Thermophysical properties of U_3Si_5 to 1773 K

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Abstract

Possible use of U_3Si_5 as a nuclear reactor fuel requires knowledge of its thermophysical properties as a function of temperature. While limited data is available for U–Si compounds containing higher uranium densities, no investigations of U_3Si_5 have been presented in the literature to date. High purity U_3Si_5 was fabricated to facilitate a set of experiments to determine the coefficient of thermal expansion, heat capacity, thermal diffusivity, and thermal conductivity from room temperature to 1773 K. Each measurement on nearly stoichiometric U_3Si_5 showed the existence of a phase transformation at 723 K, which is not consistent with the most recently published phase diagram.

Keywords: Uranium silicide, U_3Si_5 , laser flash analysis, thermal conductivity

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1. Introduction

Compounds from the U–Si binary system have received historic interest as nuclear reactor fuels for specialized applications. Most familiar of these are U_3Si and U_3Si_2 , which have been used for many years as fuels for research reactors [1]. U–Si compounds with higher silicon contents such as U_3Si_5 have been rarely investigated due to a uranium density (7.5 g-U/cm^3) significantly lower than both U_3Si (15.0) and U_3Si_2 (11.3). The uranium density of U_3Si_5 is also appreciably lower than UO_2 (9.7), more closely matching that of U_3O_8 (7.1). This suggests that use of U_3Si_5 as a reactor fuel could only be broadly envisioned if high enrichment was allowed for specialty reactor designs, or as a second fissile phase in a composite fuel where a companion high density fuel would increase the total uranium loading to necessary levels. The primary advantages of U_3Si_5 identified to date are the neutronic similarity of a UN– U_3Si_5 composite to reference UO_2 [2], which would minimize LWR operational differences from the viewpoint of the reactor operator, and greatly improved oxidation resistance compared to the more commonly cited U–Si fuel candidate, U_3Si_2 [3]. Although at this point such a fuel is hypothetical, reactor performance modeling would undoubtedly be an early investment to explore neutronics and burnup as a function of possible reactor designs, fuel loading, and many other parameters.

The importance of temperature in governing many aspects of reactor performance demands knowledge of thermophysical properties from room temperature to anticipated operating conditions and through temperatures brought about by potential transients. Even the more familiar U–Si compounds U_3Si and U_3Si_2 have, until recently [4], received minimal attention with respect to their thermophysical properties at elevated temperatures. This is primarily due to lower temperature conditions of research reactors. To date, only a few studies could be located in the literature which focus on the thermophysical properties of U_3Si_5 these consisted of sub-ambient investigations focused on fundamental properties.

This study was initiated to provide thermophysical properties for U_3Si_5 that can be used by the modeling and simulation communities to test reactor performance prior to in-pile testing. Performance of U_3Si_5 fuel under potentially off-normal conditions can also be elucidated from the high temperature data, useful for calculating accident tolerance in LWR safety design criteria.

2. Experimental

Preparation of homogeneous single phase U_3Si_5 in geometries suitable for thermophysical property measurement using differential scanning calorimetry (DSC), dilatometry, and laser flash analysis (LFA) was first necessary for execution of this work. Arc melting was chosen as the most efficient means to synthesize gram quantities of U_3Si_5 for subsequent fabrication into samples suitable for property measurement. Efforts were taken to prevent $O_2(g)$ contamination during the fabrication steps to minimize formation of oxide phases. Finally, microstructural characterization was essential to facilitate discussion of the phase content of the material measured.

2.1. Sample preparation

High purity feedstock of depleted uranium plate was used as the starting material. Inductively coupled mass spectrometry was conducted to verify impurity content of the U feedstock. Impurities for the uranium metal were below the detectable limit for all impurities with the exception of 31 ppm carbon. The plate was then wire electro-discharge machined into discs approximately 10 grams each. The silicon used was Alfa Aesar stock with 99.999% purity in the form of small irregular shapes up to 5 mm in size. The silicon charge was measured such that stoichiometric U_3Si_5 would be achieved. Samples were weighed before and after each arc melting to confirm that minimal mass loss occurred during the arc melting process.

Buttons of U_3Si_5 were prepared by arc-melting the uranium and silicon feedstock to produce an approximate mass of 10 g each. Fabrication was performed in an arc melter (5TA Reed Tri-Arc, Centorr Vacuum Industries, USA) constant current welder connected to a water cooled 2% thoriaated tungsten electrode and a water cooled copper hearth. A gettered argon gas stream fed the arc melter chamber with an oxygen mole fraction (χ_{O_2}) less than 10^{-10} parts per million (ppm). A molten titanium getter was also utilized inside the arc melter itself to capture any remaining oxygen in the chamber. Following arc melting, U_3Si_5 buttons were heat treated at 1570 K for 48 hours in a W-metal furnace to homogenize the solidified melt. U_3Si_5 is reported to form congruently at 2043 K according the most recent published phase diagram [5].

2.2. Sintering U_3Si_5 powder

Specimens for thermophysical property measurements were prepared by a powder metallurgy route. Arc-melted U_3Si_5 buttons were comminuted

in a high energy SPEX mill (8000M, SPEX Sample Prep, USA) using a stainless steel jar and milling media. The resulting powder was sieved to -200 mesh within a nitrogen glove box maintained between 1–20 ppm O₂ concentration to minimize oxidation of the powder. Sieved powders were then pressed at 300 MPa in a steel die set, which utilized Zn stearate as a die lubricant. Binders were not used during fabrication of the pellets in order to minimize oxygen contamination. Pellets were sintered using a W metal furnace on Ta foil under flowing Ar gas. The Ar gas stream was gettered through a Cu charge to minimize the oxygen content in the gas stream, which was monitored throughout the furnace profile. Densities were determined through immersion density measurement according to ASTM B 962–08 [6] using Fluorinert FC–43 as the immersion fluid. The balance used to determine masses in this study was calibrated to 0.01 mg. Resulting pellets were between 96–98% of the theoretical density of U₃Si₅ taken as 9.06 g/cm³.

Representative samples for chemical analysis were taken from the comminuted button that was used to fabricate the pellets used in this study. Inductively coupled plasma–optical emission spectroscopy (ICP–OES) was used to determine transition and transuranic elements, while the WO₃ combustion catalyst method was utilized to determine H, C, and N content. Elemental O analysis is not possible using this experimental technique, and was therefore not evaluated in this study. ICP–OES required 50 mg of powder to be digested in a solution of nitric, hydrofluoric, and hydrochloric acid. Chemical analysis was by ALS Environmental of Tuscon, Arizona (USA). Three measurements were conducted on powder from the representative pellet to explore potential chemical variations within the feedstock. The results of the chemical analysis for detectable elements are shown in Table 1. Sintered pellets analyzed in this work are Si–lean relative to the anticipated content (16.4%) of stoichiometric U₃Si₅ by 0.4 weight percent (w/o).

2.3. Microstructure analysis

Powder X–ray diffraction (XRD) was performed on a Bruker D8 diffractometer using CuK α radiation. The instrument was fitted with a graphite monochromator to remove CuK β from the diffracted beam. Measurements were conducted in a Bragg–Brentano geometry from 20 – 140° 2 θ with a step size of 0.01°. Powder specimens were prepared by comminuting ingots using a mortar and pestle. This was done inside an inert atmosphere (He) glovebox to minimize oxygen contamination. The powder was mounted on a Si crystal zero–background plate using a thin layer of vacuum grease, and

109 then sealed inside a beryllium container while inside the glovebox . An XRD
110 pattern using the prescribed method collected on a U_3Si_5 specimen following
111 powder metallurgy and sintering as described below is shown in Figure 1.

112 Figure 1 confirms that U_3Si_5 is the dominant phase present in the sample.
113 For comparison, the characteristic peaks of other U–Si phases in the vicinity
114 of U_3Si_5 are shown, along with the peaks of UO_2 . A primary peak of UO_2
115 is evident at roughly 28° , and evidence of other peaks at higher angles can
116 be observed. Two peaks at 33° and 37° 2θ were not identified via the XRD
117 database for any known U–Si or U–O compounds.

118 Scanning electron microscopy (Inspect, FEI, Hillsboro, Oregon) was also
119 used to further investigate the microstructures of the synthesized materials.
120 Samples of U_3Si_5 were cross sectioned, ground, and polished with $0.05\ \mu\text{m}$
121 colloidal silica used as the final step. Although the majority of the polished
122 sample was observed as a single phase, two secondary phases were identi-
123 fied using electron backscatter detection (see Figure 2). The first phase,
124 appearing brighter in the backscatter image indicating higher uranium con-
125 tent, was generally observed as $5\text{--}10\ \mu\text{m}$ precipitates. These constituted far
126 less than one volume percent. Qualitatively, these precipitates appeared to
127 be somewhat localized with several being collected in a $100\ \mu\text{m}$ region but
128 being totally absent from surrounding areas. Energy dispersive spectroscopy
129 (EDS) measurements confirmed that this secondary silicide phase consisted
130 only of U and Si, and was U–rich compared to the surrounding matrix. It is
131 suspected that the secondary phase is USi based on the accepted phase dia-
132 gram. However, recent reports [see 7, and references therein] have suggested
133 the existence of U_4Si_5 , which could also be possible based on the EDS data.
134 Further characterization of the specimen with neutron diffraction or conver-
135 gent beam electron microscopy would be necessary for decisive assignment.

136 A second precipitate roughly the same size as the first was also identified
137 in the backscatter SEM images, appearing darker than the matrix. These
138 precipitates were observed less frequently than the U–rich phases. EDS mea-
139 surement of these precipitates identified the presence of Si, U, and O. It is
140 assumed that this phase is UO_2 given the XRD analysis, and that the Si EDS
141 signal is likely due to the interaction volume of the electron beam penetrating
142 the $5\text{--}10\ \mu\text{m}$ particles.

143 2.4. Differential scanning calorimetry

144 Specimens for heat capacity measurements were prepared according to
145 §2.2 using a 6 mm punch and die set. Resulting cylindrical pellets weighed

0.170 g and had diameters of 4.58 mm $\pm$ 0.01 mm and thickness of 1.17 mm $\pm$ 0.01 mm. Measurements in the DSC used Pt pans with Al₂O₃ liners, which prevented reaction of the U₃Si₅ phase with the pans and thermocouples. Specimen mass varied by <0.01 mg between measurements.

The ratio method was utilized to determine the specific heat capacity,* c_p , of the specimens in a differential scanning calorimeter (Pegasus 404C, Netzsch Instruments, Germany). Measurements were conducted at a heating rate of 20 K·min⁻¹ to a final temperature of 1243 K. The atmosphere in the DSC was comprised of ultrahigh purity Ar(g) that flowed through a Cu getter source (2A-100, Centorr Vacuum Industries, USA), which decreased the O₂(g) content in the gas stream to 10⁻¹⁵ ppm. Oxygen content on the gas stream was monitored on the exhaust by an in-stream oxygen sensor (Rapidox 3100 OEM, Cambridge Sensotec, UK) to verify minimal O₂(g) contamination in the furnace chamber. Thermocouple and sensitivity calibrations were conducted using melt point standards over the entire range of temperatures investigated. Based on the temperature calibrations, the instrument had an error in temperature of $\pm$ 1 K. Onsets for phase transformations were calculated using a linear intercept method within the software provided by the manufacturer of the equipment [8].

2.5. Dilatometry

Thermal expansion specimens were prepared according to §2.2 using a 6 mm punch and die set. Mass for a typical thermal expansion specimen was 0.794 g and had diameters of 4.57 mm $\pm$ 0.01 mm and thicknesses of 5.35 mm $\pm$ 0.02 mm.

Measurement of the physical coefficient of thermal expansion, α_P , was determined using a dilatometer (DIL 402CD, Netzsch Instruments, Germany). A heating rate of 2.5 K·min⁻¹ was used to a maximum temperature of 1732 K. A baseline correction was applied to the data to correct for the thermal expansion of the Al₂O₃ fixturing. The Ar atmosphere was monitored with an oxygen sensor on the outlet. Initial χ_{O_2} values were 0.1–1 ppm, which dropped to 10⁻¹² ppm during the measurement and returned to the initial value on cooling. Specimen mass increased by <0.5 mg between measurements, which is attributed to surface oxidation of the specimen. Approxi-

*Heat capacity values were converted to molar values using a molecular weight of 854.56 g mol⁻¹.

179 mation of the phase transformation temperature was achieved using a linear
180 intercept method similar to the DSC.

181 2.6. Thermal diffusivity measurements

182 Cylindrical specimens were fabricated according to §2.2 using a 13 mm
183 punch and die set. The specimen weights were between 2 g and 2.7 g with
184 thickness between 2.19 mm and 2.95 mm with a standard error of ± 0.02
185 mm. Pellet diameters were $11.4 \text{ mm} \pm 0.1 \text{ mm}$ in size. Diffusivity values
186 were determined by fitting the temperature rise signal with a Cape-Lehman
187 model [9]. Calibration of the thermocouple used to measure the sample
188 temperature was achieved using the Curie temperature of Fe; the minimum
189 in the diffusivity curve produced was located at 1045.2 K, slightly above the
190 accepted value of 1043 K. As such, an uncertainty of $\pm 3 \text{ K}$ is ascribed to the
191 temperatures of each measurement.

192 The LFA (LFA 427, Netzsch Instruments, Germany) technique was uti-
193 lized to determine the thermal diffusivity, D , of the specimens. In this tech-
194 nique, a laser is pulsed on one side of the specimen, while the heat rise is
195 determined on the opposite side by measuring the infrared blackbody radia-
196 tion. All surfaces of the sample were coated with a graphite coating (Graphit
197 33, Kontakt Chemie) to improve absorption of the laser energy on the bottom
198 face and enhance emissivity of the upper face. Diffusivity data was collected
199 from room temperature to 1773 K in 50 K increments on cooling. Additional
200 data was collected between 273 K and 1174 K on heating and cooling to
201 investigate hysteresis that was observed in the specimens. Reaction temper-
202 atures were determined qualitatively using a linear intercept method similar
203 to the DSC. Reactions were observed to be sigmoidal in nature on heating
204 in the diffusivity measurements. Given that two reaction temperature inter-
205 cepts were determine, the higher reaction temperature value was accepted
206 due to local heating of about 50 K that is induced by the laser [10] and
207 the value was closer to the temperature observed in the DSC (see also in-
208 set of Figure 5). Three laser shots were collected at each temperature step
209 and averaged to produce the diffusivity values reported in this study. Al_2O_3
210 fixturing was used throughout the sample chamber, and gettered argon was
211 again flowed throughout the measurement. Oxygen content of the outlet gas
212 stream was monitored with an oxygen sensor during each measurement and
213 was $< 10^{-15}$ ppm for all measurements. Specimen mass gains were 1–3 mg,
214 which is attributed to surface reaction with the graphite coating.

215 3. Results

216 Each of the three techniques were used to obtain the datasets as de-
217 scribed above. The measured thermal expansion was used to determine the
218 temperature-dependent density based upon room temperature immersion
219 data collected as described in §2.2. The product of c_p , ρ , and D results in
220 the thermal conductivity, λ . The results of all three measurements as well
221 as calculation of the thermal conductivity are discussed below.

222 3.1. Coefficient of thermal expansion

223 Specimen length change (dL/L_0) and physical coefficient of thermal ex-
224 pansion (α_p) for U_3Si_5 are shown in Figure 3 as a function of temperature
225 to 1673 K. The specimen dL/L_0 increases linearly with temperature over
226 the entire temperature range. Deviations from linearity begin at 726 K and
227 return to linear behavior at 732 K (see inset of Figure 3).

228 3.2. Heat capacity

229 The molar heat capacity of U_3Si_5 as determined by the ratio method in
230 the DSC is shown in Figure 4. Values for c_p increase linearly over the entire
231 measurement range, with the exception of the endothermic peak with an
232 onset at 723 K. Sato *et al.* and Miyadai *et al.* determined the heat capacity
233 of U_3Si_5 for $T < 40$ K in a magnetometer [11, 12], which is the only c_p data
234 in the literature to the authors' knowledge.

235 The endothermic peak observed in the DSC at 723 K is an apparent
236 molar heat induced by the enthalpy of an as yet unidentified phase transfor-
237 mation discussed below. Use of DSC to determine heat capacity will result
238 in superposition of such effects, and they must be removed to arrive at the
239 true heat capacity of the material of interest. The linear behavior of the
240 heat capacity measured below and above the peak facilitated a least squares
241 minimization fit to approximate the heat capacity in the region of the phase
242 transformation. This result, plotted in red in Figure 4, was used to determine
243 the thermal conductivity.

244 3.3. Thermal diffusivity

245 Thermal diffusivity for U_3Si_5 as a function of temperature to 1773 K is
246 shown in Figure 5. Both heating and cooling data are shown, which produce
247 different diffusivity values for $T < 1174$ K. On heating from room temper-
248 ature a linear dependence with temperature is observed. Deviations from

249 linearity are observed at two different temperatures: 723 K and 874 K. The
250 positive deviation from linearity at 723 K is highlighted in the inset of Fig-
251 ure 5. Above 723 K, the diffusivity continues to increase linearly until a sharp
252 increase is observed for $874 < T < 1074$ K. Above 1074 K, the measured dif-
253 fusivity values continue to increase linearly until the maximum temperature
254 determined in this study.

255 Cooling from 1773 K follows a linear decrease in diffusivity to 723 K,
256 with $R^2 = 0.999$. Values below 723 K decrease below the linear trend. At
257 550 K a discontinuity in the diffusivity is observed, before decreasing to the
258 initial heating values. Cooling to room temperature returned the thermal
259 diffusivity values to the original magnitude. To the authors' knowledge, no
260 previous thermal diffusivity studies have been conducted on U_3Si_5 .

261 3.4. Thermal conductivity

262 The calculated thermal conductivity of U_3Si_5 is shown in Figure 6 as
263 a function of temperature to 1773 K. A propagation of errors analysis was
264 conducted based on the errors introduced from measuring α_p , c_p , and D from
265 the DIL, DSC, and LFA techniques, respectively. The result of the error
266 analysis calculates the error in thermal conductivity values at 5%, consistent
267 with that expected of the LFA technique. Thermal diffusivity data on heating
268 was also neglected in this analysis.

269 4. Discussion

270 4.1. Solid state reaction at 723 K

271 The existence of a phase transformation is observed at 723 K in each of
272 the thermophysical property measurements. The closest reaction on the most
273 recent phase diagram [5] is the peritectoid reaction at 723 K, reproduced in
274 Figure 7. This reaction was first postulated by Brown and Norreys [13], who
275 concluded that USi_2 decomposes to USi_3 and $\text{USi}_{1.88}$ and later confirmed
276 to be exothermic in nature. Observation of a reaction at this same exact
277 temperature in nominally U_3Si_5 samples would initially suggest severe off-
278 stoichiometry or incomplete arc melting, as slightly Si-rich U_3Si_5 would be
279 expected to contain small amounts of $\text{USi}_{1.88}$ rather than USi_2 . However,
280 XRD, elemental analysis by ICP-OES, and SEM results described above
281 confirm that the samples synthesized here are of the composition and room
282 temperature structure attributed to U_3Si_5 , and are devoid of any substantial
283 fraction secondary U–Si phase. Furthermore, the DSC signal is *endothermic*
284 suggesting a different reaction mechanism applies.

285 Therefore, the results of this study reproduce the reported peritectoid
286 reaction temperature, but the composition and energetics are inconsistent
287 with the literature. A more detailed investigation of previous studies reveals
288 conflicting results regarding phase stability in the U–Si system near the U_3Si_5
289 composition. Results of Remschnig *et al.* suggest that U_3Si_5 is actually
290 a highly defective AlB_2 -type structure, which exists as two isostructurally
291 similar phases that form superstructures along the *c*-axis of the unit cell when
292 annealed above 973 K [14]. Vaugoyeau *et al.* also investigated a number of
293 U–Si melt compositions near U_3Si_5 and observed that U_3Si_5 and $\text{USi}_{1.88}$ each
294 have a range of allowed stoichiometries, and are difficult to distinguish by
295 XRD [15].

296 Further uncertainty is encountered when the sources of USi_2 structural
297 data are consulted. Sasa *et al.* studied USi_2 in detail, and reports that the
298 phase is metastable and will degrade exothermically at 623 K [16]. Stoi-
299 chiometric USi_2 characterized in the work of Sasa *et al.* was synthesized by
300 leaching excess U from $\text{USi}_{1.88}$ in nitric acid. Other techniques that report
301 data for USi_2 utilize a bismuth amalgam technique [17, 13]. To the authors’
302 knowledge, no previous investigators have synthesized USi_2 using a steady
303 state technique.

304 The data of this study supports the conclusion that the U–Si phase dia-
305 gram as shown in Figure 7, while accurate at room temperature in the vicinity

of U_3Si_5 , contains inaccuracies at elevated temperatures. The results of this study do not provide any conclusions with respect to phase transformations at elevated temperatures, but it can be stated that a U–Si compound synthesized at the target composition of U_3Si_5 undergoes an endothermic phase transformation at 723 K. The reaction is shown to be reversible upon cooling; hysteresis of the thermal conductivity and possible implications of this response to the use of U_3Si_5 as reactor fuel are discussed below. Diffraction studies at elevated temperatures are needed to elucidate the complete structural behavior of this compound, but are beyond the scope of this current study.

4.2. Density dependence of U_3Si_5 with temperature

The physical coefficient of thermal expansion is solved by taking the instantaneous derivative of dL/L_0 with temperature, which is shown in Figure 3. An average value for α_p is calculated from the data at $10.7 \times 10^{-6} \text{ K}^{-1} \pm 0.5 \times 10^{-6} \text{ K}^{-1}$ for $300 \text{ K} < T < 1250 \text{ K}$, which is plotted as the red-line. Above 1250 K, dL/L_0 and corresponding α_p values deviate slightly from linearity, which increases the error in assuming a constant α_p to $\pm 2 \times 10^{-6} \text{ K}^{-1}$. Using standard error analysis techniques, the error in assuming a constant α_p generates an error in density of $< 1\%$ over the entire temperature range.

4.3. Fundamental contributions to the molar heat capacity of U_3Si_5

The molar heat capacity of metals at constant pressure is predominantly composed of harmonic lattice, anharmonic lattice, dilational, and electronic terms. The dilational term is calculated using the well known relation $c_d = \alpha_p^2 V k_T^{-1} T$, where V and k_T are the molar volume and isothermal compressibility, respectively. Compressibility values for U_3Si_5 were not found during the literature review. Values for the bulk modulus of USi_2 and USi are reported by Yagoubi *et al.* to be 140 GPa and 111 GPa, respectively [18]. Assuming that the bulk modulus for U_3Si_5 is similar to USi_2 provides an estimate to the dilatational heat capacity term. Using this value for k_T and α_p value provided in the previous section, the dilational contribution to heat capacity is calculated, which contributes less than 0.1% over the entire temperature range analyzed in this study.

Contribution to heat capacity by electronic, c_e , and anharmonic lattice, c_a , terms follow a linear dependence with temperature. Due to the complex nature of modeling the anharmonic term, it is common for this term to be summed with the electronic term as $(b + \gamma)T$, where b and γ are the

342 anharmonic and electronic constants, respectively. By expanding the Debye
 343 model, one can solve for the linear component using [see 19, and references
 344 therein]:

$$(c_v + c_e - 3NR)T^{-1} = -\frac{3NR\Theta_D^2}{20}\frac{1}{T^3} + (b + \gamma) \quad (1)$$

345 where N , R and Θ_D are the number of atoms in the unit cell, gas constant
 346 and the Debye temperature, respectively. A least squares fit of Equation (1)
 347 is shown in the inset of Figure 4. The value of $(b + \gamma)$ for U_3Si_5 from this
 348 study is $30.5 \text{ mJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$ (U_3Si_5 basis), which is within 0.5% with the
 349 value calculated from low temperature heat capacity data [11, 12]. A value
 350 of 183 K is calculated for Θ_D based on the slope of the aforementioned
 351 fit. A comparison of Θ_D with the literature is not available to the author's
 352 knowledge. Subtracting the electronic and dilational contribution from the
 353 heat capacity data calculates c_v , shown as the ($\diamond$) symbols in Figure 4. For
 354 $T < 1000 \text{ K}$, c_v is within 1% of the Dulong–Petit value ($199.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$),
 355 which is expected given the calculated Debye temperature for this system.
 356 Above 1000 K, c_v is at most 4% lower than the Dulong–Petit value. For the
 357 purposes of calculating the thermal conductivity, a linear regression analysis
 358 was assumed over the entire temperature range, represented by the red line
 359 in Figure 4.

360 4.4. Thermal diffusivity and thermal conductivity dependence with tempera- 361 ture for U_3Si_5

362 The material characterized in this study can be declared of acceptably
 363 high purity based on the XRD and SEM analyses. Although a small quan-
 364 tity of UO_2 was observed in the microstructure, which would not affect the
 365 thermal diffusivity data. The error introduced to the thermal conductivity
 366 of U_3Si_5 from second phases limited to at most a few percent each will be
 367 less than the error of the calculation (5%), and as such can be considered to
 368 be captured by this term.

369 Thermal transport in metallic materials can be simplified to transport
 370 of thermal energy by phonons and electrons in this temperature range. In
 371 general, the phonon term in metallic conductors is only relevant at lower
 372 temperatures ($T < 100 \text{ K}$) because the thermal conductivity is inversely
 373 dependent on temperature, while the electronic term is linearly dependent.
 374 Over the measured temperature range, a linear temperature dependence is
 375 observed suggesting U_3Si_5 is dominated by the electronic conduction term.

376 It is known that the electronic component of the thermal conductivity in
 377 metals decreases upon the formation of defects in the solid state [20]. Non-
 378 linear increases in thermal diffusivity for $874 < T < 1074$ K on heating (see
 379 Figure 5) are consistent with the removal of the defective Pmmm structure
 380 in this material on heating U_3Si_5 as reported by Remchnig *et al.* [14]. Inter-
 381 estingly, the thermal diffusivity data suggests that some degree of hysteresis
 382 exists in this phase field from the kinetics of defect removal in the system as
 383 evidenced by differential heating and cooling. As such, thermal conductivity
 384 data represented by the (- · -) in Figure 6 should be taken with caution and
 385 depends on the specimen history. It is suspected that the defective structure
 386 does not form on cooling until well below 723 K, although more detailed
 387 diffraction work as a function of temperature is necessary to evaluate this
 388 hypothesis. Furthermore, the sharp transition observed at $T_{tr} = 550\text{K}$ is
 389 not understood given the analysis techniques utilized in this study. Further
 390 diffraction work is again required to elucidate the fundamental mechanisms
 391 involved in the transition.

392 The thermal conductivity of UO_2 , which is dominated by phonon trans-
 393 port in the temperature range of this study, is shown as a function of tem-
 394 perature in Figure 6 [21]. At room temperature, the thermal conductivity of
 395 U_3Si_5 is $\sim 60\%$ lower in value than UO_2 . On heating, the thermal conductiv-
 396 ity of U_3Si_5 overtakes the UO_2 values at 574 K and continues to increase with
 397 temperature. For comparison, data for UN from Hayes *et al.* is also included
 398 [22]. Thermal conduction in UN has a similar metallic behavior to U_3Si_5
 399 although the magnitude for UN is $\sim 60\%$ larger over the entire temperature
 400 range conducted in this study.

401 It is expected that U_3Si_5 is metastable on heating above or cooling be-
 402 low the reaction temperature at 723 K, which impacts the thermal transport
 403 in this system. For a reactor application, it is reasonable that portions of
 404 U_3Si_5 fuel elements would operate for extended periods of time within the
 405 temperature region where the phase transformation is observed. At a mini-
 406 mum, the hypothesized phase transformation has been demonstrated in this
 407 work to perturb the thermal conductivity of U_3Si_5 by over 30%. Such an
 408 uncertainty in the thermal conductivity of a reactor fuel at service tempera-
 409 tures would require conservatism detrimental to the demands of commercial
 410 units. Unknowns regarding the kinetics of defect recovery in this system were
 411 not investigated in this study, but are relevant to understanding U_3Si_5 as a
 412 fuel element. Clearly the performance of U_3Si_5 under irradiation testing is
 413 paramount to validating this fuel in a reactor setting. However, the details of

414 this phase transformation, as well as the impact of irradiation on the stability
415 of highly-defective structures that are reported to populate this portion of
416 the U–Si binary system, are first essential even before in-pile testing if U_3Si_5
417 is to be considered for nuclear reactor applications.

418 5. Conclusions

419 The coefficient of thermal expansion, molar heat capacity, thermal dif-
420 fusivity, and thermal conductivity of U_3Si_5 were determined as a function
421 of temperature to 1773 K. A constant coefficient of thermal expansion was
422 determined over the entire temperature range of $10.7 \times 10^{-6} \text{ K}^{-1}$. Electronic
423 contributions to the molar heat capacity measured in this study were con-
424 sistent with values presented in the literature and the Dulong-Petit law is
425 observed once the electronic component is neglected. Metallic thermal con-
426 duction is observed in U_3Si_5 which increases linearly with temperature. An
427 endothermic phase transformation was observed at 723 K in all measure-
428 ments executed here. Although this temperature is consistent with the USi_2
429 peritectoid reaction located further into the Si-rich portion of the binary,
430 neither XRD nor SEM revealed its existence in samples synthesized here.

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435 auspices of the U.S. Department of Energy.

7. References

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Table 1: Chemical analysis conducted on as-sintered U_3Si_5 pellets. Elements included in the analysis, but below the detection limit are included as follows: Al, Sb, Ba, Be, Cd, Ca, Cr, Fe, Pb, Li, Mg, Mo, Ni, P, K, Se, Na, Sr, Sn, Ti, Zn, Zr, B, Gd, Nb, Ta, and W.

Elements	Si	C	H	N	Cu	V	As	Co	Mn	Hf
Contents (w/o)	16.00	0.23	0.27	0.16	0.008	0.005	0.03	0.005	0.01	0.02

Figure 1: XRD pattern collected on a sintered U_3Si_5 specimen that was crushed and sealed within a Be sample holder. Reference files are from: 04-003-3432 (U_3Si_5) [11], 04-008-2456 (UO_2) [23], 04-003-0522 (USi) [24], and 04-003-3437 ($\text{USi}_{1.88}$) [12].

Figure 2: Scanning electron microscope of the U_3Si_5 microstructure collected with a backscatter electron detector.

Figure 3: Specimen length change normalized to original specimen length and physical coefficient of thermal expansion as a function of temperature for U_3Si_5 . The calculated average α_p value is shown as the red line. An inset for dL/L_0 centered at the phase transformation temperature, which is highlighted by the meshed rectangle.

Figure 4: Molar heat capacity of U_3Si_5 collected from 353 K to 1423 K ($\square$), with calculated c_v ($\diamond$) and Dulong–Petit value ($-\cdot-$). Least squares minimization fit of the data ($-$), which was used to calculate the thermal conductivity. The inset includes a $(c_v - 3NR)T^{-1}$ against T^{-3} plot with a linear fit according to Equation (1).

Figure 5: Thermal Diffusivity data collected on heating ($\triangle$) and cooling ($\square$) for U_3Si_5 . The inset includes a meshed rectangle to highlight the heating data near the phase transformation temperature at 723 K. Specific attention is drawn to the qualitative assessment of the phase transformation temperature in the inset, which is further described in the text.

Figure 6: Thermal conductivity data as a function of temperature for U_3Si_5 ($\square$) with a least squares minimization fit of the data ($-$). Arrows indicate differences in heating and cooling values for U_3Si_5 . Reference data for UO_2 ($\diamond$, [21]) and UN (∇ , [22]) are included for comparison.

Figure 7: U-Si partial phase diagram based on the full binary as reported by Okamoto [5].