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Synthesis and structure of the new oxide fluoride $Sr_2TiO_3F_2$ from the low temperature fluorination of Sr_2TiO_4: an example of a staged fluorine substitution/insertion reaction

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In this paper we report the synthesis of the new oxide fluoride, $Sr_2TiO_3F_2$, from the low temperature reaction of Sr_2TiO_4 with fluorinating agents (NH_4F, transition metal difluorides). The reaction involves involves substitution/insertion with 2 F replacing 1 O, with the extra anions entering interstitial sites within the structure. The fluorination results in a significant reduction in the unit cell along *a*, *b* ($\approx$2%) along with a large expansion along *c* ($\approx$23%): $Sr_2TiO_3F_2$, $a = b = 3.8017(1)$, $c = 15.536(1)$ Å. Structural refinement using powder neutron diffraction data indicates that the reaction is a staged process leading to alternate layers of full and empty interstitial sites (space group *P*4/*nmm*). The occupancy of the interstitial sites also results in a substantial distortion in the Ti coordination away from the octahedral coordination of the Sr_2TiO_4 starting material, with one very long bond such that the coordination approximates to square pyramidal.

Introduction

This work reports the synthesis and structure of a new inorganic oxide fluoride, $Sr_2TiO_3F_2$. Such materials have been attracting significant interest in recent years. High temperature synthesis and structural studies of a range of materials, *e.g.* $BaScO_2F$, have been reported by Needs *et al.*[1–4] The number of oxide fluorides that can be prepared by the high temperature route is however limited by the high stability of the simple fluoride starting materials relative to the intended products. Other routes have therefore been attempted to overcome this problem, *i.e.* high pressure synthesis and the low temperature fluorination of precursor oxides. High pressure synthesis has been successful in the preparation of new superconducting copper oxide fluorides,[5,6] but suffers from the fact that the technique requires expensive equipment and the sample sizes are small. The use of low temperature synthesis routes appears therefore to be more favourable, and such routes have also been successfully applied to cuprate systems. Studies by Al Mamouri *et al.* showed that the low temperature (220 °C) reaction of Sr_2CuO_3 with F_2 gas yielded the superconducting oxide fluoride $Sr_2CuO_2F_{2+\delta}$.[7] Further work showed that other fluorinating agents, NH_4F, MF_2 (M = Cu, Ni, Zn), XeF_2 could also be employed to prepare this oxide fluoride.[8–10] These low temperature routes have been demonstrated to be suitable for the fluorination of a wide range of cuprate materials,[11–16] and the successful synthesis of new manganese, iron and zirconium based oxide fluorides have been recently reported.[17–20]

The K_2NiF_4 structure has attracted particular interest in respect of low temperature fluorination, due to its ability to incorporate extra interstitial anions. In previous studies, we showed that it was possible to prepare the new oxide fluoride, $Ba_2ZrO_3F_2{\cdot}xH_2O$ ($x \approx 0.5$) from the low temperature fluorination of the K_2NiF_4 type oxide Ba_2ZrO_4.[20] The reaction represents a substitution of 2 fluorine atoms for 1 oxygen atom, leading to an increase in the anion content, the excess anions occupying the interstitial sites within the structure. Due to the water sensitivity of these Ba based systems, we also found the presence of H_2O in the interstitial sites.

In this paper we report the fluorination of Sr_2TiO_4 to give $Sr_2TiO_3F_2$, showing the widespread applicability of low temperature methods for the synthesis of inorganic oxide fluorides. Of particular relevance to this work, is the recent report on the fluorination of $LaSrMnO_4$ to give $LaSrMnO_4F$ by Aikens *et al.*[19] In this paper the authors reported that the fluorination is a staged insertion process resulting in alternating full and empty interstitial sites. In this paper we show a similar staged fluorination process (in this case substitution/insertion) for the fluorination of Sr_2TiO_4.

Experimental

The precursor oxide, Sr_2TiO_4 was prepared from high purity $SrCO_3$ and TiO_2. The starting materials were intimately mixed in the correct stoichiometry and heated to 1100 °C for 14 hours in air, before regrinding and reheating at the same temperature for a further 14 hours. Two fluorination routes can be employed for the synthesis of the fluorinated phase, reaction with NH_4F (method 1), and reaction with MF_2 (M = Cu, Zn) (method 2). For each method the fluorination was performed on approximately 1g samples of precursor.

In the case of method 1, Sr_2TiO_4 was ground with 2.4 mol equivalents of NH_4F (representing a 20% excess over the stoichiometric reaction). The resulting mixture was then held at 90 °C for 2 hours, before raising the temperature to 250 °C for 15 hours. The mixture was then reground and reheated at the same temperature for a further 15 hours.

Method 2 involved the addition of anhydrous CuF_2 or ZnF_2 (1.05 mol; 5% excess) to the Sr_2TiO_4; the mixture was ground, then held at 90 °C for 2 hours before raising the temperature to 250 °C for 15 hours. As for method 1, the mixture was reground and reheated at 250 °C for a further 15 hours.

Both methods are not quite ideal. The first method suffers from the fact that partial decomposition occurs during the

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reaction to give small but significant SrF_2 and $SrTiO_3$ impurities, presumably as a result of the water liberated from the reaction.

There is no such decomposition for method 2, but in this case there is transition metal oxide impurity (ZnO, CuO) from the fluorinating agent.

Attempts were also made to prepare the fluorinated phase by reaction with the CuF_2/ZnF_2 kept separate, so as to avoid CuO/ZnO impurity, as reported previously for some cuprate systems.[11,13] This method, although successful, proved also to be not ideal. In particular, it proved difficult to prevent overfluorination of the sample at the surface, leading to SrF_2 impurity as well as a higher fluorine content phase, as yet not fully characterised.

Therefore, for the neutron diffraction sample, the second method was used, involving the mixing of ZnF_2 with the sample. The ZnO impurity was included in the refinement as a second phase.

Characterisation

X-Ray diffraction

The products were characterised by powder X-ray diffraction (Cu K_α radiation Seifert XRD 3003TT diffractometer) with both methods giving similar results. After fluorination a large shift in the X-ray diffraction peaks was observed (Fig. 1). Refinement of the cell parameters indicated that the *c* axis undergoes a very large expansion ($\approx$23%), while a contraction ($\approx$2%) along *a*, *b* was observed.

$$Sr_2TiO_4,\ a = b = 3.894(1),\ c = 12.625(2)\ \text{Å}$$

$$Sr_2TiO_3F_2,\ a = b = 3.8017(1),\ c = 15.536(1)\ \text{Å}$$

Since there is no possibility, in the sample studied, for there to be an increase in metal oxidation state, it is reasonable to assume that the fluorination is a substitution process, with 2 F atoms replacing one O atom to give a general formula $Sr_2TiO_3F_2$. The actual fluorine content was determined by fluorine analysis (ion selective electrode), as outlined below.

Fluorine analysis

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.* 0.025 g of sample was dissolved in 5 cm^3 of 1 M HCl, to which was added 95 cm^3 of distilled water followed by 50 cm^3 of a pH *ca.* 5.3 total ionic strength 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, CuF_2, ZnF_2) was present in any of the samples analysed. Potential errors in the analysis are due to the presence of SrF_2 impurities. There was negligible amount of this impurity present for the samples prepared using CuF_2/ZnF_2 and so these samples were the ones analysed by fluorine analysis (the presence of CuO/ZnO in the sample was taken into account in the subsequent calculation of the fluorine content). 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.

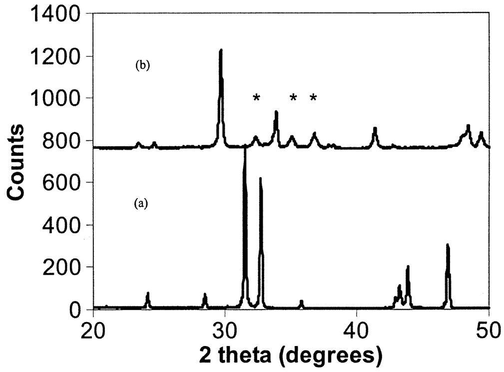

Fig. 1 X-Ray diffraction pattern for (a) Sr_2TiO_4 and (b) $Sr_2TiO_3F_2$ prepared *via* reaction with ZnF_2 (ZnO peaks are marked with an asterisk).

For the composition $Sr_2TiO_3F_2$ a fluorine content of 12.3% should be observed. The actual average value obtained from analysis of 3 samples was 12.1%

Other support for this composition is the fact that heating this sample to high temperature (>500 °C) results in decomposition to give SrF_2 and $SrTiO_3$ in complete agreement with the composition $Sr_2TiO_3F_2$

$$i.e.\ Sr_2TiO_3F_2 \rightarrow SrF_2 + SrTiO_3$$

Unlike for the fluorination of Ba_2ZrO_4, this Sr based system does not suffer from additional water incorporation as shown by TGA studies, which showed no evidence of any weight loss on heating to elevated temperature (500 °C).

Neutron diffraction

Neutron diffraction data were collected on a 1 g sample fluorinated with ZnF_2 on diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. Structure refinement was employed using the GSAS suite of programs.[21] The ZnO from the fluorinating agent was entered into the refinement as a secondary phase.

Structure refinement

Attempts to refine the structure using the model (space group *I*4/*mmm*) obtained previously for $Ba_2ZrO_3F_2{\cdot}xH_2O$ resulted in a poor fit to the data. In contrast, use of the model (space group *P*4/*nmm*) reported by Aikens *et al.* for $LaSrMnO_4F$[19] gave a good fit to the data indicating that there was an ordering of the anions in the interstitial sites. As observed for $LaSrMnO_4F$, it was found that there were alternate layers of full and empty interstitial sites consistent with the composition $Sr_2TiO_3F_2$ for which the total anion content is 5. Thus it appears as if the fluorination reaction is a staged process as observed for $LaSrMnO_4F$.[19] There were, however, still some slight discrepancies in the model; namely the O3/F3 (apical) and O4/F4 (interstitial) occupancies refined to values slightly below 1 and there were high anisotropic displacement parameters (particularly U_{33}) for these atoms and also for Sr1 and Ti. Attempts to account for these discrepancies, by trying to place some oxygen in the empty interstitial site were unsuccessful, with the occupancy of this site refining to zero. Other modifications to the refinements were also attempted, *i.e.* displacement of atoms off site, split sites *etc.*, but these attempts generally resulted in either no improvement to the fit or unstable refinements. We can propose that the reason for these discrepancies may be a small degree of disorder in the structure, such that we do not have completely ordered alternating full and empty interstitial sites. Such a disorder is extremely difficult to fit, and cannot be simply modelled by the incorporation of anions into the empty interstitial site, since the presence of anions in this site would result in significant localised atom shifts. The fact that it is U_{33} that is high supports

Table 1 Refined structural parameters for $Sr_2TiO_3F_2$[a]

Atom	Site	x	y	z	sof	Anisotropic displacement parameters/Å^2		
						$100U_{11}$	$100U_{22}$	$100U_{33}$
Sr1	2c	0.75	0.75	0.0967(3)	1.0	1.1(1)	1.1(1)	3.1(2)
Sr2	2c	0.75	0.75	0.3976(2)	1.0	0.97(7)	0.97(7)	0.6(1)
Ti	2c	0.25	0.25	0.2592(5)	1.0	0.44(8)	0.44(8)	1.8(2)
O1	4f	0.25	0.75	0.2934(2)	1.0	0.12(5)	1.08(8)	1.6(1)
O2/F2	2c	0.25	0.25	0.1504(3)	1.0	1.35(9)	1.35(9)	0.7(1)
O3/F3	2c	0.25	0.25	0.4413(4)	0.89(2)	1.9(2)	1.9(2)	6.0(5)
O4/F4	2a	0.25	0.75	0.0	0.91(2)	1.5(1)	1.5(1)	3.3(3)

[a] Tetragonal, *P*4/*nmm*; $a = b = 3.8017(1)$, $c = 15.5358(1)$ Å, $R_p = 4.11\%$, $R_{wp} = 2.32\%$.

this view of a small degree of disorder as the atom shifts would be likely to be along the z direction.

The final refined parameters are given in Table 1, along with selected bond distances in Table 2 and the neutron diffraction profiles in Fig. 2. It is impossible to distinguish oxygen and fluorine by either neutron diffraction or X-ray diffraction, and so we have assumed that the fluorine is preferentially located in the apical and interstitial sites, in agreement with modelling studies of related systems.[22,23] Therefore these sites are labelled O/F, with the equatorial site labelled O.

Discussion

We have shown that the low temperature fluorination of the K_2NiF_4 phase Sr_2TiO_4 is possible to give the new oxide fluoride $Sr_2TiO_3F_2$, the structure of which is given in Fig. 3. As observed by Aikens *et al.* for the fluorination of $LaSrMnO_4$ to give $LaSrMnO_4F$,[19] the fluorination process appears to be staged resulting in the ordered occupancy of the interstitial sites (alternating full and empty sites). However, whereas the fluorination of $LaSrMnO_4$ is a simple insertion process, the fluorination of Sr_2TiO_4 is a more complicated substitution/insertion process in which 2 fluorine atoms replace one oxygen atom. The more complicated nature of the process in this case may account for the discrepancies in the refinement (high values for U_{33} for some atoms, occupancy < 1 for O3/F3 and O4/F4), which have been attributed to a small degree of disorder.

Table 2 Selected bond distances for $Sr_2TiO_3F_2$

Bond	Bond distance/Å
Ti–O1	1.973(2) [×4]
Ti–O2/F2	1.691(7)
Ti–O3/F3	2.829(7)
Sr1–O2/F2	2.815(2) [×4]
Sr1–O4/F4	2.423(3) [×4]
Sr2–O1	2.497(2) [×4]
Sr2–O3/F3	2.773(2) [×4]
Sr2–O3/F3	2.503(5)

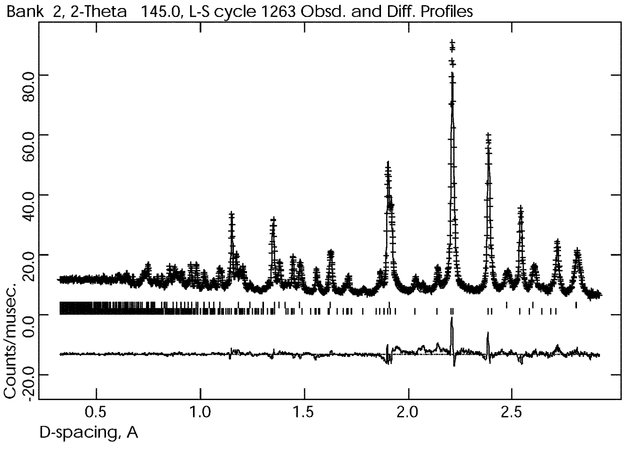

Fig. 2 Observed, calculated and difference neutron diffraction profiles for $Sr_2TiO_3F_2$.

It might be expected that the fluorination proceeds such that an apical oxygen is replaced by an apical fluorine, with the additional fluorine atom to maintain charge neutrality entering the adjacent interstitial site. If this was the case then the O2/F2 and O4/F4 sites would be fully occupied by fluorine, with the

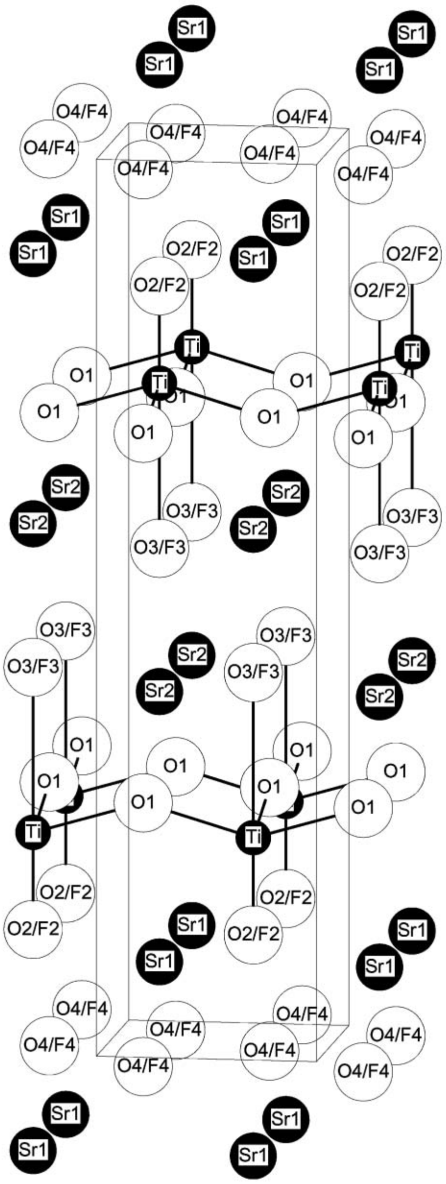

Fig. 3 The structure of $Sr_2TiO_3F_2$ showing alternating full and empty interstitial sites (small black spheres = Ti, large black spheres = Sr, large white spheres = O/F).

Table 3 Results of bond strength calculations for $Sr_2TiO_3F_2$ showing the apparent favourability of the anion distribution, O1, O2, F3, F4

O/F arrangement	Bond strength sum for Ti	Bond strength sum for Sr1	Bond strength sum for Sr2
O1, O2, F3, F4	4.07	1.95	2.23
O1, F2, F3, O4	3.87	2.22	2.23
O1, F2, O3, F4	3.87	1.81	2.45

O3/F3 fully occupied by oxygen. However, bond strength calculations[24,25] suggest an alternative situation with the O2/F2 site occupied by oxygen and the O3/F3 (the apical site furthest from the interstitial anions), and O4/F4 sites (interstitial site) occupied by fluorine (Table 3). This is somewhat surprising, suggesting large restructuring on fluorination. Detailed modelling work is, however, required to confirm the results obtained from the bond strength calculations.

In the undoped phase, Sr_2TiO_4, the coordination of the Ti is octahedral. On fluorination there are major changes to the apical anion positions around the Ti resulting in a significant change in the Ti coordination. The apical anion site (O2/F2) closest to the occupied interstitial anions site is repelled by these latter anions resulting in a very short Ti–O/F bond distance (1.691 Å). In contrast the other apical anion site (O3/F3) is brought closer to the Sr sites resulting in a very long Ti–O/F bond (2.829 Å). Because of the length of this latter bond, the Ti coordination approximates to square pyramidal, which represents a rather unusual coordination for Ti.

There are also two distinct Sr sites, one 8-coordinate (around the occupied interstitial site) and one 9-coordinate (around the empty interstitial site). In comparison, for the undoped phase there is only one type of Sr and the coordination number is 9, comparable to the coordination of the Sr next to the empty interstitial site in the fluorinated phase.

In summary we have shown that the low temperature fluorination of Sr_2TiO_4 is possible to give the new oxide fluoride $Sr_2TiO_3F_2$. The fluorination process is staged giving alternate occupied and empty interstitial sites, although slight discrepancies in the refinements suggests that there may be some disorder within the system. Further studies have shown evidence for a higher fluorine content phase (fluorination with 1.5 mol of ZnF_2), and work is ongoing trying to determine the structure of this system. The results demonstrate the versatility and widespread applicability of low temperature fluorination methods for the synthesis of new inorganic oxide fluorides. The work is also of relevance to those working in the field of oxygen excess K_2NiF_4 systems. In particular oxygen excess K_2NiF_4 systems have been recently attracting attention for possible use as oxygen separation membranes, due to the observed high oxide ion conductivity through the interstitial sites.[26] Studies on these fluorine containing systems can aid our understanding of the former, since higher interstitial levels are possible in the case of the oxide fluorides, making the structural characterisation of the nature of these interstitial sites easier. In particular, the fact that staging of the interstitial anion incorporation has been observed in both $Sr_2TiO_3F_2$ and $LaSrMnO_4F$[19] suggests the possibility that this may also take place to some degree in related oxygen excess systems. If this were indeed the case, then it might have a significant influence on the conducting properties of these materials.

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