Fluorination of the Ruddlesden–Popper type cuprates, $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (Ln = La, Nd; A = Ca, Sr)

Peter R. Slater,*[a] Jason P. Hodges,[b] M. Grazia. Francesconi,[b] Colin Greaves[b] and Marcin Slaski[c]

[a]*School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST*
[b]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*
[c]*School of Physics and Space Research, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*

The low-temperature (200–350 °C) fluorination of the Ruddlesden–Popper type cuprates, $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (Ln = La, Nd; A = Ca, Sr) using F_2 gas, CuF_2, and NH_4F is reported. The incorporation of large levels of fluoride ions is observed for each of these fluorinating agents. The general characteristics of each method are discussed, and it is shown that for this system, fluorination mainly occurs by insertion of fluorine for reaction with F_2, substitution of fluorine for oxygen for NH_4F, and a mixture of the two processes for CuF_2. For A = Sr, it is assumed that fluorine inserts mainly between the two CuO_2 layers, since large expansions of the unit cell along the *c* direction are observed. No evidence for bulk superconductivity has so far been observed after fluorination.

Recently we have reported that the reaction of the alkaline-earth cuprates A_2CuO_3 (A = Ca, Sr) with F_2 gas at low temperatures (*ca.* 200 °C) yields the oxide fluorides $A_2CuO_2F_{2+\delta}$, with superconductivity (T_c *ca.* 46 K) being observed for A = Sr.[1,2] We have subsequently demonstrated two other simple low-temperature solid-state fluorination routes to these oxide fluorides, involving the facile reaction (at *ca.* 230 °C) of A_2CuO_3 with NH_4F[3] or transition-metal difluorides (*e.g.* CuF_2, ZnF_2).[4] Moreover partial substitution of Ba for Sr has been shown to raise the T_c as high as 66 K, significantly the highest T_c for any phase with the confirmed La_2CuO_4 structure. Since for other cuprates, it has been shown that T_c increases with increasing number of Cu layers (generally up to three layers), it was of extreme interest to look at related materials with multiple Cu layers. Sr_2CuO_3 may be considered as the first member of the homologous series, $Sr_{n+1}Cu_nO_{2n+1+\delta}$. The $n = 2$ member has been prepared by high-pressure synthesis,[5] but for ambient pressure synthesis, rare-earth elements, Ln, are required to partially substituted for the alkaline-earth metals, and this represents the widely known Ruddlesden–Popper type double-layer cuprates, $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (Ln = rare-earth, A = Ca, Sr).[6–9] As in the case of Sr_2CuO_3, significant oxygen vacancies are located in these phases, mainly between the double CuO_2 layers such that the coordination of Cu is square pyramidal (Fig. 1). These phases are non-superconducting as synthesised, but a number of groups have induced superconductivity (T_c up to 60 K) using a variety of routes including high-oxygen-pressure annealing, control of synthesis conditions, or use of an oxidizing agent such as $KClO_3$.[10–12] Our aim was to attempt to induce superconductivity through fluorination.

In phases with high Sr content, *e.g.* $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$, significant vacancies are also located in the CuO_2 planes, and an ordering of these vacancies occurs leading to a tripled cell along one direction.[9] This gives rise to a unique one-dimensional tunnelled copper–oxygen sublattice built from vertex linked CuO_5 square pyramids (Fig. 2), where it should be possible to insert fluorine similar to the case of A_2CuO_3 (A = Ca, Sr, Ba). In this paper we report detailed studies on the fluorination of these double-layer cuprates, showing the extent and characteristics of fluorination by each method. In addition we highlight the differences in the characteristics of the three methods.

Experimental

High-purity Nd_2O_3, La_2O_3, $SrCO_3$, $CaCO_3$, and CuO were used to prepare the following samples, $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$, $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ and $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$. The intimately ground powders were heated in air at a temperature between 1050 and 1075 °C for 18 h, reground, and then reheated at the same temperature for a further 18 h, followed by furnace cooling.

Fluorination by solid/F_2 gas reaction

The samples were heated in 10%F_2–90%N_2 (passed over NaF to remove HF) at a temperature between 200 and 250 °C for a time ranging from 15 to 150 min. The temperature used depended on the system [$Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ (205 °C), $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ (240 °C), $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$ (250 °C)] and reaction times, which ranged from 15 min to 5 h, determined the extent of fluorination.

Fluorination by NH_4F (solid-state reaction)

For fluorination using NH_4F a reaction temperature of 300–350 °C was required and up to 20 mol of NH_4F were used

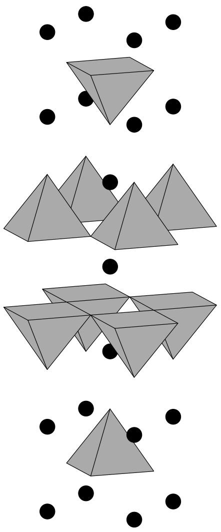

Fig. 1 Structure of $La_2ACu_2O_6$ (A = Ca, Sr) showing square-pyramidal Cu (spheres: A, Sr)

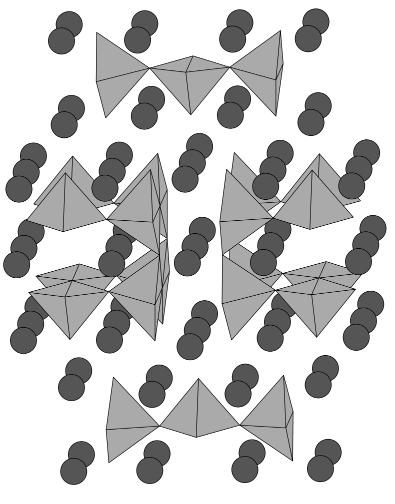

Fig. 2 Structure of $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ showing square-pyramidal Cu (spheres: Nd, Sr)

to prepare samples with the highest F content. In order to minimize SrF_2 impurities at higher F levels, the NH_4F was added in stages, *e.g.* for 10 mol of NH_4F, 5 mol was added first and reacted at 300–350 °C; the sample was then reground with a further 5 mol of NH_4F and heated as before.

Fluorination by CuF_2 (solid-state reaction)

Anhydrous CuF_2 (0–2 mol) was added to the precursor oxides; the mixture was ground and heated in the range 245–350 °C in air for 12 h.

Autoclave method (solid–gas reaction with CuF_2)

The drawback of the CuF_2 route is the presence in the samples of CuO impurity deriving from the decomposition of CuF_2. In order to avoid this problem, a number of experiments have been performed in enclosed vessels with the starting oxides and CuF_2 separated. In this route, the oxides were weighed out into a Teflon vessel and the required amount of CuF_2 was then placed in a small nickel pot, which was put into the Teflon vessel, and the lid fitted. The Teflon vessel was then placed in an autoclave and heated to 245 °C. Similar results were obtained to the solid-state reaction with CuF_2, with the exception that no CuO impurities were observed in this case, as the CuF_2 was kept separate.

Characterization methods

The resulting products were characterised by powder X-ray diffraction (Cu-Kα_1 radiation, Siemens D-5000 diffractometer). Potential superconducting properties were examined using a DC SQUID magnetometer (Cryogenics Model S100).

The fluorine contents were determined using a fluoride ion selective electrode. Prior to measurements being made, the electrode was calibrated using freshly prepared solutions containing known concentrations of NaF. The sample solution was then prepared as follows: *ca.* 0.02–0.05 g of sample was dissolved in 5 cm^3 of 0.5 M HCl, to which was added 45 cm^3 of distilled water followed by 50 cm^3 of a pH *ca.* 5.3 total ionic strength adjustment buffer (TISAB) solution (preparation described below). The fluorine content of the sample was then determined from the electrode reading of the solution using the NaF calibration graph. No noticeable residual fluorinating agent (NH_4F or CuF_2) was present in any of the samples analysed. The major errors in the analysis resulted from any presence of Sr/CaF_2 impurities which tended to be observed mainly for samples with high fluorine contents. The presence of this impurity will result in a higher apparent fluorine content for the sample. The fluorine contents of samples containing significant amounts of this impurity should therefore be treated as only approximate, and this is referred to further in the results section.

The TISAB solution was prepared as follows; 57 cm^3 glacial acetic acid, 58 g of NaCl and 4 g of *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*,*N*-tetraacetic acid were dissolved in 500 cm^3 of distilled water, and sufficient 5 M NaOH was added to adjust the pH to *ca.* 5.3. The buffer solution was then made up to 1000 cm^3 with distilled water.

Copper oxidation states were determined by iodometric titration. Two complementary titrations were performed for each sample. The first titration involved dissolving *ca.* 0.05 g of the sample in 50 cm^3 of distilled water by the addition of dilute (2 M) HCl. The solution was then boiled to ensure complete conversion of any Cu^{3+}/Cu^{+} to Cu^{2+}, before excess KI was added. The I_2 generated was then titrated under N_2 against standard (0.02 M) $Na_2S_2O_3$ solution. This titration determines the total amount of Cu in the sample. The second titration involved dissolving under N_2 the same mass of sample in excess KI solution by addition of dilute HCl. The liberated I_2 was then titrated as before. From the difference in the titration values obtained, the copper oxidation state can be determined. In samples fluorinated by direct solid-state reaction with CuF_2, CuO is present as an impurity, and so this will influence the titration. The quantity of CuO present is however known (equal to the amount of CuF_2 added) and so this can be corrected for in the determination of the Cu oxidation state of the sample: good agreement between the Cu oxidation state calculations was obtained for samples fluorinated to a similar extent by the direct solid-state reaction method and the autoclave method (where the CuF_2 is kept separate and so no correction is required).

Results

Fluorination of $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (L = La, Nd; A = Ca, Sr)

Powder X-ray diffraction suggested significant fluorine incorporation for all fluorination methods, with large peak shifts in most cases. The magnitude of the shifts increased with increased fluorine content. Fig. 3–5 show the X-ray diffraction patterns for the starting materials, and the 'fully' fluorinated products for each method.

(a) Reaction with NH_4F. In order to successfully fluorinate the double-layer cuprates by this method, a higher temperature (300–350 °C) was required compared with similar reactions with $Sr_{2-x}A_xCuO_3$ (230 °C). Moreover, since the double-layer materials appear to be less moisture sensitive, Sr/CaF_2 impurities were only observed for samples with the highest fluorine levels. Tables 1 and 2 list cell parameters and fluorine contents for a range of samples prepared by this method. The presence of Sr/CaF_2 impurities in the high fluorine content samples means that the calculated fluorine contents for these samples should be viewed as only approximate.

For $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ and $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ there was no change in cell symmetry but the cell parameters increased by up to *ca.* 5% along *a* and *b*, and *ca.* 1% along *c* after fluorination. Fluorination of $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ proved more interesting. In this system at low fluorine contents the cell was tetragonal as for the parent compound, while for high fluorine levels the cell became orthorhombic. At intermediate fluorine contents both phases were observed (Fig. 6), with the ratio of the phases with low fluorine content (tetragonal, $a=b\approx3.92$, $c\approx20.14$ Å) and high fluorine content (orthorhombic, $a\approx3.86$, $b\approx3.90$ Å, $c\approx21.68$ Å) varying with overall fluorine content; at high fluorine levels, only the latter phase was observed. In the low fluorine content phase, the largest changes in cell parameters were along *a* and *b* (similar to $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$

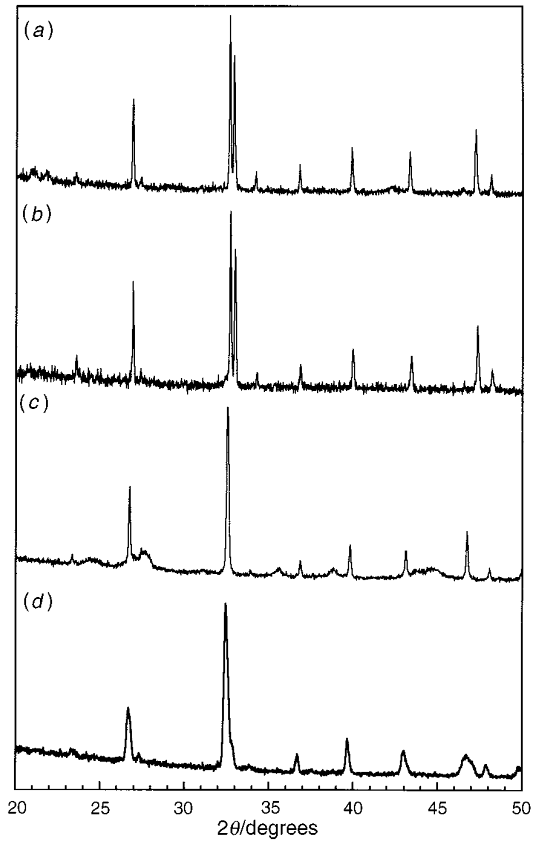

Fig. 3 Powder X-ray diffraction patterns for (*a*) $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$, (*b*) $La_{1.9}Ca_{1.1}Cu_2O_{5.95}F_{0.4}$ (F_2 gas), (*c*) $La_{1.9}Ca_{1.1}Cu_2O_{5.3}F_{1.3}$ (NH_4F) and (*d*) $La_{1.9}Ca_{1.1}Cu_2O_{5.5}F_{0.9}$ (CuF_2, 350 °C)

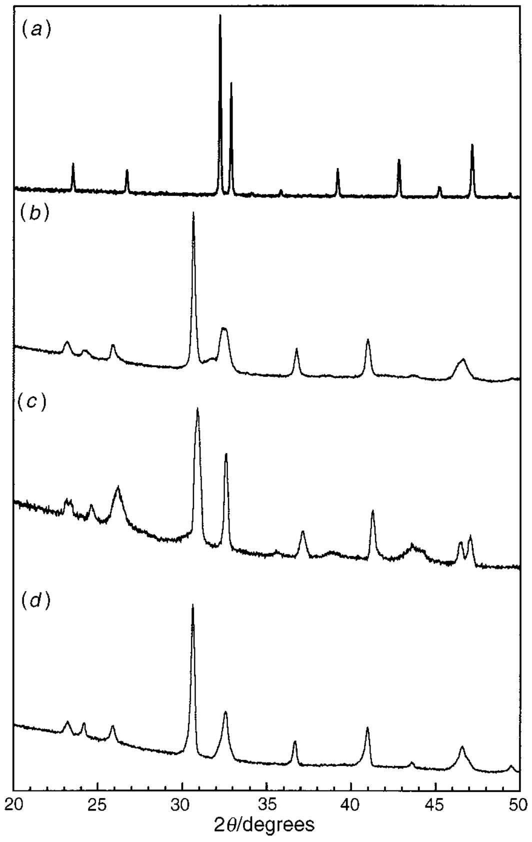

Fig. 4 Powder X-ray diffraction patterns for (*a*) $La_{1.9}Sr_{1.1}Cu_2O_{6.05}$, (*b*) $La_{1.9}Sr_{1.1}Cu_2O_{6.05}F_{1.5}$ (F_2 gas), (*c*) $La_{1.9}Sr_{1.1}Cu_2O_{4.9}F_{2.3}$ (NH_4F) and (*d*) $La_{1.9}Sr_{1.1}Cu_2O_{5.45}F_2$ (CuF_2, 245 °C autoclave method)

and $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$) whereas an expansion along *c* by 8% was observed for the high fluorine content phase, with much lower expansions along *a* and *b* (Table 1). If we consider the change in cell parameters from the low to the high fluorine content phase, then we can see that *a* and *b* actually contract slightly, with a large expansion along *c*. Moreover a change from tetragonal to orthorhombic symmetry is observed which may be related to an ordering of O/F and vacancies. It is possible that the cell may be tripled along *b* similar to that observed for $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$, although there is no conclusive evidence for this.

Iodometric titrations indicated a negligible increase in the copper oxidation state following fluorination, with the copper oxidation state for all three systems remaining close to 2.0+. Thus fluorination *via* NH_4F appears to be essentially a non-oxidative process, and so probably involves a substitution reaction in which one oxygen is replaced by two fluorine atoms.

The reaction with NH_4F appears to proceed *via* the addition of HF, derived from the decomposition reaction $NH_4F \rightarrow NH_3 + HF$. Evidence for this is provided by an attempt to fluorinate $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ *via* a quantitative reaction with a solution of NH_4F in H_2O in a hydrothermal bomb. Reaction at 100 °C suggested only a minor change in cell parameters, and subsequent heating of the filtered and washed solid at 350 °C resulted in a large change in cell parameters indicating successful fluorine incorporation. Moreover, the filtrate was alkaline, suggesting that the cuprate had incorporated HF, leaving NH_3 in solution. Monitoring the reaction more carefully with a pH meter showed that at 60 °C, a fast reaction (total reaction time *ca.* 10 min) occurred with the pH changing from acidic to alkaline as the cuprate was added to the aqueous solution of NH_4F. A similar experiment performed at room temperature, however, showed a pH change to neutral

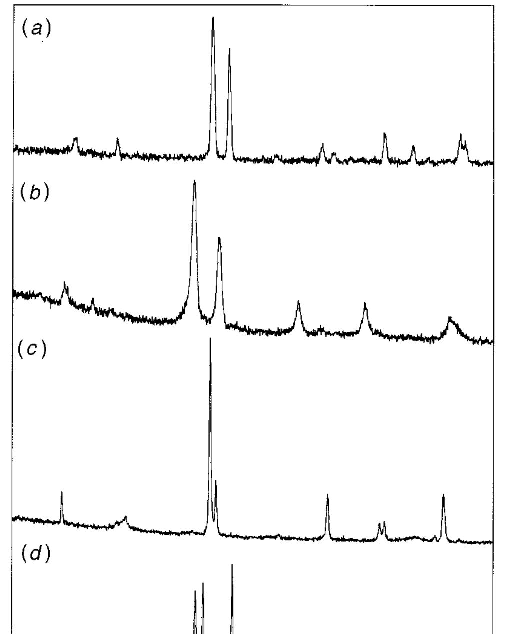

Fig. 5 Powder X-ray diffraction patterns for (*a*) $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$, (*b*) $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}F_{1.8}$ (F_2 gas), (*c*) $Nd_{1.3}Sr_{1.7}Cu_2O_{4.65}F_2$ (NH_4F) and (*d*) $Nd_{1.3}Sr_{1.7}Cu_2O_{4.8}F_{2.8}$ (CuF_2, 245 °C autoclave method)

Table 1 Cell parameters for $La_{1.9}Sr_{1.1}Cu_2O_{6.05}$ (LSC), $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ (LCC) and $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$ (NSC) fluorinated using NH_4F

compound	mol. NH_4F	a/Å	b/Å	c/Å
LCC	—	3.828(1)	$=a$	19.410(3)
LCC	1	3.831(1)	$=a$	19.442(6)
LCC	2	3.834(1)	$=a$	19.475(5)
LCC	10	3.895(2)	$=a$	19.56(1)
LCC	20	3.899(1)	$=a$	19.57(1)
LSC	—	3.851(1)	$=a$	20.048(6)
LSC	0.5	3.896(3)	$=a$	20.12(2)
LSC	1	3.922(1)	$=a$	20.141(9)
LSC	2	3.929(1)	$=a$	20.177(7)
LSC	5	3.937(1)	$=a$	20.199(5)
LSC	20	3.859(2)	3.903(2)	21.68(1)
NSC	—	3.767(3)	11.366(9)	20.10(1)
NSC	0.5	3.798(5)	11.49(1)	20.29(4)
NSC	1	3.818(4)	11.54(1)	20.35(3)
NSC	2	3.847(1)	11.555(6)	20.38(2)
NSC	5	3.851(2)	11.56(1)	20.37(2)
NSC	10	3.863(3)	11.62(1)	20.31(2)
NSC	20	3.944(3)	11.92(1)	20.10(3)

Table 2 F contents, Cu oxidation states and suggested final compositions for selected samples of $La_{1.9}Sr_{1.1}Cu_2O_{6.05}$ (LSC), $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ (LCC) and $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$ (NSC) fluorinated using NH_4F

compound	mol. NH_4F	F content mol^{-1}	Cu oxidation state	suggested composition of sample
LCC	—	—	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.95}$
LCC	1	0.5	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.7}F_{0.5}$
LCC	2	0.7	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.6}F_{0.7}$
LCC	10	1.3	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.3}F_{1.3}$
LSC	—	—	2.1	$La_{1.9}Sr_{1.1}Cu_2O_{6.05}$
LSC	1	0.6	2.1	$La_{1.9}Sr_{1.1}Cu_2O_{5.75}F_{0.6}$
LSC	20	2.3	2.1	$La_{1.9}Sr_{1.1}Cu_2O_{4.9}F_{2.3}$
NSC	—	—	2.0	$Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$
NSC	5	1.2	2.0	$Nd_{1.3}Sr_{1.7}Cu_2O_{5.05}F_{1.2}$
NSC	10	1.8	2.0	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.75}F_{1.8}$
NSC	20	2.0	2.0	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.65}F_{2.0}$

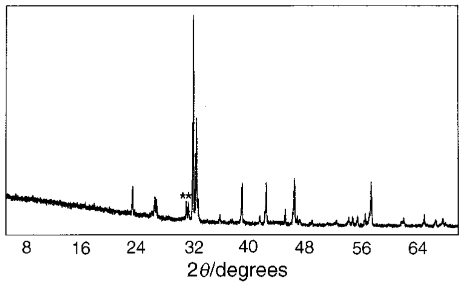

Fig. 6 Powder X-ray diffraction patterns for $La_{1.9}Sr_{1.1}Cu_2O_6$ fluorinated with 7.5 moles of NH_4F, showing two fluorinated phases: main peaks from the high fluorine content phase are marked*

only, suggesting that NH_4F itself was adsorbed by the sample, with no decomposition to HF and NH_3 occurring at this temperature.

(b) F_2 gas. In order to achieve successful fluorination, the samples $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$ and $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ required a higher temperature (240–250 °C) than $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ (205 °C), which may relate to the slightly different structures. Moreover, at temperatures >205 °C the Nd containing phase decomposed to give SrF_2. The fluorine content was observed to increase with increasing reaction time at these temperatures.

Fluorination of $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$ resulted in a small increase in the cell parameters, indicating a low incorporation of fluorine (Table 3), whereas $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ and $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ showed larger expansions, consistent with high fluorine levels. For these phases the largest increase in cell parameters was along the c direction, suggesting the probable incorporation of F between Cu ions in adjacent CuO_2 layers. Unlike the case of the fluorination of A_2CuO_3 ($A=Ca$, Sr, Ba), where fluorination led immediately to a large structural change to the oxide fluoride $Sr_2CuO_2F_{2+\delta}$, with little non-stoichiometry range (δ) for F, the fluorination of the $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ ($L=Eu$, Nd) showed a wide fluorine solid solution from the oxide endmember to the highest fluorine content, the XRD peaks shifting to lower 2θ values as the fluorine content was increased. Indeed, broad peaks, or shoulders on peaks were commonly observed, indicating a mixture of compositions with slightly different cell parameters in the sample, due to the inhomogeneity of fluorination.

As in the case of fluorination using NH_4F, a distinct two-phase region (high and low F content phases) was observed for $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ at intermediate F levels, the cell parameters for these two phases being vastly different due to a large expansion along c for the high F content phase ($a=b\approx3.90$, $c\approx20.32$ Å compared to $a=b\approx3.90$, $c\approx22.11$ Å). In this case, however, no change to orthorhombic symmetry was observed for the high fluorine content phase. The fluorine contents for a range of samples prepared using F_2 gas are given in Table 3. These results show that for the phases with $A=Sr$, very high fluorine contents are achieved, such as 1.8 fluorine atoms per formula unit after fluorination of $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$.

Iodometric titrations showed that the reaction with F_2 gas was highly oxidative, as might be expected, with the copper oxidation state increasing with increasing fluorination up to values close to 3.0+ (Table 3). These results, and the fluorine contents determined, suggest that the fluorination of the double-layer cuprates by F_2 gas proceeds *via* a simple insertion process, in which the anion site vacancies are gradually filled by fluorine. The fluorine contents and copper oxidation states determined, however, indicate that fluorine must also occupy some interstitial sites for high fluorine contents, similar to that observed in $Sr_2CuO_2F_{2+\delta}$, since, for $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}F_{1.8}$ and $La_{1.9}Sr_{1.1}Cu_2O_6F_{1.5}$ there are seven 'ideal' anion sites, leaving the remaining 0.45 or 0.5 fluorine atoms to occupy interstitial sites presumably in the Ln/Sr ($L=Nd$, La) bilayers. The alternative possibility of partial substitution of fluorine for oxygen was not supported by the copper oxidation state determinations. Slightly higher fluorine contents were also observed on prolonged fluorination, demonstrated by larger peak shifts. The $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$ sample heated at 205 °C for >2.5 h showed a shoulder at higher d-spacing, which increased with increasing fluorination time, thus indicating the presence of two phases, $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}F_{1.8}$ and a phase with larger peak shift and therefore presumably higher F content. Unfortunately, at these high fluorination levels, it is extremely difficult to avoid decomposition to give SrF_2, and it was not possible to isolate the pure phase with the higher F content. Fluorine analysis of the mixed sample gave an anomalously high fluorine content, 3.5, presumably due to the presence of the SrF_2 impurity, and so the exact fluorine content of this phase is not known.

(c) CuF_2 method (solid-state and autoclave routes). Both the solid-state and the autoclave methods gave similar results, although the latter had the advantage that because the sample and CuF_2 were kept separate, no CuO impurity was observed. Cell parameters, copper oxidation states and F contents are given in Tables 4 and 5.

At high temperatures (>300 °C) the XRD patterns of the products were similar to those from reaction with NH_4F, whereas at lower temperatures (*ca.* 245 °C) the reaction appeared to be similar to reaction with F_2 gas. Iodometric titrations supported this view, with the copper oxidation state

Table 3 Cell parameters, Cu oxidation states and F contents (x) for $La_{1.9}Sr_{1.1}Cu_2O_{6.05}F_x$ (LSC), $La_{1.9}Ca_{1.1}Cu_2O_{5.95}F_x$ (LCC) and $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}F_x$ (NSC) prepared using F_2

compound	reaction temp./°C	reaction time/min	a/Å	b/Å	c/Å	Cu oxidation state	x
LCC	—	—	3.828(1)	$=a$	19.410(3)	2.0	—
LCC	250	15	3.834(2)	$=a$	19.475(5)	2.1	0.2
LCC	250	50	3.839(1)	$=a$	19.506(4)	2.15	0.4
LSC	—	—	3.851(1)	$=a$	20.048(6)	2.1	—
LSC	220	30	3.853(1)	$=a$	20.05(1)	2.1	0.1
LSC	220	60	3.876(3)	$=a$	20.18(4)	2.25	0.4
LSC	240	15	3.898(1)	$=a$	20.32(2)	2.3	0.6
LSC	240	60	3.893(1)	$=a$	21.95(1)	2.9	1.5
NSC	—	—	3.767(3)	11.366(9)	20.10(1)	2.0	—
NSC	205	20	3.787(4)	11.399(6)	20.18(1)	2.15	0.2
NSC	205	60	3.842(3)	11.544(7)	20.54(2)	2.3	0.8
NSC	205	120	3.837(1)	11.600(4)	21.04(2)	2.6	1.3
NSC	205	150	3.851(2)	11.679(5)	21.37(2)	2.9	1.8

Table 4 Cell parameters for $La_{1.9}Sr_{1.1}Cu_2O_{6.05}$ (LSC), $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ (LCC) and $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$ (NSC) fluorinated using CuF_2

compound	mol. CuF_2	reaction temp./°C	a/Å	b/Å	c/Å
LCC	—	—	3.828(1)	$=a$	19.410(3)
LCC	0.5	245	3.827(1)	$=a$	19.427(5)
LCC	1	245	3.834(1)	$=a$	19.51(1)
LCC	2	245	3.843(3)	$=a$	19.58(2)
LCC	1	350	3.860(2)	$=a$	19.50(1)
LSC	—	—	3.851(1)	$=a$	20.048(6)
LSC	0.25	245	3.898(3)	$=a$	20.18(2)
LSC	0.5[a]	245	3.902(2)	$=a$	20.14(2)
LSC	1[b]	245	3.887(7)	$=a$	21.99(6)
LSC	1.5	245	3.896(5)	$=a$	22.09(2)
LSC	2	245	3.93(1)	$=a$	22.2(1)
LSC	1.5	300	3.864(2)	3.929(2)	21.53(2)
LSC	1.5	350	3.856(1)	3.911(1)	21.45(1)
NSC	—	—	3.767(3)	11.366(9)	20.10(1)
NSC	0.25	245	3.817(1)	11.455(1)	20.33(1)
NSC	0.5	245	3.832(3)	11.55(1)	20.50(2)
NSC	1.25[b]	245	3.804(1)	11.690(4)	21.70(2)
NSC	1.5	245	3.798(1)	11.699(2)	21.91(1)
NSC	1.5	270	3.823(1)	11.746(4)	21.75(2)
NSC	1.5	300	3.937(1)	11.800(2)	19.96(1)
NSC	1.5	350	3.884(7)	11.81(1)	19.89(2)

[a] Sample consisted of two phases: the cell parameters for the lower F content (most abundant) phase are given. [b] Sample consisted of two phases: the cell parameters for the higher F content (most abundant) phase are given.

increasing at low temperatures, while remaining close to 2.0+ at higher temperatures. The maximum copper oxidation state achieved by this method was, however, lower than that obtained using F_2 gas (2.5+ compared to 3.0+), suggesting that although highly oxidative, the oxidising power of the reaction with MF_2 is not as great as for the reaction with F_2 gas. Copper oxidation states and fluorine contents for selected samples are listed in Table 5. Taken together, the copper oxidation states and fluorine contents indicate that at high temperatures the reaction proceeds *via* substitution (2F≡1O), whereas at low temperatures the reaction is probably a mixture of insertion (as in the case of F_2) and substitution. Suggested final compositions of the samples after fluorination were determined from the fluorine contents and copper oxidation states and are reported in Table 5. The slight difference in the MF_2 (low temperature) and F_2 reaction routes is demonstrated by the fact that for $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$, the orthorhombic splitting at the highest fluorine content, designated by the ratio $a:b/3$, was significantly larger for samples derived from the MF_2 route (*ca.* 1.025 compared to *ca.* 1.01).

In all three methods, the fluorine content could be varied by suitable control, *e.g.* amount of CuF_2/NH_4F or temperature and time for F_2 gas. For the CuF_2 and F_2 methods, the copper oxidation state can also be controlled between 2+ and 3.0+, such that it is quite readily possible to prepare samples with copper oxidation states in the region 2.2–2.3+, which should be optimum for superconductivity.

All samples were examined for possible superconductivity. For the sample $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$, a very weak superconducting signal (*ca.* 0.1% volume fraction), T_c *ca.* 20 K, was observed after light fluorination using CuF_2 (*ca.* 0.1–0.2 moles). Under such conditions, samples showed broad X-ray peaks consistent with a mixture of fluorine contents. Further work has failed to increase the superconducting fraction, or increase

Table 5 F contents, Cu oxidation states and suggested final compositions for selected samples of $La_{1.9}Sr_{1.1}Cu_2O_{6.05}$ (LSC), $La_{1.9}Ca_{1.1}Cu_2O_{5.95}$ (LCC) and $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$ (NSC) fluorinated using CuF_2

compound	mol. CuF_2	reaction temp./°C	F content mol^{-1}	Cu oxidation state	suggested composition of sample
LCC	—	—	—	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.95}$
LCC	2	245	0.5	2.1	$La_{1.9}Ca_{1.1}Cu_2O_{5.8}F_{0.5}$
LCC	1	350	0.9	2.0	$La_{1.9}Ca_{1.1}Cu_2O_{5.5}F_{0.9}$
LSC	—	—	—	2.1	$La_{1.9}Sr_{1.1}Cu_2O_{6.05}$
LSC	0.25	245	0.4	2.25	$La_{1.9}Sr_{1.1}Cu_2O_{6.0}F_{0.4}$
LSC	1.5	245	2.0	2.5	$La_{1.9}Sr_{1.1}Cu_2O_{5.45}F_{2.0}$
LSC	1.5	300	1.8	2.15	$La_{1.9}Sr_{1.1}Cu_2O_{5.2}F_{1.8}$
LSC	1.5	350	1.7	2.1	$La_{1.9}Sr_{1.1}Cu_2O_{5.2}F_{1.7}$
NSC	—	—	—	2.0	$Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$
NSC	0.5	245	0.7	2.2	$Nd_{1.3}Sr_{1.7}Cu_2O_{5.5}F_{0.7}$
NSC	1.5	245	2.8	2.55	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.8}F_{2.8}$
NSC	1.5	270	2.5	2.35	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.75}F_{2.5}$
NSC	1.5	300	2.2	2.1	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.65}F_{2.2}$
NSC	1.5	350	1.8	2.1	$Nd_{1.3}Sr_{1.7}Cu_2O_{4.85}F_{1.8}$

T_c. No evidence for superconductivity was found for any other sample.

Discussion

The results clearly demonstrate that the Ruddlesden–Popper type cuprates, $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (L = Nd, La, Eu; A = Sr, Ca) can incorporate significant fluorine levels. This system is interesting because it demonstrates some different characteristics of each of the three fluorination routes leading to large differences in the final fluorinated products. In particular, reaction with F_2 gas appears to proceed *via* fluorine insertion, while reaction with NH_4F appears to involve fluorine substitution for oxygen. The reaction with CuF_2 at low temperatures (*ca.* 245 °C) probably involves both insertion and substitution mechanisms, while at higher temperatures (> 300 °C) the substitution process dominates, and the copper oxidation state remains at 2.0+. In addition, it has been found that heating samples prepared by the F_2 gas route to temperatures > 300 °C also results in a similar XRD pattern to reaction with NH_4F. Thus the high copper oxidation states are only stable at low-temperatures (*ca.* 200–250 °C), and so this fact can be used as a post-synthesis means of control of the fluorine content and copper oxidation state.

If we consider the reactions with F_2 gas and MF_2 (low temperature), the highest fluorine levels were achieved for A = Sr leading to a large expansion of the lattice parameters along *c* (up to 2 Å) for such samples, suggesting that fluorine is being inserted into the vacant sites between the CuO_2 layers, so that the copper coordination changes from square pyramidal to octahedral. The magnitudes of the changes in *c* are also consistent with the expansion that would be needed for insertion of fluorine between the CuO_2 layers to give two Cu—F bonds of reasonable length (*ca.* 1.8 Å). There is also evidence that some excess fluorine is introduced in these systems, which must be located in interstitial sites, presumably between the Ln/Sr bilayers, similar to the interstitial fluorine sites between the Sr bilayers in $Sr_2CuO_2F_{2+\delta}$.[4] A further interesting point is the distinct two-phase character observed for $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ on fluorination, suggesting the stability of the high fluorine content phase. In the case of A = Ca, lower fluorine levels are observed, and the expansion along *c* is small (*ca.* 0.17 Å), suggesting that very little, if any, fluorine is now located between the CuO_2 layers, with the fluorine possibly being located in the interstitial sites instead.

These results can be explained by considering the size of the cation separating the two CuO_2 layers. For phases with A = Sr, there is a mixture of rare earth, Ln, and Sr separating the CuO_2 layers, whereas for phases containing Ca, it is the Ca that occupies these sites.[13] Thus for the former systems the larger size of Sr compared to Ca (ionic radii for 8-coordination, Sr^{2+} 1.26 Å, Ca 1.12 Å)[14] means that the separation of the layers is larger (*e.g.* $La_2SrCu_2O_6$ *ca.* 3.7 Å, $La_2CaCu_2O_6$ *ca.* 3.3 Å)[13] and so fluorine can be inserted much more readily into the vacant sites between the layers.

An interesting point is the fact that for the reactions with NH_4F and CuF_2 (high temperature) the samples $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ and $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ showed different behaviour, whereas for the other methods they behaved similarly. For the former, a large increase in *c* was observed along with a distinct two-phase region similar to that observed for reaction with F_2 and MF_2 (low temperature). In contrast, for both $La_{1.9}Ca_{1.1}Cu_2O_{6-y}$ and $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ the major expansion was along *a* and *b*, with little change along *c*. The origin of this difference is unclear. Further work, including powder neutron diffraction studies and Eu Mössbauer experiments on $Eu_{1.3}Sr_{1.7}Cu_2O_{6-y}$ (isostructural with $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$), is planned to help rationalise this result. We suggest that the high fluorine content phase has a composition $La_{1.9}Sr_{1.1}Cu_2O_5F_2$ (*i.e.* the substitution of one oxygen atom by two fluorine atoms in $La_{1.9}Sr_{1.1}Cu_2O_6$), with octahedral copper similar to the situation in $Sr_2CuO_2F_{2+\delta}$. This is supported by fluorine analysis (Table 2) although the presence of SrF_2 impurities at the higher fluorine levels does cast some doubts over the absolute reliability of the values. Such a compound, with all the anion sites filled, might be expected to be very stable, and this perhaps explains the two-phase region. The reason why fluorination of $Nd_{1.3}Sr_{1.7}Cu_2O_{6-y}$ with NH_4F does not form a similar phase may be related in some way to the slightly different structure of the parent oxide or to the fact that the starting oxygen content is lower ($y \approx 0.35$) so that an anion content (O + F) of 7.0 is not achieved after fluorination of this phase. One problem with this postulation is that the fully fluorinated $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ is orthorhombic, whereas the proposed compound $La_{1.9}Sr_{1.1}Cu_2O_5F_2$ might be expected to be tetragonal. This indicates some sort of ordering must be present, which may be related to O/F ordering, perhaps in the apical sites (if we assume that fluorine occupies only the apical sites, then the composition of the apical positions consists of one oxygen plus two fluorine atoms). Alternatively it may be related to a small excess of interstitial fluorine, which is suggested by the fluorine analysis.

The origin of the weak superconducting signal in $La_{1.9}Sr_{1.1}Cu_2O_{6-y}$ at 20 K for low fluorine levels is unclear. This signal has been seen reproducibly in a number of lightly fluorinated samples, but without any significant increase in signal strength, and is not present in the parent undoped material. It is possible that this signal may be due to the presence of a very small amount of the single copper layer phase $La_{2-x}Sr_xCuO_4$ impurity, which becomes superconducting after fluorination. The lack of bulk superconductivity in these systems may be possibly explained by the partial occupation of the anion sites between the CuO_2 layers, since the location of isolated fluorine or oxygen atoms in these sites would be expected to result in hole trapping.

Recently superconducting related phases, $Sr_2Ca_{n-1}Cu_nO_{2n+x}F_{2-y}$ ($n = 2$, 3), have been synthesised by a high-pressure route with high T_cs ($n = 2$, 99 K; $n = 3$, 111 K).[15] These results support the view that it should be possible to induce superconductivity in the systems studied by suitable synthesis control. In this respect, if we assume that the occurrence of superconductivity is quenched by hole trapping by localised oxygen or fluorine atoms linking the CuO_2 layers, then in principle, complete occupation of these anion sites should eliminate such hole trapping. However, such a situation ultimately results in copper oxidation states which are too high for superconductivity, *e.g.* for $La_{1.9}Sr_{1.1}Cu_2O_6F$ the copper oxidation state would be 2.55+. It may therefore be possible to use a combination of fluorination methods, involving the non-oxidative fluorination of the sample first with NH_4F, which we believe leads to the replacement of one oxygen by two fluorine atoms and a consequent increase in the occupation of the anion sites between the CuO_2 layers. Reaction with F_2 or MF_2 could then be used to fill the remaining sites and provide the necessary Cu oxidation. Alternatively, we have suggested that the high fluorine content phase produced by the reaction of $La_{1.9}Sr_{1.1}Cu_2O_6$ with NH_4F consists of replacement of one oxygen atom by two fluorine atoms to give a stable system $La_{1.9}Sr_{1.1}Cu_2O_5F_2$, where all the anion sites are filled, *i.e.*

$$La_{1.9}Sr_{1.1}Cu_2O_6 + 2\ F \rightarrow La_{1.9}Sr_{1.1}Cu_2O_5F_2 + 1\ O$$

(Cu oxidation state = 2.05)

Fluorine could then be inserted into the interstitial sites of this phase to raise the Cu oxidation state to the optimum level by the oxidative fluorination with F_2 gas or CuF_2, *i.e.*

$$La_{1.9}Sr_{1.1}Cu_2O_5F_2 + 0.5\ F \rightarrow La_{1.9}Sr_{1.1}Cu_2O_5F_{2.5}$$

(Cu oxidation state = 2.3)

Such two-stage fluorination processes could be used for a range of cuprate systems to vary the O/F ratio, while achieving a copper oxidation state (*ca.* 2.3+) suitable for superconductivity.

Neutron diffraction studies are planned to try to confirm these conclusions, particularly relating to the location of the fluorine atoms. In addition Eu Mössbauer studies of the $Eu_{1.3}Sr_{1.7}Cu_2O_{5.65}$ system are planned to examine the variation in the Eu environment with increasing F content. With respect to this system, and the related Nd-containing system, $Nd_{1.3}Sr_{1.7}Cu_2O_{5.65}$, one might expect that fluorine would initially insert along the one-dimensional channels in the structure (Fig. 2). Then after these sites have been filled, the fluorine would presumably occupy the sites between the CuO_2 sheets.

Despite the lack of superconductivity, these results taken together with previous studies on A_2CuO_3 (A = Ca, Sr, Ba), show that low-temperature fluorination is a powerful tool for the incorporation of fluorine in samples of this type. Moreover, these results on the double-layer cuprates show a clear difference between the nature of the fluorination processes. Namely the fluorination with NH_4F appears to be essentially a non-oxidative substitution reaction, although the fact that superconducting $Sr_2CuO_2F_{2+\delta}$ can be prepared from Sr_2CuO_3 suggests that some oxidation, probably aerial oxidation, can occur.[3] In contrast, the fluorination with F_2 gas appears to proceed *via* an oxidative insertion reaction in this system, while reaction with MF_2 (low temperature) involves both substitution and insertion. The reaction with Sr_2CuO_3 to give $Sr_2CuO_2F_{2+\delta}$ shows that the fluorination by F_2 gas can also involve partial substitition in addition to oxidative insertion.

Summary

The results clearly demonstrate that large amounts of fluorine can be incorporated into the Ruddlesden–Popper type cuprates $Ln_{2-x}A_{1+x}Cu_2O_{6-y}$ (L = La, Nd; A = Ca, Sr). Despite the lack of superconductivity, these results further demonstrate that low-temperature fluorination is a powerful tool for the incorporation of fluorine and control of copper oxidation states in cuprates. Recent preliminary results have shown that these fluorination routes can also be applied to non-cuprate systems.

We thank the EPSRC for financial support.

References

1 M. Al-Mamouri, P. P. Edwards, C. Greaves and M. Slaski, *Nature* (*London*), 1994, **369**, 382.
2 M. Al-Mamouri, P. P. Edwards, C. Greaves, P. R. Slater and M. Slaski, *J. Mater. Chem.*, 1995, **5**, 913.
3 P. R. Slater, P. P. Edwards, C. Greaves, I. Gameson, J. P. Hodges, M. G. Francesconi, M. Al-Mamouri and M. Slaski, *Physica C*, 1995, **241**, 151.
4 P. R. Slater, J. P. Hodges, M. G. Francesconi, P. P. Edwards, C. Greaves, I. Gameson and M. Slaski, *Physica C*, 1995, **253**, 16.
5 Z. Hiroi, M. Takano, M. Azuma and Y. Takeda, *Nature* (*London*), 1993, **364**, 315.
6 N. Nguyen, L. Er-rakho, C. Michel, J. Choisnet and B. Raveau, *Mater. Res. Bull.*, 1980, **15**, 891.
7 C. Michel and B. Raveau, *Rev. Chim. Miner.*, 1984, **21**, 407.
8 N. Nguyen, C. Michel, F. Studer and B. Raveau, *Mater. Chem.*, 1982, **7**, 413.
9 N. Nguyen, J. Choisnet and B. Raveau, *Mater. Res. Bull.*, 1982, **17**, 567.
10 R. J. Cava, B. Batlogg, R. B. van Dover, J. J. Krajewski, J. V. Waszczak, R. M. Fleming, W. F. Peck Jr., L. W. Rupp Jr., P. Marsh, A. C. W. P. James and L. F. Schneemeyer, *Nature* (*London*), 1990, **345**, 602.
11 K. Kinoshita, H. Shibata and T. Yamada, *Physica C*, 1991, **176**, 433.
12 R. Mahesh, R. Vijayaraghavan and C. N. R. Rao, *Mater. Res. Bull.*, 1994, **29**, 303.
13 R. C. Lobo Ph.D. Thesis, University of Birmingham, 1990.
14 R. D. Shannon, *Acta. Crystallogr., Sect. A*, 1976, **32**, 751.
15 T. Kawashima, Y. Matsui and E. Takayama-Muromachi, *Physica C*, 1996, **256**, 313.

Paper 7/03735J; *Received 29th May*, 1997