

A Study on the Preparation and Physical Property Determination of NaVO_2

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Received April 6, 1987; in revised form September 14, 1987

Stoichiometric and near-stoichiometric NaVO_2 phases have been prepared by the hydrogen reduction of NaVO_3 or mixtures of Na_2CO_3 and V_2O_5 at 650°C . The black reduction products react instantly with air to generate nonstoichiometric Na_xVO_2 phases with the formation of NaOH . Stoichiometry of the compound could be maintained by working in a dry box under a gettered argon atmosphere. Pure NaVO_2 was characterized by X-ray diffraction studies, thermoanalytical methods, and magnetic measurements. The semireversible crystallographic transition was noted at 115°C by means of a differential scanning calorimetry experiment. This transition, however, is very weak and quite broad. At room temperature, NaVO_2 appears to be orthorhombic, but above the transition temperature, it adopts the $\alpha\text{-NaFeO}_2$ structure. The magnetic properties indicate a moderate interaction between vanadium centers which reduces the overall magnetic moment to a value of approx $1.2 \mu\text{B}$, a moment which is much lower than that expected for the spin-only moment for trivalent vanadium. © 1988

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Introduction

In a continuing study of ternary oxides containing the V^{3+} ion, a reinvestigation of the compound NaVO_2 was carried out. This compound was first reported in 1954-1956 (1-3). A brief report on its magnetic properties was presented in a thesis (4) in 1957. The compound remained unstudied for several years until a careful thermodynamic study was carried out by Barker and Hooper in 1973 (5-7). This compound was of interest to us since we recently reported the synthesis, structure, and physical properties of the lithium analog, LiVO_2 (8, 9). The objectives of this investigation were to

synthesize pure NaVO_2 and to determine its physical and chemical properties.

Experimental

Reagents

The reactants used in this study were all reagent-grade chemicals which were further examined by X-ray diffraction prior to use. The NaVO_3 from Fisher Scientific Co., with the label $\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$, was found to be pure $\alpha\text{-NaVO}_3$ (by X-ray analysis and thermogravimetric analysis (TGA) showed less than a 6% weight loss between room temperature and 150°C). Reagent-grade Na_2CO_3 and V_2O_5 were used as received. Purified sodium orthovanadate, Na_3VO_4 , was obtained from Matheson, Coleman & Bell Co.

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Synthesis

Several techniques were used to prepare the NaVO_2 compound. The reduction of $\alpha\text{-NaVO}_3$ or stoichiometric mixtures of Na_2CO_3 and V_2O_5 in a H_2/Ar atmosphere (1:10 volume ratio) was utilized. This method led to the purest product. At a reaction temperature of $<600^\circ\text{C}$, incomplete reaction between H_2 and NaVO_3 was observed as revealed by X-ray diffraction on the products. At a temperature of $>750^\circ\text{C}$, decomposition occurred with the formation of V_2O_3 and Na_2O (which slowly volatilized). The optimal time and temperature conditions for the reduction of NaVO_3 with hydrogen were found to be 650°C and 18–24 hr for a 3- to 5-g sample of the oxide-carbonate mixture.

The reaction vessel was also an important factor in the isolation of a pure product. A platinum boat was found to be superior to a ceramic (Al_2O_3 or ZrSiO_4) vessel. The reaction of hydrogen and/or Na_2O with the ceramic boats was quite pronounced. An attempt to reduce Na_3VO_4 under the optimal conditions given above failed to produce any NaVO_2 , the reactant was recovered unchanged.

A stoichiometric mixture of well-mixed Na_2CO_3 and V_2O_5 in a platinum cylinder, contained in a fused-silica tube, was heated to 650°C in a vacuum system to decompose the carbonate. The oxide mixture was then further heated to 750°C for 4 hr. The fused silica tube was then sealed under vacuum. The twin assembly was heated to 750°C for 4 days then quenched to room temperature. Na_2O was found to have escaped from the reaction mixture and/or product. This oxide then reacted vigorously with the fused-silica tube. The reaction product within the platinum cylinder was found to be heterogeneous by microscopic examination. This product was also highly reactive with water or methanol, indicative of Na_2O formation.

It was noticed that freshly prepared

NaVO_2 was highly reactive, gaining weight on exposure to air, and that it released a considerable amount of heat when placed in water or methanol. The formation of NaOH or its hydrate is highly evident when the pure samples are exposed to air. Evidence for the presence of water was obtained from the differential scanning calorimetry (DSC) and TGA experiments conducted on air-exposed products, whereas X-ray diffraction studies indicated the presence of V_2O_3 .

The electrolytic reductions of $\alpha\text{-NaVO}_3$ or mixtures of Na_2CO_3 and V_2O_5 in fused alkali halides were carried out in SiC crucibles at 750°C with carbon electrodes at 3.0 V and currents of the order of 1 to 3 A. The only products isolated, after water treatment, were black flakes which were found to be pure V_2O_3 . In one experiment where the current was very low (approx 50 mA), black crystals of $\text{Na}_x\text{V}_2\text{O}_5$ were formed and identified by X-ray powder diffraction. The unit cell parameters determined for these crystals were: $a = 4.779(3)$, $b = 11.296(8)$, and $c = 3.605(2)$ Å. These parameters would indicate that the value of x in the general formula presented above is approximately one.

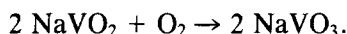
Analyses

Characterization methods included X-ray diffraction, TGA, DSC, and magnetic susceptibility measurements. A high-temperature X-ray camera (Central Research Laboratories, Inc.) was used to obtain the powder diffraction patterns of polycrystalline samples above and below the transition temperature which had been previously reported (4, 6). The source used in all the X-ray experiments was averaged, Ni-filtered, $\text{CuK}\alpha$ radiation. The thermal analyzer was a DuPont Model 990 unit and the magnetic data were obtained by the Faraday method using a Cahn microbalance. The magnetic apparatus was calibrated with a $\text{HgCo}(\text{SCN})_4$ reference standard. Temperature

and diamagnetic core corrections were made.

Results

Many difficulties were encountered in the synthesis of pure NaVO_2 and also during the characterization procedures in which the products were exposed to air (even for a short period of time). Most of the oxidations carried out in the thermal balance in air or flowing oxygen led to significantly low values for oxidation, indicative of an already higher oxidation state for vanadium in our samples. Typically a weight increase of only 5 to 10% was observed for the air-exposed samples. Furthermore these samples were also found to change color from black to a gray-white solid in air and the process was accompanied by a threefold increase in volume. The theoretical weight gain expected for stoichiometric NaVO_2 is 15.10%. The chemical equation for the oxidation of NaVO_2 is



In the later stages of our studies, where the products were maintained in a dry-argon atmosphere, weight gain results indicated an increase of 14.9%. The thermogram showed a strong exothermic change at 520°C followed by a gradual weight increase at 750°C where the oxidation was complete. A typical TGA thermogram is

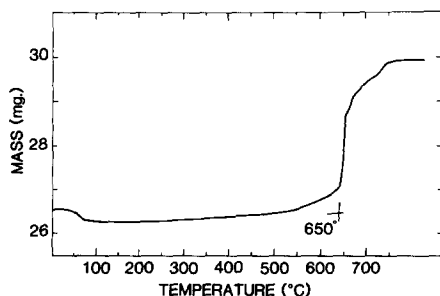


FIG. 1. A thermogravimetric analysis profile of NaVO_2 in an oxygen atmosphere.

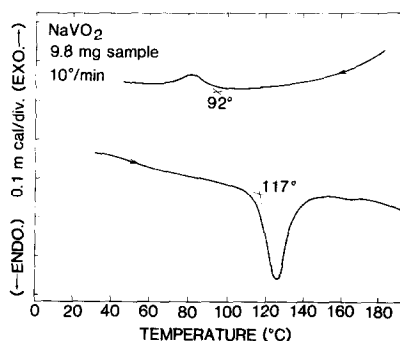


FIG. 2. A differential scanning calorimeter scan of NaVO_2 in a gettered argon atmosphere.

shown in Fig. 1. The yellow TGA residue, which had undergone a fusion, was observed by X-ray studies to be pure $\alpha\text{-NaVO}_3$.

An objective of this investigation was to determine more precisely the transition temperature noted by Barker and Hooper (6) at "ca. 200°C." A sluggish transition in NaVO_2 was noted in both the work of Bongers (4) and that of Barker and Hooper (6). In our DSC studies, utilizing the purest sample, NaVO_2 showed a weak, broad, semireversible transition at 115°C. The energy involved in this transition was of the order of 65 cal/mole. On cooling, a broad and very weak exothermic peak was observed at 95°C. The DSC scan of pure NaVO_2 , contained in sealed double pans, was carried out in an argon or dry-nitrogen atmosphere and the results are shown in Fig. 2.

The X-ray diffraction experiments at room temperature generally yielded broad-lined patterns which indicated poor crystallinity; similar results have been previously noted by other investigators (5-7). To prevent oxidation during the X-ray experiment all samples were loaded in glass capillaries inside a dry box then sealed in the absence of air. For the high-temperature X-ray experiments, quartz capillaries were used. The patterns obtained at room temperature

could not be indexed on a monoclinic basis (that observed for the ambient-temperature form of NaNiO₂ (10)). A study of the observed and reported room-temperature powder data was carried out using the Louër indexing program (11). One possible assignment was obtained from the trial program which indicated an orthorhombic cell. The unit cell parameters generated by this computer program were: $a = 9.034$, $b = 7.198$, and $c = 5.386$ Å. Successful indexing of Barker and Hooper's room-temperature data and that obtained in this study was achieved using this cell. The results of a least-squares refinement on the room temperature powder data are given in Table I.

The high-temperature X-ray powder diffraction data (at 200 and 250°C), were readily indexed based on the hexagonal α -

TABLE I
CRYSTALLOGRAPHIC UNIT CELL PARAMETERS FOR
THE ROOM-TEMPERATURE FORM OF NaVO₂

a (Å)	b (Å)	c (Å)	Vol. (Å ³)	Reference
9.074(6)	7.184(2)	5.375(2)	350.4(2)	Data from (7)
9.099(4)	7.163(8)	5.386(9)	351.1(6)	This work
9.027(13)	7.162(7)	5.375(9)	347.5(6)	This work
9.044(5)	7.173(7)	5.333(4)	346.0(4)	This work

Observed and calculated d spacings for an indexed powder diffraction pattern of NaVO₂

h	k	l	I (obs.)	d (obs.)	d (calc.)
1	1	0	20	5.617	5.620
0	0	1	70	5.316	5.333
2	2	0	15	2.808	2.810
0	0	2	30	2.681	2.667
1	0	2	15	2.555	2.558
3	1	1	50	2.467	2.465
0	3	1	100	2.180	2.182
4	0	2	25	1.721	1.725
1	1	3	25	1.695	1.695
2	4	1	75	1.589	1.591
3	1	3	40	1.500	1.498
1	5	1	15	1.371	1.369
0	1	4	20	1.309	1.311
7	1	1	30	1.236	1.237
8	1	1	20	1.093	1.093
7	0	3	20	1.052	1.045
8	2	2	25	1.000	0.9996

Note. Doublet (5.5 Å) peaks observed in the powder pattern. The numbers in parentheses, here and elsewhere in the text, are estimated standard deviations in the last quoted decimal place.

TABLE II
CRYSTALLOGRAPHIC UNIT CELL PARAMETERS FOR
THE HIGH-TEMPERATURE FORM OF NaVO₂

Temp. (°C)	Hexagonal		Vol. (Å ³)	Rhombohedral		Reference
	a (Å)	c (Å)		a (Å)	α (°)	
200	2.86	17.0	120.4	—	—	(1)
200	3.00	16.30	127.0	—	—	(7)
200	2.995(2)	16.29(1)	126.6	5.700	30.46	This work
250	2.992(2)	16.24(1)	125.9	5.684	30.52	This work

Note. Rhombohedral α -NaFeO₂ structure. Hexagonal and rhombohedral parameters are given.

NaFeO₂ structure. The refined hexagonal parameters (from the 250°C data) are: $a = 2.992(2)$ and $c = 16.24(1)$ Å; unit cell volume = 125.9(1) Å³. The parameters for our observed results and those reported in the literature are presented in Table II.

It should be noted that the hexagonal c/a ratio is quite large, as in the case of LiVO₂, and not consistent with the normal c/a ratios observed for other compounds with the α -NaFeO₂ structure. The calculated c/a ratio from our data at 200°C is 5.44; the typical value for other sodium compounds with this structure is approx 5.3, and therefore this ratio represents a much larger unit cell.

The magnetic data taken on both air-exposed and argon-protected samples of NaVO₂ showed paramagnetic behavior in the range 80–600 K. The air-exposed material, however, had a magnetic moment of only 0.8 μ B in the low-temperature region of 80–300 K. A relatively pure sample of NaVO₂, which has handled under argon, showed a slightly higher magnetic moment (0.9 μ B) at room temperature and exhibited a magnetic transition at approximation 125°C, where the magnetic moment gradually increased to 1.2 μ B. On cooling and recycling, a transition was observed but the magnetic moment was once again reduced, possibly the result of some oxidation of V³⁺. The various heat cycles in the magnetic experiment are shown in Fig. 3.

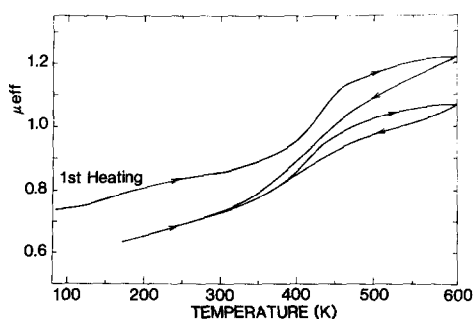


FIG. 3. The effective magnetic moment of NaVO_2 as a function of temperature (K). The arrows indicate the results obtained during the two heating and cooling cycles.

An electrochemical reduction and oxidation on stoichiometric NaVO_2 was carried out by Dr. J.-M. Tarascon of Bell Communications Research Lab. The data showed that the material could not be further reduced (increasing x in the formula Na_xVO_2) at 0.5 V. The compound, however, can be oxidized (charged in the electrochemical cell) but undergoes a nonreversible decomposition to a stable phase where the value of x in Na_xVO_2 is approximately 0.6. At this composition the oxidized phase is highly stable and cannot be further reduced or oxidized. The X-ray of the "charged" product was quite different from that of the starting material. The strong doublet present in pure NaVO_2 converges into a single peak in the same region of the X-ray pattern for $\text{Na}_{0.6}\text{VO}_2$. Similar X-ray patterns were also observed on air-exposed products. These powder diffraction patterns (oxidized phases) could be indexed on the NaMoO_2 basis (the $\alpha\text{-NaFeO}_2$ structure) but showed different unit cell parameters than those obtained for the high-temperature form of stoichiometric NaVO_2 (see Table III). The powder pattern for oxidized $\text{Na}_{0.6}\text{VO}_2$ is remarkably similar to that of V_2O_3 and the high-temperature form of NaVO_2 ; portions of all three powder patterns are reproduced in Table IV for comparison.

TABLE III
CRYSTALLOGRAPHIC UNIT CELL PARAMETERS FOR
THE PARTIALLY OXIDIZED NaVO_2

Remarks	a (Å)	c (Å)	Vol. (Å ³)
Exposed to air for 1 week	2.872(3)	16.96(4)	121.2(4)
After magnetic experiment	2.859(10)	17.13(9)	121.3(1.0)

Note. Singlet (5.3 Å) peak in powder pattern. Rhombohedral $\alpha\text{-NaFeO}_2$ (or NaMoO_2) structure type. Hexagonal parameters are given.

Discussion

The synthesis of NaVO_2 was found to be most difficult in that the normal ceramic-type methods of preparation led to a product which appeared to be the stoichiometric product, but this material instantaneously and irreversibly reacted with air to yield an oxidized product. The air sensitivity of this compound was heretofore not mentioned in the literature and is quite pronounced in comparison to the lithium analog recently described (9). This air instability was not

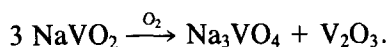
TABLE IV
COMPARISON OF THE X-RAY DATA OF V_2O_3
AND NaVO_2 HIGH-TEMPERATURE AND
OXIDIZED FORMS)

V_2O_3		NaVO_2 (at 200°C)		Oxidized form, Na_xVO_2	
d (Å)	I (rel.)	d (Å)	I (rel.)	d (Å)	I (rel.)
		5.440	55	5.626	100
3.658	71				
2.713	100	2.714	15	2.827	20
		2.564	12		
2.477	80	2.468	22	2.462	10
2.189	36	2.183	100	2.151	50
2.052	34	2.025	2	2.113	20
1.699	85	1.734	12	1.748	10
1.580	7	1.603	20	1.598	10
1.472	24	1.498	15		
1.430	31	1.445	5	1.435	25
1.332	14	1.378	5		

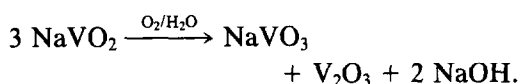
expected for such an oxide prepared at high temperature and it was a surprise to witness the decomposition of these compounds during the examination under the microscope. The necessity of handling all the freshly reduced products in an argon-filled dry box is imperative. The structure of NaVO₂ at room temperature appears to be distorted from that formed at high temperature. The simplified pattern for the high-temperature phase appears to be that of α -NaFeO₂, a rhombohedral structure based on the ordered sodium chloride cell wherein layers of sodium ions alternate with vanadium ions, all in octahedral interstices formed by the oxygen layers. The lower symmetry for the room-temperature phase could arise from V³⁺-V³⁺ interactions within the layers, as in LiVO₂. The transition is very sluggish and quite weak in comparison with the lithium-vanadium-oxide analog. The onset of transition appears to be at 115°C and is possibly not reversible. Continued cycling results in the loss of transition possibly caused by oxidation or decomposition. The exact structure of the room-temperature phase is unknown but it is not isostructural with α -NaNiO₂. The high-temperature phase appears to have the same rhombohedral structure as that of α -NaFeO₂. LiVO₂ and NaNiO₂ both transform to the α -NaFeO₂ structure at high temperature.

The low magnetic moment indicates that the V³⁺ ions, with a d^2 electronic configuration, have delocalized electrons which are involved in some type of metal-to-metal interaction. This interaction is not entirely eliminated at higher temperatures since the samples show augmented magnetic moments but these are also weaker (ca. 1.2 μ B) than that expected for a d^2 system ($\mu_s = 2.83 \mu$ B). The V-V internuclear distance in the high-temperature form of NaVO₂ is 2.99 Å, whereas the critical separation for V³⁺-V³⁺ in oxide compounds is calculated to be about 2.94 Å (12).

The chemistry involved in the air oxidation/decomposition of NaVO₂ is complex and can be described as partial oxidation and decomposition in terms of the following chemical equation:



Any Na₃VO₄ formed in the rearrangement reaction could not be further reduced in the H₂ reduction experiment, and this would generate low weight-gain values in the oxidation analysis. The antiferromagnetic V₂O₃ phase would yield low magnetic moments for impure samples in the magnetic experiment. A decomposition reaction can be presented if a partial oxidation and hydrolysis were to occur:



The presence of these products would once again account for the TGA and magnetic results obtained on the air-exposed samples of NaVO₂.

For the argon-protected NaVO₂ product, however, the TGA results are consistent with a stoichiometric compound. There could exist a solid solution series of the type: Na_xVO₂ or Na_xVO_{2+y}, which would complicate the results. This is probable since such a series was observed in the Na_xV₂O₅ system studied by Pouchard (13). The magnetic properties obtained on the compounds in that particular system also showed low magnetic moments, moments which were much lower than those expected for the presence of some V⁴⁺ (a d^1 ion).

Acknowledgment

S.K.P. would like to acknowledge participation in the NSF-Sponsored Multi-Institutional Summer Research Program in Solid State Chemistry during 1986.

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