MULTIALIQUOT CELL APPROACH FOR STRUCTURE DETERMINATION
FROM POWDER DIFFRACTION OF HIGH SYMMETRY COMPOUNDS

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ABSTRACT
The algorithm employing extended figures of merit (ExFoMs) is formulated in order to allow an automatic structure determination from powder diffraction (SDPD) for high-symmetry lattices. Application of aliquot cells as building units for the larger cell of high symmetry is expected to facilitate the structure solution with direct space methods, in order to decrease time for the model search in a large-scale unit cell. Indexing and structure solution with one calculated pattern of the known pyrochlore \( \text{Tl}_2\text{Nb}_2\text{O}_7 \) and one experimental synchrotron powder pattern of the new pyrochlore \( \text{K}_{0.88}\text{Nb}_2\text{O}_{7.58}\text{H}_{4.28} \) (Fd3m, \( a = 10.64536(5) \) Å) are demonstrated as simple experimental examples.

INTRODUCTION
Nowadays the structure solution from single crystal diffraction data appears fully automatic managed with well-known software packages, e.g., Crystals (Watkins et al., 1996). In situations when the preparation of large single crystals is challenging, numerous techniques for the structure solution from powder data (SDPD) are available (David et al., 2006), but the software allowing a fully automatic SDPD, desirable for rapidly developing materials and drugs industries, is still in the stage of development (Smirnova, in progress). An example of the semi-automatic SDPD interface, progressing from indexing to a structure solution is EXPO2004 (Altomare et al., 2004). However, it requires the creative contribution of a crystallographer at each step. Indexing is known as a “bottleneck” in structure solution from powder diffraction data and sometimes requires a complicated choice among several possible cells. Though the optimal would be to try structure determination for all good cells proposed by an indexing program, that is time and effort consuming. Presently well-known, efficient and popular indexing programs like CRYSFIRE (Shirley, 2000), TREOR (Werner et al., 1985) and DICVOL (Boutif et al., 2004) employ figures of merit (FoM) suggested by De Wolff (1968) and Smith & Snyder (1979) to estimate the correctness of proposed cells. For both cases, the higher the FoM, the better solution is considered. More complicated and computer-power-demanding programs, like McMaille (Le Bail, 2006), may employ more sophisticated figure of merit including Bravais lattice...
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type, symmetry and profile matching result, that weight higher symmetry cells by multiplying the FoM by an integer. As the structure solution from powder diffraction becomes more and more automatic, as for single crystals, the role of figures of merit increases as uniform criteria to choose the best proposed cell. In this context, presently most popular F(20) and M(20) figures of merit cannot serve for the final decision, but can only help to chose 5-10 best solutions, understanding that the highest FoM does not necessarily correspond to the correct cell. This manuscript presents extended figures of merit formulated in order to facilitate the automatic structure determination from powder data and outlines the algorithm in the background of future automated SDPD software, patent pending, (Smirnova, in progress).

**EXPERIMENTAL**

The powder pattern (Fig.1) of example pyrochlore-type compound Tl$_2$Nb$_2$O$_7$ (Fourquet et al., 1995) is calculated using FullProf &Winplotr software (Rodriguez-Carvajal, 1990), utilizing atomic coordinates deposited in the Crystallography Open Database (www.crystallography.net). Octahedral colorless single crystals of K$_{0.88}$(OH)$_{0.69}$H$_{1.81}$(H$_2$O)$_{0.89}$Nb$_2$O$_6$ were obtained by hydrothermal reaction of Nb$_2$O$_5$ and KOH (at Nb$_2$O$_5$:KOH molar ratios of 1:7 or 1:8) in Teflon-lined autoclaves.

**Table 1.** Experimental details for the data collection and structure refinement of the new pyrochlore

| Formula unit | K$_{0.88}$Nb$_2$O$_{7.58}$H$_{4.28}$ | No. of parameters | 16 |
| Symmetry     | Cubic                             | Profile function  | Pseudo-Voight |
| Space group  | Fd3m                              | U                 | 0.0106(5)     |
| Z            | 8                                 | V                 | -0.0040(1)    |
| Cell parameter a = 10.64546(5) Å | W                         | 0.0015(1)         |
| Radiation    | Synchrotron (SPring-8)            |                   |               |
| Equipment    | Debye-Sherer BL B-02              |                   |               |
| Monochromator| Silicon (111)                     |                   |               |
| Wavelength   | 0.77704 Å                        |                   |               |
| Temperature  | 300 K                             |                   |               |
| Container    | Quartz                            |                   |               |
| 2Θ interval  | 2–40°                             |                   |               |
| 2Θ step      | 0.01°                             |                   |               |
| Software     | FullProf                          |                   |               |
| No. of points| 74                                |                   |               |
Reaction temperatures from 453 to 513 K were used, and the reaction times ranged from 12 hours to 3 days. The details of the structure solution from laboratory single crystal X-ray diffractometer data are described elsewhere (Smirnova, 2010). A higher-resolution and lower background powder pattern of $\text{K}_{0.88}\text{Nb}_2\text{O}_{7.58}\text{H}_{4.28}$ has been collected at the SPring-8 synchrotron radiation facility (Japan) and treated with FOX (Favre-Nicolin et al. 2002) and FullProf &Winplotr (Rodriguez-Cravajal, 1990) suites including DICVOL04 (experimental details are listed in Table 1).

RESULTS AND DISCUSSION

The figures of merit (De Wolff et al., 1968 and Smith & Snyder, 1979) employed in the indexing software mentioned above are formulated as follows:

$$M_{20} = \frac{Q_{20}}{2 \bar{e} \cdot N_{20}}$$

where $N_{20}$ is the number of calculated $Q$ values up to $Q_{20}$; $Q_{20}$ is the $Q$ value for the 20th observed and indexed line; $\overline{2 \bar{e}}$ is the average discrepancy in $Q$ for these 20 lines

$$F_{20} = \left(\frac{1}{|\Delta 2 \Theta|} \cdot \frac{N}{N_{poss}}\right)$$

and

where $N_{poss}$ is the number of independent diffraction lines possible up to the $N$th observed line and $|\Delta 2 \Theta|$ is the average absolute discrepancy between observed and calculated $2 \Theta$ values.

**Table 2.** Indexing solutions proposed by DICVOL04 for the powder patterns of pyrochlore compounds $^*$.  

<table>
<thead>
<tr>
<th>System</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>M(20)</th>
<th>F(20)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Calculated pattern</em></td>
<td><strong>Tl$_2$Nb$_2$O$_7$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cubic</td>
<td>10.6224</td>
<td>10.6224</td>
<td>10.6224</td>
<td>386.9</td>
<td>257.4</td>
</tr>
<tr>
<td>tetragonal</td>
<td>7.5112</td>
<td>7.5112</td>
<td>10.6224</td>
<td>329.8</td>
<td>215.8</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>10.6224</td>
<td>7.5112</td>
<td>2.5037</td>
<td>536.7</td>
<td>341.4</td>
</tr>
</tbody>
</table>

* the true cell solutions are marked with green while the highest FoMs are marked with red color
As it is observed in the Table 2, for the calculated powder pattern of Tl$\text{Nb}_2\text{O}_7$, ($Fd-3m$, $a = 10.6224$ Å) the program suggests several possible solutions and the correct solution of highest symmetry among them. The higher M(20) and F(20) for the orthorhombic cell are confusing and require a crystallographer’s eye to select the correct cell. Notionally extending the observation to more complicated situations, the repetition of the same lattice described by different cells is considered as the indication of the correct indexing solution. Therefore, an extension to indexing algorithms, taking into account lower symmetry cells for the same lattice described by high-symmetry cell, and the extended figures of merit are formulated as follows:

$$M_m(20) = M(20)_h \cdot N_m$$
$$F_m(20) = F(20)_h \cdot N_m$$

where $M(20)_h$ and $F(20)_h$ are $M(20)$ and $F(20)$ for the highest symmetry cell $N_m$ is the number of multialiquot cells for the same lattice;

or

$$M_{sm} = \Sigma M(20)_m$$
$$F_{sm} = \Sigma F(20)_m$$

where $\Sigma$ - sums of FoMs for all multialiquot cells describing the same lattice.

A similar, but not identical situation to Tl$\text{Nb}_2\text{O}_7$ is observed when indexing the experimental synchrotron powder pattern of K$_{0.88}$Nb$_{2}$O$_{7.58}$H$_{4.28}$ (Table 2, bottom). The single crystal structure solution points to the pyrochlore cubic cell (Smirnova, 2010), while the DICVOL shows higher FoMs for the orthorhombic cell (Table 2) when indexing the high-resolution synchrotron powder pattern. One may note the orthorhombic cell is related to the cubic cell as: $a' = a\sqrt{3}$, $b' = \frac{1}{2}a\sqrt{2}$, $c' = a/4$. Thus the correct choice to start structure solution would be a smallest cubic unit of $c' = a/4$ size.
Figure 1. Observed synchrotron (circles), calculated (line, top) and difference (line, bottom) patterns of $K_{0.88}Nb_2O_{7.58}H_{4.28}$. Vertical lines indicate Bragg peak positions.

Figure 2. The polyhedral models of the $K_{0.88}Nb_2O_{7.58}H_{4.28}$ pyrochlore-type crystal structure as refined from synchrotron powder data in two representations: left - traditional $Nb_2O_6^{2-}$ framework view (green octahedra $NbO_6$, grey spheres – K, red spheres – $O_{aq}$); right - built of $Nb_4$ or $K_4$ tetrahedral units (green tetrahedra - $Nb_4$, grey tetrahedra – $K_4$, red spheres – $O(48f)$).
Table 3. The atomic parameters of $K_{0.88}Nb_2O_{7.58}H_{4.28}$ as refined from the synchrotron powder data.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyck.</th>
<th>Fraction</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{iso}, \text{Å}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>16d</td>
<td>0.44(-)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.84(6)</td>
</tr>
<tr>
<td>$O_{aq}(1)$</td>
<td>16d</td>
<td>0.288(-)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.77(5)</td>
</tr>
<tr>
<td>Nb</td>
<td>16c</td>
<td>1.0(-)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.93(1)</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
<td>1.0(-)</td>
<td>0.3105(2)</td>
<td>0.125</td>
<td>0.125</td>
<td>0.77(5)</td>
</tr>
<tr>
<td>$O_{aq}(2)$</td>
<td>32e</td>
<td>0.222(-)</td>
<td>0.4297(5)</td>
<td>0.4297(5)</td>
<td>0.4297(5)</td>
<td>0.77(5)</td>
</tr>
</tbody>
</table>

Indeed, the final structure extracted from the higher resolution and lower background synchrotron powder data (Tables 1,3; Figures 1-2) contains the cubic building units ($c' = a/4$) – the $Nb_6$ and $K_6$ tetrahedra of 3.7651 Å edges (Figure 2, right). Thus the multialiquot cells found amongst extra indexing programs are useful as building blocks when solving structure by direct space methods. Moreover, the approach is expected to decrease time necessary for the simulated annealing of a structure model search and may appear particularly useful for organic structures with large cells. According to the concept, one may start to search for the structural model applying a cell of lower/volume symmetry with the hope that it may represent a building unit for the larger cell of higher symmetry, and then switch to the true cell. It is important to note these observations start from relatively small pyrochlore cubic cell. Turning to the automation of SDPD processes, the multialiquot cell allows one to select the only true indexing solution; thus, the fully automatic structure solution from powder data become possible (Smirnova, in progress). Considering the powder reflections overlap, the program may create several structure models fitting the powder data and validate the feasibility with bond valence sums calculations (Brown et al., 1985) or with the new wave method (Smirnova, 2010).

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