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Scandium Titanite and Scandium Vanadite, $ScTiO_3$ and $ScVO_3$[1]

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$ScTiO_3$ has been prepared by solid-state reaction of Sc_2O_3, TiO_2, and Ti at 1700°; $ScVO_3$, by reaction of Sc_2O_3 and V_2O_3 at 1500° and by reduction of $ScVO_4$ with hydrogen at 950°. X-Ray intensities of $ScTiO_3$ and $ScVO_3$ closely correspond with those of Sc_2O_3, indicating a C-type R_2O_3 face-centered-cubic structure. The magnetic susceptibility of $ScVO_3$, measured by the Gouy method over the range 77–300°K, shows normal paramagnetic behavior corresponding to $\mu_{eff} = 2.98$ BM. The optical reflection spectrum of $ScVO_3$, showing four bands at 4130, 9750, 13,900, and 20,200 cm^{-1}, is consistent with V^{3+} in lower than trigonal symmetry. $ScTiO_3$ shows moderate powder conductivity, but its magnetic susceptibility indicates that most of the d^1 electrons are localized on Ti^{3+}. The optical reflection spectrum of $ScTiO_{3.00}$ shows a continuous absorption from 28,000 to 3800 cm^{-1}, possibly superimposed on a Ti^{3+} ligand-field absorption band at 20,000 cm^{-1}.

Introduction

Morin[3] has argued persuasively that the breadth of the 3d conduction band in the transition metal oxides should increase from right to left in the periodic table consistent with increasing overlap of the 3d orbitals. The compounds of scandium, consequently, should be the most favored of the first-row transition series in showing wide conduction band characteristics, hence, high carrier mobility in a suitably populated system. As part of a program to investigate transport properties in transition metal compounds, it was undertaken to synthesize $ScTiO_3$ and $ScVO_3$ and to examine their electric and magnetic behavior. The possibility existed that these compounds might be metallic if they conformed to a model in which a scandium 3d conduction band is populated by electron excitation from Ti^{3+} ($3d^1$) or V^{3+} ($3d^2$) as easily ionized donor centers.

Experimental Section

Starting Materials.—Sc_2O_3, 99.5%, obtained from the Australian Mineral Development Laboratories, South Australia, contained 0.3% SiO_2 as principal impurity. V_2O_5, 99.9%, was obtained from the Vanadium Corp. of America. Ti metal, 99.8%, was obtained as a −300-mesh powder from Metal Hydrides, Inc. The magnetic susceptibility of TiO_2 obtained by oxidation of the Ti metal powder showed the latter to contain 0.2% Fe. After being dried in air at 100° it showed 96% Ti metal by weight, as determined by weight gain at 1000°. V_2O_3 was prepared by hydrogen reaction[4] of V_2O_5 at 950°. TiO_2 was Fisher Certified reagent.

Preparation of $ScTiO_3$.—$ScTiO_3$ was prepared by heating under vacuum at 1700° a compacted mixture of composition $2Sc_2O_3 \cdot 3TiO_2 \cdot Ti$. The oxides were both sieved through 300-mesh screens and dried at 400° before thorough admixture and grinding with Ti metal. Some oxidation of Ti metal occurred during grinding, and allowance was made for this by addition of more Ti and less TiO_2 in successive preparations, always in such proportions as to keep the Sc:Ti ratio at unity. The Ti^0 and Ti^{3+} contents of the reaction mixtures and products, respectively, were checked by determining their weight gain when heated in air at 1000°. For the sample of $ScTiO_3$ closest to stoichiometry, for example, the gain in weight of the initial reaction mixture was 99.70% of theoretical, and after firing that of the product was 99.50% of theoretical, corresponding to a composition $ScTiO_{3.003}$.

Reaction mixtures were heated in either an iridium or molybdenum crucible, less sticking of the fired pellets occurring with the latter. The crucibles were supported on inverted alumina or zirconia crucibles and surrounded by a section of alumina or mullite tube to act as a radiation shield. The reaction assembly was contained in a 64-mm diameter quartz tube evacuated to a pressure of less than 10^{-6} torr. Samples were carefully outgassed at low temperature before final heating. Temperatures were estimated to ±20° by sighting with an optical pyrometer into a small hole in the crucible lid, substantially blackbody conditions being obtained.

Reaction was incomplete at 1300° but complete in 2 hr at 1650° or above. No change in the positions or intensities of the powder diffraction peaks was obtained on regrinding and heating of the product for a further period. Sintered pellets of $ScTiO_3$ were black and very hard. The compound melted somewhat above 1800°.

Preparation of $ScVO_3$.—Attempts to produce $ScVO_3$ by reaction of Sc_2O_3 with V_2O_3 at 1650° under vacuum resulted in a cubic phase but also in sublimation of shiny black columnar crystals onto the inside of the crucible lid. These highly electrically conducting crystals were found to be V_2O_3, their X-ray pattern matching closely that reported on ASTM Card No. 1-1293. Reaction of Sc_2O_3 and V_2O_3 in a sealed platinum capsule at 1500° gave complete reaction, but, more conveniently, $ScVO_3$ was found to be the stoichiometric product of reduction by hydrogen at 950° of $ScVO_4$. $ScVO_4$[5,6] was made by reaction of intimate mixtures of Sc_2O_3 and V_2O_5 at 900–1000° for 10–15 hr. It has been shown that weight losses for such preparations are less than 0.1% even at 1200°. After thorough grinding, $ScVO_4$ was weighed into an alumina boat and heated in a slow stream of hydrogen purified by passage through a palladium diffuser. Reduction was carried out first at 450–500° and finally at 950° for several hours. The weight loss by $ScVO_4$ in forming $ScVO_3$ was within 0.3% of that calculated, and reheating $ScVO_3$ in air at 700° gave a weight gain also within 0.3% of that calculated. $ScVO_3$ powder prepared by hydrogen reduction was dark brown and apparently air stable.

X-Ray Diffraction.—X-Ray powder diffraction peaks were recorded at slow scan rates on a General Electric XRD-5 diffractometer. Peak positions were fixed by calibration of the 2θ scale with silicon, tungsten, and Sc_2O_3 powder samples, and also by inclusion of Sc_2O_3 and W as internal standards. Intensities were obtained by measuring peak areas with a planimeter. For the recording of $ScVO_3$ peak areas, the fluorescence background was arbitrarily suppressed. Radiation was Cu Kα.

Magnetic Susceptibility.—Samples were meshed to a given size range and packed in 3-mm diameter precision-bore Pyrex tubes

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[2] On leave from the Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia.

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[4] W. Klemm and P. Pirscher, *Optik*, **3**, 75 (1948).

[5] L. H. Brixner, *J. Electrochem. Soc.*, **112**, 70 (1965).

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constructed with a central septum and evacuated tail. A tube correction was found to be unnecessary. Calibration of the Gouy balance with nickel chloride solution and with $HgCo(NCS)_4$[7] sieved to a given size range gave calibration values agreeing within 0.3%. Room-temperature susceptibility was checked by repacking samples in the same tube. In the case of $ScTiO_{3.003}$, which showed an unexpectedly high susceptibility, measurements over the temperature range were also made using different tubes and a different Gouy balance in another laboratory, but results obtained were identical. In all cases measurements were made over a range of magnetic fields from 2500 to 10,000 gauss, and gram susceptibilities were extrapolated by χ_g *vs.* $1/H$ plots to zero reciprocal field. $ScTiO_3$ was found to gain oxygen slightly when finely ground in air; samples for magnetic and spin resonance measurements were minimally crushed until they passed a 100-mesh but not a 170-mesh sieve.

Optical Spectra.—Ultraviolet, visible, and near-infrared spectra were recorded as diffuse-reflectance spectra on a Beckman DK-2A double-beam spectrophotometer fitted with a reflectance sphere. Sc_2O_3 was used as an isomorphous reference sample.

Electron Paramagnetic Resonance.—Powder samples were examined at 77°K at a frequency of 9 Gc/sec with a standard homodyne system using balanced crystal detection with 100-kc/sec field modulation and phase-sensitive detection.

Results

The observed X-ray diffraction intensities and lattice constants of $ScTiO_3$ and $ScVO_3$ are given in Tables I and II. Those for Sc_2O_3 are included for comparison. Similar X-ray patterns with similar intensities were observed for compositions $ScTiO_{3.053}$, $ScTiO_{3.095}$, and $ScTiO_{3.17}$. Compositions nominally $ScTiO_{3.25}$ and $ScTiO_{3.5}$ gave a similar phase with, however, separation of some TiO_2 (rutile), indicating a limiting composition below $ScTiO_{3.25}$.

Neither $ScTiO_{3.003}$ nor $ScVO_3$ gave an electron paramagnetic resonance signal at 77°K, but $ScTiO_{3.053}$ gave a strong single peak corresponding to a g galue of 1.98. Magnetic susceptibility data for these compositions are given in Table III, and the plots of reciprocal χ per gram-atom of M^{3+} *vs.* T are shown in Figure 1. For $ScTiO_{3.053}$ and $ScVO_3$ the field dependence of susceptibility was small (approximately 0.5 and 2% extrapolations from 10,000 gauss to infinite field, respectively), and normal Bohr magneton numbers were obtained as shown in Table III. For $ScTiO_{3.003}$, although it was prepared from the same starting materials as $ScTiO_{3.053}$, the field dependence was relatively high, and the linear plots of χ_g *vs.* $1/H$ extrapolated to a value 25% below that at 10,000 gauss. These differences in behavior suggest that Fe impurity known to be present in the starting Ti metal was reduced to free Fe, at least in part, in $ScTiO_{3.003}$ but was all present as Fe^{2+} or Fe^{3+} in $ScTiO_{3.053}$. Reflectance spectra for $ScTiO_{3.003}$ and $ScVO_3$ are shown in Figure 2. The reflectance scales, in units of log (R_0/R), are arbitrary with respect to true optical absorption coefficients.

The electrical conductivities of sintered pellets of $ScTiO_3$ and $ScVO_3$ were checked simply with an electrometer resistance bridge and two probes. $ScTiO_{3.003}$ showed a resistivity of about 10^4 ohms cm, but the resistivity of $ScVO_3$ was approximately 10^8 ohms cm. (A

Table I

Comparison of Observed Diffraction Intensities

$h^2 + k^2 + l^2$	Sc_2O_3[a]	$ScTiO_3$	$ScVO_3$
6	30	34	32
12	100[b]	200	200
14	4	2	4
16	15	16	21
18	8	8	8
20	3	3	
22	26	24	27
24	4	2	
26	20	22	21
30	9	8	7
32	78	86	90
34	5	4	
36	2	1	
38	10	7	11
40	4	2	
42	9	9	9
44	33	36	44
46	12	14	13
48	4	5	4
50	4	3	
52	3	2	
54	8	7	10
56	3	3	
62	3	3	
64	7	10	8
66	5	6	
68	4	3	
70	3	3	
72	3	4	
74	4	5	
76	8	13	11
78	2		
80	3	7	
84		3	
86		4	
90		4	

[a] Values for Sc_2O_3 from H. E. Swanson, R. K. Fuyat, and G. M. Ugrinic, National Bureau of Standards Circular 539, Vol. III, U. S. Government Printing Office, Washington, D. C., 1954. [b] This value appears to be in error by a factor of 2. Admixture of Sc_2O_3 with $ScTiO_3$ or $ScVO_3$ gave a double set of diffraction peaks with the same relative intensities throughout—*i.e.*, the compounds are closely isomorphous and show similar intensities.

Table II

Lattice Constants[a] and Composition

Compound	a_0, A	Ti^{3+} as % of total Ti
Sc_2O_3	9.845[b]	
$ScTiO_{3.003}$	9.709 ± 0.003	99.5
$ScTiO_{3.053}$	9.710 ± 0.003	89.4
$ScTiO_{3.095}$	9.717 ± 0.003	81.0
$ScVO_3$[c]	9.602 ± 0.003	

[a] Cu $K\alpha_1$, λ 1.5405 A; Sc_2O_3 (a_0 = 9.845 A) and W powder (a_0 = 3.1648 A) as internal standards. [b] See reference given in footnote *a* of Table I. [c] $ScVO_{3.000 \pm 0.0015}$.

Table III

Paramagnetic Constants[a] for $ScTiO_3$ and $ScVO_3$

χ/g-atom of $M^{3+} = C/(T + \theta)$ cgs units

	C	θ	μ_{eff}
$ScTiO_{3.003}$	0.570 ± 0.005	93 ± 2	2.14
$ScTiO_{3.053}$	0.362 ± 0.004	45 ± 2	1.71
$ScVO_3$	1.103 ± 0.025	117 ± 4	2.98

[a] After correction for diamagnetism using the values of P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956.

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(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4196 (1958).

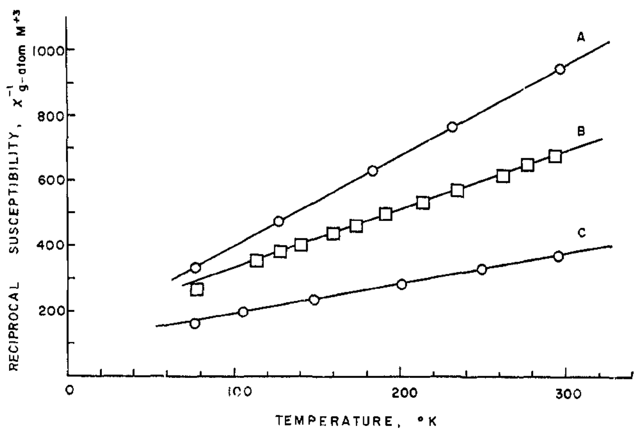

Figure 1.—Reciprocal susceptibility per gram-atom of M^{3+} *vs.* absolute temperature: A, $ScTiO_{3.053}$; B, $ScTiO_{3.003}$; C, $ScVO_3$.

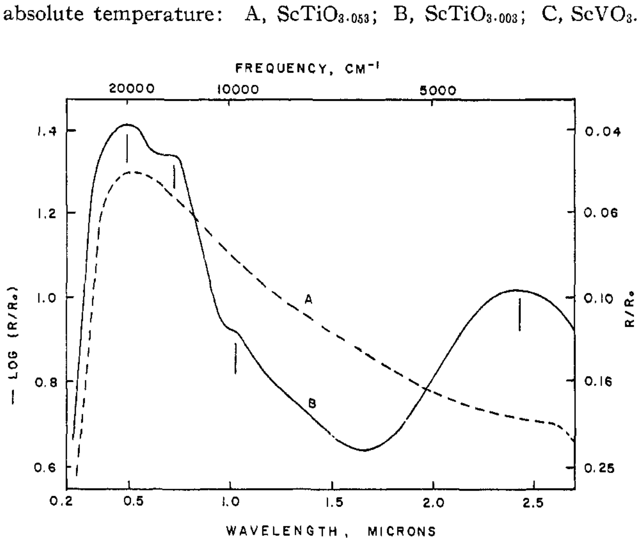

Figure 2.—Electronic absorption spectra for $ScTiO_{3.003}$ (A) and $ScVO_3$ (B) with Sc_2O_3 as reflection reference.

section of alumina rod had a resistivity of 10^{10} ohms cm under similar conditions.)

Discussion

The close correspondence of the X-ray intensity data for $ScTiO_3$ and $ScVO_3$ with those for Sc_2O_3 shows that these three compounds are isostructural. The scattering powers of Ti^{3+} and V^{3+} are very close to those for Sc^{3+}, and almost identical reflection intensities are to be expected whether the Ti^{3+} or V^{3+} ions are ordered or random with respect to $Sc.^{3+}$

A number of C-type metal oxides are known, including Sc_2O_3, $(Fe,Mn)_2O$ (bixbyite), Ce_2O_3, and Y_2O_3.[8] A single-crystal refinement of the structure of Y_2O_3 has been recently reported.[8] Of the 32 metal ions in the unit cell, 8 are at $^1/_4$, $^1/_4$, $^1/_4$, each surrounded by six oxygen atoms at the corners of a slightly distorted cube with two oxygens missing from diagonally opposite corners, and 24 are at the more general positions u, 0, $^1/_4$ with six oxygen atoms at the corners of a cube with two oxygens missing from the opposite corners of one face. The structure thus approximates a fluorite type with one-quarter of the oxygens missing.

The presently described compounds exhibit considerable "cubic solid solubility" in that oxidation of some Ti^{3+} to Ti^{4+} or V^{3+} to V^{4+} does not alter the crystal structure, the additional oxygen evidently being accommodated in the empty oxygen spaces in the lattice with very little change in lattice constant (Table II). This behavior parallels that of a number of reported solid solutions between M'_2O_3 and $M''O_2$ oxides[9,10] in the low M_2O_3 region. However, at compositions $Sc_2O_3 \cdot 2TiO_2$ and $Sc_2O_3 \cdot TiO_2$, while the predominant phase (or solid solution) was the face-centered cubic $(Sc,Ti)_2O_{3+x}$, unreacted TiO_2 was present at the first composition and a small quantity of a second phase, not identifiable as any of TiO_2, pyrochlore, fluorite, or pseudobrookite, was present at the second. This behavior is considerably different from that shown, for example, by Y_2O_3 with TiO_2 where $Y_2O_3 \cdot 2TiO_2$ forms a pyrochlore phase and $Y_2O_3 \cdot TiO_2$ forms a fluorite phase.[9]

As well as accommodating Ti^{4+} or V^{4+} in their structures, the $ScTiO_3$ and $ScVO_3$ phases can presumably, since they have the same structure as Sc_2O_3, form solid solutions with it from the $Ti_2O_3 \cdot Sc_2O_3$ and $V_2O_3 \cdot Sc_2O_3$ compositions up to 100% Sc_2O_3. Such behavior has been observed for the Fe_2O_3–Sc_2O_3 and Cr_2O_3–Sc_2O_3 systems,[11,12] where for 0–50 mole % Fe_2O_3 or Cr_2O_3 sintered with Sc_2O_3 at 1300°, the Sc_2O_3-type structure was retained with a change of lattice constant proportional to Fe_2O_3 and Cr_2O_3 concentrations. In the present systems, extensive volatilization of V_2O_3 from initially stoichiometric $ScVO_3$ heated at 1700° still produced the C rare earth oxide phase, as expected.

The magnetic susceptibility data for $ScTiO_{3.053}$ corresponding to $\mu_{\text{eff}} = 1.71$ BM are normal, indicating one, or statistically very close to one, unpaired electron per Ti^{3+} atom. Likewise, the moment of 2.98 BM observed for $ScVO_3$ is only slightly higher than the spin-only predicted value of 2.83 BM for V^{3+} $(3d^2)$. However, the 2.14 BM observed per Ti^{3+} in $ScTiO_{3.003}$ is clearly higher than expected. Although it was observed that sintered pellets of the black $ScTiO_{3.003}$ showed an apparent resistivity of 10^4 ohms cm, the true resistivity of the structure is possibly considerably lower, but the presence of Fe must not be overlooked. However, the magnetic results suggest that the $3d^1$ electron must be substantially localized on the Ti^{3+} sites; consequently, $ScTiO_3$ is probably not metallic but an intrinsic semiconductor. The existence of at least a small number of conduction electrons in the black compound is evidenced by the optical reflection spectrum, which shows the presence of a continuous absorption from approximately 28,000 to 3800 cm^{-1}, probably superposed on a Ti^{3+} ligand-field absorption band at 20,000 cm^{-1}.

The dark brown $ScVO_3$, with a resistivity of approximately 10^8 ohms cm, shows a magnetic susceptibility and optical reflection spectrum consistent with localized $3d^2$ electrons. Of the four absorptions observed (at 4130, 9750, 13,900, and 20,200 cm^{-1}), the upper two

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[12] J. E. Young, Jr., private communication

probably correspond[13] to the normal $3d^2$ octahedral transitions $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$. For VF_3 complexes[14] with a trigonal distortion of a cubic field, three bands at 10,200, 14,800, and 23,000 cm^{-1} have been observed. The upper two correspond to undistorted "cubic" transitions, and the lowest, to the spin-forbidden transition $^3T_{1g} \rightarrow {}^1E_g, {}^1T_{2g}$. The $ScVO_3$ band at 9750 cm^{-1} evidently corresponds to this transition. The actual lowering of the local V^{3+} symmetry to or below trigonal can also allow strong splittings of the "cubic" levels, in particular that of the ground state. For V^{3+} in Al_2O_3 the ground state is split[15] by 1200 cm^{-1} and, in the present case, by 4130 cm^{-1}. The absence of a spin resonance signal for stoichiometric $ScTiO_3$ or $ScVO_3$ at 77°K is probably due to strong spin–lattice interaction; for $ScTiO_{3.053}$, the additional oxygen may reduce this interaction.

The moderate conductivity of $ScTiO_3$ suggests that the 3d orbitals of scandium, together with the 3d orbitals of titanium, participate in establishing conduction band states, and studies on pure crystals could be most interesting. In the absence of completely iron-free Ti starting metal or single crystals of the stoichiometric compounds, conductivity and other physical properties were not further investigated. The sensitivity of the spin resonance and presumably carrier density and mobility to oxygen content in the $ScTiO_{3+x}$ phase suggests a fruitful study of the M_2O_{3+x} region in the C metal oxide–fluorite system.

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Phase Equilibria in the System $Ca_3(PO_4)_2$–$Zn_3(PO_4)_2$

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Phase relationships in the system $Ca_3(PO_4)_2$–$Zn_3(PO_4)_2$ were determined by quenching, strip-furnace, and high-temperature X-ray diffraction methods. The data were used to construct phase diagrams which show the effect of solid solubility on the inversion temperatures of $Ca_3(PO_4)_2$ and $Zn_3(PO_4)_2$ polymorphs and those of the intermediate compound, $CaZn_2(PO_4)_2$. The stable and metastable forms of $CaZn_2(PO_4)_2$ and the metastable existence of "γ-$Zn_3(PO_4)_2$" (the $Mg_3(PO_4)_2$ structure) are discussed in detail.

The alkaline earth orthophosphates as well as those of zinc and cadmium are important phosphor hosts. Of particular interest are divalent tin-activated β-$Sr_3(PO_4)_2$ and divalent manganese-activated β-$Zn_3(PO_4)_2$ which have been used as a color corrector in high-pressure mercury vapor lamps and as the red component in color television screens, respectively. The investigation of the phase equilibrium relationships in the system $Ca_3(PO_4)_2$–$Zn_3(PO_4)_2$ was undertaken as part of a general study on the phase relations in the system $Sr_3(PO_4)_2$–$Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$–$Zn_3(PO_4)_2$.

The phase relations in the system $Ca_3(PO_4)_2$–$Zn_3(PO_4)_2$ have not been reported; however, considerable information has been published on the end members.

Welch and Gutt[1] found that pure calcium orthophosphate melts at 1756° and has three stable polymorphs labeled β, α, and α′ in order of increasing temperature. The phase transitions may be represented by

$$\beta \overset{1125°}{\rightleftarrows} \alpha \overset{1430°}{\rightleftarrows} \alpha'$$

The β ⇄ α inversion can be studied by the quenching technique, but these authors did not comment on the rate of the α ⇄ α′ inversion. The systems $Ca_3(PO_4)_2$–$Sr_3(PO_4)_2$ and $Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$ have been studied by Sarver, Hoffman, and Hummel[2] and by Ando,[3] respectively. β-$Ca_3(PO_4)_2$ takes both Sr^{2+} and Mg^{2+} into solid solution, and in both cases the β → α inversion temperature increases rapidly as the concentration of impurity ions increases. Koelmans, Engelsman, and Admiraal[4] reported the existence of two low-temperature phase transitions at −40° and +35° and speculated that these may be connected with ordering effects in the β-$Ca_3(PO_4)_2$ structure.

Zinc orthophosphate was found by Katnack and

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