Synthesis and Structure of Ba_2InO_3F: Oxide/Fluoride Ordering in a New K_2NiF_4 Superstructure

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Ba_2InO_3F has ordered anions producing a K_2NiF_4 superstructure with alternating sections of oxide and fluoride ions separating infinite InO_2 layers.

The structures of complex transition metal oxyhalides, particularly those with layer structures, have recently come under considerable scrutiny due to the potential of developing new high temperature superconducting cuprates. Sowa *et al.* have prepared materials such as $Ca_3Cu_2O_4Cl_2$ with an anion-deficient Ruddlesden–Popper $Sr_3Ti_2O_7$-type structure with CuO_2 layers and apical Cu–Cl bonds.[1] A similar structure exists for $Ba_3In_2O_5Cl_2$ where the chloride ions again order onto the apical sites around the small cation.[2] More significantly, Edwards *et al.* have reported the synthesis of superconducting $Sr_2CuO_2F_{2+\delta}$;[3] structural studies of these materials indicate that the fluoride ions occupy preferentially the apical sites within the K_2NiF_4 structure adopted, Fig. 1. However, distinguishing oxide and fluoride ions using the normal structural methods, X-ray and neutron diffraction, is impossible due to practically identical scattering powers for these two atoms. Assignments of oxide and fluoride ions to various sites within a mixed oxyfluoride, therefore, relies upon the other experimental methods, *e.g.* ^{19}F MAS–NMR or interpretation of the anion coordination geometry; fluoride ions, having only a single negative charge, normally interact much more weakly than oxide with the cations in the structure. We have recently prepared a new oxyfluoride, Ba_2InO_3F, in which fluoride ion ordering produces a novel superstructure of K_2NiF_4. We report here the synthesis of this compound, its structure (obtained by the refinement of powder X-ray diffraction data) and the significance of this work in designing and understanding the structure of oxyfluoride cuprate superconductors.

Ba_2InO_3F was prepared by the reaction of a well ground mixture of $BaCO_3$, In_2O_3 and BaF_2 in the correct stoichiometric proportions at 1050 °C. Powder X-ray diffraction data collected from the pale grey–green product showed a pattern in which all the peaks could be indexed on a tetragonal unit cell of dimensions a = 4.164 Å and c = 13.950 Å, reasonable for a compound crystallising with a K_2NiF_4 type structure. However, a number of reflections were found which are not permitted in the *I4/mmm* space group, for example the [104] reflection was moderately strong (Fig. 2). Careful inspection of the powder diffraction pattern showed a number of lines requiring a primitive unit cell; full indexing of the data showed the systematic absences, [$hk0$], $h + k = 2n$ and [$h00$], $h = 2n$, consistent with the space group *P4/nmm*, in which the body centring condition is replaced with an n glide plane. This space group is adopted by the so called T* phases with the stoichiometry A_2BX_4 found for rare-earth cuprates in which sections of the K_2NiF_4 structure are interleaved with those with the Nd_2CuO_4 structure.[4] In Nd_2CuO_4 the oxide ions in the NdO layers occupy sites non-apical to Cu, producing a fluorite type arrangement, *i.e.* differences in the positions/type of interlayer or apical anions produce the new lower symmetry.

Data for structure refinement were collected over a 20 h period in the 2θ range 20–120° with a step size of 0.02°. The refinement was undertaken using Rietveld profile analysis employing the GSAS program suite.[5] The starting model was taken from the coordinate description of $Nd_{1.32}Sr_{0.41}Ce_{0.27}CuO_{4-y}$,[4] in the space group *P4/nmm* but with barium replacing neodymium–strontium, indium substituting for copper and the anions, labelled X and all given the oxygen scattering factor curves, on the same sites, 4f, 2c and 2a. This produces layers of vertex sharing MX_5 square-based pyramids with alternating orientations. Refinement of the heavy atom positions gave a moderately good fit to the data, producing reasonable intensity in the primitive peaks. However, introduction of the refinement of the anion positions and temperature factors showed that the atom (X3) assigned to 2a (0.75, 0.75, 0) was unstable, demonstrating that this site was unoccupied. This anion was, therefore, returned to the K_2NiF_4-type apical site near (0.75, 0.75, 0.1). Refinement proceeded smoothly in this description giving a final χ^2 of 1.45. Final atomic positions are given in Table 1; important derived bond lengths have been deposited. The final profile fit is shown in Fig. 2. Fig. 1(*b*) shows the unit cell content.

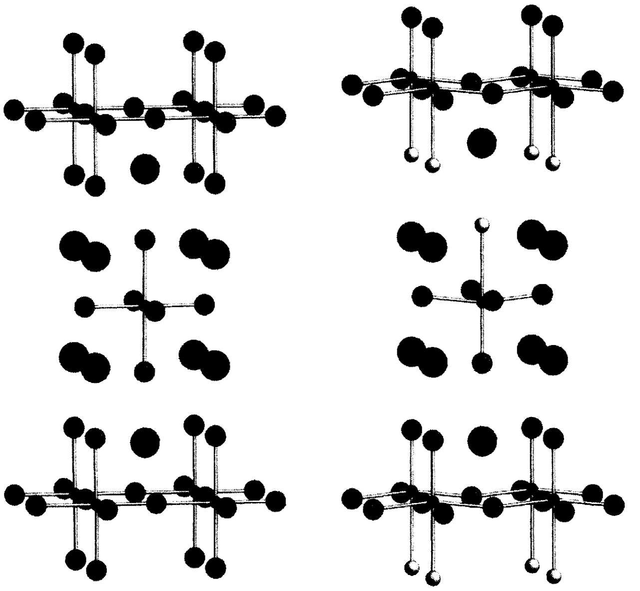

Fig. 1 The structures of K_2NiF_4 and Ba_2InO_3F. Ba/K large dark spheres, In/Ni small dark spheres, anions medium sized spheres. In the Ba_2InO_3F structure (right), the fluoride (light) and oxide (dark) ion sites are distinguished by shading.

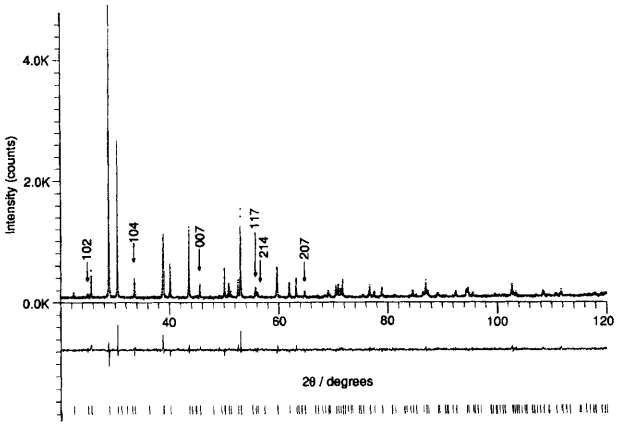

Fig. 2 Powder X-ray diffraction data obtained from Ba_2InO_3F. The strongest reflections from the primitive lattice are marked. Data points are marked as crosses, profile fit as the upper continuous line and difference as the lower continuous line. Reflection positions are shown as tick marks.

Table 1 Final crystallographic data for Ba_2InO_3F with e.s.d.'s given in parentheses

Atom	Site	x	y	z	$B_{iso}/Å^2$
X(1)/O	4f	$\frac{3}{4}$	$\frac{1}{4}$	°.2521(19)	3.9(4)
X(2)/F	2c	$\frac{3}{4}$	$\frac{3}{4}$	°.4205(25)	3.9(4)
X(3)/O	2c	$\frac{3}{4}$	$\frac{3}{4}$	°.0887(24)	3.9(4)
Ba(1)	2c	$\frac{1}{4}$	$\frac{1}{4}$	°.3817(3)	1.46(23)
Ba(2)	2c	$\frac{1}{4}$	$\frac{1}{4}$	°.1026(3)	2.13(27)
In	2c	$\frac{3}{4}$	$\frac{3}{4}$	°.2348(4)	1.39(20)

a = 4.16328(3), c = 13.9494(2) Å; space group *P*4/*nmm*. χ^2 = 1.45 R_{wp} = 0.112

Table 2 Bond valence sums for individual cation–anion interactions

		X(2)		X(3)		Cation valence	
	O(1)	F	O	O	F	X(2) = F X(3) = O	X(2) = O X(3) = F
In	2.37	0.12		0.69		3.19	
			0.16		0.52		3.04
Ba(1)	1.11	0.66		—		1.78	
			0.87		—		1.98
Ba(2)	0.67	—		1.02		1.69	
			—		0.78		1.45
Anion valence	2.08[a]	0.78	1.03	1.71	1.30		

[a] O(1) bond valence is half of column sum

Ordering of the oxide and fluoride ions in Ba_2InO_3F, which results in the reduction of symmetry from *I*4/*mmm* to *P*4/*nmm*, is a result of the different preferred interaction strengths between the monovalent and divalent anions and the cations in the K_2NiF_4 structure. Literature data for materials containing individual Ba···O and Ba···F interactions show that average Ba···F distances are less than average Ba···O distances, *i.e.* the ionic radius of F^- is smaller than O^{2-}.[6] However, the coordination numbers of fluoride ions are often much lower than those of oxide and assignment of fluoride and oxide to the X2 and X3 sites is best achieved by considering the full coordination geometries. The X2 site has interactions at 2.993 Å (x4 Ba1), 2.76 Å (x1 Ba1) and 2.59 Å (x1 In), whilst for X3 the corresponding distances are 2.950 Å (x4 Ba2), 2.649 Å (x1 Ba2) and 2.096 Å (x1 In). The X2 ion, therefore, interacts much more weakly with the cations and can be assigned as fluoride. This can be demonstrated clearly by considering the bond valence sums,[6] Table 2. With X2 = F and X3 = O, values of 0.78 and 1.71 are obtained for these sites, whilst X2 = O and X3 = F gives 1.02 and 1.30, respectively; the former is obviously much closer to the expected values of 1 and 2 for F^- and O^{2-}, respectively, and also avoids appreciable underbonding of Ba(2). The X2 site can, therefore, be confidently assigned to fluoride and X3 to oxide.

The coordination geometry around the indium is clearly 5(O) + 1(F); this near fivefold coordination is a geometry frequently adopted by indium, for example, $Ba_3In_2O_6$.[7] It is probably worth noting that the coordination distances around indium in $LaBaInO_4$,[8] which adopts the perfect K_2NiF_4 structure, are 4 × 2.09 Å (equatorial) and 2 × 2.23 Å (axial) showing that regular sixfold coordination around indium is not found even in a material adopting the normal K_2NiF_4 structure.

We have also investigated the structures of $Ba_3In_2O_5F_2$ and Sr_2FeO_3F. The former adopts an $Sr_3Ti_2O_7$-type phase with apical fluoride ions. The latter, in accordance with a comment made by Menil *et al.*,[9] does not have the perfect K_2NiF_4, *I*4/*mmm* structure. Preliminary refinements indicate a structure similar to that of Ba_2InO_3F in space group *P*4/*nmm*. It is therefore clear that oxide and fluoride can order in layer perovskites due to their rather different coordination preferences. This may be significant in the strategic synthesis of new layer cuprates where, for example, the separation of cuprate layers may be controlled. In addition the structure of Ba_2InO_3F shows that oxide and fluoride ions may be readily distinguished by consideration of the full coordination environment, rather than the individual bond lengths.

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