5. ZrO₂とSiCとの混合物の1600°C水素気流中での焼結によりZrCが生成した。
6. MoSi₂, SiCをそれぞれ40wt%まで含有するジルコニア試料は、電気炉抵抗発熱体として利用する場合安定性ジルコニアより利点が少ない。

文 献
4) a) たとえば着藤清六, 宗宮雅行, 工業研究, No. 23, 42-51 (1963).
   b) 宗宮雅行, “含ジルコニア系耐火物” 工業材料の進歩, 東京工業大学工業材料研究所, 201-204 (1964).

22. Solid Solubilities of FePO₄ and CrPO₄ in AlPO₄

By
Taneo KOBAYASHI
(Nagoya Institute of Technology)

Abstract
Al³⁺, Fe³⁺ and Cr³⁺ are similar in their chemical properties, and their coordination number to O²⁻ is six. Their ortho-phosphates are able to have an isostructrue with SiO₂, because the ratios of the average ionic radii of the positive ions to that of oxygen ion are nearly equal to each other, —0.30, 0.31, 0.35 and 0.35 for SiSiO₄, AlPO₄, FePO₄ and CrPO₄ respectively. In practice, the quartz type, the tridymite type and the cristobalite type, have been found for AlPO₄ and only the quartz type for FePO₄, but the isostructure with SiO₂ is not yet known even now for CrPO₄. The solid solutions between AlPO₄-FePO₄ and AlPO₄-CrPO₄, which were synthesized above 1100°C, were studied in this paper.

In the AlPO₄-FePO₄ system, perfect solid solutions were made, and their crystals had the structure of the cristobalite type and the quartz type when [Al³⁺/Fe³⁺] ≥3/7, and ≤2/8 respectively.

In the range [Al³⁺]=0.55~0.3 molar fraction, the crystals were in the transition state from the cristobalite type to the quartz type.

In the AlPO₄-CrPO₄ system, the crystal structure was of the cristobalite type with the exception that δ-CrPO₄ was isolated when [Al³⁺/Cr³⁺] was below 8/2.

1. Introduction
It is well known that Al, Fe and Cr have similar chemical properties. The co-ordination number to O²⁻ is six for Al³⁺, Fe³⁺ and Cr³⁺, and the ratio of the average ionic radii of the positive ions to that of oxygen ion makes it possible for AlPO₄, FePO₄ and CrPO₄ to have an isostructure with SiO₂ geometrically. Therefore it should be possibl to form solid solutions between AlPO₄ and FePO₄, or AlPO₄ and CrPO₄. Especially AlPO₄ and FePO₄ have practically an isostructure with SiO₂, so they are much similar to each other.

On the other hand, the ionic radii of Al³⁺, Fe³⁺ and Cr³⁺ determined by Wyckoff are 0.55, 0.67 and 0.70 Å respectively. So the radius of Al³⁺ is 22 and 27 per cent smaller than those of Fe³⁺ and Cr³⁺ respectively. FePO₄ does not have a cristobalite type structure, and the CrPO₄ crystal belongs to the triclinic structure.
From these points the solid solubilities in the system AlPO₄-FePO₄ and AlPO₄-FePO₄ were studied in this paper.

2. Preparation

For the preparation of the samples, extra pure reagents ammonium alum, ferric alum, chromic alun, diammonium phosphate, ammonium acetate, and hydrochloric acid were used.

AlPO₄·2H₂O was prepared as mentioned in the previous paper: ammonium phosphate solution which contained [PO₄³⁻] of the tenfold [Al³⁺] in molar concentration was added to a dilute ammonium alun solution, and the precipitation was made by regulating pH to 4~5 with 25 per cent AcNH₄ solution, and successively the precipitates together with the mother liquid were heated on a water bath for 1~2 days, until the amorphous precipitates grew into crystals, AlPO₄·2H₂O, which were filtered washed with water, and then dried at 45°C.

Next, a part of the ammonium alun was replaced with ferric alum or chromic alun of equal moles, and thereby Fe³⁺ or Cr³⁺ was introduced partially of wholly instead of Al³⁺ into AlPO₄·2H₂O, thus the hydrates of (Al, Fe) PO₄ or (Al, Cr) PO₄ were prepared.

Sample 0.8g sample holder corundum d.t.a. couple Pt/PtRh/Pt thermo couple Pt/PtRh heating rate 6°C/min

Fig. 1. D.T.A. curves of FePO₄·2H₂O and (AlₓFeₓ)PO₄·2H₂O.

Differential thermal analysis, indicated for example in Fig. 1, showed that these hydrates lost their water of crystallization below 400°C and crystallized gradually into anhydrates at a higher temperature. The more the compounds contained FePO₄, the lower their melting points were. Therefore the hydrates were fired at relatively low temperature (1100~1170°C) for 15 hours, and some of them were sintered at this temperature.

3. Method of experiment

At first it was ascertained by chemical analysis whether the samples (anhydrates) had the chemical compositions as expected. The crystal water contents of the hydrates was determined by the weight loss up to 500°C.

In order to ascertain whether the solid solutions between AlPO₄ and FePO₄ or AlPO₄ and CrPO₄ can be made, the variation of the lattice-constants was calculated from the results of precise determination by X-ray diffractions, and the α→β inversions for the cristobalite type as well as the quartz type were observed by thermal analysis. The pleochroisms of the samples were also studied by a polarizing microscope.

Quartz was used as the internal standard substance for the precise X-ray diffractions. It was washed thoroughly with HCl, and the lattice constants were precisely determined with pure MgO. According to their values (the distances between the two crystal faces) of the quartz were calculated again.

The samples were mixed with this standard quartz and the diffractions of the faces (200) and (102) in the case of the cristobalite type, (200) and (112) in the case of the quartz type were observed precisely.

4. Results

The compositions of the samples by the chemical analysis are shown in Table 1. The results showed good accordance with the values expected from the method of synthesis of the hydrates.

Table 1. Chemical composition of (Al, Fe)PO₄ and (Al, Cr)PO₄ solid solutions.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Composition (%)</th>
<th>Mol. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO₄</td>
<td>41.8</td>
<td>58.2</td>
</tr>
<tr>
<td>(AlₓFeₓ)PO₄</td>
<td>31.9 (12.5)</td>
<td>55.6 (79.9)</td>
</tr>
<tr>
<td>(AlₓFeₓ)PO₄</td>
<td>22.9 (23.9)</td>
<td>53.2 (59.9)</td>
</tr>
<tr>
<td>(AlₓFeₓ)PO₄</td>
<td>14.6 (34.4)</td>
<td>51.0 (39.9)</td>
</tr>
<tr>
<td>(AlₓFeₓ)PO₄</td>
<td>7.0 (44.0)</td>
<td>48.9 (19.9)</td>
</tr>
<tr>
<td>FePO₄</td>
<td>52.9</td>
<td>47.1</td>
</tr>
<tr>
<td>(AlₓCrₓ)PO₄</td>
<td>39.3 (3.1)</td>
<td>57.6 (95.2)</td>
</tr>
<tr>
<td>(AlₓCrₓ)PO₄</td>
<td>36.9 (6.1)</td>
<td>57.0 (90.1)</td>
</tr>
<tr>
<td>(AlₓCrₓ)PO₄</td>
<td>32.1 (12.0)</td>
<td>55.9 (79.9)</td>
</tr>
</tbody>
</table>

(1) The quasi-binary system AlPO₄-FePO₄

The hydrates had two moles of water per mole, and the weight loss up to 500°C corresponded to the water of crystallization. From the results of the X-ray diffractions of the hydrates (Fig. 2), the structures of FePO₄·2H₂O and AlPO₄·2H₂O (-B type) — the two end members of this system— appeared to be alike. The patterns of (Al, Fe)PO₄·2H₂O varied gradually among those of the two end members, so their structures also had to be very similar.

As Fe³⁺ was substituted for Al³⁺ in AlPO₄, the
The strength of the X-ray diffraction patterns of the cristobalite type gradually became weaker. Above 80 mole per cent of Fe³⁺ the crystal structure changed into the quartz type. (see Fig. 3) Between 73-76 mole per cent the cristobalite type and the quartz type coexisted, and at 73 mole per cent the cristobalite type was dominant and on the contrary at 76 mole per cent the quartz type was so.

Even when the crystals of (Al, Fe)PO₄ took either the cristobalite form or the quartz form, the α-β inversions could be observed in the thermal analysis. (see Fig. 4)

Under the cross nicol of the polarized microscope, the samples, which contained 50 mole per cent or more of Fe³⁺ in place of Al³⁺ in AlPO₄,
increased their pleochroism to a high extent. At 73 mole per cent some quartz type crystals co-existed, and when Fe³⁺ was much more than 73 per cent, the quartz type crystals increased rapidly, while the cristobalite type, which shows a small amount of birefringence, disappeared.

(2) The quasi-binary system AlPO₄–CrPO₄

By the reaction Cr³⁺ with PO₄³⁻ in the solution, CrPO₄·6H₂O is prepared, and when it is fired at 1125°C, it changes into β-CrPO₄. When Cr³⁺ partially replaced the Al³⁺ in aluminium ortho-phosphate, the hydrates showed the structure analogous to AlPO₄·2H₂O (β type), but over 20 mole per cent, they became amorphous (see Fig. 5), though CrPO₄·6H₂O itself was also amorphous when it was prepared in this manner.

By thermal analysis the α–β inversion could be recognized also in (Al, Cr)PO₄, but its peaks were somewhat indistinct. (see Fig. 7)

5. Discussion

(1) (Al, Fe)PO₄

The hydrates had two moles of crystal water per mole and showed a similar structure for X-ray diffractions, so they are able to make solid solutions.

Both aluminium phosphate and ferric phosphate are isostructures with SiO₂, and when they are fired at high temperatures, AlPO₄ crystalises into the cristobalite type and FePO₄ into the quartz type.

The crystal systems and the lattice constants of the samples (Al, Fe)PO₄ are given in Table 2 and Fig. 8.

By the substitution of Fe⁺⁺ for Al³⁺, the lat-
The peak of the $\alpha-\beta$ inversion of pure AlPO$_4$ in the thermal analysis was fairly small at the lower temperature (206°C), and this is due to the fact that the development of the crystals of the cristobalite type is imperfect as reported in the previous paper$^7$.

From the results of the X-ray diffractions and the thermal analysis, it is clear that the crystallization of (Al, Fe) PO$_4$ to the cristobalite form is accelerated by the substitution.

At present only the quartz type is known for the crystal form of ferric ortho-phosphate$^{8,9}$. When the substitution of Fe$^{3+}$ for Al$^{3+}$ was over 80 mole per cent, the crystals were changed into the quartz type, and did not include the cristobalite type. These quartz type solid solutions made the $\alpha-\beta$ inversion worse in its sensitiveness. (see Fig. 4). In (Al$_{0.24}$ Fe$_{0.76}$) PO$_4$ the $\alpha-\beta$ inversion peak could be observed only a little. As Fe$^{3+}$ was replaced by Al$^{3+}$, the length of both $a$- and $c$-axis of the quartz type crystals began to contract. This is due to the shortness of the radius of Al$^{3+}$ to Fe$^{3+}$. In this case the temperature of the $\alpha-\beta$ inversion went down remarkably, while, as mentioned above, the substitution of Fe$^{3+}$ for Al$^{3+}$ in AlPO$_4$ had little effect on the inversion temperature.

When the substitution of Fe$^{3+}$ for Al$^{3+}$ in AlPO$_4$ was over 55 mole per cent, a new endothermic peak, which is comparable in height with the $\alpha-\beta$ inversion, appeared by the thermal analysis near 135°C, but this peak became smaller by repeating the thermal analysis. In this range the temperature of the $\alpha-\beta$ inversion becomes higher, when Fe$^{3+}$ was continued to be substituted for Al$^{3+}$ and at (Al$_{0.24}$ Fe$_{0.76}$) PO$_4$ it reached 263°C. (When the cristobalite type AlPO$_4$ makes solid solutions with other minerals, the temperature of the $\alpha-\beta$ inversion generally becomes lower than that of the end member, AlPO$_4$.) But in this range the lattice constants, calculated from the results of X-ray diffractions, did not vary, so even if the substitution was over 55 mole per cent, the unit cell dimension did not expand any more, and moreover free FePO$_4$ was not detected. When the replacement was carried on beyond 73 mole per cent of Fe$^{3+}$ the quartz type began to appear too, and at last there occurred only the quartz type.

Although the AlPO$_4$-FePO$_4$ system made solid solutions as (Al, Fe)PO$_4$ above 1100°C, AlPO$_4$ and FePO$_4$ crystallize into the cristobalite type and the quartz type respectively. So, when the composition of the solid solutions is in the range of 55~24 mole per cent for Al$^{3+}$, they will take a semi-stable structure in the transition state from the cristobalite type to the quartz type. By thermal analysis this causes the unstable endothermic peak near 135°C, and makes the $\alpha-\beta$ inversion unusually higher.

(2) (Al, Cr) PO$_4$

Cr$^{3+}$ is familiar to Al$^{3+}$ next to Fe$^{3+}$ in its chemical properties. In addition $1/2$(Cr$^{3+}$+P$^{5+}$) = 0.49, 1/2(Cr$^{3+}$+P$^{5+}$)/O$^{2-}$ = 0.35, and these relations are equal to FePO$_4$. So CrPO$_4$ has the probability of making an isostructure with SiO$_2$. But actually it does not take this structure. Nevertheless solid solutions between AlPO$_4$ and CrPO$_4$ could be produced by substituting Cr$^{3+}$ for a part of Al$^{3+}$ in AlPO$_4$. But as the ionic radius of Cr$^{3+}$ is much larger (27 per cent) than that of Al$^{3+}$, the solid solutions have less atomic density, and also the energy in the crystal lattice is in a high level owing to disturbance of the atomic arrangement. These lead to the conclusion that in these solid solutions (Al, Cr)PO$_4$, the strength of X-ray diffractions becomes weaker, and the peak of the $\alpha-\beta$ inversion by thermal
Table 3. Crystal systems and lattice constants of (Al, Cr)PO₄ solid solutions.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Crystal systems</th>
<th>a₀(Å)</th>
<th>c₀(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AlₙCrₙ)PO₄</td>
<td>tetragonal</td>
<td>5.007</td>
<td>7.022</td>
</tr>
<tr>
<td>(AlₙCrₙ)SO₄</td>
<td>tetragonal</td>
<td>5.020</td>
<td>7.069</td>
</tr>
<tr>
<td>(AlₙCrₙ)SO₄</td>
<td>triclinic</td>
<td>5.000</td>
<td>7.022</td>
</tr>
</tbody>
</table>

tetragonal system; cristobalite type
triclinic system; β-CrPO₄

Fig. 9. Lattice constants of (Al, Cr)PO₄.

Table 3 and Fig. 9 show that when Cr³⁺ is substituted for Al³⁺ in AlPO₄, elongation of the crystal axes occurs, especially toward the c-axis. The difference of the atomic radius between Al³⁺ and Cr³⁺ is so large that the solid solutions by the substitution reach saturation over 20 mole per cent of Cr³⁺, and then β-CrPO₄ is isolated. Near the saturation point precise measurement by X-ray diffractions was impossible because of the disturbance of the atomic arrangement.

6. Conclusio
(1) Both the AlPO₄-FePO₄ system and the AlPO₄-CrPO₄ system could make solid solutions when they were fired above 1100°C.
(2) In (Al, Fe)PO₄, the cristobalite type crystals were stable when [Al³⁺/Fe³⁺] ≥ 3/7, and the quartz type crystals were stable when [Al³⁺/Fe³⁺] ≤ 2/8. In the range [Al³⁺]=0.55~0.3 molar fraction, the crystals belonged to the cristobalite type, but they seemed to be in a transition state to the quartz type.
(3) In (Al, Cr)PO₄, the cristobalite type crystals were stable with the exception that β-CrPO₄ was isolated when [Cr³⁺]=0.2 molar fraction.

Acknowledgment
The author wishes to thank Dr. Goro Yamaguchi, Prof. of the University of Tokyo, for many helpful discussions and suggestions during this work.

References
2) G. Yamaguchi, Japan Analyst 6, 121–127 (1957).
4) T. Kobayashi, see 1)

[Received Sept. 15, 1965]