# Optimizing the superconducting transition temperature and upper critical field of $Sn_{1-x}In_xTe$

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$Sn_{1-x}In_xTe$ is a possible candidate for topological superconductivity. Previous work has shown that substitution of In for Sn in the topological crystalline insulator SnTe results in superconductivity, with the transition temperature, $T_c$, growing with In concentration. We have performed a systematic investigation of $Sn_{1-x}In_xTe$ for a broad range of $x$, synthesizing single crystals (by a modified floating-zone method) as well as polycrystalline samples. The samples have been characterized by x-ray diffraction, resistivity, and magnetization. For the single crystals, the maximum $T_c$ is obtained at $x = 0.45$ with a value of 4.5 K, as determined by the onset of diamagnetism.

Topological crystalline insulators (TCIs),[1] in which metallic surface states are protected by crystal point-group symmetry instead of the time-reversal symmetry that contributes to the traditional topological insulators (TIs),[2,3] have attracted great interest since their discovery. The theoretical prediction[4] of a TCI phase in SnTe has received strong experimental support from angle-resolved photoemission studies.[5,6] This, in turn, has triggered the search for possible topological superconductivity[3,7] in the SnTe system. In particular, spectroscopic studies[8,9] have recently examined In-doped SnTe, as it is a low-carrier-density superconductor based on a narrow-gap semiconductor, which satisfies the criteria of possible topological superconductivity.[8,10,11] Earlier studies of superconductivity in $Sn_{1-x}In_xTe$ have shown that one can vary $T_c$ from $<1$ K at $x = 0.02$ to 2.6 K at $x = 0.2$.[12–15] That work suggests that one should be able to raise $T_c$ by further increasing the In concentration.

Given the interest in the $Sn_{1-x}In_xTe$ system, we decided to perform a systematic study of $T_c$ and the upper critical field, $H_{c2}$, as a function of $x$. A series of both polycrystalline and single-crystal samples have been synthesized and characterized. Exploring the composition range $0 \leqslant x \leqslant 1$, single-phase samples were obtained for $x \lesssim 0.5$. The results for $T_c$ are summarized in Fig. 1. For the single crystals, where the composition is best controlled, we find that $T_c$ has a maximum of 4.5 K at $x = 0.45$, with an estimated $\mu_0 H_{c2}(T = 0) = 1.52$ T. For polycrystalline samples, we found the same maximum $T_c$ at a nominal $x = 0.40$. Following an initial presentation of our results,[16] we became aware of the work of Balakrishnan et al.,[17] who confirmed the magnitude of $T_c$ at $x = 0.4$.[18]

Polycrystalline samples with nominal composition, $Sn_{1-x}In_xTe$ $(0 \leqslant x \leqslant 1.0)$, were prepared via the horizontal unidirectional solidification method. Stoichiometric mixtures of high-purity elements [Sn (99.99%), In (99.99%), and Te (99.999%)] were sealed under vacuum in double-walled quartz ampoules. The ampoules were heated at 850 °C in a box furnace and rocked to achieve good mixing of the ingredients. Afterward, the samples were gradually cooled down to room temperature over 24 h and removed for characterization. Single crystals with a nominal In concentration of $x = 0.1$–0.5 were grown by a modified floating-zone method. The starting material was prepared as for the polycrystalline samples, after

which the quartz ampoule was mounted in a floating-zone furnace. The space around the quartz was filled with high-purity Ar at 1 bar to avoid oxygen diffusion through the quartz. A crystal growth velocity of 0.5–1 mm/h was used.

The crystal structure of each composition was characterized by x-ray powder diffraction measured with Cu $K\alpha$ radiation at room temperature. The diffraction data were analyzed with the GSAS program package.[19] For each single-crystal composition, a crushed piece was used for the diffraction measurement. Magnetic measurements were carried out in a quantum design superconducting quantum interference device (SQUID) magnetometer, for temperatures down to 1.75 K. Electrical resistivity was measured using the in-line four-point configuration, with an excitation current of 5 mA, in a quantum design physical properties measurement system (PPMS).

Each polycrystalline sample rod was approximately 10 cm in length. A piece was cut from the center for characterization. Each crystal rod grown by the modified floating-zone method was approximately 15 cm in length. Pieces cut from the center and ends were characterized by magnetization measurements. The error bars on $T_c$ in Fig. 1 reflect the observed spread in values and provide an indirect measure of compositional variation. For the x-ray diffraction and resistivity measurements, a piece from the center of each crystal rod was used.

X-ray diffraction (XRD) was used to investigate the crystal structure. As shown in Fig. 2, the peaks of the indium-free sample (SnTe) can be indexed quite well to the rocksalt structure with a lattice constant of $a = 6.318$ Å, consistent with previous studies.[4,8] Similarly, XRD patterns were obtained for each of the polycrystalline samples ($x = 0.1$–1.0) as shown in Fig. 2. Only the cubic phase is detected for $x \leqslant 0.3$, while the $x = 0.4$ sample shows a trace amount ($\lesssim 2\%$) of a secondary phase (tetragonal InTe). For $x = 0.5$, an undetermined secondary phase is present, while the tetragonal InTe phase becomes substantial for $x \geqslant 0.6$.

The XRD patterns for the single-crystal growths are plotted on a logarithmic scale in Fig. 3(a). There is no detectable second phase for $x \leqslant 0.4$. For $x = 0.45$, there is a small second phase, while $x = 0.5$ exhibits asymmetrically broadened diffraction peaks but no obvious second phase.

The lattice parameter $a$ determined for the cubic phase in the polycrystalline and single-crystal samples is illustrated in
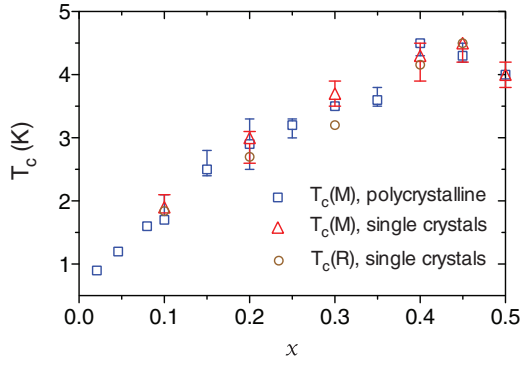
FIG. 1. (Color online) Superconducting transition temperature as a function of indium concentration $x$ for both polycrystalline (blue squares) and single-crystal samples (red triangles), obtained from magnetization measurements, and for single crystals (brown circles) from resistivity measurements. For each concentration, different parts of the as-grown crystal rod were measured to give an average value of $T_c$. Data for indium concentrations less than 10% are taken from Erickson *et al.*[14]

Fig. 3(b). According to Vegard's law, the lattice parameters of the alloy samples should vary linearly between the values of the end members. There is a complication in the present case in that the stable phase of InTe is tetragonal. The cubic phase is stable at high pressure, and it can be retained as a metastable phase at ambient pressure with reported $a = 6.177$ Å at room temperature.[20] The corresponding Vegard's law prediction is given by the dot-dashed line, which we present for completeness; however, the relevance of this line is unclear given the instability of the InTe end point.

We find that the lattice parameters of the single-crystal samples follow a straight line but with a slightly reduced slope. The polycrystalline samples follow the same line up to $x = 0.4$, but deviate from it for $x \geqslant 0.5$, where substantial amounts of the second phase are evident. Clearly, the In concentration in the cubic-phase alloy reaches its maximum at $x \sim 0.5$, and that saturation leads to the presence of the InTe second phase for larger $x$. Given the linear evolution of $a$ and the single-phase behavior for $x < 0.5$, we conclude that the actual In concentration is approximately equal to the nominal concentration in cubic phase $Sn_{1-x}In_xTe$ for $x < 0.5$.
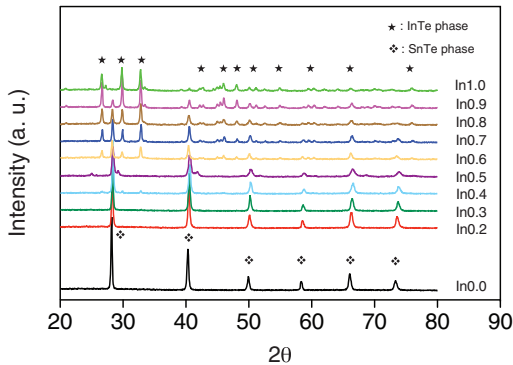


FIG. 2. (Color online) X-ray diffraction spectra for $Sn_{1-x}In_xTe$ ($Inx$) polycrystalline samples with nominal compositions $x = 0$–$1.0$.
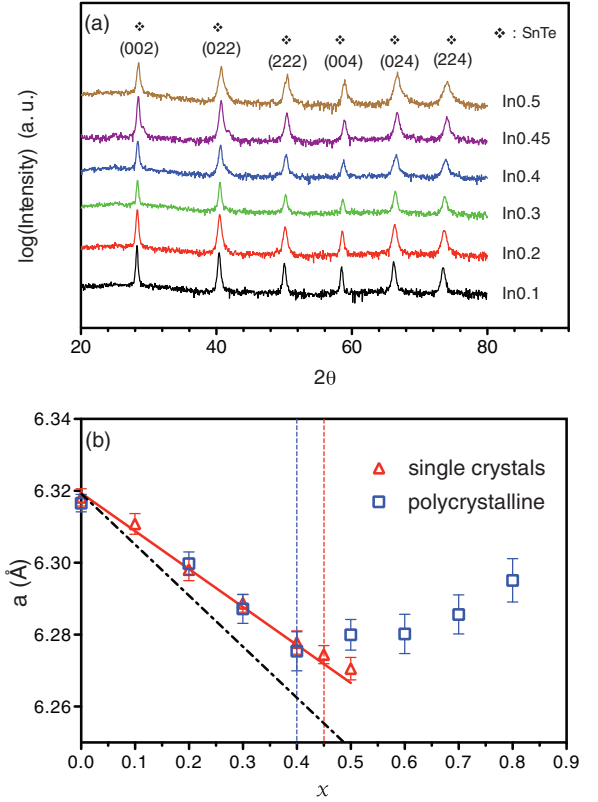


FIG. 3. (Color online) (a) X-ray diffraction measurements for the single crystals with composition $x = 0.1$–$0.5$, with intensity plotted on a logarithmic scale. (b) Lattice parameters $a$ derived from Rietveld analysis of XRD patterns of the cubic phases in polycrystalline (blue squares) and single crystal (red triangles) samples as a function of the nominal indium concentration $x$.

The superconducting transition temperature of each sample was determined by magnetization measurements. Figure 4(a) shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations for the $Sn_{0.55}In_{0.45}Te$ single crystal measured between 1.75 and 6 K under an applied field of 1 mT. The onset of the Meissner signal occurs at $T_c = 4.5$ K. The magnetic hysteresis ($M$-$H$) loops for representative $x = 0.2$ and 0.45 single-crystal samples measured at 1.75 K are compared in Fig. 4(b). Clearly the $M$-$H$ loop for In0.45 includes a larger area than that of In0.2, indicating stronger flux pinning for 45% indium substitution. The lower critical field $H_{c1}$, defined by the deviation point of the $M$-$H$ curve from its initial linear behavior, can be estimated from the data in the inset of Fig. 4(b). With higher indium concentration, $Sn_{1-x}In_xTe$ superconductors are more likely to resist magnetic flux penetration.

The superconducting critical temperature $T_c(M)$ is defined as the temperature at which the magnetic moment begins to drop sharply. The results for all samples are displayed in Fig. 1. Starting at small $x$, the polycrystalline samples show an almost linear relation between $T_c$ and $x$, reaching the highest $T_c$ of 4.5 K when $x = 0.4$.[21] The variation of $T_c$ with $x$ for single crystals shows a similar relation for $x \leqslant 0.45$. This trend confirms and extends the earlier experimental results from several groups,[12–15] and it occurs within the regime where the
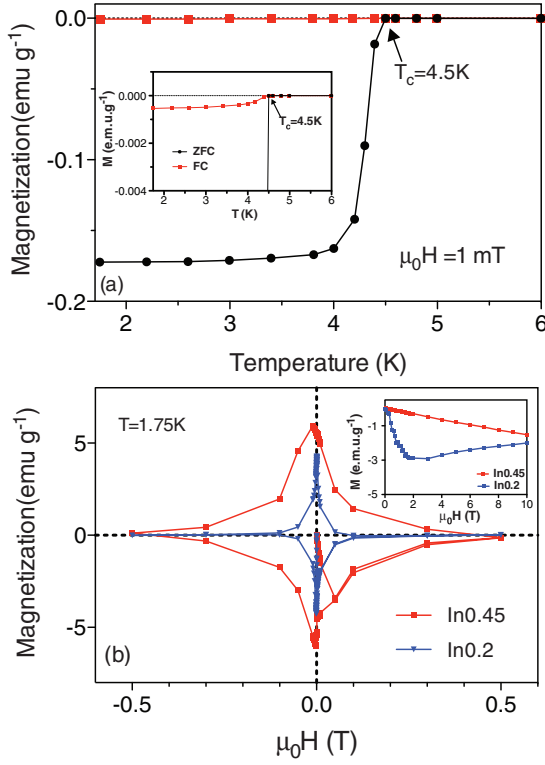
FIG. 4. (Color online) (a) Temperature dependence of magnetic susceptibility for $Sn_{0.55}In_{0.45}Te$ single crystals measured under conditions of FC (ZFC) in an applied field of 1 mT at a cooling (heating) rate of 0.1 K/min. (b) Hysteresis loop of a $Sn_{0.55}In_{0.45}Te$ single crystal measured at 1.75 K. The inset shows the initial $M$-$H$ behavior at a field less than 10 mT and 1.75 K. For magnetization measurements, samples are cut into roughly cubiclike small chunks. The demagnetization factor can be taken as 1 considering that the crystal structure is isotropic.

XRD results indicate that the samples are essentially single phase.

The resistivity of $Sn_{1-x}In_xTe$ single-crystal samples is weakly metallic in the normal state up to 300 K (not shown); the transition to zero resistance is fairly sharp, with a typical width of 0.2 K, as shown in Fig. 5. The parameter $T_c(R)$ is defined as the onset temperature for the drop in resistivity. As
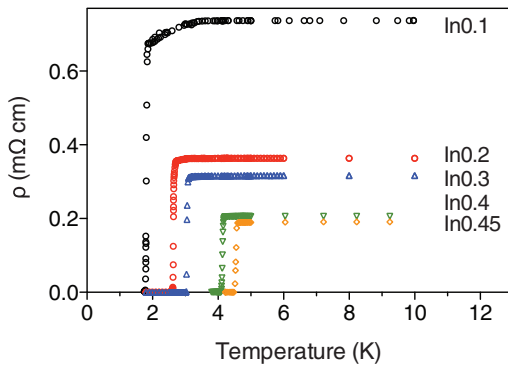


FIG. 5. (Color online) Temperature dependence of the resistivity for $Sn_{1-x}In_xTe$ single crystals.
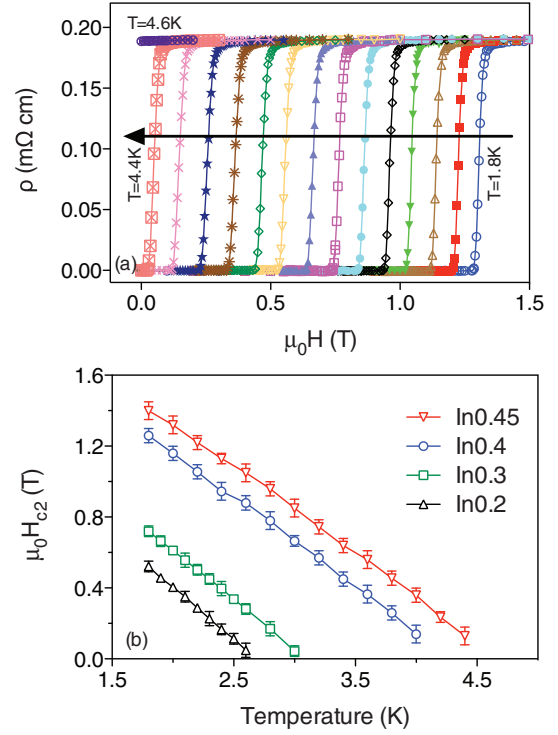


FIG. 6. (Color online) (a) Field dependence of the resistivity for the $x = 0.45$ crystal at fixed temperatures from 1.8 to 4.6 K. (b) Upper critical field $H_{c2}(T)$ determined from resistivity measurements on four single crystals.

the indium concentration increases, $T_c(R)$ changes similarly with $T_c(M)$, as shown in Fig. 1.

The magnetic-field dependence of the electrical resistivity for single crystals was also measured. Representative data for $Sn_{0.55}In_{0.45}Te$ are shown in Fig. 6(a). The upper critical field $H_{c2}$ was determined from such measurements. Specifically, $H_{c2}(T)$ is defined as the onset of the resistive transition at each fixed temperature; the results are shown in Fig. 6(b). The upper critical field at zero temperature $H_{c2}(T = 0)$ can be estimated using the Werthamer-Helfand-Hohenberg approximation,[22] $H_{c2}(0) = 0.69T_c|dH_{c2}/dT|_{T=T_c}$. From the measured curves for $\mu_0 H_{c2}(T)$, we obtain the initial slopes (at $T \approx T_c$) of $-0.58$ T/K for $x = 0.2$, $-0.55$ T/K for $x = 0.3$, $-0.49$ T/K for $x = 0.4$, and $-0.48$ T/K for $x = 0.45$. Using $T_c = 2.7$, 3.1, 4.2, and 4.5 K for the respective samples, the upper critical fields are estimated to be $\mu_0 H_{c2}(T = 0) = 1.08$, 1.18, 1.42, and 1.49 T for $x = 0.2$, 0.3, 0.4, and 0.45, respectively. These results show that a stronger applied field is needed to completely suppress the superconductivity at 0 K for $Sn_{1-x}In_xTe$ superconductors with higher indium concentrations.

To conclude, we have investigated the correlations between indium concentration, crystal structure, and superconducting properties for the In-doped SnTe system. Bulk $Sn_{1-x}In_xTe$ single crystals were successfully grown by the modified floating-zone method. In our work, we have demonstrated that the material retains a single phase of the rocksalt structure with linearly shrinking lattice parameters for $x \leqslant 0.4$ in polycrystalline samples and $x \leqslant 0.45$ in single crystals. With indium substitution, $Sn_{1-x}In_xTe$ displays bulk superconductivity at

accessible temperatures, and indium shows a significant effect on enhancing the $T_c$ of $Sn_{1-x}In_xTe$ materials. A maximum in $T_c$ around 4.5 K was achieved in both polycrystalline and single crystals at $x = 0.4$ and 0.45, respectively. Transport measurements show that raising the indium concentration toward the optimum value also leads to a higher upper critical field. For $Sn_{0.55}In_{0.45}Te$ single crystals, the $\mu_0 H_{c2}(T = 0)$ is estimated to be 1.49 T.

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