APPENDIX 1

STRUCTURAL REFINEMENT OF TAPO$_4$-5

TAPO$_4$-5 belongs to AFI topology. AFI structure has been studied by single crystal as well as by powder techniques (Bennet et al 1983, Richardson et al 1987, Qiu et al 1989, Bialeck et al 1991 and Chao et al 1992). Its topological data are given in Chapter 2. AFI crystallises in P6CC space group and its formula is T$_{24}$O$_{48}$.

A1.1 NEED FOR TAPO$_4$-5 STRUCTURAL REFINEMENT

On substitution of Ti in AlPO$_4$, it may replace either aluminium or both aluminium and phosphorus. In either case the unit cell constant should not decrease because the Ti-O bond length (1.78 Å) is higher than Al-O (1.75 Å) and P-O (1.53 Å) bonds. Actually decrease in unit cell constant was observed (Table 3.4). A similar decrease in unit cell constant was observed for silica analogue of AlPO$_4$-5 (SSZ-24), (Si-O=1.52 Å). This decrease was attributed to a decrease in bond angle from 176.5° (Al-O2-P) to 142.2° (Si-O2-Si) (Bialeck et al 1991). An attempt has been made to refine the structure of TAPO$_4$-5, with view to identify the reasons for the reduction of unit cell constants.

A1.2 RIETVELD ANALYSIS

Rietveld (1969) developed a computer based analytical procedure, for extracting full information from entire powder data, which was subsequently further developed by many groups and now their procedure is known as Rietveld analysis.
Rietveld analysis is a least square simultaneous refinement of structural model(s), instrumental factors, specimen characteristics etc., until the best fit is obtained between the calculated and the observed patterns.

In order to do the analysis, it is inevitable to have carefully collected step scan data from highly crystalline materials. With modern computerized diffractometers, the data have been collected in digital form. The Rietveld analysis can be done on X-ray and Neutron powder diffraction data.

The quantity minimized in the least square refinement is the residue ‘Res’ (Equation A1.1)

\[ \text{Res} = \sum w_i (y_i - y_{ci})^2 \]  
(A1.1)

where
\[ w_i = \frac{1}{y_i} \]
\[ y_i = \text{observed intensity at } i^{\text{th}} \text{ step} \]
and
\[ y_{ci} = \text{calculated intensity at the } i^{\text{th}} \text{ step} \]

On diffraction from each Miller plane, the obtained peak will have a peak position, peak height, peak breadth and tails, which decay gradually from peak position. The integrated area is proportional to Bragg intensity \( I_K \), where \( K \) represent Miller indices \( h,k,l \) and

\[ I_K \propto F_K^2 \]  
(A1.2)

\( F_K \) is structure factor. The observed intensity will include intensity corrections \( (L_K) \), preferred orientation function \( (P_K) \), scale factor from structural model \( (S) \), instrumental or specimen correction such as profile function \( (\phi) \) etc. Further, background \( (b_i) \) at each step will also be included in the observed intensity. Hence the calculated intensity can be represented as

\[ Y_{ci} = S \sum_k L_K F_K^2 \phi (2\theta_i - 2 \theta_K) P_K + b_i \]  
(A1.3)
and the structure factor

\[ F_k = \sum_j N_j f_j \exp \left[ 2\pi i (h x_j + k y_j + l z_j) \exp (-M_j) \right] \]

where \( M_j = 8\pi^2 \cdot \frac{\hat{s}^2 \sin^2 \theta}{\lambda^2} \) and \( N_j \) is the site occupancy multiplier of \( j \)th atom site.

### A1.2.1 Criteria of fit

The objective of Rietveld refinement is to obtain best fit of the entire calculated pattern to the entire observed pattern, by refining global and structural parameters. The fit can be judged by various indices or factors.

\[
R_p = 100 \frac{\sum_i Y_i - Y_{ci}}{\sum_i Y_i} \text{ the } R \text{ factor} \quad (A1.5)
\]

\[
R_{wp} = 100 \left( \frac{\sum W_i (Y_i - Y_{ci})^2}{\sum W_i Y_i^2} \right)^{1/2} \text{ the weighted pattern } R \text{ factor} \quad (A1.6)
\]

\[
R_{\text{expected}} = 100 \left( \frac{(N - P + C)}{\sum W_i Y_i^2} \right)^{1/2} \quad (A1.7)
\]

and \( S \), goodness of fit is the ratio of \( R_{wp}/R_{\text{expected}} \).

The numerical values of \( R_p, R_{wp} \) and \( S \) and the graphical output including difference plot will give information about the extent or quality of refinement.

### A1.2.2 DBWS program

DBWS-9006 (Wiles and Young 1981 and Sakthivel and Young 1991) is the most widely used refinement program. It has come through long successive development and improvement. The program has many features, easy to handle, run at one stroke and run in most of the environments. We have compiled the program in UNIX environment and the graphical output was viewed in PC-DOS.
The program includes seven profile functions and background correction can be done with either supplied background or linear interpolation between selected points in the pattern or by specified background function, which can be refined and the function used in the program is

\[ Y_{bi} = \sum_{m=0}^{5} B_m \left( \frac{(2\theta_i / BKPOS) - 1}{m} \right)^m \]  

(A1.8)

where BKPOS is user specified in the input control file. More than one phase refinement and quantitative analysis of phase is also possible (Hill and Howard 1987).

A1.3 DATA COLLECTION AND REFINEMENT STRATEGY

A1.3.1 Data collection

Highly crystalline, calcined TAPO₄·5 with unit cell composition Ti₀.₁₅Al₁₀.₆₀P₁₃.₁₉O₄₈ (AFI topology) was used for powder XRD data collection. The data were collected on Siemens D500 diffractometer in 2θ between 5 to 70° in steps of 0.05° using CuKα (λ = 1.54184 Å) as source with exposure of 44 sec at each step. The data collected on computer was converted to required form. The collected pattern is shown in the Figure A1.1. Nearly 1000 data points were used (5 to 45°) for refinement and the data are given in Appendix 2. The SEM picture shows that TAPO₄·5 crystallise in spherical shape (Figure 3.10 a). Hence, unwanted preferred orientation can be of minimum.

A1.3.2 Refinement strategy

The approach to structural refinement is given as flow chart in Figure A1.2.
Figure A1.1 Step scanned XRD pattern of TAP04-5
From collected data the peaks were identified and matched with standard pattern (VonBallmoos and Higgins 1990). The indexed peaks were used for least square refinement of cell parameters. The geometrical refinement was done by DLS-76 program (Baerlocher et al 1977). The structural data from Bennet et al (1983) and the refined cell constants were used as DLS-76 input. The resulting geometrically refined co-ordinates were used for structural refinement. The structural refinement was done using DBWS-9006 PC program. The global parameters were first refined, followed by structural parameter. During structural refinement, due care was taken for the refinement to lead in right direction. If unacceptable bond angles or bond distances were obtained, different strategy of refining the parameters were followed. PARST program (Nardelli 1983) was used to calculate the bond distances and bond angles.
When the best fit is obtained or when no further best fit could be achieved, then the refinement was stopped.

A1.4 REFINEMENT RESULTS

The unit cell parameters of TAPO$_4$-5 was found to be $a = b = 13.6805$ Å and $C = 8.4089$ Å by least square refinement. The input file prepared for DLS-76 is given in appendix 3, in which the following connectivity principles were used.

\[
\begin{array}{c}
\text{Al}^{**} \\
03 \\
\text{Al} - 02 - P - 01 - \text{Al}^{*} \\
04 \\
\text{Al}^{***}
\end{array}
\quad
\begin{array}{c}
P^{***} \\
04^{*} \\
P^{*} - 01^{*} - \text{Al} - 02 - P \\
03^{*} \\
P^{**}
\end{array}
\]

The obtained fractional co-ordinates are given in Table A1.1. The refinement were converged with $R = 0.053$ and $\sigma = 0.249$.

Table A1.1

Fractional co-ordinates of TAPO$_4$-5 by geometrical refinement (DLS-76)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Co-ordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>P</td>
<td>0.4627</td>
</tr>
<tr>
<td>Al</td>
<td>0.4655</td>
</tr>
<tr>
<td>01</td>
<td>0.4064</td>
</tr>
<tr>
<td>02</td>
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<tr>
<td>03</td>
<td>0.3968</td>
</tr>
<tr>
<td>04</td>
<td>0.5841</td>
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</table>
**Table A1.2**

Structural parameters of TAP04-5 refined by Rietveld's analysis

<table>
<thead>
<tr>
<th>Atom</th>
<th>Co-ordinates</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
</tr>
<tr>
<td>P</td>
<td>0.4628</td>
<td>0.3311</td>
</tr>
<tr>
<td>Al</td>
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<td>0.3369</td>
</tr>
<tr>
<td>O1</td>
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</tr>
<tr>
<td>O2</td>
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</tr>
<tr>
<td>O3</td>
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<td>0.3868</td>
</tr>
<tr>
<td>O4</td>
<td>0.5844</td>
<td>0.3947</td>
</tr>
</tbody>
</table>

\[ a = b = 13.6738 \text{ Å} \quad \text{and} \quad c = 8.3965 \text{ Å} \]

**Table A1.3**

Bond distances and bond angles of TAP04-5

<table>
<thead>
<tr>
<th>Bond distance</th>
<th>Bond angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Length(Å)</td>
</tr>
<tr>
<td>P - 01</td>
<td>1.521</td>
</tr>
<tr>
<td>P - 02</td>
<td>1.494</td>
</tr>
<tr>
<td>P - 03</td>
<td>1.514</td>
</tr>
<tr>
<td>P - 04</td>
<td>1.517</td>
</tr>
<tr>
<td>Al - 02</td>
<td>1.715</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A1.3 Graphical fit of TAPO$_4$-5 by Rietveld analysis
The geometrically refined co-ordinates were fed into the DBWS program. Totally 28 parameters such as scale factor, displacement factor, background factor, cell parameters, profile parameters and co-ordinates of all atoms were refined. The refinement were stopped after certain stage, where further refinement was not possible, and the values $R_p = 20.71$, $R_{wp} = 26.51$ and $S = 5.50$. The graphical fit is given in Figure A1.3, the refined co-ordinates are given in Table A1.2, and the DBWS input file is given in Appendix 4. From the refined structural parameters the bond angles and bond distances were calculated. The input file of PARST used is given in appendix 5 and the results obtained are given in Table A1.3.

A1.5 DISCUSSIONS

In the Rietveld analysis, the initial $R_p$ value was 120. After refining the scale factor, displacements and background parameters, the value has come down to 30.6. Further refinements of global parameters and structural parameters, brought down the $R_p$ value to 20.7. Though, the value has been reduced to 20.7, but still it is higher. The high value indicates that the structure is not refined completely, due to its structural complexity (72 atoms/unit cell). While refining the structure, water adsorbed in TAP04-5 was not taken into account and also there is no built-in soft constraints for bond distances and bond angles in the present program (DBWS). Attempts to refine further resulted in bond length and bond angles of deviation above 10%, which are unacceptable.

The bond lengths and bond angles obtained from partially refined fractional co-ordinates are within the prescribed limits. The metal-oxygen bond distances were smaller than normal values, suggesting the possibility of presence of metal oxygen double bonds (Ti=O). There was no change in the bond angles.