# Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ ($0 \leq x \leq 1.5$): The first palladium–oxide–fluorides†

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The first series of alkaline-earth palladium oxide–fluorides Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ ($0 \leq x \leq 1.5$) display the T′ structure (Nd$_2$CuO$_4$) instead of the predicted T structure (La$_2$CuO$_4$), showing that electronic factors prevail over steric factors.

Since the discovery of superconductivity in Sr$_2$CuO$_2$F$_{2+\delta}$ there has been an increased interest in ternary oxide-fluorides. Sr$_2$CuO$_2$F$_{2+\delta}$ is prepared *via* low temperature ($T = 220$ °C) reaction routes.[1] Low temperature fluorination induces an interesting structural rearrangement in the parent compound Sr$_2$CuO$_3$, which is a one-dimensional material containing linear chains of vertex sharing CuO$_4$ squares along the crystallographic *b* axis. Upon fluorination one oxygen is substituted by two fluorines and Cu$^{2+}$ becomes octahedrally coordinated by four oxygens and two fluorines. The fluorinated compound, Sr$_2$CuO$_2$F$_{2+\delta}$ displays the T structure (La$_2$CuO$_4$). Insertion of excess fluorine, $\delta$, also takes place and this fluorine occupies interstitial sites in the T structure. Similarly to Sr$_2$CuO$_2$F$_{2+\delta}$, the preparation and structural characterisation of Ca$_2$CuO$_2$F$_{2+\delta}$ was reported.[2] Although the starting material Ca$_2$CuO$_3$ is isostructural to Sr$_2$CuO$_3$, Ca$_2$CuO$_2$F$_{2+\delta}$ displays the T′ (Nd$_2$CuO$_4$) structure due to the smaller radius of Ca$^{2+}$ compared to that of Sr$^{2+}$. The substituting fluorines do not occupy an apical site of a Cu–O polyhedra but are located in the Ca–O layers, leaving Cu$^{2+}$ to maintain square planar coordination. Only a small excess of fluorine inserts ($\delta \approx 0.1$). The alkaline earth palladates with the general formula A$_2$PdO$_3$ (A = Ba, Sr) are isostructural with the A$_2$CuO$_3$ (A = Ca, Sr) materials.[3] We prepared the Ba$_{2-x}$Sr$_x$PdO$_3$ ($x = 0$–2) series and performed low temperature fluorination. Here we report the preparation and structural characterisation of the first palladium oxide–fluorides with general formula Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$. To the best of our knowledge, no binary or ternary oxide-fluorides of palladium have ever been reported. Similarities and differences with Sr$_2$CuO$_2$F$_{2+\delta}$ and Ca$_2$CuO$_2$F$_{2+\delta}$ will be discussed.

The parent compounds Ba$_{2-x}$Sr$_x$PdO$_3$ ($x = 0$–2) were prepared *via* high temperature routes.[4] The oxide solid solutions could be prepared over the entire stoichiometry range, $0 \leq x \leq 2$. To the best of our knowledge the preparation of the Ba$_{2-x}$Sr$_x$PdO$_3$ ($x = 0$–2) series has never been reported. Powder X-ray diffraction (PXRD) was used for structural characterisation and all the diffractograms showed that Ba$_{2-x}$Sr$_x$PdO$_3$ ($x = 0$–2) are isostructural to the Sr$_{2-x}$Ca$_x$CuO$_3$ compounds (space group *Immm*). The decrease in the volume of the unit cell for *x* increasing obeys Vegard's law. Inductively coupled plasma (ICP) spectroscopy was used to confirm the Ba : Sr and (Ba,Sr) : Pd ratios throughout the whole series. The preparation of Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ was achieved *via* low temperature fluorination of Ba$_{2-x}$Sr$_x$PdO$_3$, using CuF$_2$ or poly(vinylidene difluoride) (PVDF)[5] as fluorinating agents, in a starting reagent ratio Ba$_{2-x}$Sr$_x$PdO$_3$ : F$_2$ = 1 : 1. The precursor oxides were mixed with the fluorinating compounds, and heated for 14 hours at 200–250 °C (CuF$_2$) or at 300–350 °C (PVDF). PXRD showed that the fluorinated

materials could be obtained as single phases for parent compounds with a Sr content *x* < 1.5. Fluorination of Ba$_{2-x}$Sr$_x$PdO$_3$ with *x* > 1.5 always gave poorly crystallised products with large amounts of Ba(Sr)F$_2$ byproducts. The same outcome resulted from fluorination reactions involving a starting reagent ratio F$_2$ : Ba$_{2-x}$Sr$_x$PdO$_3$ > 1. PXRD indicated a structural relationship to Ca$_2$CuO$_2$F$_{2+\delta}$ (T′ structure) rather than to Sr$_2$CuO$_2$F$_{2+\delta}$ (T structure), for all the Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ ($0 \leq x \leq 1.5$) compounds. Rietveld profile analysis of the PXRD data has been used to refine the structures of Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ using the program RIETICA.[6] Refinements were carried out on Ba$_2$PdO$_2$F$_2$ (Fig. 1), BaSrPdO$_2$F$_2$ and Ba$_{0.5}$Sr$_{1.5}$PdO$_2$F$_2$.[7]

In the T′ structure palladium occupies a perovskite-like layer and is coordinated by four oxygens in square planar fashion, while barium and strontium occupy a fluorite-like layer and are coordinated by four oxygens and four fluorines in distorted cubic fashion. The structural model based on the T′ structure is supported by the preference of Pd$^{2+}$ for square planar coordination. Although X-rays cannot distinguish between oxygen and fluorine, it was assumed that the F ions are located within the Sr/Ba layers, as reported for Ca$_2$CuO$_2$F$_{2+\delta}$.[2] The O/F stoichiometry was deduced from the ratio of the starting reagents and crystallographic data. Nevertheless, we investigated the possibility of insertion of excess fluorine (chemical formula: Ba$_{2-x}$Sr$_x$PdO$_2$F$_{2+\delta}$), in analogy to the A$_2$CuO$_2$F$_{2+\delta}$ (A = Sr, Ca) series. Consequently, we considered the possibility of (1) Pd$^{2+}$/Pd$^{3+}$ or Pd$^{2+}$/Pd$^{4+}$ mixed-valence to maintain charge neutrality and/or (2) the presence of octahedrally coordinated Pd$^{3+}$ or Pd$^{4+}$. Pd$^{3+}$ and Pd$^{4+}$ are found in fluorides and usually show octahedral coordination.[8] Moreover, in Ca$_2$CuO$_2$F$_{2+\delta}$ excess fluorine is located on apical sites.[2] Magnetic measurements confirmed the absence of Pd$^{3+}$, and EXAFS spectroscopy confirmed that there is no change of oxidation or coordination number for palladium upon fluorination.

Magnetic measurements showed that both the starting and fluorinated materials are diamagnetic. These results are in
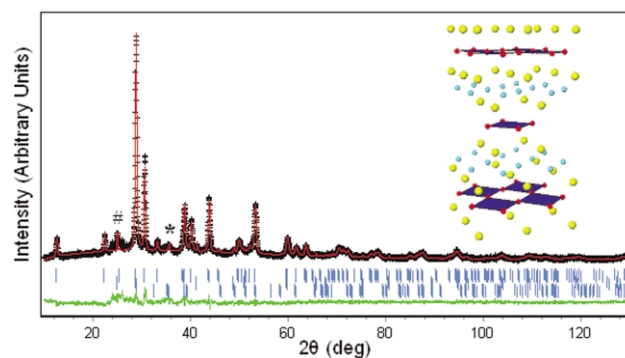


**Fig. 1** Refinement of Ba$_2$PdO$_2$F$_2$. Black line (observed), red line (calculated), green line (difference). # reflection associated with BaF$_2$, * reflection associated with CuO. (Top right) The T′ structure of the Ba$_{2-x}$Sr$_x$PdO$_2$F$_2$ compounds: Yellow spheres represent Ba (Sr) cations, blue squares represent PdO$_4$ square planes, red and light blue spheres represent O and F anions respectively.

agreement with the presence of $Pd^{2+}$ in square planar coordination in the fluorinated compounds. $Pd^{3+}$ shows a $t_{2g}^6 e_g^1$ electronic configuration and the presence of one unpaired electron cannot be reconciled with the magnetic data.

XANES spectra showed that the position and structure of the Pd K-edge[9] in all $Ba_{2-x}Sr_xPdO_3$ and $Ba_{2-x}Sr_xPdO_2F_2$ compounds are the same, indicating that there is no change of oxidation state or coordination upon fluorination. Although the Pd K-edge is very broad, it is possible to detect the presence of $Pd^{3+}$, as recent work on $LaPdO_3$ has demonstrated.[10] The Pd K-edge EXAFS indicates that the first coordination sphere around the Pd contains four oxygen atoms for all of the samples. Whilst these are split into pairs in the parent chain structures,[3] they are too close together (ca. 0.02 Å) to be refined separately, and were considered as a single shell in all cases.

The Fourier transform (FT) of Pd K-edge EXAFS of $Ba_{0.5}Sr_{1.5}PdO_2F_2$ (Fig. 2) revealed that whilst the Pd–O and Pd–Pd peaks had similar intensity to $Ba_{0.5}Sr_{1.5}PdO_3$, the peak due to the Pd–Sr and Pd–Ba contributions was reduced. The similarity of the peak intensity and the refined Debye–Waller factor for the Pd–O shell shows that the Pd square planar coordination is preserved in the fluorinated sample. In $Ba_{0.5}Sr_{1.5}PdO_3$ the Pd⋯Pd shell at ca. 4 Å is best fit by two Pd⋯Pd distances, as expected from the chain structure, whereas in $Ba_{0.5}Sr_{1.5}PdO_2F_2$ this feature is best fit by a single Pd⋯Pd distance, indicative of an increase in vertex sharing consistent with a change from a chain to sheet structure. This is also mirrored by a small increase in the Pd–O distances in $Ba_{0.5}Sr_{1.5}PdO_2F_2$. Whilst the Pd–Sr and Pd–Ba distances could be separated in $Ba_{0.5}Sr_{1.5}PdO_3$, they refine to effectively the same distance in the fluorinated sample. They are also highly correlated, and the Debye–Waller factor has increased by about 50%. Taken together this indicates a much higher level of disorder between the Pd–O sheets and the Ba/Sr–O/F sheets in the oxide–fluoride as compared to the oxide. This reduction in the intensity of the Pd–Ba/Sr shell was common to all the fluorinated samples.

There are similarities and differences between the palladium and copper oxide–fluorides. The main similarity is the structural rearrangement induced by the substitution of two fluorines for one oxygen, which transforms a one-dimensional oxide ($A_2MO_3$ with A = Ca, Sr, Ba and M = Cu, Pd) containing M–O chains into a two dimensional oxide fluoride containing M–O planes. This similarity of outcomes highlights that low-temperature fluorination is indeed one of the few synthetic routes in solid-state chemistry to allow predictability for the structure of the products.

The main difference between the palladium and copper oxide–fluorides is the stoichiometry of fluorine. $Sr_{2-x}Ca_xCuO_2F_{2+\delta}$ always contain excess fluorine, whereas $Ba_{2-x}Sr_xPdO_2F_2$ never do. Stoichiometric $Sr_2CuO_2F_2$ can only be obtained by removing the excess fluorine from $Sr_2CuO_2F_{2+\delta}$ in a reducing atmosphere.[11]

Tolerance factors have previously been used to rationalise the occurrence of the T and T′ structure in $K_2NiF_4$-like compounds.[12] We calculated the tolerance factors, $t$, for the $Ba_{2-x}Sr_xPdO_2F_2$ compounds using the equation in ref. 12 and

the numerical values for ionic radii were taken from ref. 13. The T structure occurs for $0.87 \leq t \leq 0.99$ and the T′ structure for $0.83 \leq t \leq 0.86$. The range of $t$ values for the $Ba_{2-x}Sr_xPdO_2F_2$ series is $0.863 \leq t \leq 0.90$, which indicates that $t$ predicts the T structure for all $Ba_{2-x}Sr_xPdO_2F_2$, with the $Ba_{0.5}Sr_{1.5}PdO_2F_2$ compounds on the T/T′ border. The contrast between the calculated tolerance factors and the actual structure can be explained by a competition of steric and electronic factors. The radius ratio would impose a T structure with an octahedrally coordinated palladium but a square planar coordination, i.e. a T′ structural arrangement, confers more CFSE (Crystal Field Stabilisation Energy) to transition metals with electronic configuration $nd^8$.

## Notes and references

1 M. Al-Mamouri, P. P. Edwards, C. Greaves and M. Slaski, *Nature (London)*, 1994, **369**, 382; M. G. Francesconi, P. R. Slater, J. P. Hodges, C. Greaves, P. P. Edwards, M. Al-Mamouri and M. Slaski, *J. Solid State Chem.*, 1998, **135**, 17; E. I. Ardashnikova, S. V. Lubarsky, D. I. Densenko, R. V. Shpanchenko, E. V. Antipov and G. Van Tendeloo, *Physica C (Amsterdam)*, 1995, **253**, 259.
2 M. Al-Mamouri, P. P. Edwards, C. Greaves, P. R. Slater and M. Slaski, *J. Mater. Chem.*, 1995, **5**, 913.
3 Y. Laligant, A. LeBail, G. Ferey, M. Hervieu, B. Raveau, A. Wilkinson and A. K. Cheetham, *Eur. J. Solid State Inorg. Chem.*, 1998, **25**, 237; H. D. Von Wasel-Nielen and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1970, **375**, 209.
4 Mixtures of stoichiometric amounts of $BaCO_3$, $SrCO_3$ and PdO were ground and heated in air at 1100 °C for 48 h.
5 P. R. Slater, *J. Fluorine Chem.*, 2002, **117**, 43.
6 RIETICA: B. A. Hunter, *IUCr Powder Diffraction*, 1997, **22**, 21.
7 PXRD data were collected on a Siemens D5000 diffractometer, Cu-Kα radiation ($\lambda$ = 1.541 Å), $T$ = 25 °C, range = 5–130°, stepsize = 0.02°. The structural model was based on the T′ structure (space group *I4mmm*). $Ba_2PdO_2F_2$: $a$ = 4.1398(3), $c$ = 14.0459(13) Å, $R_{wP}$ = 5.80%, $R_{exp}$ = 3.86%; $BaSrPdO_2F_2$: $a$ = 4.0911(5), $c$ = 13.4085(20) Å, $R_{wP}$ = 5.19%, $R_{exp}$ = 3.52%; $Ba_{0.5}Sr_{1.5}PdO_2F_2$: $a$ = 4.0701(5) Å, $c$ = 13.1071(26) Å, $R_{wP}$ = 7.65%, $R_{exp}$ = 5.20%. In order to account for the reflections associated with small amounts of CuO and $Ba(Sr)F_2$ impurities, multiphase refinements were performed (Fig. 1).
8 N. Bartlett, *Fluorine Compounds of the Platinum Metals, Preparative Inorganic Reactions*, Wiley-Interscience Publishers, 1965; A. Tressaud and S. Khainoum, *Z. Anorg. Allg. Chem.*, 1986, **540/541**, 291; B. Bachmann and B. G. Muller, *Z. Anorg. Allg. Chem.*, 1993, **619**, 387.
9 The Pd K-edge X-ray absorption spectra were collected in transmission mode at ca. 80 K from samples diluted in BN on station 9.2 of the Daresbury Laboratory SRS (2 GeV ca. 200 mA) using a Si(220) double crystal monochromator with 50% harmonic rejection. Three spectra were collected for each sample, averaged and calibrated using the first maximum in the first derivative of the Pd K-edge of Pd foil (24350.0 eV). Background subtraction was carried out using PAXAS [N. Binsted, PAXAS, Program for the Analysis of X-Ray Absorption Spectra, University of Southampton, 1988] by fitting the pre-edge region to a quadratic polynomial, subtracting this from the data and approximating the atomic component of the post-edge region with coupled high (typically sixth) order polynomials. Fitting of the experimental data was carried out with EXCURV98 [N. Binsted, EXCURV98, CCLRC Daresbury Laboratory Computer Program, 1998] making use of multiple scattering curved wave theory, a von-Barth ground state and a Hedin–Lundqvist exchange potential. Details of the refinements, table of data EXAFS spectra and FTs are available in the ESI.
10 S. J. Kim, S. Lemaux, G. Demazeau, J. Y. Kim and J. H. Choy, *J. Mater. Chem.*, 2002, **12**, 995.
11 J. L. Kissick, C. Greaves and P. P. Edwards, *Phys. Rev. B*, 1997, **56**(5), 2831.
12 J. F. Brindley, S. S. Trail and B. A. Scott, *J. Solid State Chem.*, 1990, **86**, 310.
13 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
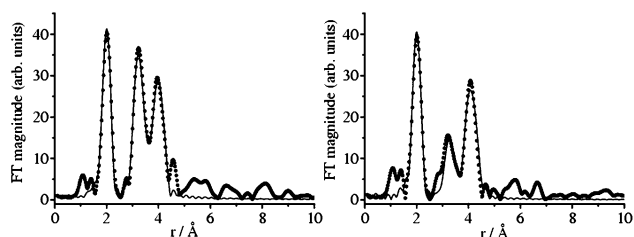
**Fig. 2** FTs of Pd K-edge EXAFS of $Ba_{0.5}Sr_{1.5}PdO_3$ (left) and $Ba_{0.5}Sr_{1.5}PdO_2F_2$ (right). Circles, experimental data; lines, calculated data.