Superconductivity in doped $\text{FeTe}_{1-x}\text{S}_x$ ($x = 0.00$ to $0.25$) single crystals

P K Maheshwari,$^{1,2}$ V Raghavendra Reddy,$^3$ B Gahtori$^1$ and V P S Awana$^{1,2}$

$^1$ CSIR-National Physical Laboratory, Dr K. S. Krishnan Marg, New Delhi-110012, India
$^2$ AcSIR – Academy of Scientific & Innovative Research-NPL, New Delhi-110012, India
$^3$ UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore-425001, India

E-mail: awana@nplindia.org

Keywords: Fe chalcogenide superconductivity, crystal growth, structural details, magneto transport and mossbauer spectroscopy

Abstract

We report self flux growth and characterization of $\text{FeTe}_{1-x}\text{S}_x$ ($x = 0.00$ to $0.25$) single crystal series. Surface x-ray diffraction (XRD) exhibited crystalline nature with growth in (00l) plane. Microstructural (electron microscopy) images of representative crystals showed the slab-like morphology and near stoichiometric composition. Powder XRD analysis (Rietveld) of single crystals exhibited tetragonal structure with $P4/nnm$ space group and decreasing $a$ and $c$ lattice parameters with increase in $x$. Electrical resistivity measurements ($\rho$-$T$) showed superconductivity with $T_c$ onset at 9.5 K and 8.5 K for $x = 0.10$ and $x = 0.25$ respectively. The un-doped crystal, i.e., $x = 0.00$, exhibited known step like anomaly at around 70 K. Upper critical field $H_{c2}(0)$, as calculated from magneto transport [$\rho (T)$-$H$], for $x = 0.25$ crystal is around 60 Tesla and 45 Tesla in $H//ab$ and $H//c$ directions. Thermal activation energy [$U_0(H)$] calculated for $x = 0.10$ and 0.25 crystals followed weak power law, indicating single vortex pinning at low fields. Mossbauer spectra for $\text{FeTe}_{1-x}\text{S}_x$ crystals at 300 K and 5 K are compared with non superconducting FeTe. Both quadrupole splitting (QS) and isomer shift (IS) for S doped crystals were found to decrease. Also at 5 K the hyperfine field for $x = 0.10$ superconducting crystal is decreased substantially from 10.6 Tesla (FeTe) to 7.2 Tesla. For $x = 0.25$ crystal, though small quantity of un-reacted Fe is visible at room temperature, but unlike $x = 0.10$, the low temperature (5 K) ordered FeTe hyperfine field is nearly zero.

Introduction

Fe based compounds were mainly known for their magnetic properties and observation of superconductivity in them was thought to be a far cry. However, the scenario changed dramatically after the discovery of superconductivity in Iron based compounds, first in Iron pnictides [1, 2] and later in Iron chalcogenides [3]. This attracted huge attention of scientific community in the field of superconductivity. Iron based superconducting compounds and high $T_c$ [HTSc] Cuprates [4, 5] are known to be outside the conventional BCS (Bardeen Cooper & Schrieffer) theory of superconductivity [6]. Another superconductor discovered after the high $T_c$ Cuprates, i.e., MgB$_2$ yet follows the BCS in its strong coupling limit [7].

The Fe chalcogenide compounds are known to possess most simple crystal structure among other Fe based superconductors. The ground state of Fe chalcogenides i.e., FeTe orders anti-ferromagnetically along with coupled structural/magnetic phase transitions at below around 70 K. The coupled structural/magnetic phase transition of FeTe is seen clearly in electrical, thermal and magnetic measurements at around the same temperature [8–10]. The substitution of S/Se at Te site in FeTe introduces superconductivity by suppressing the anti-ferromagnetic ordering [8, 11–14]. The highest superconducting temperature ($T_c$) for Fe(Fe/Se, S) chalcogenides series is achieved at approximately 15 K for FeSe$_{0.30}$Te$_{0.50}$ at ambient conditions [8, 15]. Further, the $T_c$ of Fe chalcogenide systems, increases up to 27 K under high pressure [16] and to above 50 K with favourable alkali metal intercalations [17–19].

© 2018 IOP Publishing Ltd
The single crystal growth of Fe chalcogenide superconductors is rather difficult and mainly the self flux Bridgman and the added flux (KCl/NaCl) with complicated heat treatments are employed for crystal growth [20–24]. Bridgman method is quite expensive as the same employs state of art furnaces. On the other hand flux method is marred with foreign contamination, which is difficult to remove completely; hence self flux method is preferred to grow quality single crystals. As far as growth of FeTe$_{1-x}$S$_x$ single crystals is concerned the same is rather difficult due to large difference between the ionic radius of Te$^-$ (211 pm) and S$^-$ (186 pm) [25]. Here, we report self flux crystal growth and superconductivity characterization of FeTe$_{1-x}$S$_x$ ($x = 0.00$ to $0.25$) series. After, repeated runs, we are been able to grow the single crystals of FeTe$_{1-x}$S$_x$ series by self flux method. Superconductivity occurs in FeTe$_{1-x}$S$_x$ with increase in Te site S substitution and the magnetic ordering (∼70 K) for FeTe gets gradually suppressed. Host of physical properties including structural details, morphology, superconductivity and Mossbauer spectroscopy are reported here for FeTe$_{1-x}$S$_x$ single crystal series. In our view, the fact that although Fe chalcogenide superconductivity is heavily studied for both poly and single crystal of FeTe gets gradually suppressed. Host of physical properties including structural details, morphology, superconductivity and Mossbauer spectroscopy are reported here for FeTe$_{1-x}$S$_x$ single crystal series. In our view, is the fact that although Fe chalcogenide superconductivity is heavily studied for both poly and single crystal of FeTe$_{1-x}$S$_x$ [3, 8–10, 15], the same is only scant for FeTe$_{1-x}$S$_x$ [12, 14, 25].

Experimental details

All the studied FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) single crystals are grown via melt process in a simple programmable furnace using self flux method from constituent elements of 99.99 purity. Well mixed stoichiometric powders were pelletized, vacuum sealed in quartz tube and kept in a furnace. The heating schedule involved various steps at 1000 °C, 200 °C, 300 °C and 750 °C in case of S doped crystals [26] and slightly simpler route for pristine $x = 0.0$ crystal [27]. Reference [26] deals with only $x = 0.10$ Sulfur doped crystal and very few results obtained at that time on the same were reported in a conference. The same heat treatment as used for $x = 0.10$ is applied for $x = 0.05$ and 0.25, which resulted in good crystals. Beyond $x = 0.25$ we could not grow the S doped FeTe$_{1-x}$S$_x$ crystals. The reason may be large difference between the ionic radius of Te$^-$ (211 pm) and S$^-$ (186 pm) [25]. Basicall, the crystals are grown from melt of mixed and well pulverized stoichiometric constituent elements by slow cooling with good range of Sulfur solubility at Te site of up to 25%. The transport and magnetization results are obtained on Quantum Design (QD) Physical Property Measurement System (PPMS) down to 2 K under applied magnetic field of up to 14 Tesla. $^{57}$Fe Mossbauer measurements were done on crushed powders of the synthesized single crystals in transmission mode having $^{57}$Co as radioactive source.

Results and discussion

Heat treatment schedule employed for single crystal growth of FeTe$_{1-x}$S$_x$ ($x = 0.05$ to 0.25) is shown by the schematic diagram in figure 1. This heat treatment is different than the one being employed for growth of FeTe or FeTe$_{1-x}$Se$_x$ single crystals (shown in right inset of figure 1). Only, after several trials, we could optimize the final heating schedule to grow large (cm size, left inset of figure 1) FeTe$_{1-x}$S$_x$ ($x = 0.0$ to 0.25) single crystals. The heat treatment thus employed for FeTe$_{1-x}$S$_x$ was checked for reproducibility and found alright.

SEM (Scanning electron microscopy) images and EDX (Energy dispersive x-ray analyzer) are useful for understanding the morphology and elemental analysis of the synthesized samples. SEM and EDX had been performed at room temperature for FeTe$_{0.75}$S$_{0.25}$ single crystal and the results are shown in figure 2. It is clear from the SEM image that FeTe$_{0.75}$S$_{0.25}$ crystallizes in layered structure, which is similar to the case of FeTe [27]. The EDX analysis is shown in insets (a) and (b) of figure 2. Inset (a) shows the quantitative elemental analysis of selected area for FeTe$_{0.75}$S$_{0.25}$, which is found to be near to the stoichiometric ratio i.e., close to FeTe$_{0.75}$S$_{0.25}$. Inset view (b) depicts selected area spectral analysis of FeTe$_{0.75}$S$_{0.25}$, showing that all the elements of FeTe$_{0.75}$S$_{0.25}$ are being present without contamination of any other foreign element in the matrix.

Figure 3 depicts the room temperature XRD pattern carried out on the surface of FeTe$_{1-x}$S$_x$ ($x = 0.0$ to 0.25) single crystals, indicating the crystal growth of all the samples in (001) plane only. This result confirms the evidence of single crystalline property of the as grown FeTe$_{1-x}$S$_x$ ($x = 0.0$ to 0.25) series. Further to study the detailed structural properties, we performed the powdered XRD followed by Rietveld refinement using Fullprof software. The observed powder XRD of all the studied FeTe$_{1-x}$S$_x$ crystals is shown in figure 4(a). All the samples of FeTe$_{1-x}$S$_x$ ($x = 0.0$ to 0.25) series exhibit tetragonal structure within P4/nmm space group. Also seen were small impurities of crystalline FeTe$_2$. The values of lattice parameters, co-ordinate positions, and volume obtained from Rietveld refinement are depicted in table 1. As the S concentration at Te site of FeTe$_{1-x}$S$_x$ ($x = 0.0$ to 0.25) series increases, a monotonic decrease in lattice parameters ($a$ and $c$) is clearly observed, which is in confirmation with our previous results on bulk polycrystalline samples of the same series [28]. The lattice parameters, $a$ and $c$ are seen to decrease from 3.82 Å to 3.79 Å and 6.29 Å to 6.21 Å for $x = 0.00$ and $x = 0.25$.
respectively. Inset of figure 4(a) shows the zoomed part of powder XRD of crystal series from 2θ angle of 42° to 46°, the result clearly shows shifting of peak towards the higher angle for the [003] plane, representing decrement in the c lattice parameter with S doping.

Figure 4(b) depicts the Rietveld refinement of FeTe1-xSx (x = 0.0 to 0.25) series at room temperature. Here $\chi^2$ represents the goodness of fitting of the observed and experimental data, which is in single digits. The values of $\chi^2$ for respective samples are shown in figure 4(b) as well. Although Rietveld refinement of FeTe is reported earlier [27], but the same is shown here as well for the sake of inter comparison with others samples. From the Rietveld refinement, we can safely conclude that the entire essential phase is identified and there is only small impurity (FeTe$_2$) being marked by * is found in some of the crystals; particularly in x = 0.05 and 0.10. Further small impurity of Fe$_3$O$_4$ is found in x = 0.25 crystal, which is marked by #.
Figure 3. Single crystal XRD for FeTe$_{1-x}$S$_x$(x = 0.0 to 0.25) series at room temperature.

Figure 5 despite the resistivity ($\rho$) versus temperature ($T$) measurement for FeTe$_{1-x}$S$_x$ (x = 0.0 to 0.25) crystals in temperature range from room temperature (300 K) down to 2 K and the $\rho$ is normalized at 300 K i.e. $\rho(T)/\rho_{300}$. Figure 5 clearly shows a semiconducting to metallic behavior for all the crystals except x = 0.25, which showed only semiconducting to superconducting transition. The x = 0.05 and x = 0.10 crystals also showed superconducting transition at low temperatures. For pure FeTe crystal without applying any external field, a coupled magnetic/structural transition appears at around 70 K and 65 K during warming and cooling cycles respectively. Warming/cooling cycle hysteresis of transition width ($\Delta T$) of ~5 K in temperature occurs during measurement due to the existence of latent heat throughout the cycles, which is in confirmation with our previous report [27, 29].

For FeTe crystal, neither $T_c$ onset nor $T_c$ offset ($\rho = 0$) were seen down to 2 K and rather a metallic step is seen below 70 K due to magnetic transition [27]. For x = 0.05, i.e. FeTe$_{0.95}$S$_{0.05}$ a semiconducting to metallic step occurs in $\rho$-$T$ measurement approximately at around 55 K, followed by $T_c$ onset at approximately 9 K, but no $T_c$ offset ($\rho = 0$) down to 2 K. In case of x = 0.10 i.e., FeTe$_{0.90}$S$_{0.10}$ crystal $T_c$ onset is 9.5 K and $T_c$ offset ($\rho = 0$) is found to be 6.5 K along with the metallic step due to magnetic ordering at around 48 K. For x = 0.25, i.e., FeTe$_{0.75}$S$_{0.25}$, the normal state metallic part associated with magnetic ordering is not seen and rather a semiconducting to superconducting transition occurs at $T_c$ onset of around 8.5 K and $T_c$ offset ($\rho = 0$) at 4.5 K. Inset of figure 5 depicts the zoomed view of $\rho$-$T$ plots, showing $T_c$ onset, $T_c$ offset and magnetic transition of studied FeTe$_{1-x}$S$_x$ (x = 0.0 to 0.25) single crystals. It is clear from the $\rho(T)$ results that though FeTe shows only the metallic step due to reported magnetic ordering at 70 K, the x = 0.05 and 0.10 exhibit the same but along with superconductivity onset at lower temperatures. This means in case of x = 0.05 and 0.10 both magnetic ordering and superconductivity co-exist. Interestingly, in case of the x = 0.25 the magnetic ordering associated metallic step is absent and the crystal is superconducting below 10 K.

Further to understand the superconducting response of FeTe$_{1-x}$S$_x$ single crystals, $\rho$-$T$ measurements under applied magnetic field have been performed for FeTe$_{0.75}$S$_{0.25}$ single crystal under applied magnetic field of up to 14Tesla in both direction i.e., $H//ab$ and $H//c$ and the results are shown in figures 6(a) and (b). The broadening of the $H//c$ is wider in comparison to $H//ab$ field direction, this shows that superconductivity is relatively weak in $c$-direction. The anisotropy of superconductivity being visible in $H//ab$ and $H//c$ measurements further confirm the single crystalline nature i.e., uni-directional growth of the studied material.

The upper critical field $H_c(0)$ for $H//ab$ and $H//c$ direction is calculated for FeTe$_{0.75}$S$_{0.25}$ single crystal. At absolute zero temperature, $H_c(0)$ is determined by using Ginzburg–Landau (GL) equation i.e.,

$$H_c(0) = \frac{1}{[1-(T/T_c)^2]/(1+ (T/T_c)^2)]}.$$ 

Thus calculated $H_c(0)$ of FeTe$_{0.75}$S$_{0.25}$ single crystal for $H//ab$ and $H//c$ directions are shown in inset view of figures 6(a) and (b) respectively. Further, $H_c(0)$ is calculated using normal state resistivity criteria ($\rho_n$) of 10%, 50% and 90%, which is found to be around 25Tesla, 45Tesla and 60Tesla respectively for $H//ab$ direction and 20Tesla, 35Tesla and 45Tesla for $H//c$ direction for FeTe$_{0.75}$S$_{0.25}$ single crystal. The fitted solid lines imply the extrapolated curve fitting of the GL equation, i.e. $H_c(T) = H_c(0)[1-(1-T/T_c)^2]/(1+ (1-T/T_c)^2)]$, here $t = T/T_c$ is called reduced temperature and $T_c$ is superconducting transition temperature. From fitted curve, the resultant $H_c(0)$ is valid far exceeded from the Pauli Paramagnetic limit i.e. 1.84 times of $T_c$ [30]. High $H_c(0)$ of FeTe$_{0.75}$S$_{0.25}$ single crystal indicates the highly pinned superconductor against the external applied magnetic field.
Figure 4. (a) Powder XRD patterns for crushed powders of FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) series at room temperature. Inset view is zoomed [003] plane view for the same. (b) Observed and fitted XRD of FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) series at room temperature using Rietveld refinement.

Table 1. FeTe$_{1-x}$S$_x$ ($x = 0.00$ to $0.25$) single crystals lattice parameters and coordinate positions using Rietveld refinement.

|        | $x = 0.00$ | $x = 0.05$ | $x = 0.10$ | $x = 0.25$ |
|--------|------------|------------|------------|------------|
| $a = b$ ($\text{Å}$) | 3.826(2)   | 3.803(2)   | 3.801(2)   | 3.798(2)   |
| $c$ ($\text{Å}$)    | 6.292(3)   | 6.242(3)   | 6.237(3)   | 6.212(3)   |
| $V$ ($\text{Å}^3$)  | 92.132(3)  | 90.304(3)  | 90.06(2)   | 89.6405(2) |
| Fe     | (3/4, 1/)  | (3/4, 1/)  | (3/4, 1/)  | (3/4, 1/)  |
|        | 4, 0       | 4, 0       | 4, 0       | 4, 0       |
| Te     | (1/4, 1/)  | (1/4, 1/)  | (1/4, 1/)  | (1/4, 1/)  |
|        | 4, 0, 286  | 4, 0, 289  | 4, 0, 288  | 4, 0, 280  |
| S      | (1/4, 1/)  | (1/4, 1/)  | (1/4, 1/)  | (1/4, 1/)  |
|        | 4, 0, 289  | 4, 0, 288  | 4, 0, 288  | 4, 0, 280  |
For determination of the coherence length $\xi(0)$ of FeTe$_{1-x}$S$_x$ single crystal, we use the relation of $\xi(0)$ and $H_c(0)$ as follows; $H_c(0) = \phi_0/2\xi(0)^2$, here $\phi_0$ is flux quantum, i.e., $2.0678 \times 10^{-11}$Tesla-m$^2$. For FeTe$_{0.75}$S$_{0.25}$ single crystal, at absolute zero temperature, the calculated coherence length $\xi(0)$ from above equation comes to be 23.4 Å and 27.05 Å for diamagnetic shielding of the sample, con

For further analysis of the $\rho(T)$H behaviour of the FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) series, the thermally activated flux flow (TAFF) plots, i.e., $\ln\rho$ versus $1/T$ at various applied fields are drawn for FeTe$_{0.90}$S$_{0.10}$ and FeTe$_{0.75}$S$_{0.25}$ single crystals and are shown in figures 7(a) and (b) respectively. Inset of figure 7(a) shows the $\rho(T)$H measurement of FeTe$_{0.90}$S$_{0.10}$ sample, which is reported earlier [26]. According to TAFF theory [31, 32], the TAFF region is described with the help of Arrenhius relation [33] i.e., $\ln(\rho(T, H)) = \ln(\rho(0)) - U_g(H)/k_B T$, here $\ln(\rho(0))$ is temperature dependent constant, $U_g(H)$ activation energy and $k_B$ the Boltzmann constant. $\ln(\rho)$ versus $1/T$ graph would be linearly fitted in TAFF region for both the samples as described with the above equation, TAFF fitted plots of up to 12Tesla in case of FeTe$_{0.90}$S$_{0.10}$ and up to 14Tesla in case of FeTe$_{0.75}$S$_{0.25}$ are shown in figures 7(a) and (b) respectively. All the linearly fitted extrapolated lines with magnetic fields are intercepted at the same temperature, which coincides approximately at superconducting transition temperature ($T_c$) of the compound. The resistivity broadening pattern under magnetic field in both samples is quite similar to FeSe$_{0.50}$Te$_{0.50}$ superconductor [34] and is due to the thermally assisted flux motion [35].

The thermal activation energy [$U_g(H)$] calculated for FeTe$_{0.90}$S$_{0.10}$ and FeTe$_{0.75}$S$_{0.25}$ single crystals for different magnetic fields is shown in figure 9(b). The thermal activation energy varies from 14 meV to 5.2 meV for magnetic field range from 0.5Tesla to 12Tesla for FeTe$_{0.90}$S$_{0.10}$ and 3.5 meV to 1.33 meV for magnetic field from 1Tesla to 14Tesla for FeTe$_{0.90}$S$_{0.25}$ single crystal. The calculated thermal activation energy is far lesser than the activation energy for FeSe$_{0.30}$Te$_{0.70}$ single crystal [34]. Thermal activation energy follows as power law relation i.e., $U_g(H) = K \times H^{-\alpha}$, here $U_g$ is thermal activation energy, $K$ is constant, $H$ is magnetic field and $\alpha$ is called field dependent constant. For lower magnetic field i.e., up to 2Tesla, $\alpha$ comes around 0.07 while for higher magnetic field i.e., greater than 4Tesla, $\alpha$ comes around 0.63 for FeTe$_{0.90}$S$_{0.10}$ single crystal. While for FeTe$_{0.75}$S$_{0.25}$ sample, $\alpha$ comes 0.12 up to 3Tesla magnetic field and 0.75 for high magnetic field of above 4Tesla. This result of weak power law dependence of $U_g(H)$ shows that single vortex pinning is effective at low fields for studied FeTe$_{0.90}$S$_{0.10}$ and FeTe$_{0.75}$S$_{0.25}$ single crystals [32, 36].

In order to even further explore the superconducting properties of FeTe$_{1-x}$S$_x$, the magnetization measurements have been done down to 2 K for FeTe$_{0.90}$S$_{0.10}$ single crystal, which are shown in figure 8. The real ($M'$) and imaginary ($M''$) parts of AC susceptibility for FeTe$_{0.90}$S$_{0.10}$ single crystal are taken at 10 Hz amplitude and 333 Hz frequency cooled down to 2 K in the absence of any DC magnetic field. From the figure, it is clearly seen that a sharp decrement occurs in real part of AC susceptibility below its $T_r$, i.e., at around 7 K, showing the diamagnetic shielding of the sample, confirming the bulk superconductivity of the sample. Further below $T_c$, a peak occurs in imaginary part of AC susceptibility i.e. $M''$, that’s reflecting the flux penetration effect inside the crystal. There is also no indication of two peak behaviors, thus ruling out the granularity or polycrystalline nature of studied crystal. Inset of figure 8 shows the isothermal $MH$ plot of the FeTe$_{0.90}$S$_{0.10}$ single crystal at 2 K, exhibiting a clear opening of loop at up to 1Tesla. This $MH$ plot shows the evidence of typical type-II superconductivity in our studied FeTe$_{0.90}$S$_{0.10}$ single crystal.

![Figure 5](image_url)

**Figure 5.** Normalized electrical resistivity ($\rho/\rho_{300}$) versus temperature plots for FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) series in temperature range of 2 K to 300 K. Inset view is zoomed part of same in temperature range of 2 K to 80 K.
The Mossbauer spectra of FeTe$_{1-x}$S$_x$ (x = 0.00 to 0.25) have been taken at 300 K (RT) and 5 K, which are shown in figure 9. The detailed Mossbauer analysis of x = 0.00, i.e., FeTe at 5 K and RT is reported elsewhere [37], and is included here for sake of intercomparison. The room temperature (RT) Mossbauer spectra of x = 0.05 and x = 0.10 samples show an asymmetric paramagnetic doublet representing the existence of two Fe sites, which is similar to FeTe Mossbauer spectra at room temperature [37, 38]. The RT data is fitted with a doublet and a singlet for x = 0.05 and x = 0.10 samples. At RT after fitting the curve, values of quadrupole splitting (QS) and isomer shift (IS) are found to be in the range of 0.40 ± 0.02 mm s$^{-1}$ and 0.39 ± 0.01 mm s$^{-1}$ respectively for majority doublet and IS for singlet is found to be 0.35 ± 0.03 mm s$^{-1}$ for both x = 0.05 and x = 0.10 sample. The IS decreases monotonically with doping from 0.46 ± 0.01 mm s$^{-1}$ for FeTe [37] to 0.35 ± 0.03 mm s$^{-1}$ for FeTe$_{0.75}$S$_{0.25}$ sample. The fraction of the singlet is found to increase in x = 0.10 sample (~40%) as compared to x = 0.05 (~10%). However, for x = 0.25 sample in addition to the asymmetric doublet, a magnetically split sextet is observed with a hyperfine field of about 32.8 ± 0.1 Tesla, which could be due to presence of FeO$_x$ [39]. Right frames of figure 9 show the Mossbauer spectra of all the samples measured at 5 K. For x = 0.05 and x = 0.10 samples, in addition to the asymmetric doublet distribution of hyperfine fields resulting in a broad magnetic sextet is observed. Therefore, the data is fitted with distribution of hyperfine fields.

Figure 6. Temperature dependent electrical resistivity $\rho (T)$ under various magnetic field (a) FeTe$_{0.75}$S$_{0.25}$ single crystal for $H//ab$ direction. Inset view is calculated $H_c$ in $H//ab$ direction for FeTe$_{0.75}$S$_{0.25}$ single crystal (b) FeTe$_{0.75}$S$_{0.25}$ single crystal for $H//c$ direction. Inset is $H_c$ in $H//c$ direction for FeTe$_{0.75}$S$_{0.25}$ single crystal.
and also considering the paramagnetic doublet. An average hyperfine field of about 9.4 Tesla and 7.2 Tesla is observed from the fitting and the fraction of magnetic sextet is observed to be about 55% and 64% for $x = 0.05$ and $x = 0.10$ samples respectively. For $x = 0.25$ sample, it is observed that the line width of central doublet increased at 5 K as compared to 300 K. This can be interpreted as due to the presence of small internal hyperfine fields in $x = 0.25$ sample at 5 K. It may be noted here that in un-doped FeTe complete magnetic splitting with hyperfine field of 10.6 Tesla is seen [37], which decrease to 9.4 Tesla and 7.2 Tesla for $x = 0.05$ and $x = 0.10$.

Figure 7. (a) $\ln(\rho(T, H))$ versus $1/T$ for different magnetic fields for FeTe$_{0.90}$S$_{0.10}$ single crystal corresponding fitted solid line of Arrhenius relation. (b) Thermally Activation energy $U_0(H)$ with solid lines fitting of $U_0(H) \sim H^{-\alpha}$ for different magnetic field for FeTe$_{0.90}$S$_{0.10}$ single crystal.
Therefore, with S doping in FeTe the magnetic ordering seems to be suppressed as observed from 5 K Mossbauer data.

**Conclusion**

We have successfully synthesized FeTe$_{1-x}$S$_x$ ($x = 0.0$ to $0.25$) single crystals series by self flux method i.e., without any added flux. Host of structural (XRD), micro-structural (SEM), superconducting i.e., high field low temperature down to 2 K transport and magnetization along with spectroscopy (Mossbauer) studies are carried out.
out and reported here. It is seen that FeTe$_1-x$S$_x$ superconductors are very robust against magnetic field as their superconductivity is hardly affected by the same. Mossbauer spectroscopy results concluded that the ground state compound (FeTe) magnetic order gets disappeared and superconductivity sets in with doping of S at Te site.

**Acknowledgments**

Authors would like to thank their Director NPL India for his keen interest in the present work. P K Maheshwari thanks CSIR, India for research fellowship and AcSIR-NPL for PhD registration.

**ORCID iDs**

V P S Awana [https://orcid.org/0000-0002-4908-8600](https://orcid.org/0000-0002-4908-8600)

**References**

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. **130** 3296
[2] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 Nature **453** 761
[3] Hu F C et al 2008 JPNAS **105** 14262
[4] Bednorz J and Muller K A 1986 Z. Phys. B **64** 189
[5] Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 Phys. Rev. Lett. **58** 908
[6] Bardeen J, Cooper L and Schiffer J R 1957 Phys. Rev. B **8** 1178
[7] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature **410** 63
[8] Fang M H, Pham H M, Qian B, Liu T J, Vehstedt E K, Liu Y, Spina L and Mazzoli Q 2008 Phys. Rev. B **78** 224503
[9] Li et al 2009 Phys. Rev. B **79** 054503
[10] Fedorchenko A V, Grechnev G E, Denenko V A, Panfilov A S, Gnatchenko S L, Tsurkan V, Deisenhofer J, Loidl A, Volkova O S and Vasiliev A N 2011 J. Phys. Condens. Matter **23** 325701
[11] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2009 Appl. Phys. Lett. **94** 012503
[12] Hu R, Bozin E S, Warren J B and Petrovic C 2009 Phys. Rev. B **80** 214514
[13] Lai X, Zhang H, Wang Y, Wang X, Zhang X, Lin J and Huang F 2015 J. Am. Chem. Soc. **137** 10148
[14] Mizuguchi Y, Deguchi K, Kawasaki Y, Ozaki T, Nagao M, Tsuda S, Yamaguchi T and Takano Y 2011 J. Appl. Phys. **109** 013914
[15] Yeh K W et al 2008 Europhys. Lett. **84** 37002
[16] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. **93** 152505
[17] Schindt E W, Hathwar V R, Schmitz D, Durban A, Scherer W, Mayr F, Tsurkan V, Deisenhofer J and Loidl A 2012 Eur. Phys. J. B **85** 279
[18] Zhang A-M, Xia T-Jong, Liu K, Tong W, Yang Z-B and Zhang Q-M 2013 Sci. Rep. **3** 1216
[19] Imai T, Ahilan K, Ning F-L, McQueen T M and Cava R J 2009 Phys. Rev. Lett. **102** 177705
[20] Mok B H et al 2009 Cryst. Growth Design **9** 3260
[21] Sales B C, Safat A S, McGuire A M, Jin R Y, Mandrus D and Mozharivskyj Y 2009 Phys. Rev. B **79** 094521
[22] Yeh K W, Ke C T, Huang T W, Chen T K, Huang Y L, Wu P M and Wu M K 2009 Cryst. Growth Design **9** 4847
[23] Zhang S B et al 2009 Supercond. Sci. Technol. **22** 155020
[24] Sun Y, Taen T, Yamada T, Tsuchiya Y, Pyon S and Tamegai T 2015 Supercond. Sci. Technol. **28** 044002
[25] Mizuguchi Y, Deguchi K, Ozaki T, Nagao M, Tsuda S, Yamaguchi T and Takano Y 2011 IEEE Trans. Appl. Supercond. **21** 2866
[26] Maheshwari P K and Awana V P S 2018 AIP Conf. Proc. **1953** 070010
[27] Maheshwari P K, Jha R, Gahtori B and Awana V P S 2015 J. Supercond. Nov. Magn. **28** 2893
[28] Awana V P S, Pal A, Vaipayee A, Gahtori B and Kishan H 2011 Physica C **471** 77
[29] Maheshwari P K, Jha R, Gahtori B and Awana V P S 2016 J. Supercond. Nov. Magn. **29** 543
[30] Clogston A M 1962 Phys. Rev. Lett. **9** 266
[31] Palstra T T M, Batlogg B, Schneemeyer L F and Waszczak J V 1988 Phys. Rev. Lett. **61** 1662
[32] Blatter G, Feigelman M V, Geshkenbein V B, Larkin A I and Vinokur V M 1994 Rev. Mod. Phys. **66** 1125
[33] Jaroszynski J et al 2008 Phys. Rev. B **78** 174514
[34] Maheshwari P K, Jha R, Gahtori B and Awana V P S 2015 AIP Adv. **5** 097112
[35] Shahzadi M, Wang X L, Shekhar C, Srivastava O N and Dou S X 2010 Sup. Sci. & Tech. **23** 105008
[36] Lei H, Hu R and Petrovic C 2011 Phys. Rev. B **84** 014520
[37] Maheshwari P K, Reddy V R and Awana V P S 2018 J. Supercond. Nov. Magn. **31** 1659
[38] Mizuguchi Y, Furubayashi T, Deguchi K, Tsuda S, Yamaguchi T and Takano Y 2010 Physica C **470** 5338
[39] Skyarova A, Linden J, Rautama E L and Karrpinen M 2013 J. Magn. Magn. Mater. **329** 129