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.

Acknowledgment.—The authors are indebted to Dr. Harolyn Perkins for electron spin resonance examination of the compounds described and to Dr. A. D. Wadsley for a number of helpful discussions. The technical assistance of Marie-Paule Chieux is gratefully acknowledged.

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[13] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[14] C. J. Ballhausen and F. Winther, *Acta Chem. Scand.*, **13**, 1729 (1959).

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

BY ERIC R. KREIDLER AND F. A. HUMMEL

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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 $\beta \rightleftarrows \alpha$ inversion can be studied by the quenching technique, but these authors did not comment on the rate of the $\alpha \rightleftarrows \alpha'$ 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 $\beta \rightarrow \alpha$ 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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[1] J. H. Welch and W. Gutt, *J. Chem. Soc.*, 4442 (1961).

[2] J. F. Sarver, M. V. Hoffman, and F. A. Hummel, *J. Electrochem. Soc.*, **108**, 1103 (1961).

[3] J. Ando, *Bull. Chem. Soc. Japan*, **31**, 202 (1958); "Phase Diagrams for Ceramists," E. M. Levin, C. R. Robbins, and H. F. McMurdie, Ed., The American Ceramic Society, Columbus, Ohio, 1964, p 214, Figure 613.

[4] H. Koelmans, J. J. Engelsman, and P. S. Admiraal, *Phys. Chem. Solids*, **11**, 172 (1959–1960).

Hummel[5] to undergo a sluggish reversible inversion ($\alpha \rightleftarrows \beta$) at 942° and to melt congruently at 1060°. The "γ-$Zn_3(PO_4)_2$" form discovered by Smith[6] is actually a set of solid solutions having the $Mg_3(PO_4)_2$ structure,[7] and pure zinc orthophosphate does not possess this structure at any temperature. Zinc orthophosphate solid solutions having the $Mg_3(PO_4)_2$ structure have been observed in the systems $Zn_3(PO_4)_2$–$Mn_3(PO_4)_2$,[8] $Zn_3(PO_4)_2$–$Mg_3(PO_4)_2$,[7] and $Zn_3(PO_4)_2$–$Cd_3(PO_4)_2$.[9] Calvo[10,11] has determined the structures of "γ-$Zn_3(PO_4)_2$" and α-$Zn_3(PO_4)_2$. The major difference between the two structures is that in the α form all of the divalent cations are tetrahedrally coordinated whereas in the γ form one-third of the cations are octahedrally coordinated. Calvo concludes that the γ form is stabilized by cations having a preference for octahedral coordination.

Experimental Procedure

Samples were prepared by allowing mixtures of chemically pure $CaCO_3$, ZnO, and $(NH_4)_2HPO_4$ to react in the solid state. The samples were heated for 15 hr at temperatures of 500, 750, and 900° in platinum crucibles. After each heat treatment the samples were thoroughly ground under acetone to ensure homogeneity. The subsolidus equilibria were studied by the conventional quenching technique.

Since the system was nonglass-forming, the melting behavior was studied by slowly heating 1-cm pellets in a Globar furnace and observing the temperature and extent of melting. These data were supplemented by experiments done on a platinum strip furnace equipped with an optical pyrometer and by determination of the temperature at which an angular fragment showed the first signs of melting when held for 20 min at constant temperature in a quench furnace. The furnace temperature was raised by 5° after each check on the sample condition. These three methods gave results which were in good agreement with each other.

Temperatures were measured to an accuracy of ±1° with Pt—Pt–10% Rh thermocouples which were frequently calibrated against the gold point and against a thermocouple calibrated by the National Bureau of Standards. Phases were identified by X-ray diffraction using Ni-filtered Cu Kα radiation and a Norelco diffractometer set at maximum sensitivity. Scanning rates from $^1/_8$ to 2° (2θ)/min were employed. The polymorphism of $CaZn_2(PO_4)_2$ was studied by high-temperature X-ray diffraction using a Tem-Pres X-ray furnace mounted on the Norelco diffractometer.

Results and Discussion

The results of the quench experiments are in Table I.[12] Owing to the complexity of the system, compositions were spaced as closely as 1 mole %, particularly in the regions near the compounds $CaZn_2(PO_4)_2$ and $Zn_3(PO_4)_2$. The melting behavior of pressed pellets as a function of temperature and composition is given in Table II.[12] The data in Tables I and II, the literature values for melting and phase transitions in the end members, and the results of the high-temperature X-ray study on $CaZn_2(PO_4)_2$ were used to construct the equilibrium diagrams shown in Figures 1 and 2.

TABLE III

X-RAY DIFFRACTION PATTERNS OF $CaZn_2(PO_4)_2$ POLYMORPHS

α-$CaZn_2(PO_4)_2$ at Room Temperature

d, A	I/I_1	d, A	I/I_1	d, A	I/I_1
4.19	52	2.62	50	2.06	11
4.13	70	2.52	35	2.04	31
3.95	39	2.47	59	1.92	7
3.85	31	2.42	17	1.88	13
3.80	30	2.36	22	1.85	5
3.75	46	2.28	9	1.84	5
3.63	20	2.26	7	1.82	5
3.58	55	2.22			
			20	1.79	5
3.24	11	2.21			
3.01	59	2.16	7	1.77	15
2.95	100	2.13	20	1.74	7
2.90	17	2.09		1.70	15
2.78	35		24	1.69	18
		2.08			
2.71	11			1.66	30

β-$CaZn_2(PO_4)_2$ at 937° Held 3 Hr

d, A	I/I_1	hkl	d, A	I/I_1	hkl
4.46	46	100	1.81	56	113
3.85	100	101, 002	1.76	35	104
2.91	95	102	1.68	7	210, 203
2.57	60	110	1.64	19	211
2.44	65	111	1.54	26	212
2.23	3	200	1.48	28	300
2.14	35	201, 112	1.45	26	204, 301
1.93	9	202	1.38	7	302

Hexagonal: $a = 5.13$ A, $c = 7.67$ A

γ-$CaZn_2(PO_4)_2$ at 1012° Held 2 Hr

d, A	I/I_1	d, A	I/I_1	d, A	I/I_1
4.37	16	3.05	42	2.03	53
4.31	90	2.91	16	2.01	39
4.06	100	2.87	37	1.98	7
3.87	45	2.63	11	1.93	10
3.75	50	2.57	8	1.82	8
3.25	18	2.38	14	1.73	57
3.08	42	2.15	45		

δ-$CaZn_2(PO_4)_2$ at Room Temperature

d, A	I/I_1	d, A	I/I_1	d, A	I/I_1
4.23	60	2.99	40	2.34	37
4.11	39	2.90	13	2.33	48
4.00	71	2.78	18	2.26	18
3.87	34	2.76	77	2.24	10
3.80	18	2.75	45	2.19	6
3.65	32	2.59	30	2.16	8
3.53	23	2.56	26	2.13	21
3.36	5	2.47	8	1.99	18
3.20	100	2.43	8	1.96	34
3.04	11	2.36	19	1.95	19
3.02	14				

+ reflections

β-$Ca_3(PO_4)_2$ Solid Solutions

β-$Ca_3(PO_4)_2$ takes 10 mole % of $Zn_3(PO_4)_2$ into solid solution at 1000°. This value was determined by slowly scanning ($^1/_8$° (2θ)/min) over the 46.9° β-$Ca_3(PO_4)_2$ peak and plotting the 2θ values against the bulk

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(5) F. L. Katnack and F. A. Hummel, *J. Electrochem. Soc.*, **105**, 125 (1958).

(6) A. L. Smith, *ibid.*, **98**, 363 (1951).

(7) J. F. Sarver, F. L. Katnack, and F. A. Hummel, *ibid.*, **106**, 960 (1959).

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(10) C. Calvo, *Phys. Chem. Solids*, **24**, 141 (1963).

(11) C. Calvo, *Can. J. Chem.*, **43**, 436 (1965).

(12) Tables I and II have been deposited as Document No. 9207 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

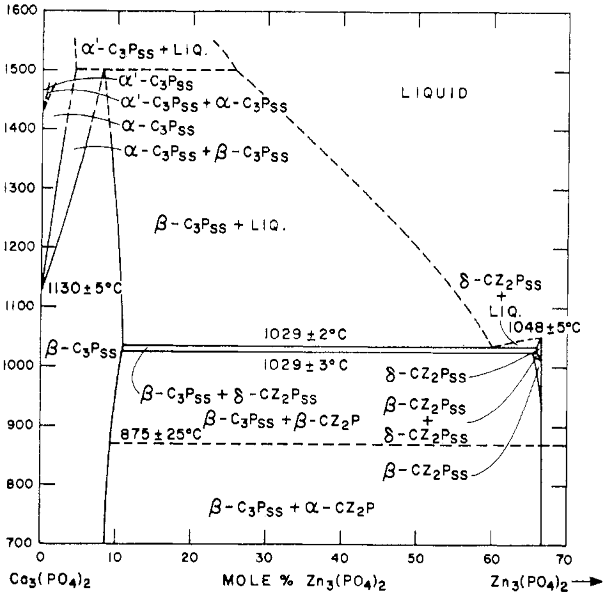

Figure 1.—The system $Ca_3(PO_4)_2$–$CaZn_2(PO_4)_2$.

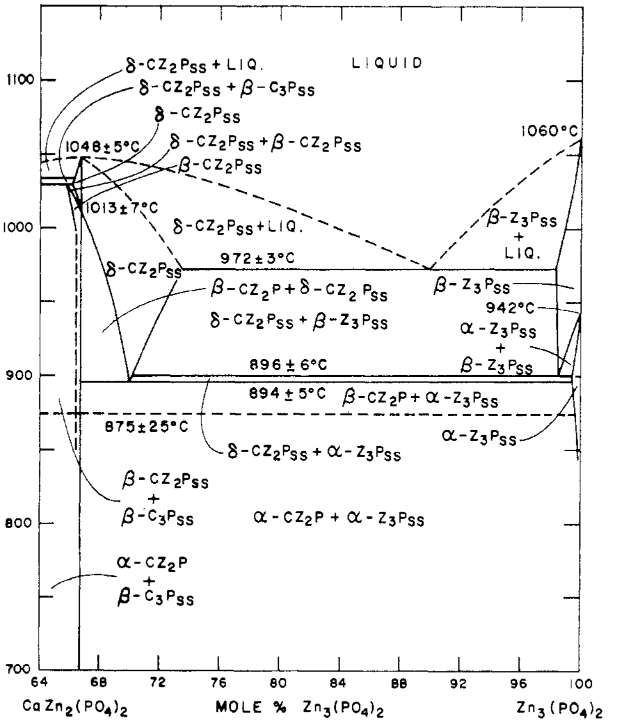

Figure 2.—The system $CaZn_2(PO_4)_2$–$Zn_3(PO_4)_2$.

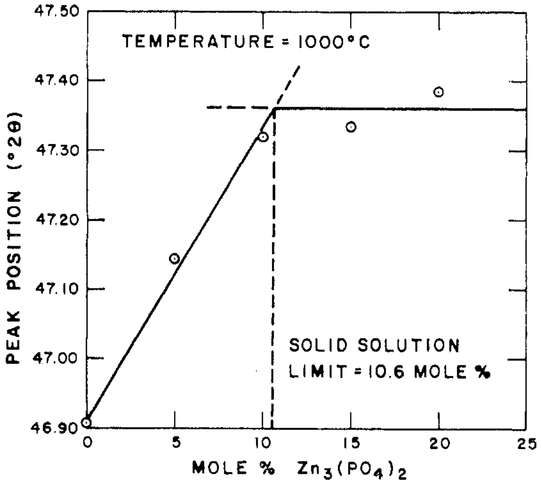

Figure 3.—Change in 2θ values as a function of composition for $(Ca,Zn)_3(PO_4)_2$ solid solutions.

sample composition (Figure 3). The samples used in this study were pressed into pellets and equilibrated at 1000° for 48 hr before the measurements were made. The solid solution of $Zn_3(PO_4)_2$ in β-$Ca_3(PO_4)_2$ resulted in a sharp increase in the $\beta \rightarrow \alpha$ inversion temperature. The same behavior was observed with β-$(Ca,Mg)_3(PO_4)_2$[3] and β-$(Ca,Sr)_3(PO_4)_2$[2] solid solutions. The $\alpha \rightleftarrows \alpha'$ inversion in $Ca_3(PO_4)_2$ was not studied.

Polymorphism in $CaZn_2(PO_4)_2$

One compound, $CaZn_2(PO_4)_2$, which melts congruently at 1048 ± 5°, was found in the system. This compound has the same type of stoichiometry as the $SrMg_2(PO_4)_2$ and $SrZn_2(PO_4)_2$ compounds reported by Sarver, Hoffman, and Hummel,[2] and a visual comparison of the X-ray patterns revealed possible structural similarities between β-$CaZn_2(PO_4)_2$ and $SrMg_2(PO_4)_2$ and between α-$CaZn_2(PO_4)_2$ and α-$SrZn_2(PO_4)_2$.

High-temperature X-ray diffraction and quenching experiments revealed the existence of four polymorphic forms of $CaZn_2(PO_4)_2$. The X-ray patterns of these polymorphs are listed in Table III. The inversions detected by the high-temperature X-ray study may be represented by

$$\alpha \xrightleftharpoons{870 \pm 25^\circ} \beta \xrightleftharpoons{997 \pm 22^\circ} \gamma$$

The $\alpha \rightleftarrows \beta$ inversion is rapidly reversible and the β form cannot be quenched to room temperature. The X-ray pattern of β-$CaZn_2(PO_4)_2$ has been successfully indexed on a hexagonal unit cell with a = 5.13 A and c = 7.67 A. The diffraction patterns of the other forms are too complex to be easily indexed.

The X-ray patterns of the γ form continuously change with time when the sample is held at 1020° for periods of up to 2 hr. Some lines disappear while new ones appear and others undergo drastic relative intensity changes. This change in the patterns was not caused by changes in the composition of the sample since, when cooled to room temperature, the α form was again obtained and there were no impurity phases present. Upon rapid cooling the γ form does not revert to β, but does revert to α at about 840°. Upon slow cooling the sequence $\gamma \rightarrow \beta \rightarrow \alpha$ was observed. This behavior demonstrates that the $\beta \rightleftarrows \gamma$ inversion is sluggish.

The quenching study revealed the existence of the fourth (δ) form of $CaZn_2(PO_4)_2$. The δ form was obtained by quenching pure $CaZn_2(PO_4)_2$ which had been held at temperatures above 1013 ± 7° for 10 hr or more. When the δ form was reheated to temperatures below 1013° and then quenched, the α form was obtained. Thus from the quenching experiments, there was apparently only one phase transformation $\alpha \rightleftarrows \delta$ occurring at 1013°. The $\alpha \rightleftarrows \beta$ inversion was not detected because the β form was nonquenchable.

The facts (a) that the X-ray patterns of the γ form undergo continuous changes with time and (b) that the γ form was not observed in the quenching studies suggest that γ-$CaZn_2(PO_4)_2$ is a nonequilibrium phase. A schematic pressure *vs.* temperature diagram which accounts for the observed thermal behavior of $CaZn_2(PO_4)_2$ is given in Figure 4. In this diagram the α, β, and δ forms are regarded as the stable polymorphs, and the γ form is regarded as a metastable phase obtained by superheating β-$CaZn_2(PO_4)_2$. Under suitable experimental conditions the γ form can revert directly to the α, β, or δ forms as shown by the arrows in Figure 4. The γ → α and γ → β reactions were observed in the high-temperature X-ray study by cooling the γ form at different rates. With rapid cooling the γ → α inversion was observed, and with slower cooling the γ → β inversion was observed. The γ → δ inversion probably takes place when the γ form is heated above 1013° for a relatively long time. This would explain the occurrence of the δ phase in quenched samples. This hypothesis was used in constructing the equilibrium diagrams shown in Figures 1 and 2.

It is interesting to note that β-$CaZn_2(PO_4)_2$ and hexagonal $BaAl_2Si_2O_8$ (Sorrell[13]) are isostructural, with lattice parameters $a = 5.13$, $c = 7.67$ A and $a = 5.25$, $c = 7.84$ A, respectively.

There may be isostructural relationships between monoclinic $BaAl_2Si_2O_8$ and α-$CaZn_2P_2O_8$, but the diffraction patterns are not sufficiently similar to allow indexing by analogy. The structure of monoclinic $BaAl_2Si_2O_8$ was determined by Newnham and Megaw,[14] and that for the hexagonal phase by Takeuchi.[15] In both phases, Al and Si are in four-coordination, and ordering occurs between Si and Al. It is likely that Zn and P are in four-coordination in β-$CaZn_2P_2O_8$, and ordering probably occurs between Zn and P.

Solid Solution in $CaZn_2(PO_4)_2$

A series of δ-$CaZn_2(PO_4)_2$ solid solutions exists between $CaZn_2(PO_4)_2$ and $Zn_3(PO_4)_2$. The solid solutions extend from 66.7 to a maximum of 74 mole % $Zn_3(PO_4)_2$ and have an eutectoid at 70 mole % $Zn_3(PO_4)_2$ and 894 ± 4°. Solid solutions of $Zn_3(PO_4)_2$ in α- and β-$CaZn_2(PO_4)_2$ were not detected. A small amount of solid solution of $Ca_3(PO_4)_2$ in β- and δ-$CaZn_2(PO_4)_2$ was detected by a 15° increase in the β ⇄ δ inversion temperature. The samples used to detect this temperature increase were simultaneously heated in the same quench furnace, hence the difference was not due to variations in sample temperature or equilibration time.

Since the α ⇄ β inversion in $CaZn_2(PO_4)_2$ was nonquenchable, the inversion temperature was assumed to be independent of composition when constructing Figures 1 and 2.

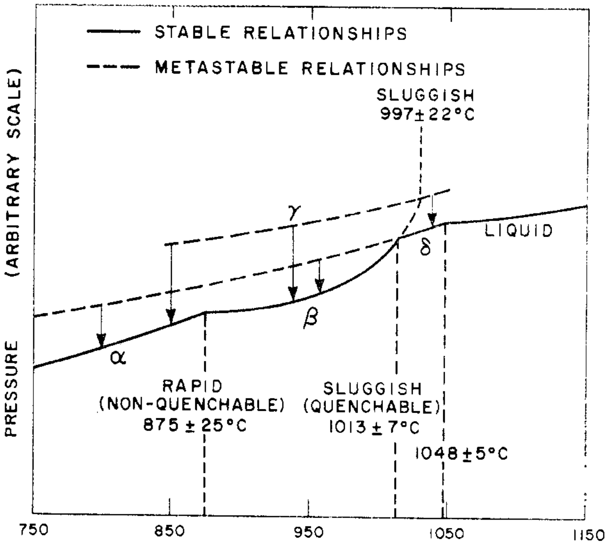

Figure 4.—Schematic pressure *vs.* temperature diagram for $CaZn_2(PO_4)_2$.

Solid Solution in $Zn_3(PO_4)_2$

A small amount of solid solution of $Ca_3(PO_4)_2$ in α- and β-$Zn_3(PO_4)_2$ was detected by a 45° decrease in the α ⇄ β inversion temperature. This lowering of the inversion temperature is in agreement with the findings in other zinc orthophosphate systems.[2,7,9] About 1.5 mole % of $Ca_3(PO_4)_2$ can be dissolved in β-$Zn_3(PO_4)_2$.

Metastable γ-$Zn_3(PO_4)_2$ Solid Solutions

Calvo[10] mentioned the existence of γ-$Zn_3(PO_4)_2$ solid solutions in the system $Ca_3(PO_4)_2$–$Zn_3(PO_4)_2$. This phase was found to be metastable in the present study. Metastable γ-$Zn_3(PO_4)_2$ could be prepared by two methods: (a) by quenching compositions containing about 70–95 mole % $Zn_3(PO_4)_2$ from temperatures above the solidus or (b) by heating samples containing α-$Zn_3(PO_4)_2$ for relatively short periods at temperatures slightly above the α ⇄ β inversion temperature (896°).

When melted at 1050° and quenched, a composition of 90% $Zn_3(PO_4)_2$–10% $Ca_3(PO_4)_2$ yielded γ-$Zn_3(PO_4)_2$ plus a trace of δ-$CaZn_2(PO_4)_2$. When this sample was reheated at 900° the γ phase persisted for a long time, but as the reheating temperature was raised or lowered from 900° the time persistence of the γ phase decreased rapidly, and the true equilibrium phases as shown in Figure 2 were obtained.

Essentially pure γ-$Zn_3(PO_4)_2$ was obtained by heating a composition of 97.5% $Zn_3(PO_4)_2$–2.5% $Ca_3(PO_4)_2$ at 911° for 5 hr. The starting material contained α-$Zn_3(PO_4)_2$ and a trace of α-$CaZn_2(PO_4)_2$. The phases observed after various times of heat treatment at 905° are shown in Table IV. Apparently, α rapidly changes to γ when heated above the inversion temperature and

TABLE IV

PERSISTENCE OF METASTABLE "γ-$Zn_3(PO_4)_2$" AT 905°

Heating time, hr	Phases present[a]
0	α-Z_3P
5	γ-Z_3P
38	γ- + β-Z_3P
93	β-Z_3P

[a] Major phase listed first; composition, 97.5 mole % $Zn_3(PO_4)_2$.

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(13) C. A. Sorrell, *Am. Mineralogist*, **47**, 291 (1962).
(14) R. E. Newnham and H. D. Megaw, *Acta Cryst.*, **13**, 303 (1960).
(15) Y. Takeuchi, *Mineral. J.* (Sapporo), **2**, 311 (1958).

γ then changes slowly into the stable β form. This fact conclusively shows that the calcium-stabilized γ-$Zn_3(PO_4)_2$ solid solutions are metastable.

The extent of the γ-solid solutions as a function of the radius of the stabilizing ion is given in Table V. As the radius of the stabilizing cation increases, the composition range of the solid solutions rapidly decreases. The calcium ion represents the limiting case for the existence of γ-solid solutions. Larger ions such as Sr^{2+} do not yield γ-solid solutions, whereas ions smaller than Ca^{2+} yield thermodynamically stable solid solutions.

Table V

Composition Range of "γ-$Zn_3(PO_4)_2$" Solid Solutions As a Function of the Radius of the Stabilizing Cation

Compn range, mole % $Zn_3(PO_4)_2$	Stabilizing cation	Radius of ion, A	Ref
0–97	Mg^{2+}	0.67	7
4–27	Mn^{2+}	0.80	8
2–7	Cd^{2+}	0.97	9
Metastable	Ca^{2+}	0.99	This paper
Not observed	Sr^{2+}	1.12	2

Conclusions

β-$Ca_3(PO_4)_2$ takes a maximum of 10 mole % $Zn_3(PO_4)_2$ into solid solution. The β ⇄ α inversion temperature increases rapidly as the concentration of $Zn_3(PO_4)_2$ increases. This behavior is the same as that observed in the $Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$[8] and $Ca_3(PO_4)_2$–$Sr_3(PO_4)_2$[2] systems.

One compound, $CaZn_2(PO_4)_2$, was found in the system. The compound melts congruently at 1048 ± 5° and has three stable polymorphs with the transition temperatures

$$\alpha \overset{870 \pm 25^\circ}{\rightleftarrows} \beta \overset{1013 \pm 7^\circ}{\rightleftarrows} \delta$$

A metastable phase, labeled γ-$CaZn_2(PO_4)_2$, was found to exist above 997 ± 22° by high-temperature X-ray diffraction. Only the α and δ forms were observed in quenched samples. δ-$CaZn_2(PO_4)_2$ forms solid solutions with $Zn_3(PO_4)_2$ extending from 66.7 to 74 mole % $Zn_3(PO_4)_2$. These solid solutions have a eutectoid at 894° and 70 mole % $Zn_3(PO_4)_2$. Slight amounts of $Ca_3(PO_4)_2$ go into solid solution in β- and δ-$CaZn_2(PO_4)_2$.

Approximately 1.5 mole % of $Ca_3(PO_4)_2$ goes into solid solution in β-$Zn_3(PO_4)_2$. The α ⇄ β inversion temperature decreases as the Ca^{2+} concentration increases. Similar behavior was observed in other systems.[7–9]

γ-$Zn_3(PO_4)_2$ solid solutions were observed in the system, but these are metastable. The composition range of the γ-solid solutions is inversely related to the size of the stabilizing cation. The Ca^{2+} ion represents the limiting size for the existence of such solid solutions, and with calcium these are metastable. Ions smaller than Ca^{2+} produce stable γ-solid solutions whereas ions larger than Ca^{2+} do not even produce metastable γ-solid solutions.

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The Rate and Mechanism of the Iodine–Formate Reaction in Dimethyl Sulfoxide–Water Solvents

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The kinetics of the reaction $I_3^- + HCOO^- \rightarrow 3I^- + CO_2 + H^+$ have been studied spectrophotometrically in water, in pure dimethyl sulfoxide, and in several dimethyl sulfoxide–water mixtures. The reaction was found to be first order in triiodide ion, first order in formate ion, and inverse first order in iodide ion in the various solvents. Metal ion–formate ion-pair dissociation constants and values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from the kinetic data. The deuterium isotope effect using deuterioformate was examined and values of k_H/k_D were found to change from 2.2 in dimethyl sulfoxide to 3.8 in water. Values of the triiodide ion dissociation constants were measured and found to decrease as the mole fraction of dimethyl sulfoxide in the solvent increased. The mechanism proposed involves a rate-determining attack of iodine on the formate anion. Because water molecules strongly solvate the formate anion *via* hydrogen bonding, the rate of reaction decreases as the water content of the solvent increases.

Introduction

In this paper we report the results of a kinetic study of the iodine–formate reaction

$$I_3^- + HCOO^- \longrightarrow 3I^- + CO_2 + H^+ \qquad (1)$$

This work represents a continuation of our evaluation of solvent effects on inorganic reactions in water–dimethyl sulfoxide (DMSO) solvents.[2] In particular, our objective has been to examine changes in rate and

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(1) To whom inquiries should be addressed.

(2) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).