Refinement Details for Pd K-edge EXAFS data for Ba$_2$PdO$_3$, Ba$_{0.5}$Sr$_{1.5}$PdO$_3$ and Ba$_{0.5}$Sr$_{1.5}$PdO$_2$F$_2$.

All of the refinements were carried out using EXCURV98. Although it was possible to use the literature XRD bond lengths for Ba$_2$PdO$_3$ and just refine the Debye-Waller factors to give a very good fit, this is not a practicable approach when refinement of the bond lengths is required (e.g. the mixed Sr-Ba compounds or the fluorinated materials) as the difference between the two Pd-O bond lengths in Ba$_2$PdO$_3$ is less than 0.02 Å. Therefore, the first Pd-O shell was always refined as a single distance. In all cases, the coordination number was fixed at 4, and this was verified by mapping the R factor against the coordination number and the Debye-Waller factor. This gave the best fit to around 3.5 in all cases. For the other shells, the appropriate values were used. In order to reduce the number of refined parameters the Debye-Waller factor for the Pd-Ba and Pd-Sr shells was constrained to have the same value. In the chain structures, only half of the Pd-Pd shell at ca. 4 Å is involved in multiple scattering through an intervening O atom, whereas in the sheet structure all of the Pd-Pd shells are involved in multiple scattering. Whilst the full cluster approach to multiple scattering is the best, in this case there are a larger number of shells, and it was decided to use the "units" version of multiple scattering within EXCURV98 to model the multiple scattering. For the chain structures this entails using a split Pd-O first shell but constraining the bond lengths and Debye-Waller factors to be identical for both pairs. Likewise, there are two Pd-Pd shells defined at ca. 4 Å, but both were constrained to have identical Debye-Waller factors. As the Pd-Pd shell involved in the multiple scattering has the greatest intensity in both the EXAFS and the FT this will dominate the spectrum. Using the reduced $\chi^2$ approach a preference for two Pd-Pd shells was shown in the data for Ba$_{0.5}$Sr$_{1.5}$PdO$_3$ but not for Ba$_{0.5}$Sr$_{1.5}$PdO$_2$F$_2$. This is interpreted to indicate a change from a chain to a sheet structure.

The number of refined parameters was always kept below the number of independent points ($2\Delta r\Delta k/\pi$). The details of the refinements are given below, and the EXAFS and FTs are shown on the following page.

Refined EXAFS parameters for Ba$_2$PdO$_3$, Ba$_{0.5}$Sr$_{1.5}$PdO$_3$ and Ba$_{0.5}$Sr$_{1.5}$PdO$_2$F$_2$ (a)

<table>
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<tr>
<th></th>
<th>Pd-O $r^{0(1)}$/Å</th>
<th>2σ$^{1(0)}/Å^2$</th>
<th>Pd-Sr $r$/Å</th>
<th>2σ$^{2}/Å^2$</th>
<th>Pd-Ba $r$/Å</th>
<th>2σ$^{3}/Å^2$</th>
<th>Pd-Pd $r$/Å</th>
<th>2σ$^{4}/Å^2$</th>
<th>$E_f^{(0)}/$V</th>
<th>R$^{(0)}$</th>
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<tr>
<td>Ba$_2$PdO$_3$ (XRD)</td>
<td>2 x 2.026</td>
<td>2 x 2.040</td>
<td>8 x 3.411</td>
<td>2 x 3.836</td>
<td>2 x 4.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba$_2$PdO$_3$</td>
<td>4 x 2.057(6)</td>
<td>0.0044(10)</td>
<td>8 x 3.404(4)</td>
<td>0.0098(4)</td>
<td>2 x 3.981(25)</td>
<td>0.0046(18)</td>
<td>1.73(88)</td>
<td>32.5</td>
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</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{1.5}$PdO$_3$</td>
<td>4 x 2.025(4)</td>
<td>0.0055(7)</td>
<td>6 x 3.285(4)</td>
<td>0.0120(11)</td>
<td>2 x 3.916(23)</td>
<td>0.0046(13)</td>
<td>2.48(82)</td>
<td>26.6</td>
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<tr>
<td>Ba$<em>{0.5}$Sr$</em>{1.5}$PdO$_2$F$_2$</td>
<td>4 x 2.033(5)</td>
<td>0.0055(7)</td>
<td>6 x 3.375(13)</td>
<td>0.0186(25)</td>
<td>4 x 4.085(4)</td>
<td>0.0070(5)</td>
<td>2.61(87)</td>
<td>30.8</td>
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(a) Standard deviation in parentheses; (b) ref. 2; (c) this work; (d) given as occupation number x distance, the estimated systematic errors in EXAFS bond lengths are ±1% for well-defined co-ordination shells; (e) 2σ$^2$ is the Debye-Waller factor; (f) $E_f$ is a single refined parameter to reflect differences in the theoretical and experimental Fermi levels;

$^{(g)}$ $R = \left| \frac{\int \mid \chi^2 - \chi^2 \mid k^2 dk}{\int \mid \chi^2 \mid k^2 dk} \right| \times 100\% .$

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\[ \text{Ba}_2\text{PdO}_2\text{F}_2 \]

\[ a = 4.13979(32)\text{Å}; \ b = 4.13979(32)\text{Å}; \ c = 14.04595(134)\text{Å} \]
\[ \alpha = 90.0000(0)^\circ; \ \beta = 90.0000(0)^\circ; \ \gamma = 90.0000(0)^\circ \]

\begin{tabular}{|c|c|c|c|c|c|}
\hline
HISTOGRAM & Rp & Rwp & Rexp & GOF & R\text{BRAGG} \\
\hline
1 & 4.48 & 5.80 & 3.86 & 2.25 & 2.45 \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
ATOMS & x (0) & y (0) & z (0) & B\text{iso} (0) & N (0) \\
\hline
Ba & 0.0000(0) & 0.0000(0) & 0.3652(1) & 1.83(6) & 1.000 \\
Pd & 0.0000(0) & 0.0000(0) & 0.0000(0) & 1.24(7) & 0.500 \\
O & 0.0000(0) & 0.5000(0) & 0.0000(0) & 1.00(0) & 1.000 \\
F & 0.0000(0) & 0.5000(0) & 0.2500(0) & 1.00(0) & 1.000 \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|}
\hline
ATOM1 & ATOM2 & DISTANCE & ERROR \\
\hline
Ba & Ba & 4.1398 & 0.0003 \\
Ba & Ba & 3.7879 & 0.0004 \\
Ba & Ba & 4.3629 & 0.0004 \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|}
\hline
ATOM1 & ATOM2 & DISTANCE & ERROR \\
\hline
Ba & Pd & 3.4865 & 0.0003 \\
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Ba & O & 2.8056 & 0.0002 \\
Ba & F & 2.6270 & 0.0002 \\
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\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|}
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ATOM1 & ATOM2 & DISTANCE & ERROR \\
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Pd & O & 2.0699 & 0.0002 \\
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\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|}
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ATOM1 & ATOM2 & DISTANCE & ERROR \\
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O & O & 4.0762 & 0.0004 \\
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O & F & 2.9273 & 0.0002 \\
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\hline
ATOM1 & ATOM2 & DISTANCE & ERROR \\
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O & F & 3.5115 & 0.0003 \\
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\end{tabular}

\[ \text{Ba}_{0.5}\text{Sr}_{1.5}\text{PdO}_2\text{F}_2 \]

\[ a = 4.07008(55)\text{Å}; \ b = 4.07008(55)\text{Å}; \ c = 13.10725(264)\text{Å} \]
\[ \alpha = 90.0000(0)^\circ; \ \beta = 90.0000(0)^\circ; \ \gamma = 90.0000(0)^\circ \]

\begin{tabular}{|c|c|c|c|c|c|c|}
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HISTOGRAM & Rp & Rwp & Rexp & GOF & R\text{BRAGG} \\
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1 & 5.88 & 7.66 & 5.20 & 2.17 & 1.56 \\
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$\text{Ba}_{0.5}\text{Sr}_{1.5}\text{PdO}_2\text{F}_2$