Stabilization of V^{4+} State in Vanadium Compounds

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Abstract

Relative stabilities of various oxidation states and the importance of stabilizing low oxidation states of vanadium in its compounds are discussed. With a brief introduction to solid-state-reaction method of synthesizing vanadium compounds, prevalent techniques of stabilizing low oxidation states (V^{3+}, V^{4+}) are presented. The role of P-T-*x* diagrams in such synthesis is explained and discussed with specific reference to synthesis of lower-oxidation-state vanadium compounds. A novel route to synthesis of a V^{4+} compound is presented. Results of experimental work based on P-T-*x* diagrams with specific focus on successful synthesis of $Zn_2VO(PO_4)_2$ are presented.

Key words: Lower Oxidation State, Vanadium Compounds Refrigerants

1. Introduction

Vanadium oxides such as VO, VO_2, V_2O_3 1 are known to show metal-insulator transition property which has huge significance in electronic switching applications 2 while vanadium compounds such as CaV_2O_5 3, 4, α'-$Na_2V_3O_7$ 5, Li_2VOSiO_4 6, $Zn_2VO(PO_4)_2$ 7 are known to exhibit exotic magnetic properties. Magnetism in vanadium based compounds arises due to existence of one or more unpaired electrons in the outermost shell of vanadium ion. When a neutral atom of vanadium with electronic configuration [Ar] $3d^3 4s^2$ sheds its outermost electrons and becomes a vanadium 'ion' it can have a spin. Depending on the number of electrons removed, it can exist in three different oxidation states, V^{3+}, V^{4+} and V^{5+} with electronic configurations [Ar] $3d^2$, [Ar] $3d^1$ and [Ar] $3d^0$ respectively. Of the three, only V^{3+} and V^{4+} carry a spin and hence are magnetic. As there is no unpaired electron in V^{5+}, it is non-magnetic.

Compounds of vanadium are generally synthesized by solid-state-reaction method in which two or more oxides of constituent elements are mixed in a stoichiometric proportion and heated to a temperature high enough to facilitate the reaction between them and for duration long enough to take the reaction to completion. Since vanadium can exist in varying oxidation states, the stability of a given oxidation state is a strong function of oxygen partial pressure, $p[O_2]$, in which the reaction takes place. When the reaction is carried out in air, a vanadium 5+ state is stabilized.

Compounds with vanadium in lower oxidations states, such as V^{3+} and V^{4+} are less stable and hence the atmosphere in which the reaction is carried out needs to be controlled in terms of $p[O_2]$ during their synthesis. Once the compounds with desired oxidation state are formed, the metastable state can be retained upon cooling to room temperature provided the same $p[O_2]$ is maintained during cooling. The P-T-x diagrams of a system of oxides are good tools using which a suitable reaction environment can be predicted.

In this article, methods of synthesis of variable-oxidation-state vanadium compounds in general, and use of P-T-x diagrams in arriving at a new method for synthesis of a tetravalent vanadium compound, in particular, are discussed in detail. Experimental data proving the successful synthesis of $Zn_2VO(PO_4)_2$ based on this new method are also presented.

2. Experimental Procedure

The reaction to synthesize $Zn_2VO(PO_4)_2$ needs to be carried out in two steps. In the first step an intermediate compound *viz.*, $Zn_2P_2O_7$ is synthesized and in the second step VO_2 is added to it to obtain the title compound.

2.1. Synthesis of $Zn_2P_2O_7$

In the first step, an intermediate compound *viz.*, $Zn_2P_2O_7$ was synthesized using ZnO and $NH_4H_2PO_4$ as sources of Zn and P respectively. The reaction was carried out according to equation (1)

$$2ZnO\ (s) + 2NH_4H_2PO_4\ (s) \quad \rightarrow \quad Zn_2P_2O_7\ (s) + 2NH_3\ (g) + 3H_2O\ (g) \tag{1}$$

Powders of 5.3424 g of ZnO (Merck, ≤99%) and 7.5529 g of $NH_4H_2PO_4$ (Merck, ≤99%) were mixed and ground in an Agate mortar with a pestle using 1-propanol as the grinding medium. The mixed powders were then dried and pressed in to pellets using a steel die of 10 mm diameter. The pellets were heated in an alumina container in a muffle furnace at a ramping rate of 4 °C/min to 600 °C from room temperature and held at 600 °C for 24 h in air and furnace-cooled (natural cooling) to room temperature. These pellets were crushed and the powder was ground and palletized again and heated for the second time at 800°C for 24 h. The pellets were then crushed and dry-ground and stored in an air-tight container.

2.2. Synthesis of $Zn_2VO(PO_4)_2$

Synthesis of $Zn_2VO(PO_4)_2$ was carried out according to equation (2)

$$Zn_2P_2O_7(s) + VO_2\ (s) \quad \rightarrow \quad Zn_2VO(PO_4)_2\ (s) \tag{2}$$

Powders of 3.4161 g of $Zn_2P_2O_7$ (synthesized as explained in section 2.1) and 0.9298 g of VO_2 (Aldrich, 99.9%) were ground and pressed into pellets as explained above and heated in flowing argon atmosphere at 900°C for 24 h in a tubular furnace and cooled to room temperature. These pellets were crushed, dry-ground and stored in a container.

2.3 Characterization

Powder X-ray diffraction data were collected on as-prepared powder samples of $Zn_2P_2O_7$ and $Zn_2VO(PO_4)_2$ on an X-ray diffractometer (*D-8 Discover Bruker-AXS*) using a Cu-K_α radiation (λ = 1.5418 Å). The experimental patterns were compared with the standard powder X-ray diffraction patterns 8 to confirm the formation of the respective compounds. Rietveld quality data were collected in the 2θ range 10°– 90° with a step size of 0.02°. The Rietveld analysis was carried out using the computer program *Fullprof* 9, 10.

3. Results and discussions

When a vanadium compound needs to be synthesized by solid state reaction technique, depending on the composition of the desired compound, one or more sources of elements are mixed and heated at a suitable temperature. For example, the non-magnetic compound of vanadium *viz.*, $Zn_2V_2O_7$ can be easily prepared by heating at 800 °C for 12 h, a mixture of powders of ZnO and V_2O_5 taken in the stoichiometric proportion according to equation (3)

$$2ZnO\ (s) + V_2O_5\ (s) \rightarrow Zn_2V_2O_7(s) \qquad (3)$$

Similarly, $Zn_2P_2O_7$ which is an intermediate compound in the synthesis of $Zn_2VO(PO_4)_2$ can be synthesized from ZnO and P_2O_5 analogous to reaction (1). However due to extreme deliquescence of P_2O_5, $NH_4H_2PO_4$ is generally used as a source of phosphorous. In such a reaction, NH_3 and H_2O will be evolved as volatile species which will be driven out during the reaction in an open atmosphere.

When the synthesis of a vanadium compound is carried out in open atmosphere, invariably, a compound in which vanadium is in V^{5+} oxidation state forms as a major fraction of the reaction product. This is because of the fact that V^{5+}, due to its inert-gas-atom-like electronic structure, $[Ar]3d^0$, is the most stable oxidation-state and hence a stable non-magnetic compound will be formed.

When a vanadium-compound with lower oxidation state (and hence magnetic) such as V^{3+} and V^{4+} is required, the $p[O_2]$ of the environment in which the reaction takes place needs to be maintained at an optimum level throughout the reaction. If the reaction is carried out in air, even a stoichiometric initial mixture corresponding to a composition such as *e.g.*, $SrVO_3$ (with V^{4+} state) will result in the most stable pentavalent vanadium compound such as $Sr_2V_2O_7$. Therefore control of $p[O_2]$ during the reaction is very important.

The information on temperature of reaction and $p[O_2]$ of the reaction-environment can be obtained by the so called P-T-x diagram of the system. Figure 1 shows a schematic of the P-T-x diagram of vanadium-oxygen (V-O) system. The original diagram with actual data is available in literature 11. It can be seen from the figure that there is a small range of temperatures for a given $p[O_2]$ in which a given oxide phase is stabilized. Once the temperature and pressure range for a desired phase, *e.g.*, VO_2 is chosen, the same conditions should to be maintained during the reaction to synthesize a compound in which V is in tetravalent oxidation state as in VO_2.

Commonly used technique is to carry out the reaction in dynamic vacuum. In this technique, a stoichiometric mixture of reactants in the solid state is heated in a furnace which is being evacuated continuously by a vacuum pump, preferably, a turbo molecular pump capable of producing a vacuum of 10^{-6} torr. In this technique, one has no control over $p[O_2]$, nevertheless, $p[O_2]$ in such an environment has been found to be suitable for stabilizing a V^{4+} state in some selected compositions.

Alternatively, with the knowledge of P-T-x diagram of the system of interest (V-O in this case), accurate information on the required $p[O_2]$ can be obtained. For example, if one were to attempt the synthesis of a V^{3+} compound such as $LaVO_3$, the $p[O_2]$-T range in which V_2O_3 (which is a V^{3+} compound) is stable, needs to be explored, or if one were to synthesize a tetravalent vanadium compound such as Sr_2VO_4, the $p[O_2]$-T range in which VO_2 (which is a V^{4+} compound) is stable, should be explored.

Once the required $p[O_2]$-T parameters are chosen, the required $p[O_2]$ can be maintained in the reaction environment by keeping in the same reaction chamber, a buffer mixture of two-component oxide system in a pre-determined proportion (CoO-Co_3O_4, for example), which at thermal equilibrium, provides the appropriate $p[O_2]$. It is important to note that such a reaction chamber should to be a closed system such as evacuated-and-sealed quartz tube. Generally the reaction mixture and the buffer mixture, in the form of pressed pellets are kept in a single quartz tube (at two ends so that they do not touch each other) and sealed after evacuation. This reaction tube is then heated to desired temperature. The required $p[O_2]$ will be maintained only ***after*** the buffer mixture equilibrates with its environment at a given temperature and not *during* the temperature-ramping stage. The information on the composition of the buffer mixture, in turn, can also be obtained from the P-T-x diagram of that system.

When the P-T-x diagram of V-O system was studied in order to obtain an appropriate P-T window for the synthesis of tetravalent vanadium compound, $Zn_2VO(PO_4)_2$, it was found that at 900°C, the commercially available high purity Argon cylinder (Grade 6.0) provides an appropriate $p[O_2]$ and hence eliminating the requirement of a buffer mixture and the use of evacuated-and-sealed quartz tube. The Argon in stock cylinder with 99.9999% purity, has an oxygen content of ≤ 0.5 ppm ($\leq 0.5\times10^{-6}$). If we assume that this argon gas is passed over the reaction mixture at atmospheric pressure, *i.e.*, 101325 Pa, the oxygen partial pressure, according to Dalton's law is given by $101325\times0.5\times10^{-6}$ Pa which is equal to 0.0506625 Pa. The value of $\log_{10}(0.0506625)$ is then -1.29 which falls well within the VO_2 stability window at 900°C as given in Fig.1. Since vanadium is in 4+ oxidation state in VO_2, the same P-T conditions should be appropriate for stabilizing V^{4+} in $Zn_2VO(PO_4)_2$. An additional advantage of using such argon flow is that $p[O_2]$ will be maintained right from room temperature through temperature-ramping stage to furnace-cooling stage. The details of the synthesis procedure are given in Sec. 2.

Figure 1 A schematic P-T-*x* diagram of the V-O system

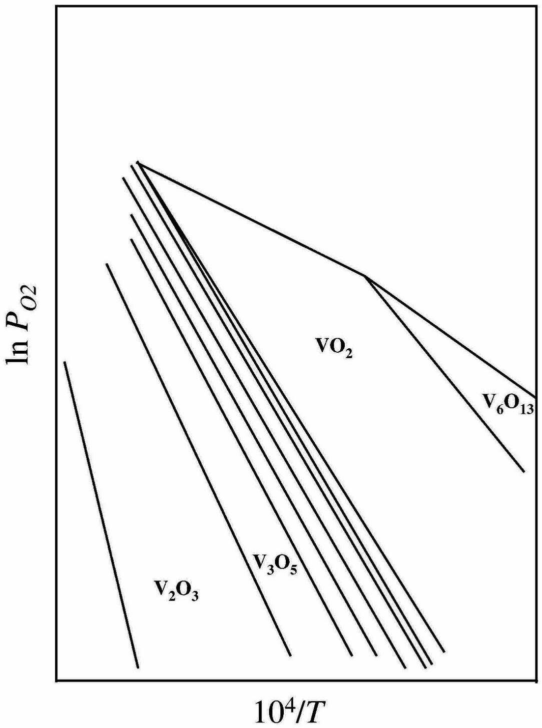
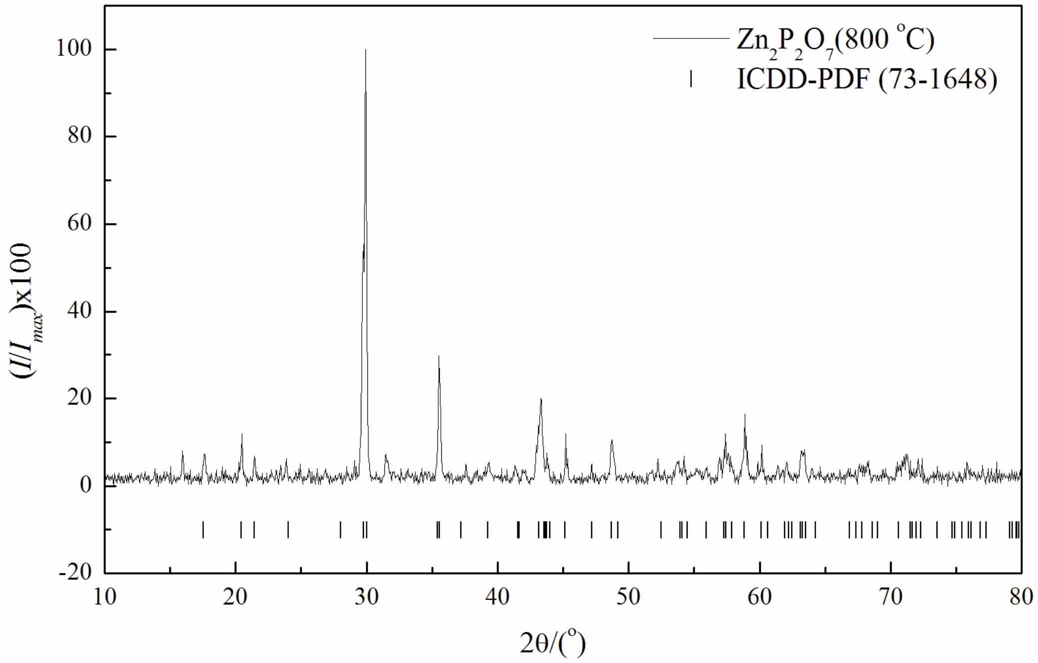


Figure 2 shows the powder X-ray diffraction pattern obtained on $Zn_2P_2O_7$ after the second heating at 800 °C in air. The observed pattern was compared to the standard ICDD-PDF pattern (card No. 73-1648). In the figure, the line-symbols below the observed pattern indicate the positions of the peaks expected according to the standard pattern. It can be seen that all the observed peaks match with the expected peak positions. This confirms the formation of the desired phase. $Zn_2P_2O_7$ crystallized with a monoclinic structure with the space group *C2/m* (No.12) and lattice parameters a = 6.61(a) Å, b = 8.29(a) Å, c = 4.51(a) Å and β = 105.400(2).

Figure 2 The experimental Powder X-ray diffraction data for $Zn_2P_2O_7$.



The formation of single phase $Zn_2VO(PO_4)_2$ was similarly confirmed by comparing the observed data with the reported standard pattern (ICDD-PDF card No.80-1927). However, to refine its crystal structure, Rietveld analysis was carried out using a high quality experimental data. Rietveld analysis is a refinement process in which a given crystal structure is refined using the experimental powder X-ray diffraction data. When the crystal structure is known from literature, a powder diffraction data can be simulated using the computer program and compared with the observed pattern. Various crystal-structure-parameters such as lattice constant, atomic positions and occupancies are refined so as to obtain the best fit with the experimental pattern.

From literature, it is known that the compound $Zn_2VO(PO_4)_2$ crystallizes in a tetragonal space group *I4cm* with lattice parameters a = 8.9227(13) Å and c = 9.039(3) Å 11. Figure 3 shows the Rietveld plot for the powder X-ray diffraction data of $Zn_2VO(PO_4)_2$. The absence of peaks at positions other than those specified by the standard pattern is a clear indication of single phase nature of $Zn_2VO(PO_4)_2$ showing that the synthesis method in which Argon flow was used to maintain the optimum $p[O_2]$ is successful. The crystal structure parameters refined by the Rietveld method are listed in Table 1. In total 42, parameters were refined including 25 background points. Only an overall thermal parameter was refined and was found to be 0.208(34) $Å^2$. The various reliability factors of the refinement process are R_p= 5.74, R_{wp} = 7.71, Rexp = 5.83, χ^2 =1.75.

Figure 3 Rietveld analysis plot for $Zn_2VO(PO_4)_2$

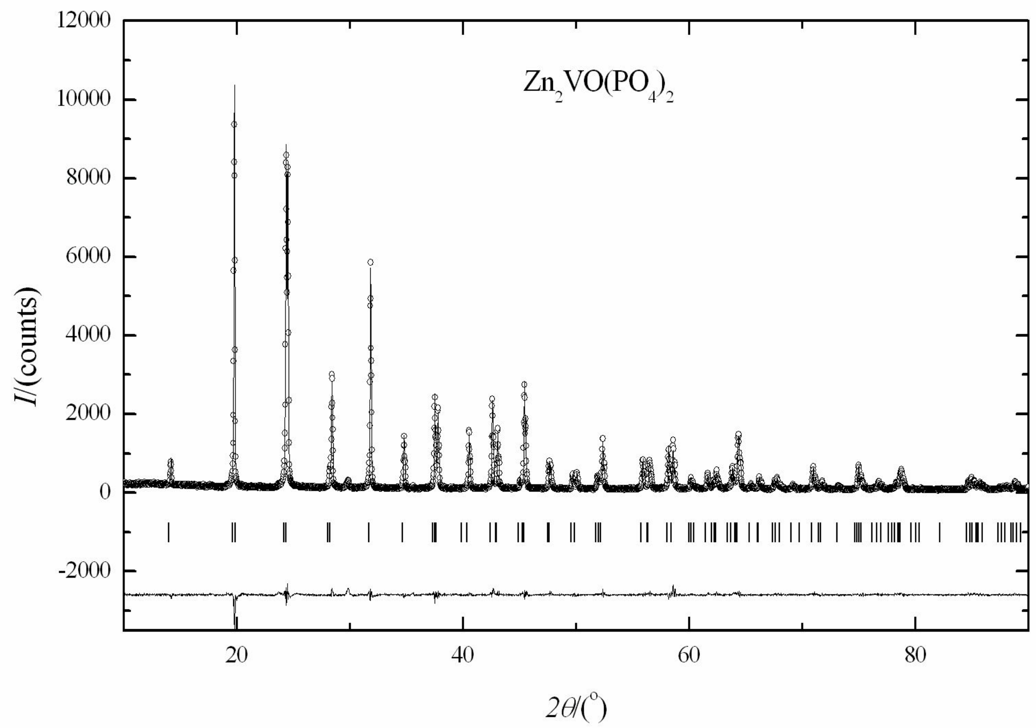


Table 1 Refined crystal structure parameters for $Zn_2VO(PO_4)_2$ in space group *I*4*cm*
(a = 8.92688(17) Å, c = 9.04139(16) Å. R_p = 8.55, R_{wp} = 10.3, χ^2 = 1.69)

Atoms	Position	*x*	*y*	*z*	F_{occu}^*	$m^\dagger$
Zn	8*c*	0.61835(14)	0.11835(14)	0.26804(51)	0.500	8
V	4*a*	0.00000	0.00000	0.10281(54)	0.250	4
P	8*c*	0.30650(28)	0.19350(28)	0.12179(70)	0.500	8
O1	16*d*	0.82710	0.13407	0.15414	1.000	16
O2	8*c*	0.65322	0.15322	0.46616	0.500	8
O3	4*a*	0.00000	0.00000	0.41723	0.250	4
O4	8*c*	0.39504	0.10496	0.24053	0.500	8

$^*F_{occu}$ = Occupancy factor, $^\dagger m$ = multiplicity factor, Oxygen atom positions are not defined.

4. Conclusion

P-T-*x* diagrams are a useful source of information in the synthesis of lower oxidation state compounds of vanadium. High purity argon flow during the reaction can provide an oxygen partial pressure suitable for stabilizing the V^{4+} state in some vanadium compounds. Single phase $Zn_2VO(PO_4)_2$ was successfully synthesized by solid state reaction technique using an Argon flow during the synthesis for providing optimum oxygen partial pressure to stabilize V^{4+} state.

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