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Iodine as an Oxidant in the Topotactic Deintercalation of Interstitial Iron in $Fe_{1+x}Te$

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Abstract: The layered telluride, $Fe_{1+x}Te$, is a parent compound of the isostructural and superconducting phases, Fe_{1+x}(Te, Se, S). Here we show that, through a simple reaction of I_2 vapor with both powder and single crystal samples, the interstitial iron can be removed from the FeTe framework topotactically. Neutron powder diffraction and X-ray single crystal diffraction confirm that the iron being extracted is the partially occupied site that lies between the 2-D blocks of edge-sharing $FeTe_4$ tetrahedra. The deintercalation process has consequences for both magnetic and crystallographic phase transitions in the compound at low temperatures. This technique could be of use for the tuning of stoichiometry of the superconducting phases and therefore enable more careful studies on how chemical composition affects magnetic and superconducting properties.

The iron-based superconductors offer new opportunities to explore the relationships between chemical composition, magnetism, and superconductivity. Since the discovery in $LaO_{1-x}F_xFeAs$ at $T_c \approx 26$ K,[1] superconductivity has been revealed in several structural families that possess two-dimensional layers of $(FeAs)^-$, which are separated by cationic layers, or are simple van der Waals solids of FeX (X = chalcogenides). Their phase diagrams universally exhibit a close proximity between superconductivity and an ordered magnetic regime,[2] which is controlled by composition or external applied pressure. The iron chalcogenides have been shown to be particularly sensitive to stoichiometry. For example, β-$Fe_{1.01}Se$ is superconducting at $T_c \approx 8.5$ K, whereas β-$Fe_{1.03}Se$ is neither magnetic nor superconducting, demonstrating that the excess interstitial iron is detrimental to the superconducting properties.[3,4] $Fe_{1+x}Te$, which possesses the same anti-PbO structure, has only been reported for $0.067 < x < 0.17$, with additional interstitial Fe located within the edge-shared $FeTe_4$ tetrahedral units (see Figure 1).[5,6] The amount of interstitial Fe controls the material's structure and magnetism; at low temperature for $x < 0.11$ the system is orthorhombic and has a commensurate magnetic structure, whereas the material at higher values of interstitial iron is monoclinic and has an incommensurate magnetic structure. $Fe_{1+x}Te$ becomes superconducting upon substitution of selenium or sulfur for tellurium,[6,7] but this substitution also affects the iron stoichiometry, and how these two factors contribute to the changes in electronic structure are unknown. To better illuminate these issues, the ability to exactly control the composition is essential. Here we report a simple chemical procedure to deintercalate the interstitial iron from both single crystal and powder samples of $Fe_{1+x}Te$ through a low temperature reaction with iodine that leaves the central FeTe framework intact, thus allowing access to new $Fe_{1+x}Te$ compositions.

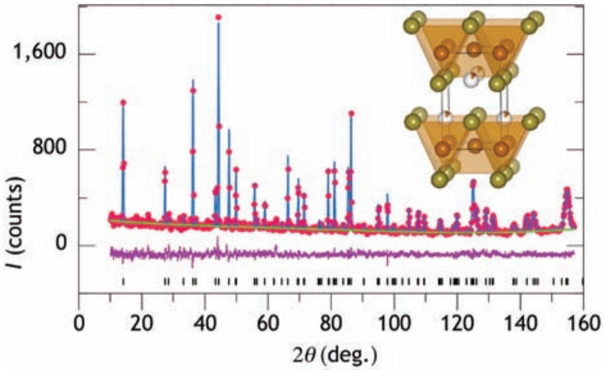

Figure 1. Observed (red), calculated (blue), and difference (purple) intensity of the neutron powder diffraction patterns of $Fe_{1.04}Te$. Inset shows the layered anti-PbO structure of $Fe_{1+x}Te$, with partial occupancy of the interstitial Fe atoms (white). The residual of the fit was $R_{wp} = 6.7\%$ and the $\chi^2 = 1.367$.

Powder samples of nominal composition $Fe_{1.15}Te$ were prepared by heating stoichiometric mixtures of Fe powder and Te powder in evacuated quartz ampules. The samples were first heated to 425 °C at 1 °C/min for 24 h, followed by 48 h at 700 °C and then slow cooling at 2 °C/min down to 25 °C. From the resulting product, compound **1**, approximately 500 mg of sample were mixed with 90−110 mg of I_2 crystals and sealed in a 10 cm^3 quartz ampule. The ampule was then heated at 300 °C for 18 h, leading to compound **2**, after which the samples were allowed to furnace cool to room temperature and examined by powder X-ray diffraction. Compound **3** was made by further reacting **2** under the same conditions, using 500 mg of sample for every 34 mg of I_2. All products were washed with methanol under sonication, centrifuged, and dried at room temperature under vacuum after decanting the solvent. The single-phase materials with the anti-PbO structure of $Fe_{1+x}Te$ were measured on the BT-1 neutron powder diffractometer (NPD) at the National Institute of Standards and Technology Center for Neutron Research. The NPD data were collected at various temperatures between 5 and 300 K, using either a Ge311 monochromator ($\lambda = 2.079$ Å) or Cu311 monochromator ($\lambda = 1.540$ Å). Structural refinements were carried out using the GSAS Rietveld refinement program.[8] The resulting structural parameters are presented in the Supporting Information (SI). Observed and calculated powder patterns for sample **3** at 100 K are shown in Figure 1, with the equivalent patterns for **1** and **2** given in SI. Lattice constants and relevant bond distances and angles are presented in Table 1.

A comparison of the NPD patterns for the I_2-reacted and unreacted samples revealed significant differences in relative

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Table 1. Results from Structure Refinements of Compounds **1** through **3** Using Neutron Powder Diffraction Data Taken at 100 K, for Tetragonal Space Group *P*4/*nmm*[a]

Compound	*a* (Å)	*c* (Å)	Te−Fe1−Te (deg)	Fe1−Fe1 (Å)	Fe1−Fe2 (Å)	Fe1−Te (Å)	Fe2−Te (Å)
1 $Fe_{1.118(5)}Te$	3.81188(2)	6.24684(6)	117.58(2); 94.25(4)	2.69541(1)	2.592(4)	2.601(1)	2.69544(4); 2.721(6)
2 $Fe_{1.051(5)}Te$	3.81374(4)	6.2547(1)	117.25(4); 94.83(7)	2.69672(3)	2.61(2)	2.590(2)	2.6969(4); 2.72(3)
3 $Fe_{1.042(5)}Te$	3.81431(5)	6.2569(1)	117.18(5); 95.0(1)	2.69712(3)	2.64(3)	2.588(2)	2.698(1); 2.68(4)
4 $Fe_{1.119(4)}Te$	3.8197(1)	6.2587(2)	117.552(6); 94.30(1)	2.7009(1)	2.596(4)	2.6051(2)	2.7010(2); 2.728(6)
5 $Fe_{1.095(5)}Te$	3.8139(3)	6.2631(9)	117.501(8); 94.39(2)	2.6968(2)	2.596(6)	2.5993(3)	2.6968(2); 2.736(8)

[a] Single crystal X-ray results for **4** and **5** at 250 K are also presented. Standard uncertainties, which represent $\pm 1\sigma$, are shown in parentheses.

intensities of Bragg reflections as a result of the large coherent Fe neutron scattering length of 9.45 fm, compared to 5.80 fm for Te. These differences afforded an accurate determination of the amount of interstitial iron even at such low occupancies. Rietveld refinement with the data gave **1** to have a composition of $Fe_{1.118(5)}Te$, compared to $Fe_{1.051(5)}Te$ and $Fe_{1.042(5)}Te$ for **2** and **3**, respectively. In all samples, the sites within the $FeTe_4$ tetrahedra refined with full occupancy, suggesting that the I_2 was preferentially removing iron from the interstitial site labeled Fe2 and not the other site labeled Fe1. Since the occupancy of Te also refined to unity within the standard uncertainty, we rule out the possibility of Te being oxidized or the anionic substitution of I^- for Te^{2-} (see SI for structural parameters). Further inspection of the structural parameters revealed that this topotactic deintercalation of the powders is associated with a small expansion of the tetragonal crystal lattice in both the *a* and *c* directions, implying that the interstitial Fe bonding, within and between the layers, has the effect of drawing the lattice together. Furthermore, the reaction with I_2 has the overall effect of oxidizing the iron framework, which would also result in a lattice expansion. These structural changes on Fe2 extraction resulted in the Fe1−Fe2 distances increasing, while the Fe1−Te bond distance actually decreases. Likewise, the variance of the Te−Fe1−Te tetrahedral angles also decreased with Fe2 extraction (variance is an average of the differences of the tetrahedral angles from the ideal 109.5°). Figure 2 shows a comparison of part of the NPD data for unreacted **1** and I_2-reacted **2** at base temperature and 100 K. It demonstrates that, at low temperatures, **1** has an incommensurate magnetic propagation vector and is orthorhombic, whereas **2** has a commensurate propagation vector and is monoclinic. These observations are consistent with the change in stoichiometry.

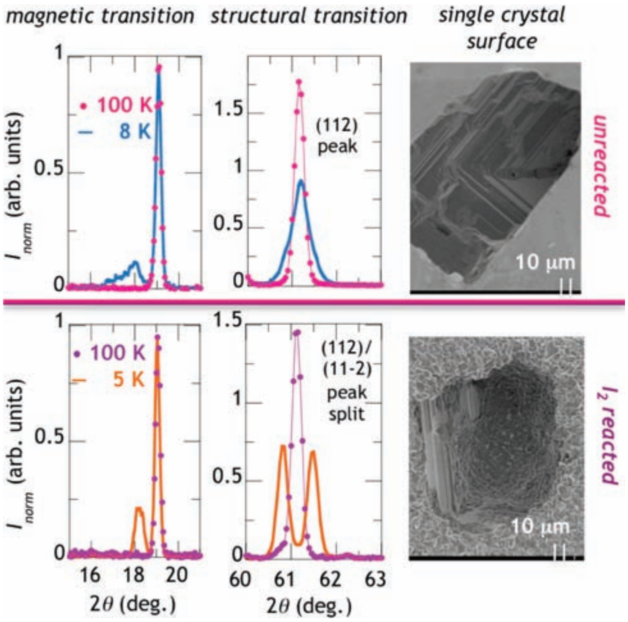

Figure 2. Magnetic and structural transitions for the unreacted $Fe_{1.118(5)}Te$ and I_2-reacted $Fe_{1.051(5)}Te$ compounds. On right, SEM photographs of the surfaces of unreacted single crystal **4** and I_2 reacted single crystal **5**.

To further confirm the deintercalation technique as a bulk effect, single crystals of $Fe_{1.119(4)}Te$ were reacted in a similar manner to the powder samples. The starting single crystals, compound **4**, were prepared by melting of the powder samples at 700 °C for several days followed by slow cooling. The composition was determined by single crystal diffraction, details of which are given in the SI. Compound **5** was prepared by combining 36.7 mg of single crystal **4** with 8.2 mg of I_2 in a sealed evacuated quartz ampule with the same heating procedure used for **2**. Structural parameters for **4** and **5** are shown in Table 1. The effects on the lattice parameters and stoichiometry by the deintercalation are less pronounced in the single crystals than in the powder samples. Figure 2 shows Scanning Electron Microscopy (SEM) photographs that demonstrate how the deintercalation process has affected the morphology of the crystal surfaces; crystal **5** has considerable terracing and aberrations compared to the unreacted and well-defined crystal **4**. The crystallographic information files as well as details of the single crystal XRD measurements and refinements are presented in the SI.

In summary, we have demonstrated that the amount of interstitial iron in the layered anti-PbO structure of $Fe_{1+x}Te$ can be diminished by reaction with iodine. Previously, iodine in a solvent has been employed to deintercalate layered alkali metal chalcogenides,[9] although our procedure is more closely related to the chemical vapor transport (CVT) methodology.[10] However, instead of heating the reactants to a temperature that would decompose the FeTe framework, in our CVT-inspired technique, we add only enough heat to boil the I_2 to remove the excess iron from the layers topotactically. It has previously been reported that substitution of Te with Se or S to produce superconductivity has two effects. First, there is suppression of the low temperature structural and magnetic phase transitions. Second, there is a reduction of the interstitial iron content such that the optimal superconducting composition $FeTe_{0.5}Se_{0.5}$ has little or no excess iron.[11] The capability of controlling iron content through the technique introduced here will allow for the investigation of larger regions of the iron chalcogenide phase diagrams, as well as allow for the two factors upon substitution to be controlled and evaluated independently.

Supporting Information Available: Structural parameters for compounds **1** through **5**; observed and calculated NPD profiles for **1** and **2**; description of single crystal XRD methods; and crystallographic information files for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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