 12 N. Suzuki, T. Noritake, N. Yamamoto and T. Hioki, *Mater. Res. Bull.*, **26** (1991) 1, 75.
- 13 S. Takeno, S.-I. Nakamura, T. Nomaki, N. Fukushima and K. Ando, *J. Solid State Chem.*, **94** (1991) 432.
- 14 N. Ohashi, Y. Teramoto, H. Ikawa, O. Fukunaga and J. Tanaka, *J. Solid State Chem.*, **97** (1992) 434.
- 15 T. Shin-ike, T. Sakai, G. Adachi and J. Shiokawa, *Mater. Res. Bull.*, **11** (1976) 249.
- 16 S. Takeno, S.-I. Nakamura, N. Fukushima and K. Ando, *J. Alloys Comp.*, **187** (1992) 31.
- 17 M.J. Rey, Ph. Dehaut, J.C. Joubert, B. Lambert-Andron, M. Cyrot and F. Cyrot-Lackmann, *J. Solid State Chem.*, **86** (1990) 101.
- 18 M.P. Clement and J. Rodden, in *National Nuclear Energy Series, Tech. Sec., Div. VIII, Vol. 1. Analytical Chemistry of The Manhattan Project*, McGraw-Hill, New York, 1950, p. 208.
- 19 R.B. Bradstreet, *Anal. Chem.*, **26** (1954) 185.
- 20 R. Marchand, P. Antoine, P. L'Haridon and Y. Laurent, *Eur. Patent Appl. EP 286,503*, 1988; *Fr. Patent Appl. 87/4,287*, 1987.
- 21 J. Guyader, F.F. Grekov, R. Marchand and J. Lang, *Rev. Chim. Minér.*, **15** (1978) 431.
- 22 Y. Furukawa and N. Sera, *Jpn. Kokai Tokkyo Koho 79, 44,590*, 1979, p. 631.
- 23 W.K. Ham, G.F. Holland and A.M. Stacey, *J. Am. Chem. Soc.*, **110** (1988) 5214.
- 24 B.L. Chamberland and P.S. Danielson, *J. Solid State Chem.*, **3** (1971) 243.
- 25 T. Palanisamy, J. Gopalakrishnan and M.V.C. Sastri, *Z. Anorg. Allg. Chem.*, **415** (1975) 275.
- 26 Von A. Feltz and S. Schmalfus, *Z. Anorg. Allg. Chem.*, **417** (1975) 137.
- 27 M.A. Chaar, D. Patel, M.C. Kung and H.H. Kung, *J. Catal.*, **105** (1987) 483.
- 28 M. Katsura, *J. Alloys Comp.*, **182** (1992) 91.
- 29 F.I. Ajami and R.K. MacCrone, *J. Phys. Chem. Solids*, **36** (1975) 7.