

Control of F-Doping in Pnictide High-Temperature Superconductors

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The recent discovery of high-temperature superconductors (HTSC) in F-doped iron arsenide $\text{LaFeAsO}_{1-x}\text{F}_x$ (with a critical temperature, T_C , of 26 K) has triggered a huge amount of experimental work in this field.¹ Preparation of new phases with different rare earths (RE) has led to the discovery of the highest T_C (greater than 50 K) in the $\text{SmFeAsO}_{1-x}\text{F}_x$ member of this family of HTSC.² The number of experimental reports on pnictide oxides published up to now, and those appearing everyday in the current literature, show quite a significant spread in the reported results, even for some basic information such as the T_C vs F trend. Most of this disagreement may be related to the difficulties in the synthesis of F-doped pnictide oxides where a possible loss of F has been suggested. Also, a secondary phase of RE oxy-fluoride is often present in addition to the main phase and its amount increases with F-doping.³ Quite surprisingly, up to now all the papers related to these HTSCs deal with "nominal" values for the stoichiometries of both cations and F. In addition, there is a total lack in the current literature of proper determination of the amount of any secondary phase and of the possible related stoichiometry fluctuations which derives from the presence of a spurious phase. As a consequence, in this paper we present the results of the preparation and characterization of some samples of the $\text{SmFeAsO}_{1-x}\text{F}_x$ system where we provide information about the "real" F-content as determined from electron microprobe analysis (EMPA). In addition, we present some suggestions about the different sources of chemical stoichiometry variation that can be found in the pnictide oxides.

The synthesis of $\text{SmFeAsO}_{1-x}\text{F}_x$ samples has been carried out employing one of the most "popular" synthetic routes, i.e., starting from proper amounts of SmAs, Fe, Fe_2O_3 , and FeF_2 . Each sample batch was ~ 1 g. SmAs was prepared starting with Sm rods (NewMetals, >99.9%) from which Sm powder was obtained working in a glovebox under Ar flux. Pellets of SmAs have been prepared and fired at 500 °C for 2 h and then to 900 °C for 18 h in quartz tubes sealed under vacuum (ca. 10^{-5} bar). The reagents were mixed, pressed into the form of pellets, wrapped in tantalum foils, and left to react at 1160 °C for 48 h in vacuum (ca. 10^{-5} bar) sealed quartz tubes. There are some remarks to be made related to the synthesis procedures which need to be seriously taken into account when preparing a series of these compounds.

One fundamental issue not yet properly considered in the current literature is the control of the starting RE arsenides. These are usually prepared at relatively high temperatures (>500 °C). However, careful control of the lattice parameters and even cation stoichiometry of the starting arsenides is required. The reason is that it is well-known that rare earth arsenides are nonstoichiometric compounds. Both anion and cation lattice sites can be partially occupied. Taylor et al.⁴ showed that a range of arsenic solubility is observed in all cases, and for example, in samarium arsenide at 700 °C, it extends from $\text{Sm}_{0.98}\text{As}_{0.81}$ to $\text{Sm}_{0.98}\text{As}_{0.98}$. Over part of the solubility range at the arsenic-rich end, variations in arsenic content can occur with no detectable change in the lattice

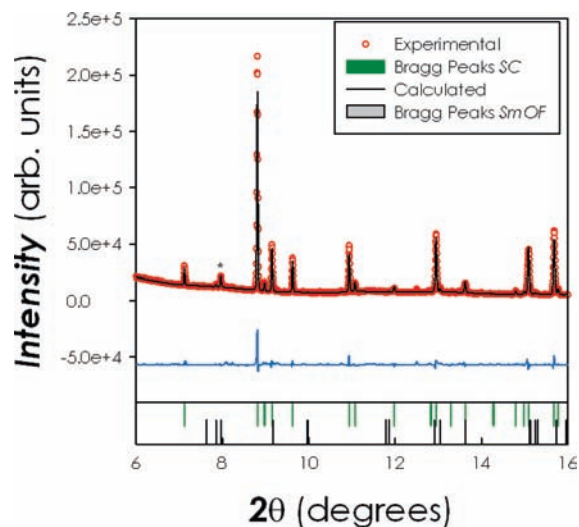


Figure 1. Rietveld refined pattern of $\text{SmFeAsO}_{0.90}\text{F}_{0.10}$ at room temperature. Red empty circles represent the experimental pattern, the black line the calculated one, while vertical green and black bars at the bottom of the pattern are the Bragg peak positions for the superconductor phase and SmOF phase, respectively. The blue line is the difference between calculated and experimental patterns.

parameters. A further decrease in arsenic content can occur at 700 °C in all but Y, Ho, Er, and Yb arsenides and is accompanied by a reduction in the lattice parameters. A range of metal solubility exists at high temperatures for all phases and results in a considerable reduction of the lattice parameters at the lower metal concentrations. This issue is of central importance. Starting with nonstoichiometric reagents clearly lead to poor control in the final product (i.e., in the superconductor) stoichiometry. This aspect may be a cause for the observed discrepancy in the reported results for these HTSCs and clearly requires strict control to prepare "correct" and comparable samples. In addition, the amount of secondary phases can be also related to stoichiometry fluctuations in the starting materials.

The samples of the $\text{SmFeAsO}_{1-x}\text{F}_x$ composition considered in this work have nominal x -values of 0.10, 0.15, 0.20, and 0.23. X-ray diffraction (XRD) data have been acquired on the samples to check the phase purity, amount of secondary phases (through Rietveld refinement), and structural parameters. Figure 1 shows a synchrotron XRD pattern ($\lambda = 0.443\ 910$ Å) for the nominal $x = 0.10$ sample.

XRD data of high quality are needed to provide a reliable quantitative estimation of the impurity phase. The Rietveld refinement with a two-phase model ($\text{SmFeAsO}_{0.90}\text{F}_{0.10} + \text{SmOF}$) allowed us to estimate that the Sm oxy-fluoride amount in the $x = 0.10$ sample is $\sim 2.70(6)\%$. An analogous estimation was made for the other samples showing a progressive increase of the SmOF amount as the F-content increases. This kind of trend can be observed in other papers present in the current literature.^{2,5} However, it seems

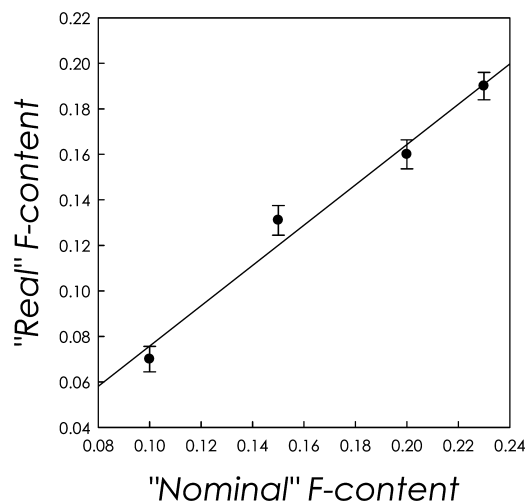


Figure 2. Correlation between the nominal F-contents and the measured F-contents.

more than reasonable to start questioning the use of nominal F-contents when the amount of this phase starts becoming a significant part of the whole sample and even at low percentages the influence on the real F-content in the SC phase cannot be ignored. In addition, the possible loss of F due to its volatile nature cannot be ruled out. Unfortunately, most of the papers published on pnictide oxides do not even report the corresponding X-ray diffraction patterns, and nothing is said about the nature and amount of impurity phases.

On the samples prepared we have checked the F-content by means of EMPA. Measurements have been done on selected grains of pure pnictide oxide phase, thus avoiding any interference coming from the samarium oxy-fluoride. To obtain the best accuracy in the EMPA measurements we took great care in sample preparation which included the use of sintered pellets that have been polished to a 0.25 μm final polish to achieve planar samples on the micrometer scale. The other important issue was the selection of standards for calibration. We selectively chose materials which contained a similar amount of the measured elements as the amount found in the pnictide phase. We also selected standards that enabled the cations and arsenic to be in the same oxidation state as that in the measured samples. In addition, we used a low current density and checked that no F-loss was present during the EMPA measurements.

Together with the F-content we have measured the cation stoichiometries and As concentration. These have been found to be in very good agreement with the nominal stoichiometries within measurement error. Let us note that all the samples have been prepared using samarium arsenides with the same lattice parameters which in turn were in agreement with those reported in the structure database.

Figure 2 shows the nominal F-contents vs the measured F-contents which are also reported in Table 1 together with the T_C of the superconducting samples.

As can be appreciated there is a linear correlation between the nominal and calculated F-contents. The measured ones are always lower than the expected ones.

Table 1. Nominal F-Contents, Measured F-Contents, and T_C Values for the Superconducting Samples

nominal F	measured F	T_C
0.10	0.071(6)	—
0.15	0.131(6)	44.2
0.20	0.160(5)	47
0.23	0.192(5)	52.1

This result has some important implications and is of general interest and importance. It is clear that by using a routine method for the preparation of F-doped iron based HTSCs, the final stoichiometries are quite far from the nominal ones. The precise definition, for example, of the lower limit of F-content for the insurgence of superconductivity and of the T_C vs F trends require strict control of F-stoichiometry. Since F is volatile any change in the synthesis conditions or even type of starting materials would require further control of sample stoichiometries. In the present case, for example, the sample with a nominal $x = 0.10$ and a real F-content of 0.071(5) does not present bulk superconductivity while the other samples show net superconducting transitions.

It is clear that the role played by the F-content in pnictide HTSCs has several similarities with the role played by the oxygen content in cuprate superconductors. In a similar way, after the discovery of HTSC in cuprates some time was needed before the accurate and precise determination of oxygen content was recognized as the basic issue to provide reliable and comparable results in those materials. This paper just reported an example of F-content determination, but any other feasible analytical method, with even a higher accuracy, may be of help in this respect (for example, X-ray fluorescence, F^- determination by electroanalytical methods, etc.).

The main aim of this work was to provide direct evidence that F-doped pnictide oxides prepared by means of a commonly used method present a large fluorine under-stoichiometry with respect to the nominal concentrations. This implies that reliable and comparable experimental data on these materials will be only obtained by controlling this parameter and also the correct stoichiometry of starting materials (i.e., RE arsenides).

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Supporting Information Available: Rietveld refined structural data for the $\text{SmFeAsO}_{1-x}\text{F}_x$ samples and magnetic susceptibility curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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