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Valence States of Layered Vanadium Chalcogenophosphates, VPS_3 and $V_{0.78}PS_3$

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VPS_3 and $V_{0.78}PS_3$ have been synthesized by calcination of elementary mixtures prepared in the ratios of V:P:S = 1:1:3 and 0.78:1:3, respectively. Their X-ray diffraction patterns indicate that they have the same crystalline structure and orientation of crystal growth. The X-ray photoelectron spectra of V2p show that the vanadium in $V_{0.78}PS_3$ is in a mixed valence state and the compound is expressed by the formula of $(V^{2+}_{0.3}V^{3+}_{0.7})_{0.78}PS_3$.

Since new metal chalcogenophosphates, MPX_3 (M = metal, X = S, Se), have been prepared by Hahn and Klingen,[1] their properties have been studied by means of X-ray diffraction,[2-9] magnetic susceptibility,[3,4] Mössbauer spectroscopy,[3] Raman spectroscopy,[10] and so on.[11-14] From these studies, it has been clarified that the structure of MPS_3, which belongs to the monoclinic space group C2/m, is similar to that of $CdCl_2$, and the formal valence is given as $M^{2+}(P^{4+}S^{2-}_3)^{2-}$. The phosphorus and sulfur in MPS_3 show characteristics of covalent bonding. As to the constitution of a V-P-S system, the formula of VPS_3 has been reported by Hahn et al.,[1,2] while the formula of $V_{0.78}PS_3$ has been given for the explanation of a microprobe elemental analysis and an X-ray structural analysis by Ouvrard et al.,[6-8] in which the valence state of vanadium is assumed as $V^{2+}_{0.34}V^{3+}_{0.44}(\text{vacancy})_{0.22}$, though both of them have been synthesized from the starting materials prepared in the same atomic ratios as V:P:S = 1:1:3. It has been generally considered that vanadium chalcogenophosphate includes vacancies.

In this study, we examined the X-ray photoelectron spectra of VPS_3 and $V_{0.78}PS_3$, and revealed the valence state of vanadium in the V-P-S system.

VPS_3 and $V_{0.78}PS_3$ were synthesized from powder-mixtures of V (Nakarai Chem. Ltd., powder of 99% purity), P (Tsutsumi Chem. Ltd., powder 99.5%) and S (Nakarai Chem. Ltd., powder 99.5%) prepared in the atomic ratios of 1:1:3 and 0.78:1:3, respectively. Each powder-mixture in a quartz tube was degassed at room temperature for 6 h by a conventional glass high-vacuum system equipped with an oil-diffusion pump. The quartz tube was then sealed off, and calcination was carried out at 400 °C for 2 weeks.

The structures of VPS_3 and $V_{0.78}PS_3$ obtained were examined by means of powder X-ray diffraction using an Fe-target, and the X-ray photoelectron spectra were measured by the aid of a VG ESCA system with a probe of MgKα X-rays (1253.6 eV) under vacuum-conditions, below 7×10^{-7} Pa.

The X-ray diffraction confirmed that both VPS_3 and $V_{0.78}PS_3$ possessed the same crystalline structure, i.e., the observed angles for (001), (100), $(20\bar{1})$, and (130) diffractions corresponded almost to those reported for VPS_3 and $V_{0.78}PS_3$, as shown in Table 1. In addition, the orientation of crystal growth was found to be the same for both compounds, since the observed relative intensity of diffraction peaks was the same. The X-ray diffraction did not show any inclusion of impure phase such as VS with a detectable amount.

Table 1. The interplanar spacings d_{hkl} of VPS_3 and $V_{0.78}PS_3$ observed by powder X-ray diffraction (Å)

(hkl)	VPS_3	$V_{0.78}PS_3$	$V_{0.78}PS_3$ [a)]
(001)	6.36	6.36	6.364
(100)	5.75	5.75	5.608
$(20\bar{1})$ (130)	2.88	2.88	2.899
(200) $(13\bar{1})$	2.77	2.77	2.804
(040)	2.57	2.57	2.541
(131) (202)	2.50	2.50	2.499

a) $V_{0.78}PS_3$: a=5.867(1), b=10.160(2), c=6.657(1), ß=107.08° (Ref.6)
VPS_3 : a=5.85, b=10.13, c=6.66, ß=107.1° (Ref.2)

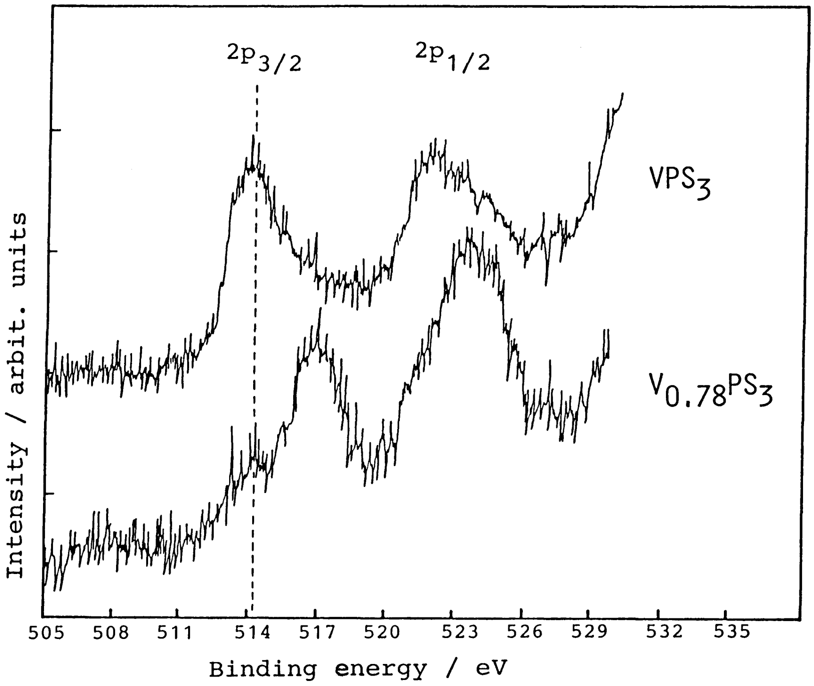

Fig. 1. X-Ray photoelectron spectra of vanadium for VPS_3 and $V_{0.78}PS_3$.

Figure 1 shows the X-ray photoelectron spectra of V2p for VPS_3 and $V_{0.78}PS_3$, where the binding energy observed was corrected to C1s of 284.7 eV. The binding energies for $2p_{1/2}$ and $2p_{3/2}$ of vanadium in VPS_3 were determined as 522.0 and 514.2 eV, respectively. On the other hand, $V_{0.78}PS_3$ showed extra peaks at 524.4 and 516.9 eV. Though the binding energy of $V2p_{3/2}$ for VPS_3 was different from that (512.7 eV) reported for VS and $V_{0.92}S$,$^{15,16)}$ this state was assigned to divalent on the basis of the known formal charge of MPS_3. The binding energy of the new $V2p_{3/2}$ peak appearing in the spectrum of $V_{0.78}PS_3$ was found to be similar to the chemical shift reported for V_2O_5,$^{15,16)}$ but the full-width at half-maximum (FWHM) was different; ca. 2.3 eV for the new peak and 1.64 eV for V_2O_5. The former was rather close to the value reported for VCl_3 (2.40 eV) and $V(hfcac)_3$ (2.66 eV),$^{17)}$ for which the chemical shift and the spin-orbit splitting width have not been reported. From these results, it was concluded that the new peak corresponded to a trivalent state. The bonding state will be discussed elsewhere on the basis of further analysis on chemical shift, spin-orbit splitting width, and so on.

The relative intensity between the peaks of $V2p_{3/2}$ appearing at 514.2 and 516.9 eV gives a ratio of divalent to trivalent vanadium in $V_{0.78}PS_3$, on the assumption that the efficiency of photoelectron emission is independent of valence state. The observed intensity ratio of 3 to 7 determines fractions of divalent and trivalent vanadium as $(V^{2+}_{0.3}\ V^{3+}_{0.7})_{0.78}$. The total formal charge is thus evaluated as ca. 2.1, which is nearly equal to the value reported for MPS_3. The determined fraction, therefore, confirms experimentally the valence state of vanadium in $V_{0.78}PS_3$ assumed by Ouvrard et al.$^{6-8)}$ This result leads to the view that vacancies included do not possess significant charge and the mixing of trivalent state accompanied with vacancy compensates the total charge.

From this study, it is concluded that VPS_3 and $V_{0.78}PS_3$ behave as individual phase, i.e., the stoichiometric phase exists originally in the V-P-S system, and a fraction x in V_xPS_3 is variable in a relatively wide range from 0.67 to 1.0. The constitutional formula is expressed by $(V^{2+}_{0.3}V^{3+}_{0.7})_{0.78}PS_3$ on the basis of the ratio of divalent to trivalent vanadium in $V_{0.78}PS_3$.

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