INL/CON-20-57562-Revision-0

Influence of Irradiation-induced Microstructural Defects on Thermal Transport in Single Crystal Thorium Dioxide

February 2020

Changing the World's Energy Future

Amey Rajendra Khanolkar, Zilong Hua, Cody Andrew Dennett, Tiankai Yao, Lingfeng He, Jian Gan, David H Hurley, Yuzhou Wang, Vinay Chauhan, Anter El-Azab, M. Khafizov, J.M. Mann

Idaho National Laboratory

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Center for Thermal Energy Transport under Irradiation

Influence of Irradiation-induced Microstructural Defects on Thermal Transport in Single Crystal Thorium Dioxide

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Idaho National Laboratory

The Ohio State University

University of Central Florida

Oak Ridge National Laboratory

Purdue University

AFRL

Columbia University in the City of New York

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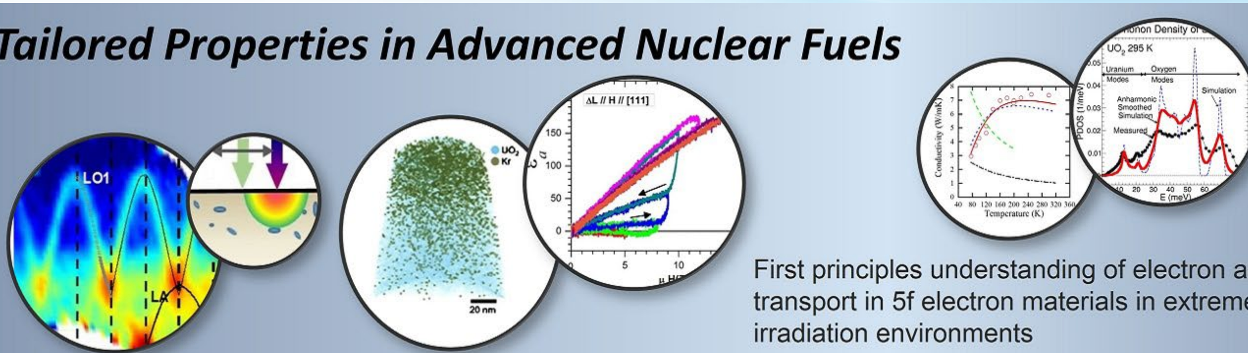
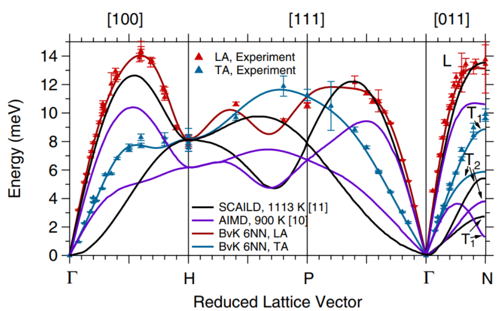
Tailored Properties in Advanced Nuclear Fuels



First principles understanding of electron and phonon transport in 5f electron materials in extreme irradiation environments

Science Question 1

What is the impact of 5f electrons on phonon and electron structure in $Th_{1-x}U_xO_2$ and UZr alloys?

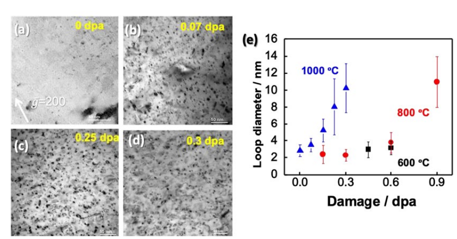


Brubaker, Z.E. et al., Phys. Rev. B. (2019)

Atom scale   *Dynamic Mean Field Theory*   ARPES   First principles   Quantum Oscillations   **Neutron scattering**   *Defect free*

Science Question 2

How do intrinsic and irradiation-induced defects self-organize in $Th_{1-x}U_xO_2$ and UZr alloys, and what are their impacts on electron and phonon scattering?

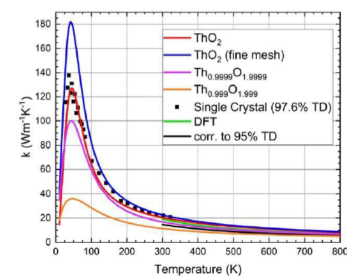


Yao, T., et al., in prep. (2020)

HRTEM   Atom scale   Defects   Electron and phonon scattering   **Input**   Atom probe tomography

Science Question 3

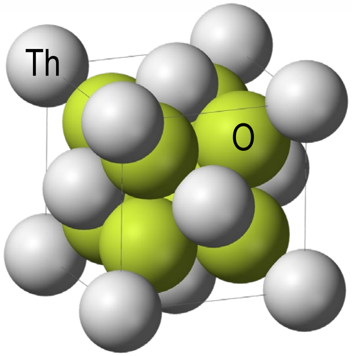
What are the collective effects of defects, defect ordering, and defect supersaturation on thermal transport of $Th_{1-x}U_xO_2$ and UZr alloys?



Deskins, R.,et al., in prep. (2020)

Modulated thermoreflectance   Operando   Thermal conductivity   Output   Mesoscale complexity   **Boltzmann**

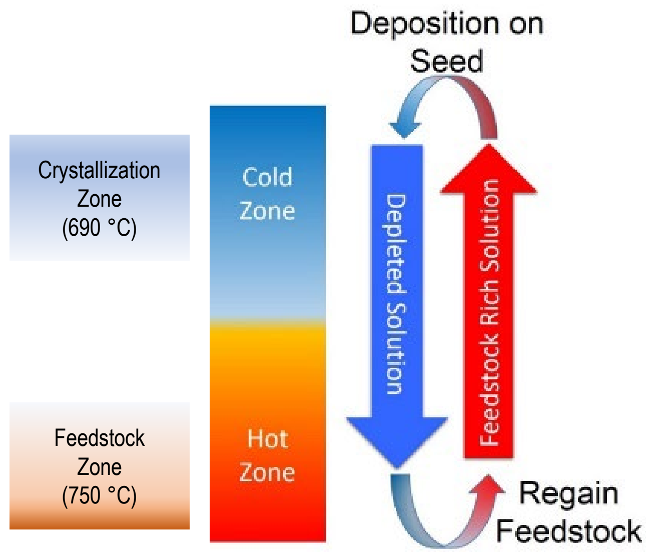
Thorium Dioxide Crystal Structure and Synthesis



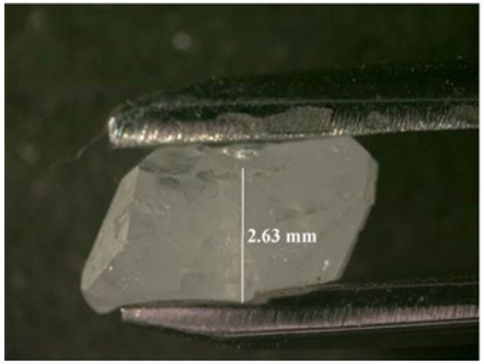
Physical Properties

Elastic Constants[§]	C_{11} = 367 GPa C_{12} = 106 GPa C_{44} = 79.7 GPa
Density[¶]	10.01 g/cm^3
Melting Point[‡]	3,350° C
Boiling Point[‡]	4,400° C
Molar Mass	264.037 g/mol
Refractive Index (n) [¶]	2.105 (at 589.3 nm) 2.135 (at 435.8 nm)

Hydrothermal Crystal Synthesis Method



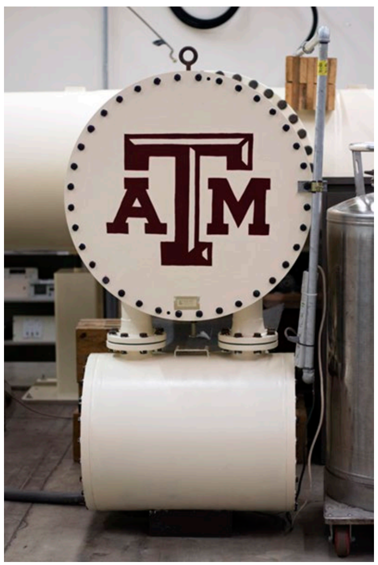
- Spontaneous nucleation performed in silver ampoules
- ThO_2 feedstock powder placed in silver ampoule
- 6M CsF mineralizer solution used to dissolve feedstock and transport it to crystallization zone
- Water counter-pressure applied to silver ampoule
- Reaction conditions maintained for 10 days



J. Castilow, et al., Mater. Res. Soc. Symp. Proc. Vol. 1576 (2013)

§ P. Macedo, W. Capps, J. Wachtmann/ J. Amer. Ceram. Soc. (1964)
¶ J. Belle, R.M. Berman, DOE/NE—0060, (1984)
‡ W.M.Haynes, Handbook of Chemistry and Physics (92nd ed.). (2011)

Ion Irradiation at Texas A&M Accelerator Laboratory



Sample ID	Avg. dpa in Plateau Region (0 – 12.5 μm)	H^+ ion energy	H^+ ion irradiation fluence (ions/cm^2)	Irradiation Temperature
ThO2-SN-8f	Pristine	N/A	N/A	N/A
ThO2-SN-8h	0.01 dpa	2 MeV	1.73×10^{17}	Room Temperature
ThO2-SN-8j	0.05 dpa	2 MeV	8.635×10^{17}	Room Temperature
ThO2-SN-8c	0.1 dpa	2 MeV	1.73×10^{18}	Room Temperature

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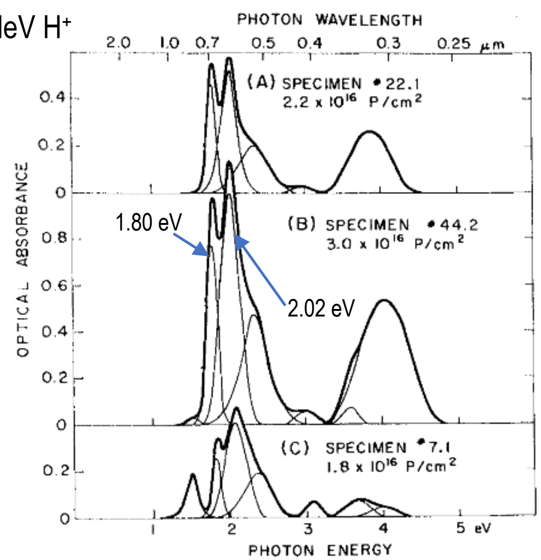
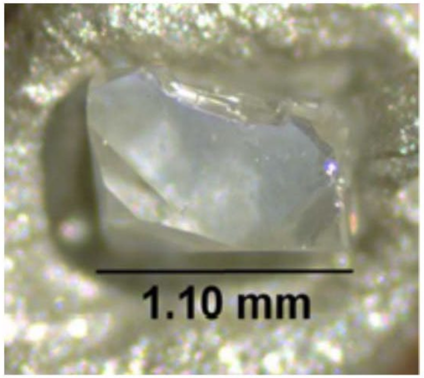
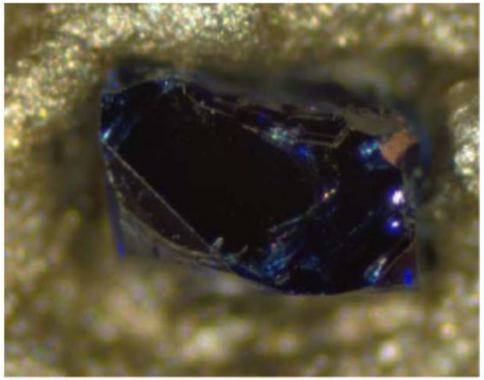
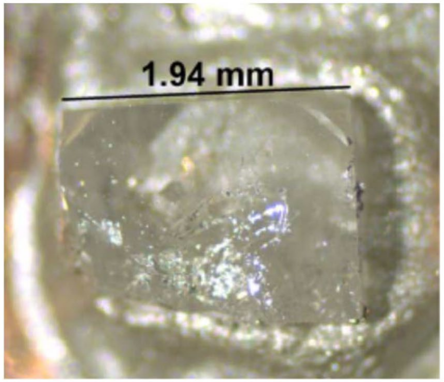
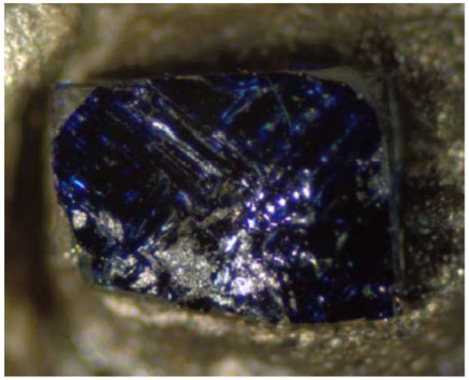
Changes in Optical Absorption after Ion Irradiation

- Proton irradiation changed thorium dioxide a colorless crystal to a dark blue appearance
- Change in optical absorption due to electrons trapped in point defects that create states within the bandgap

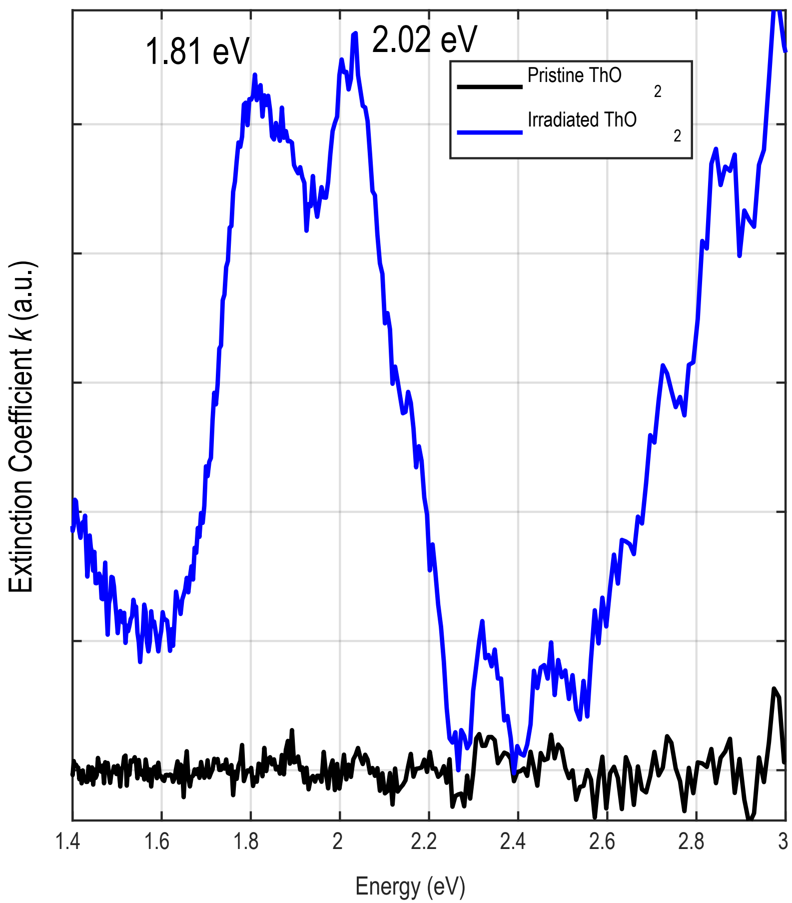
18 MeV H^+



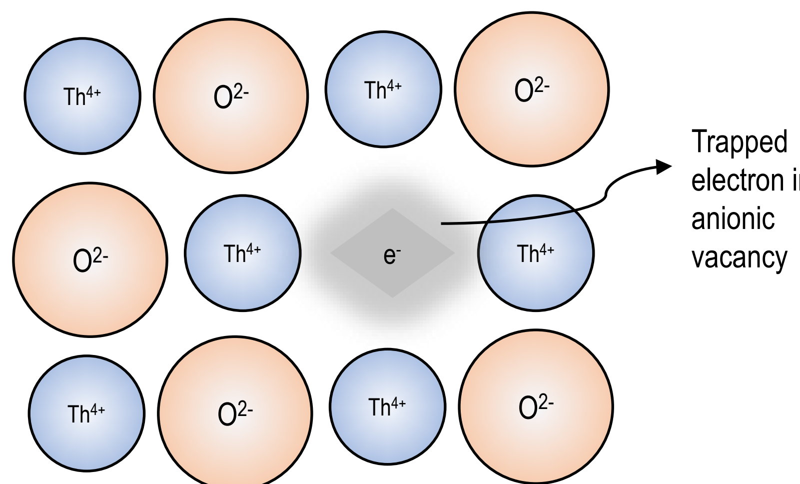
B.G. Childs, P.J. Harvey, and J.B. Hallett, Color centers and point defects in irradiated thoria. J. Am. Cer. Soc., 53(8), 431-435 (1970).

	Pre-Irradiation	Post-Irradiation
ThO2-SN-8h <u>0.01 dpa</u> Avg. Plateau Displacement Damage		
ThO2-SN-8j <u>0.05 dpa</u> Avg. Plateau Displacement Damage		

Characterization of Microstructural Damage via Optical Spectroscopy

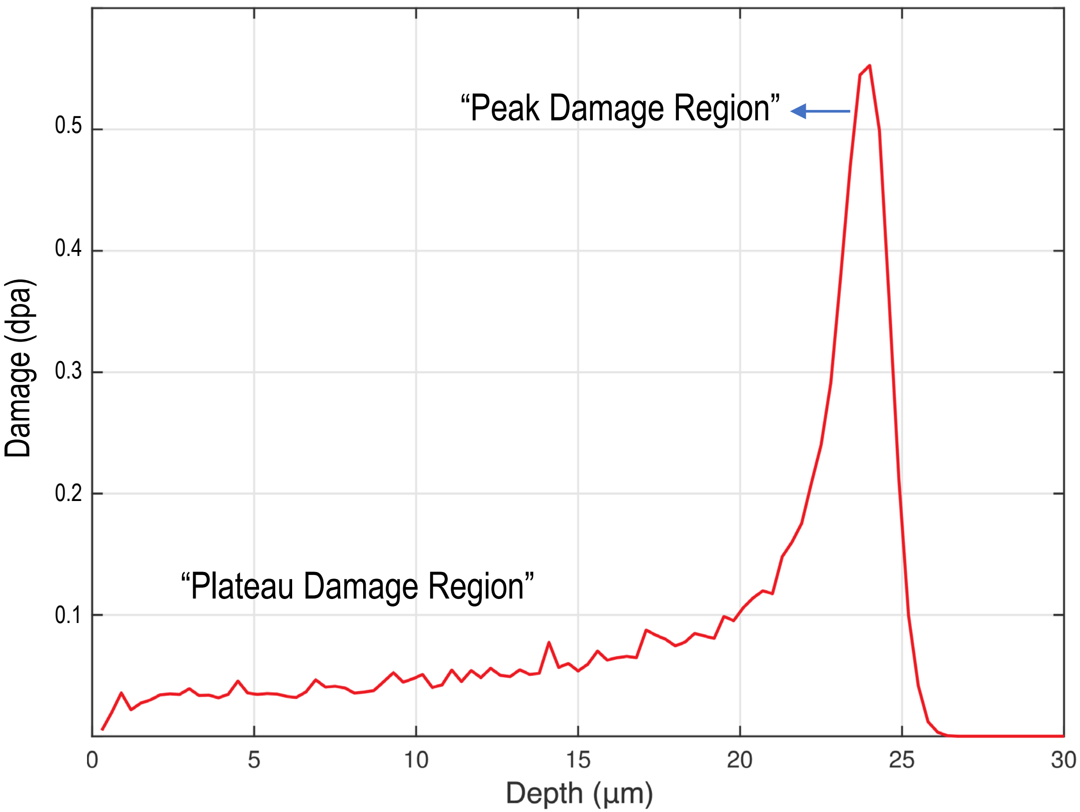


- Optical Absorption/ emission could be influenced by electronic transitions from intervalence bands created by irradiation-induced defects, or by charged defects
- Intensities of absorbed/ emitted spectra may be used to correlate with displacement damage levels



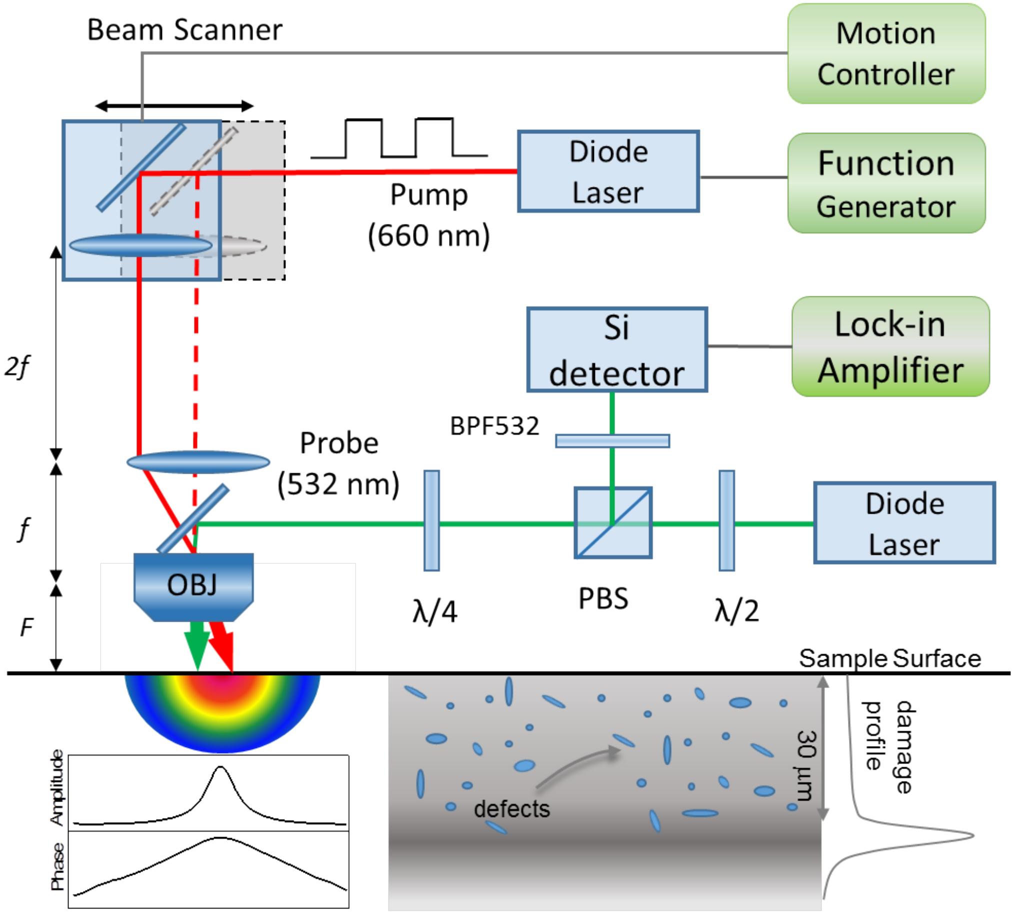
Damage Profile using SRIM

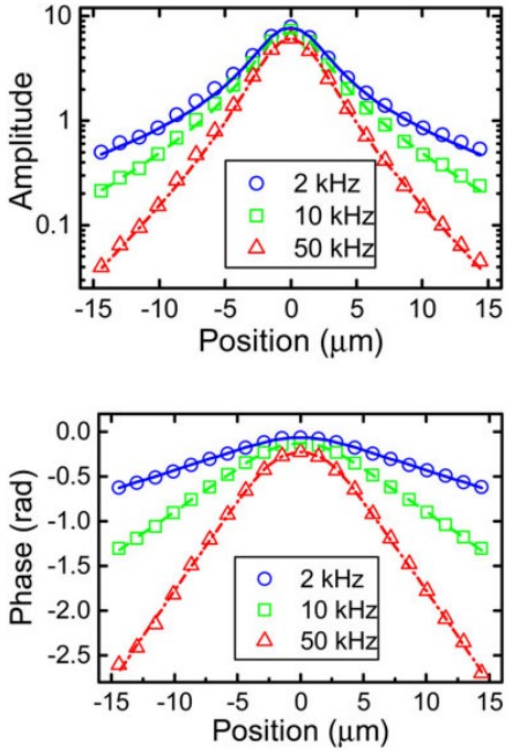
- 2 MeV H^+ ions at normal incidence
- Total fluence: 8.65 x 10^{17} ions/cm^2
- Kinchin-Pease Method



R.E. Stoller, M.B. Toloczko, G.S. Was, A.G. Certain, S. Dwaraknath, and F.A. Garner: On the use of SRIM for computing radiation damage exposure. Nucl. Instrum. Methods Phys. Res., Sect. B. 310, 75 (2013).

Laser-based Modulated Thermoreflectance Method





Thermal Wave Diffusion Depth

$$L_D = \sqrt{\alpha/\pi f_0}$$

M. Khafizov, V. Chauhan, Y. Wang, F. Riyad, N. Hang, D.H. Hurley, Investigation of thermal transport in composites and ion beam irradiated materials for nuclear energy applications. J. Mater. Res., 32(1), 204-216 (2017).

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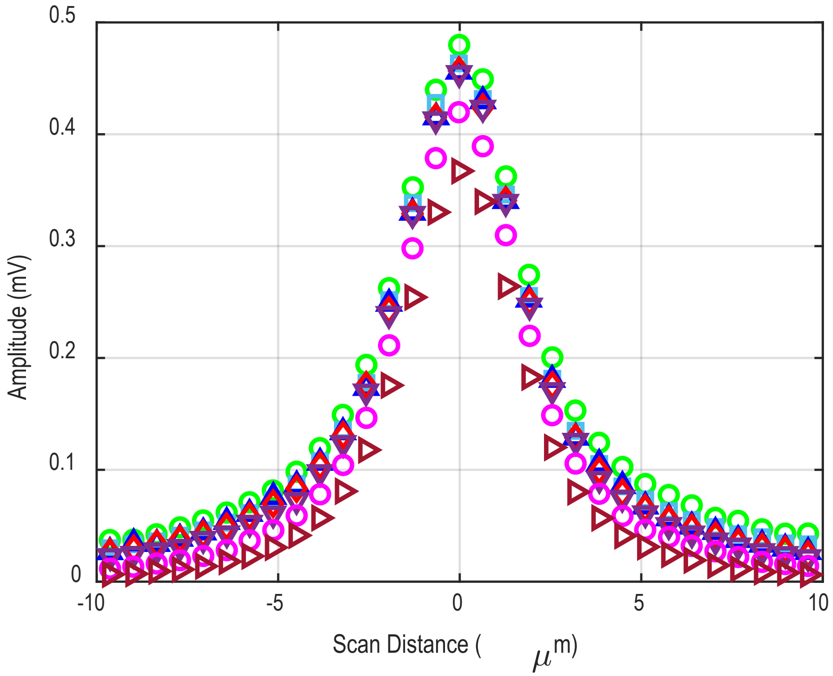
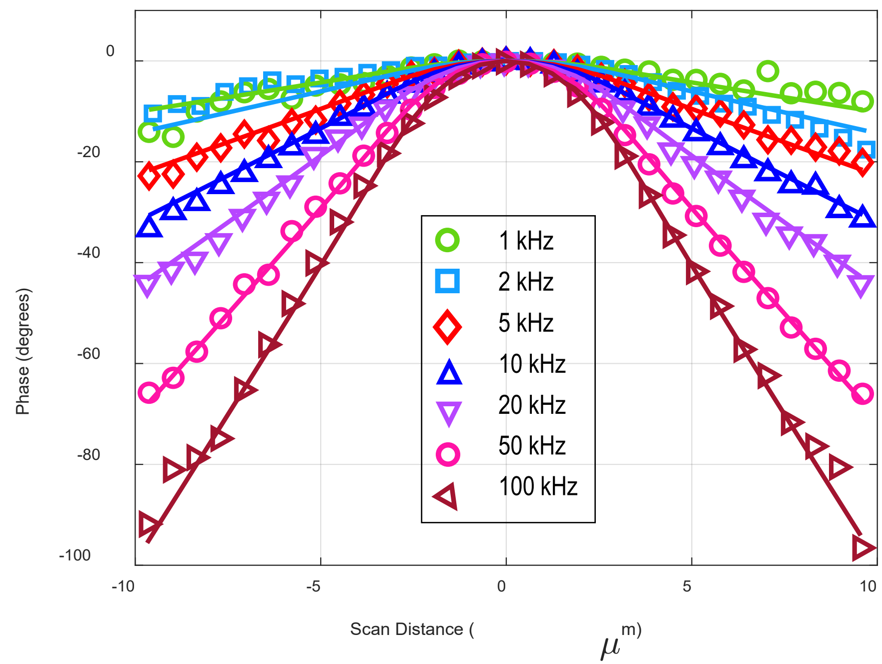
Thermal Wave Amplitude & Phase Profiles in Pristine ThO_2

Room Temperature Measurements

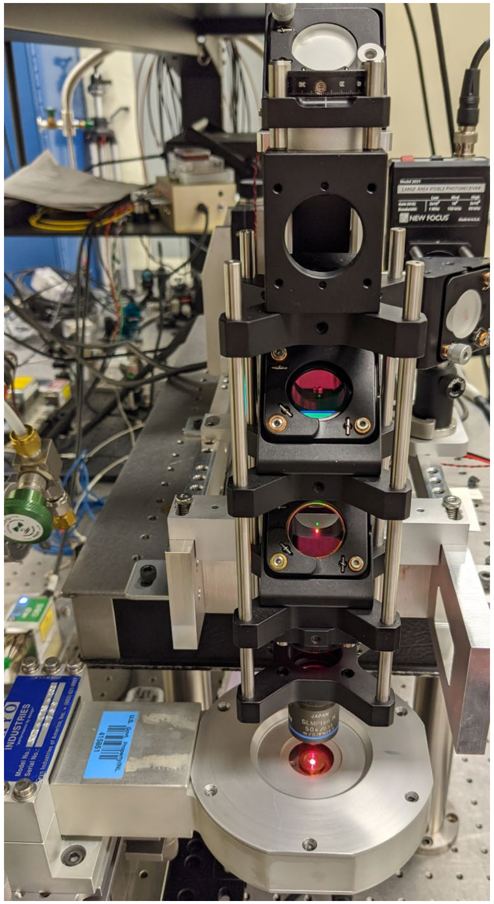


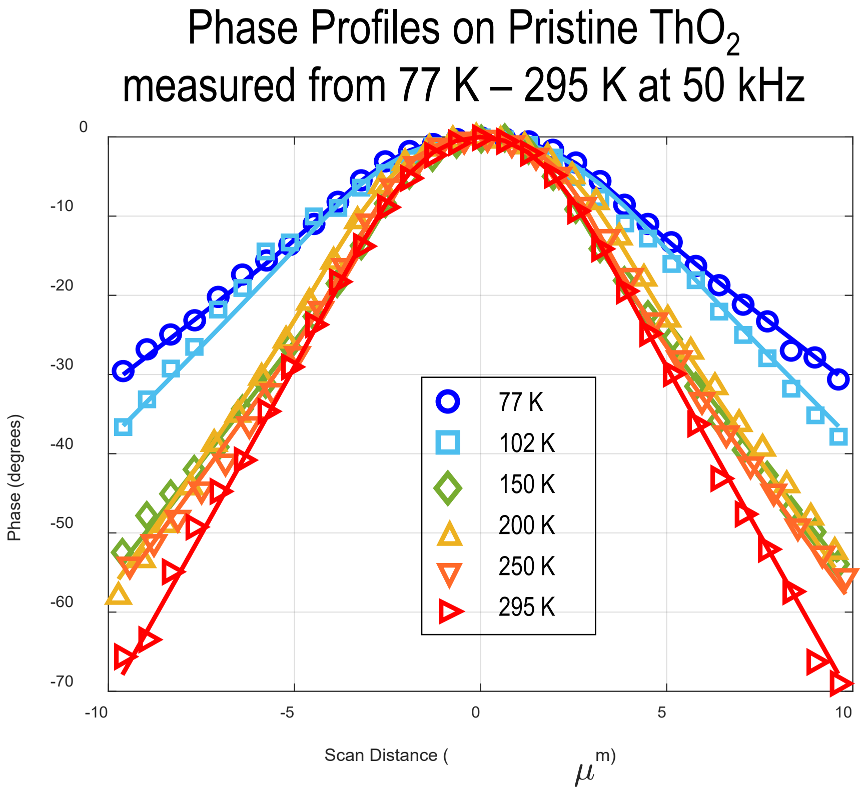


Fitted room temperature thermal diffusivity of pristine ThO_2: $\alpha = 7.66 \pm 0.7\ mm^2/s$

Using room temperature density $\rho = 10.01\ g/cm^3$ and heat capacity $C_p = 229.1$ J/(kg K), the thermal conductivity of pristine ThO_2 is: $\kappa = 17.56$ W/(m K)

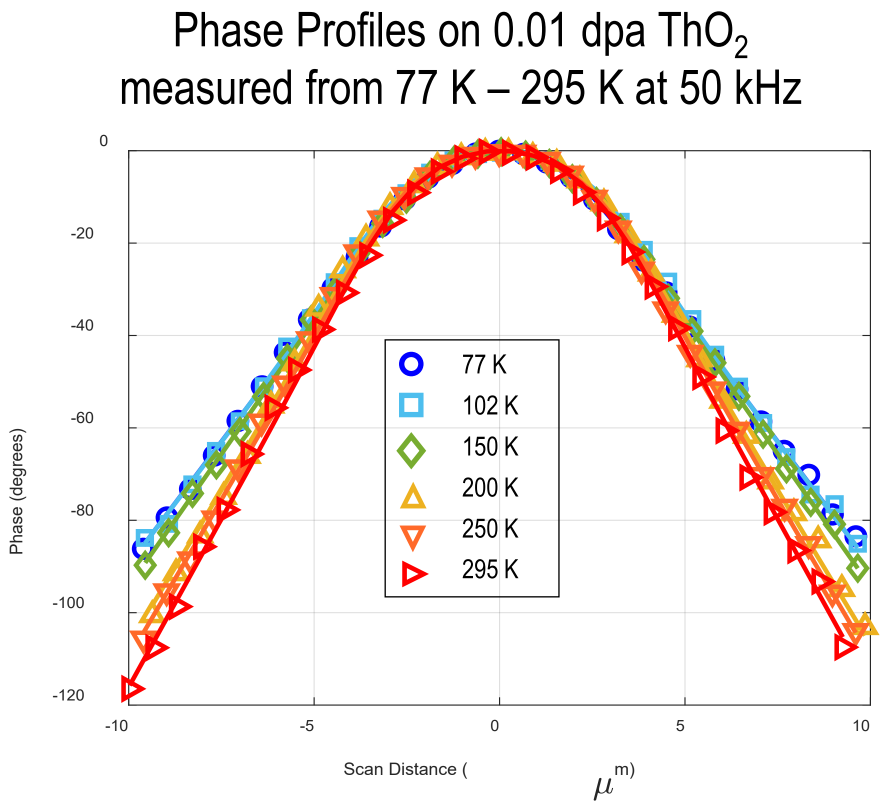
Temperature-dependent Phase Profiles in Pristine ThO_2

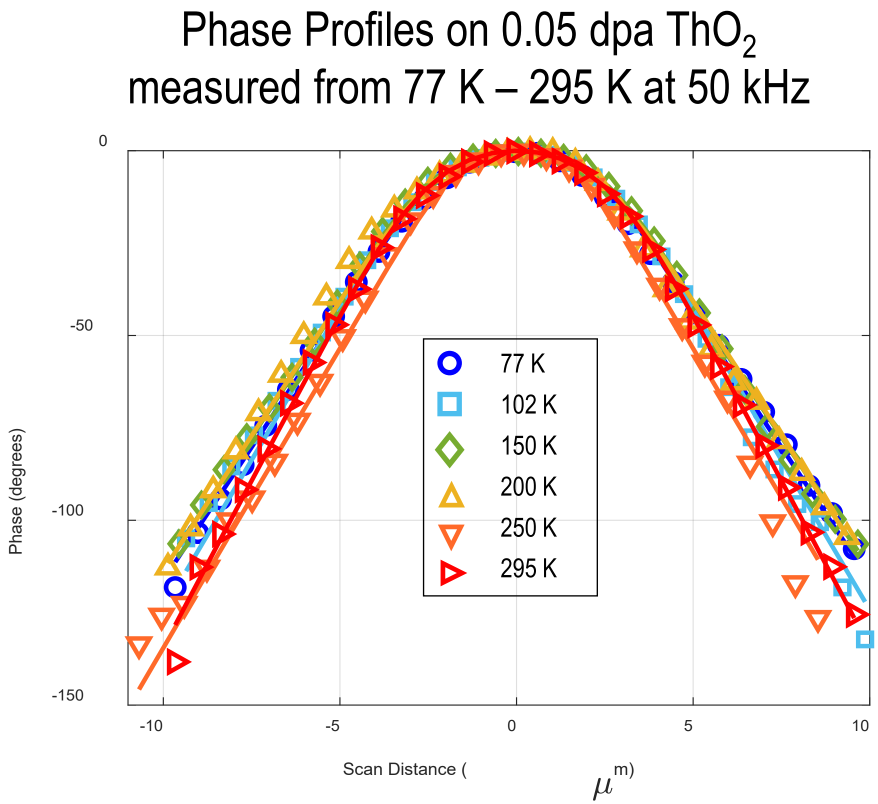




- Phase profiles become more steep with increasing temperature
- Indicates change in thermal diffusivity with temperature

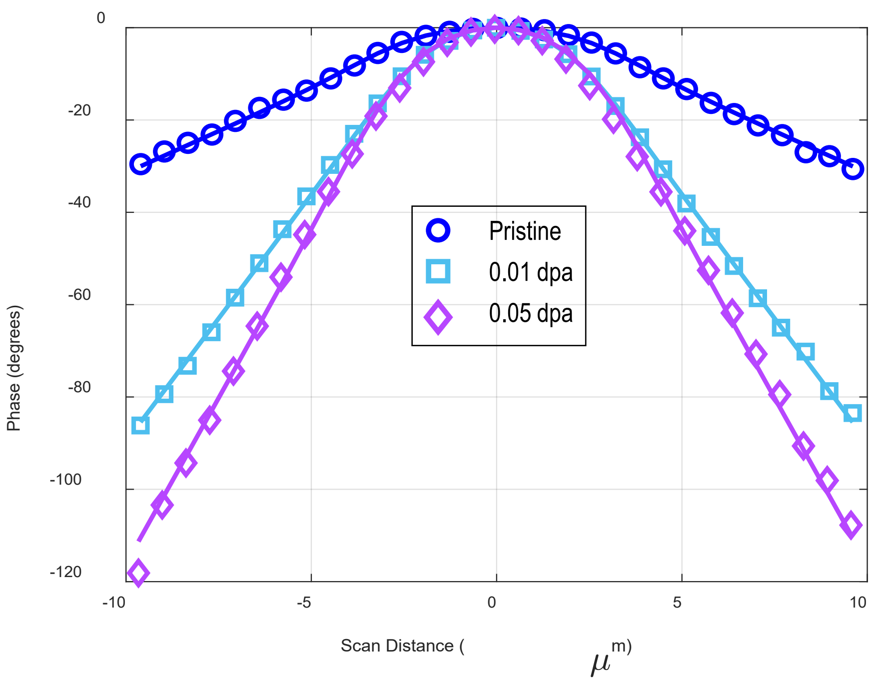
Temperature-dependent Phase Profiles in Irradiated ThO_2



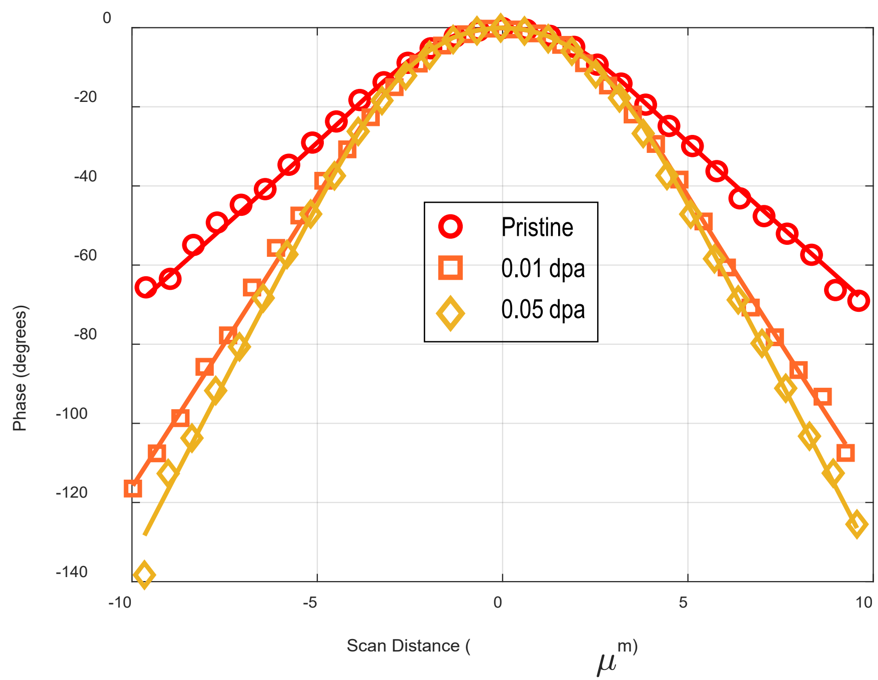


Damage Dose Dependence of Thermal Wave Phase Profiles

Phase Profiles for different damage doses measured at 50 kHz and 77 K

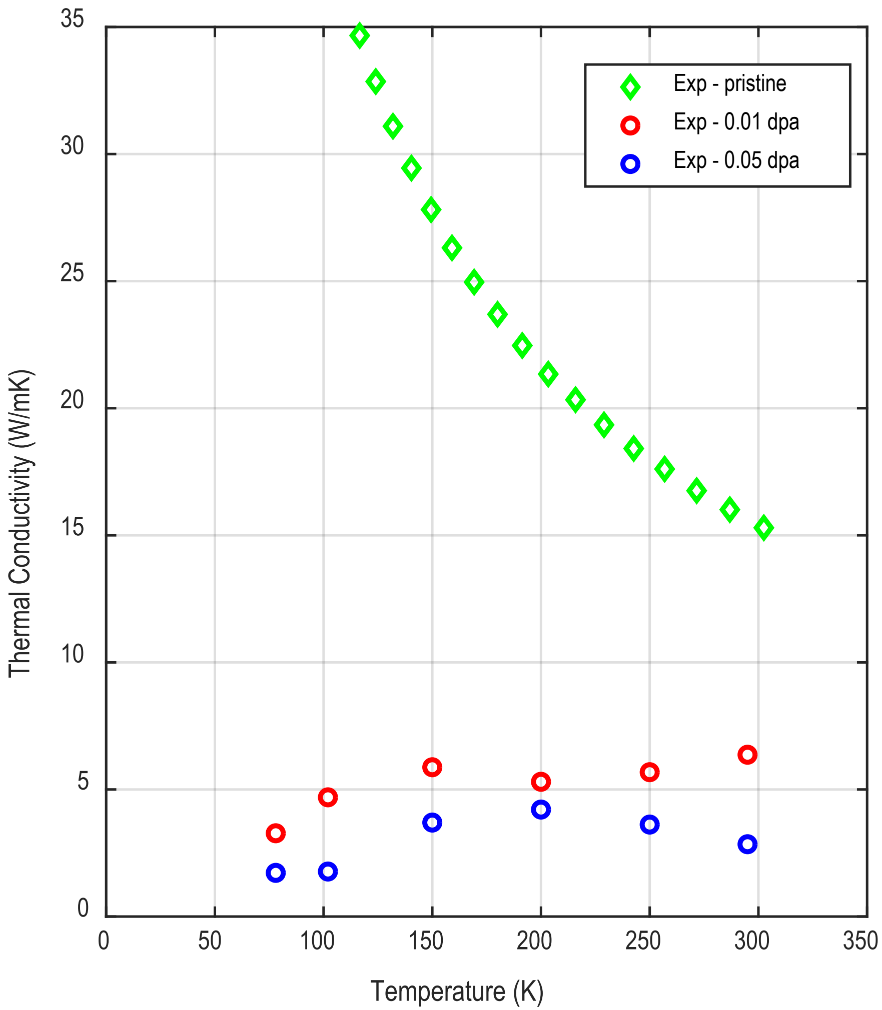


Phase Profiles for different damage doses measured at 50 kHz and 295 K



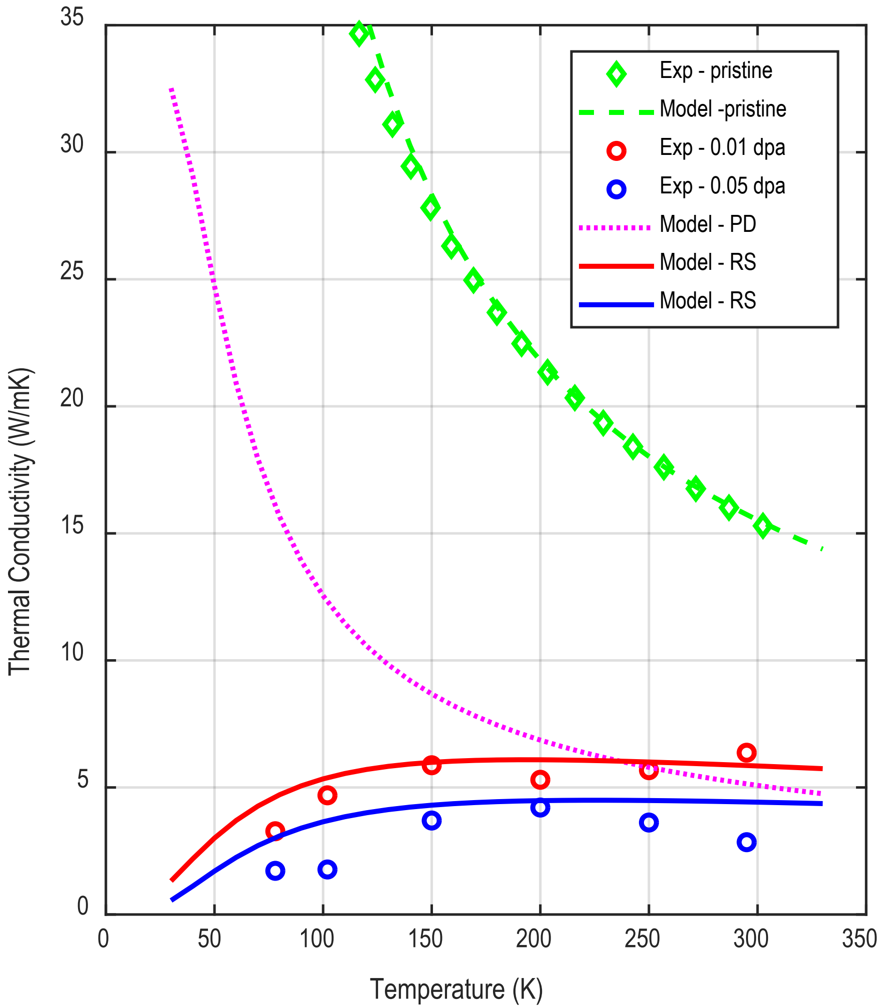
- Phase profiles become steeper with increasing displacement damage
- Change in slope more pronounced at low temperatures

Temperature- and Dose-Dependent Thermal Conductivity



- Reduction in thermal conductivity with temperature in pristine ThO_2 – three-phonon processes mediated by lattice anharmonicity
- Strong influence of irradiation-induced defects - ~60% & ~80% reduction in 0.01 dpa and 0.05 dpa, respectively at room temperature.
- Low temperature dependence in irradiated samples, with slight decrease at lower temperature

Temperature-Dependent Thermal Conductivity using Boltzmann Transport Formalism



BTE with relaxation time approximation:

$$\kappa_0 = \frac{k_B}{2\pi^2 v}\int_0^{\omega_D} \frac{C\omega^2 d\omega}{\tau^{-1}}, \quad C(\omega) = \frac{\hbar^2\omega^2 e^{\hbar\omega/k_BT}}{k_BT^2\left(e^{\hbar\omega/k_BT}-1\right)^2}$$

Phonon scattering rate τ^{-1} due to different processes is given by:

$$\tau_{anh}^{-1}(\omega) = B\omega^2 T$$

Lattice anharmonicity

$$\tau_{pd}^{-1}(\omega) = A\omega^4 + B\omega^2 T$$

Isolated point defects

$$\tau_{rs}^{-1}(\omega) = \frac{D}{(\omega-\omega_0)^2 + \Delta\omega^2} + B\omega^2 T$$

Resonant scattering of phonons from quasi-local impurity modes produced by F-centers

- Point defects in irradiated ThO_2 trap electrons and holes that result in resonant phonon scattering
- Existence of shallow hole and deep electrons states is suggested by DFT. Latter is confirmed by optical absorption and photoluminescence measurements

R. O. Pohl, Influence of F centers on the lattice thermal conductivity in LiF. Physical Review, 118(6), 1499 (1960).

Summary & Conclusions

- Investigated the influence of microstructural defects induced by irradiating single crystal ThO_2 samples with 2 MeV H^+ ions at room temperature
- Irradiation-induced optical absorption peaks suggest formation of F-center defects in crystal lattice
- Spatially-resolved thermal transport measurements performed on the length-scale of microstructural heterogeneity (within the damage layer) using a modulated thermoreflectance approach
- Irradiation-induced damage strongly affects thermal diffusivity/ conductivity – ~83% reduction from pristine to 0.05 dpa at 295 K
- BTE model with scattering rates for different processes shows that resonant scattering from strain fields associated with F-centers
- Future outlook:
  - DFT modeling of electronic transitions will be compared with optical absorption ellipsometry measurements

TETI

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