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Yttrium Phosphate–Yttrium Vanadate Solid Solutions and Vegard's Law

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Previously reported deviations from Vegard's law for the YVO_4–YPO_4 system have now been demonstrated to be due to side reactions occurring during the preparation of the solid solution. Several methods of preparation were investigated and their solid solution yields were evaluated. An aqueous coprecipitation method offers a 100% yield. Using precipitated YPO_4 as a source of phosphate results in good yields of solid solution; the poorest yields are obtained by using $(NH_4)_2HPO_4$ as the source of phosphate, the method used by prior investigators. The yields are affected by the formation of polyphosphates and polyvanadates. The produced solid solution particles are pseudomorphs of the original YPO_4 particles.

Introduction

The rare earths form a homologous series of phosphates, arsenates, chromates, and vanadates, as has been shown by Feigelson,[1] Stubican and Roy,[2] and notably by Schwarz.[3] These compounds crystallize either in the tetragonal xenotime or monoclinic monazite structures, depending upon the lanthanide involved. A more detailed discussion has appeared recently, in regard to the dimorphism of $LaVO_4$.[4]

These isomorphic compounds should form complete solid solutions and the lattice parameters should be subject to Vegard's law. However, it appears to be accepted that solid solutions of $Y(PO_4)_{1-x}(VO_4)_x$ deviate appreciably from Vegard's law.[5] This conclusion may also be culled from the X-ray data of Aia.[6] (It is significant, however, that both of these authors employed $(NH_4)_2HPO_4$ as a reactant in solid solution formation.) His graphical representation of the lattice parameters a_0 and c_0 of the tetragonal unit cell for these solid solutions indicate that at the 50% mole fraction of vanadate, both a_0 and c_0 suffer a sizable decrease from the values deduced from Vegard's law.[6] In view of the fact that the size of the tetrahedral vanadate anion is only some 8% larger than that for the phosphate anion,[4] a value well within the 15% limit that usually bounds Vegard's law, it was decided to reinvestigate the $Y(PO_4)_{1-x}(VO_4)_x$ system of solid solutions.

Early in this work it was suspected that deviations from Vegard's law were only apparent and were due to the presence of a small amount of an additional phase in the solid solutions, the new phase being caused by a side reaction during the firing process. A number of methods of preparation of $Y(PO_4)_{1-x}(VO_4)_x$ solid solutions were examined. Fortunately, one method, that of coprecipitation, was found to yield solid solutions that adhered strictly to Vegard's law. This relationship formed a basis for the analyses of the products re-

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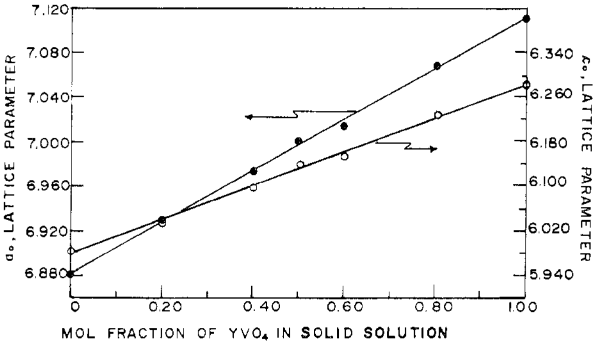


Figure 1.

sulting from the other methods. It was found that the degree of solid solution formation was dependent upon the nature of the chemical reactions employed in the preparations.

Experimental Section

The materials Y_2O_3, V_2O_5, and $(NH_4)_2HPO_4$ were commercial preparations whereas YVO_4, $YPO_4{\cdot}{}^5/{}_3H_2O$, and $Y_2(C_2O_4)_3{\cdot}4H_2O$ were prepared in the laboratory.[7] All of these materials are crystalline and were identified by their diffraction patterns.[8] The materials were mixed in desired molar proportions by grinding together selected reactants for 45 min in an automatic mortar–grinder, blending in a high-speed blender for 5 min, and regrinding for 45 min, to ensure a complete mixture for solid-state reaction. Firing was accomplished in air at 1200° for 6 hr. Normally, this is sufficient to give a complete solid-state reaction.

YPO_4 is stable to 1300° where it begins to lose P_2O_5, as indicated by TGA. YVO_4 is stable to about 1400°.[7] Thus a firing temperature of 1200° is about as high as one can go without causing decomposition of the separate phases. In those cases where refiring was done little change in the X-ray diffraction pattern occurred. In no case did we observe any separate phases of the original reactants, indicating that the given reaction was essentially completed even though complete solid solution had not occurred.

Results

(a) Coprecipitation. Both YVO_4[9] and YPO_4 can be precipitated from aqueous solution and the precipitations are quantitative.[7] Precipitated YPO_4 forms a series of hydrates, including $YPO_4{\cdot}{}^5/{}_3H_2O$, a specific mixture of mono- and dihydrates, which appears over most of the range of precipitation conditions.[7] When coprecipitated from aqueous solution and fired, the YVO_4:YPO_4 molar compositions yield the lattice parameters shown in Figure 1. Here the plotted composition, mole fraction of YVO_4, is the mole fraction in the initial aqueous preparation on a YVO_4–YPO_4 basis. Apparently, complete solid solution has taken place and Vegard's law is quantitatively followed over the entire range of composition.

The lattice parameters determined for pure YPO_4 were $a_0 = 6.880$ Å and $c_0 = 5.982$ Å, whereas those of YVO_4 were $a_0 = 7.112$ Å and $c_0 = 6.284$ Å. Corresponding literature values are as follows: YVO_4, $a_0 = 7.121$ Å and $c_0 = 6.292$ Å; YPO_4, $a_0 = 6.882$ Å and $c_0 = 6.030$ Å (6). The values are in good agreement.

(b) Solid-State Reaction of Oxides. When the components Y_2O_3, V_2O_5, and $(NH_4)_2HPO_4$ are mixed in stoichiometric amounts and fired, considerable deviation between the relative amounts of vanadate–phosphate found in the solid solution and those in the original mix are found. These results are plotted in Figure 2. Here the deviations from Vegard's law in terms of vanadate:phosphate composition have been plotted against the mole fraction of vanadate contained in the initial stoichiometric mix on a vanadate–phosphate basis. If we denote the solid solution as $Y(PO_4)_{1-x}(VO_4)_x$, then up to the composition of $x = 0.80$, a deficiency of vanadate appears in the solid solution. Small amounts of another phase were noted up to about 0.70 mole fraction of YVO_4. Identification was not certain but the extra phase appeared to be $Y_8V_2O_{17}$.[10] The formation of this compound from YVO_4 has been noted before[11]

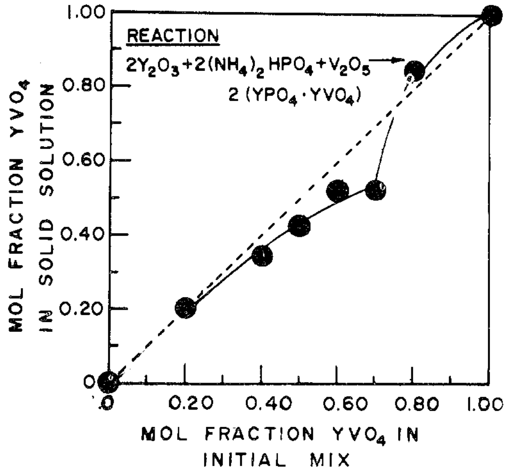


Figure 2.

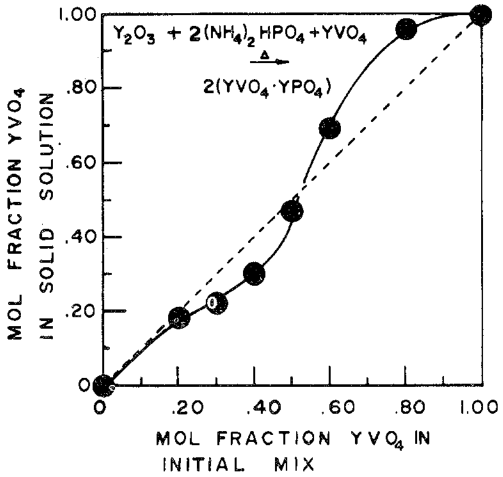


Figure 3.

$$8YVO_4 \rightarrow Y_8V_2O_{17} + 3V_2O_5\uparrow \tag{1}$$

However, we are not certain whether the appearance of $Y_8V_2O_{17}$ is due to direct formation from the oxides or to a decomposition reaction from YVO_4, as shown by the reactions

$$\begin{aligned} &Y_2O_3 + V_2O_5 \rightarrow 2YVO_4 \\ &4Y_2O_3 + V_2O_5 \rightarrow Y_8V_2O_{17} \end{aligned} \tag{2a}$$

$$Y_2O_3 + 2(NH_4)_2HPO_4 \rightarrow 2YPO_4 + 4NH_3 + 3H_2O \tag{2b}$$

$$\begin{aligned} &8YVO_4 \rightarrow Y_8V_2O_{17} + 3V_2O_5 \\ &YVO_4 + YPO_4 \rightarrow YVO_4{\cdot}YPO_4 \end{aligned} \tag{2c}$$

Reactions 2a and 2c could be simultaneous. At any rate, it was evident that the side reaction to form $Y_8V_2O_{17}$ was responsible for the vanadate-deficient compositions. A substantiating factor was the slight yellow body color observed in these compositions. $Y_8V_2O_{17}$ possesses a brilliant yellow reflectance.[11]

(c) Yttrium Vanadate Precipitate. When YVO_4 precipitate is employed in the reaction with $(NH_4)_2HPO_4$ and Y_2O_3, two entirely different situations develop depending upon the relative amount of YVO_4 present. This is shown in Figure 3. Only at about $x = 0.50$ is a stoichiometric product observed. At low vanadate, the product contains excess phosphate and the same low intensity lines attributed to $Y_8V_2O_{17}$ are seen. But at high vanadate, the products are low in phosphate. A few lines were observed which were not identifiable. It is highly

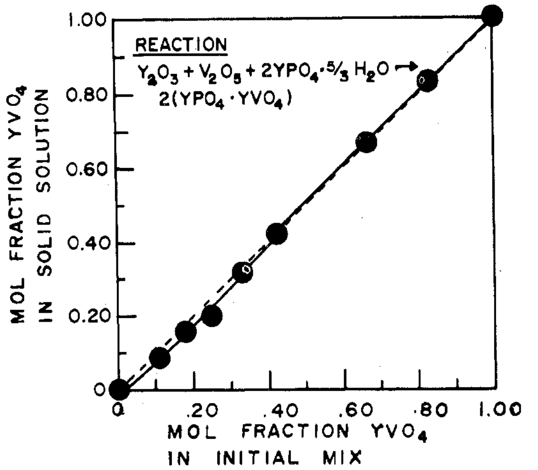


Figure 4.

probable that in addition to YPO_4 formation, the formation of a polyphosphate occurs

$$Y_2O_3 + 10(NH_4)_2HPO_4 \rightarrow 2YP_5O_{14} + 20NH_3 + 15H_2O \qquad (3)$$

Normally, the reaction to form YPO_4 from the oxides would proceed as in reaction 2b. However, if reaction 3 occurred to form the pentaphosphate, then an excess of Y_2O_3 would be expected. Since free Y_2O_3 as a separate phase was not observed (it is likely that the amount of Y_2O_3 present was too low to be detectable by X-ray diffraction analysis), we cannot completely account for the reaction (see below). The substitution of the oxalate $Y_2(C_2O_4)_3 \cdot 4H_2O$ for Y_2O_3 in the solid-state reactions produced a curve like that of Figure 3 to within a few mole percent.

(d) Yttrium Phosphate Precipitate. When $YPO_4 \cdot {}^5/_3H_2O$ is used as a reacting component along with Y_2O_3 and V_2O_5, then the produced phases follow an almost exact mole ratio as in the initial preparation as shown in Figure 4. Even the reaction with YVO_4 precipitate produced solid solutions up to about $x = 0.70$ that followed the composition of the initial preparation (see Figure 5). The sample at $x = 0.80$ was rich in vanadate ($x = 0.92$) and appeared to be unique in the series. Distinct lines appeared which we have attributed to the pentaphosphate phase YP_5O_{14}. But in addition, Y_2O_3 diffraction lines *were* observed. It is thus evident that it is the orthophosphate which decomposes to form a polyphosphate (at high vanadate levels), i.e.

$$YPO_4 \cdot {}^5/_3H_2O \xrightarrow{\Delta} YPO_4 + {}^5/_3H_2O\uparrow \qquad (4)$$

$$5YPO_4 \xrightarrow{\Delta} YP_5O_{14} + 2Y_2O_3 \qquad (5)$$

It is probable that the deviation from stoichiometry noted in Figure 3 at low phosphate levels is due to the formation of the orthophosphate, YPO_4, which then decomposes to form the pentaphosphate, YP_5O_{14}. It should be noted that the existence of the pentaphosphate is known,[12] and, indeed, its structure has been reported to be monoclinic with a space group of $P2_1/c$.[13]

Discussion

It has been shown that previously reported deviations from Vegard's law for the YVO_4–YPO_4 system are due to the presence of side reactions in the formation of the solid solutions. These side reactions depend upon the method of preparation, as well as the relative amounts of phosphate and/or vanadate present in a given preparation. All conditions for substitutional solid solution over the complete range of composition are met for the YVO_4–YPO_4 system; the 8% difference in the size of the anions is well within the 15% limit for adherence to Vegard's law.

Of the various methods of preparation of the solid solutions, the greatest apparent deviations from Vegard's law occur when $(NH_4)_2HPO_4$ is the source of the phosphate. In phosphate-rich compositions, a competing side reaction involves the formation of a polyvanadate via reaction 2a or 2c. Apparently, it makes little difference whether the reacting components are YVO_4 (precipitate) or $Y_2O_3 + V_2O_5$. However, this is not true for vanadate-rich compositions where YPO_4 is first formed and then decomposes to form a pentaphosphate. The trimetaphosphate, YP_3O_9, is also known,[14] and it may be this compound which is a reaction product in the degradation of YPO_4 during the solid solution formation

$$3YPO_4 \rightarrow YP_3O_9 + Y_2O_3 \qquad (6)$$

When $YPO_4 \cdot {}^5/_3H_2O$ is used, the ratio of vanadate to phosphate in the preparation is the same as in the solid solution up to about $x = 0.70$. Only the coprecipitation method produces solid solutions having the same composition as that in the initial preparation over the complete composition range.

Aia's[6] method of preparation of $YPO_4 \cdot YVO_4$ solid solutions is comparable to our method b, the important common step

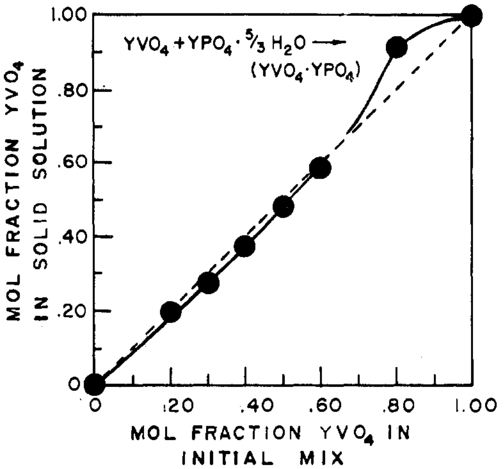
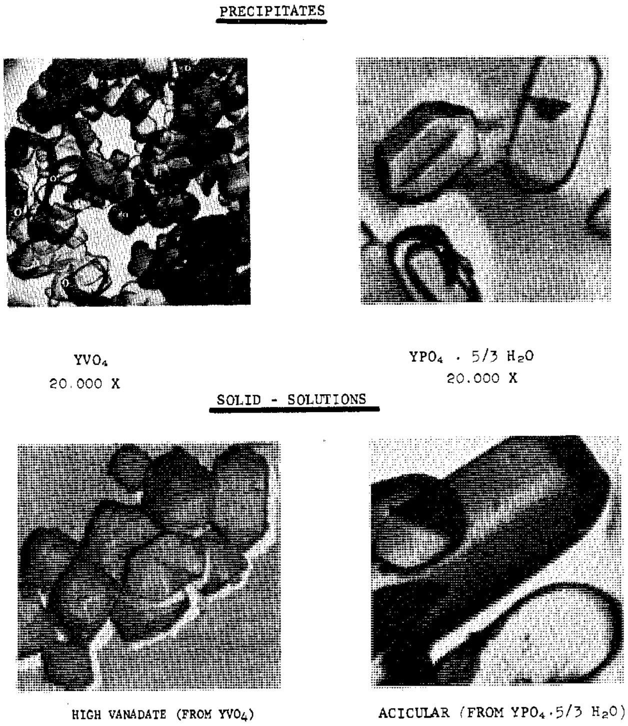


Figure 5.



PRECIPITATES

YVO_4
20.000 X

$YPO_4 \cdot 5/3\ H_2O$
20.000 X

SOLID - SOLUTIONS

HIGH VANADATE (FROM YVO_4)
10,000 X

ACICULAR (FROM $YPO_4 \cdot 5/3\ H_2O$)
20,000 X

Figure 6. Photomicrographs of several particle morphologies.

Table I. Comparison of Apparent Deviations from Vegard's Law

Mol % VO_4 in prepn	Mol % VO_4 in solid soln (Aia[6])	Mol % VO_4 in solid soln (method b)
25	22.0	23.0
50	41.5	43.0
75	75.0	75.0

being the use of $(NH_4)_2HPO_4$. Examining his X-ray data, we find that they yield values for apparent deviations from Vegard's law close to our own. This can be seen from the values in Table I.

It is interesting to note that the particle habit of $YVO_4 \cdot YPO_4$ solid solutions follows that of the $YPO_4 \cdot {}^5/_3H_2O$ used in preparation. As shown in Figure 6, precipitated YVO_4 occurs as 0.1–1.0-μ platelets while YVO_4 made by solid-state reaction of oxides is a regular dodecahedron. Precipitated $YPO_4 \cdot {}^5/_3H_2O$ is acicular with many of the particles (2–6 μ) clustered from a central growth point to form a spiny sphere.[7] For high vanadate (>70–80% VO_4), the dodecahedrons prevail. For $(NH_4)_2HPO_4$-reacted particles, the particles are not uniform.

When $YPO_4 \cdot {}^5/_3H_2O$ is employed as a reactant, an acicular product results, for both high-phosphate and high-vanadate portions of the phase compositions (see Figure 6). Apparently, the phosphate acts as a reaction base for particle formation and the product is a pseudomorph. This is similar to a much better known case of pseudomorphism where the particle morphology of $CaHPO_4 \cdot 2H_2O$ (octagonal, square platelets, rectangular platelets, and acicular) is carried through the reacting $CaHPO_4$ to form pseudomorphic $Ca_5FCl(PO_4)_3$.

Registry No. YVO_4, 13566-12-6; YPO_4, 13990-54-0.

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Kinetics of Chromium(III)–Chromium(II) Electron Transfer and Equilibria in the Chromium(II)–Acetate System

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The reactions $Cr(NH_3)_5X^{2+} + Cr^{II}$ in acetate buffer media (X = Cl, Br) obey the rate law $-d \ln [Cr(NH_3)_5X^{2+}]/dt = {}^1/_4 k_M{}^X K_D(-1 + (1 + 8[Cr^{II}]_T/K_D)^{1/2})$ where K_D is interpreted as the dissociation constant of the chromium(II) acetate dimer and $K_M{}^X$ as the specific rate of reaction of $Cr(NH_3)_5X^{2+}$ with chromium(II) monomer. At 25° in acetate buffer with $[OAc^-] = [HOAc] = 0.50\ M$ and ionic strength 1.0 M ($NaClO_4$), $K_D = (5.2 \pm 2) \times 10^{-4}\ M^{-1}$, $k_M{}^{Cl} = 0.60 \pm 0.2\ M^{-1}\ sec^{-1}$; at 25° with $[OAc^-] = [HOAc] = 0.10\ M$, $k_M{}^{Cl} = 0.34 \pm 0.1\ M^{-1}\ sec^{-1}$; at 30° with $[OAc^-] = [HOAc] = 0.10\ M$, $k_M{}^{Br} \simeq 5\ M^{-1}\ sec^{-1}$. Values of K_D and k_M for other acetate ion concentrations are tabulated. The dependences of $k_M{}^{Cl}$ and K_D upon acetate ion concentration are interpreted in terms of bimolecular electron-transfer steps $Cr(NH_3)Cl^{2+} + Cr(OAc)_n{}^{(2-n)+}$ with second-order specific rates k_n, where $0 \leq n \leq 3$, and equilibria defined by $K_n = [Cr(OAc)_n{}^{(2-n)+}]/[Cr(OAc)_{n-1}{}^{(3-n)+}][OAc^-]$ and $K_{D0} = [Cr(OAc)_2]^2/[Cr_2(OAc)_4]$. At 25° and ionic strength 1.0 M ($NaClO_4$), $k_0 = (3.0 \pm 0.2) \times 10^{-2}\ M^{-1}\ sec^{-1}$, $(k_1 - k_0)K_1 = (3.8 \pm 0.3)\ M^{-2}\ sec^{-1}$, $K_2 \approx 5\ M^{-1}$ and $K_{D0} = (4 \pm 1) \times 10^{-4}\ M$.

In an earlier study[1] of the reaction of chloropentaamminechromium(III) ion with chromium(II) in acetate media it was concluded that the effective reducing species were monomeric chromium(II) complexes present at low concentration in equilibrium with the chromous acetate dimer, and independent evidence of such equilibria was obtained from spectrophotometric measurements. It was not, however, possible to identify the chromium(II) complexes involved except to say that under the conditions used the average acetate: chromium ratio in the monomeric complexes was the same as that in the dimers. In view of the scarcity of data on chromium(II) complex equilibria and on mechanisms of reaction of metal–metal bonded species, we considered it worthwhile to undertake a further kinetic study under a wider range of conditions. From the new data we are now able to define the complexes involved in the electron-transfer processes and to estimate the stability of the chromium(II) acetate dimer.

Experimental Section

Preparation of Materials. Bromopentaamminechromium(III) bromide was prepared from rhodochromic chloride[2] as follows. The crude chloride salt was dissolved in hot water, treated with concentrated hydrobromic acid, and cooled in ice to obtain the corresponding bromide, which after being filtered off was heated with concentrated hydrobromic acid on the steam bath for 1 hr. The sparingly soluble product was washed with cold water and ethanol. Anal. Calcd for $Cr(NH_3)_5Br_3$: N, 18.6; H, 3.98. Found: N, 17.6, 18.0; H, 4.19, 4.03 (two samples). Attempts to obtain the perchlorate salt by the method previously used for the corresponding chloro complex led to extensive aquation; hence the bromide was used in all kinetic experiments. Chloropentaamminechromium(III) perchlorate was prepared and recrystallized from time to time as previously described.[1]

Chromium(II) perchlorate solutions were prepared by reduction of hexaaquochromium(III) perchlorate solutions both by zinc amalgam[1] and by electrolysis.[3] No difference in kinetic behavior could be detected between the two preparations. Storage and handling of the air-sensitive solutions are described elsewhere.[1]

Kinetic Measurements. For the slowest reactions a Hilger and Watts single-beam UVISPEK spectrophotometer was used with automatic cell changer allowing observation of up to three reactions at one time, a fourth cell being used as reference. Otherwise a Beckman DB spectrophotometer was used with a 10-in. chart recorder giving photometric accuracy better than ±0.2% transmission. Temperature control was achieved by two modifications: an aluminum box through which cooling water could be circulated was placed between the lamphouse and the cell compartment, and the latter was rebuilt with double walls for circulation of water from an external thermostat.

Data Treatment. Primary kinetic data obtained as pen-recorder