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Impact of Irradiation-induced Lattice Defects and Dopants on Thermal Transport in Oxide Nuclear Fuels

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Changing the World's Energy Future

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Idaho National Laboratory

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TETI — Center for Thermal Energy Transport under Irradiation

U.S. DEPARTMENT OF ENERGY — Office of Science

Thermal Transport in Ceramic Oxide Nuclear Fuels

- Transport of thermal energy liberated from fissile atoms underlies the physics basis for electricity generation in nuclear power plants
- Actinide oxides (UO_2, ThO_2, and $U_xTh_{1-x}O_2$) have garnered considerable attention owing to their use as ***nuclear fuels*** *in commercial and next-generation reactors*
- A complete atomistic-to-fuel scale understanding of thermal transport in actinide oxides remains a ***grand challenge*** due to complexities associated with accurately treating *electron correlation* in UO_2. ThO_2 is a model fuel material for studying thermal transport without the complexities associated with electron correlation effects.
- Doping with U-atoms ($U_xTh_{1-x}O_2$) enables systematic study of the effect of *5f* electrons on thermal transport in actinide oxide fuels

Impact of Microstructure on Fuel Performance

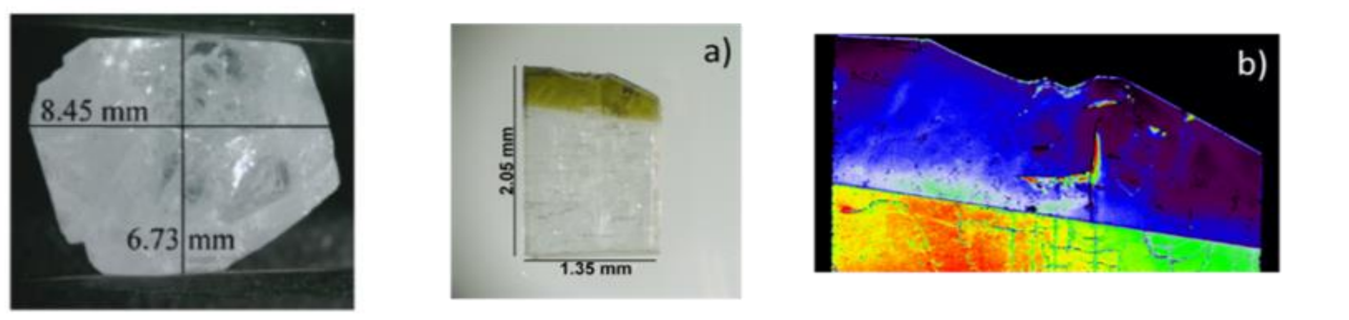
- The performance of ceramic oxide nuclear fuels is directly tied to their thermal conductivity, which in turn, is dictated by the fuel microstructure.
- Under coupled extremes of temperature and radiation fields, the microstructure can rapidly evolve, and lead to the formation of ***atomic level*** as well as extended length-scale ***structural defects.***
- Microstructural defects introduce lattice distortions that act as scattering sites for phonons and can drastically alter ***thermal*** properties.
- Comprehensive understanding of the effect of radiation-induced lattice defects on phonon-mediated thermal transport in oxide nuclear fuels is directly tied to reactor efficiency and safety

Characterizing Early-Stage, Small-scale Lattice Defects

- Characterizing statistically-significant populations of atomic-scale defects is challenging even with ultra-high resolution electron microscopy
- This has motivated the use of ***indirect approaches*** such as optical, photoluminescence and Raman spectroscopy, as well as X-ray diffraction and spatially-resolved laser-based mesoscale measurements of thermal and elastic to quantify the presence of ***lattice point defects*** and ***small-scale defect clusters.***
- When coupled with conventional characterization tools such as electron microscopy, indirect tools can provide vital information needed to accurately model defect evolution

Hydrothermal synthesis of high-quality ThO_2 and $U_xTh_{1-x}O_2$ single crystals with (001) surface orientation

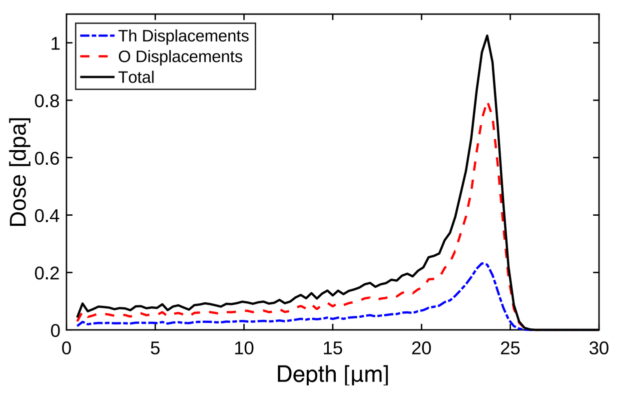
ThO_2 single crystal / U-doped ThO_2 single crystal



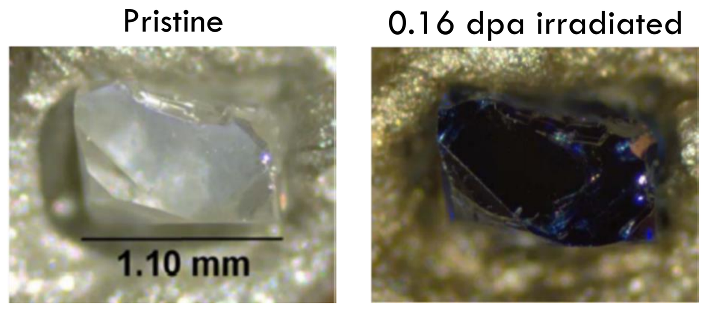
Top-down microscope images of hydrothermally-grown ThO_2 single crystal (left) and $U_xTh_{1-x}O_2$ layer (pale green) on a ThO_2 single seed crystal (clear section) (center). Raman map of T_{2g} intensity of the fluorite structure was used to determine regions with homogeneous U-doping

Seeding lattice defects in ThO_2 via bombardment with energetic protons

SRIM-calculated lattice displacement damage dose profile

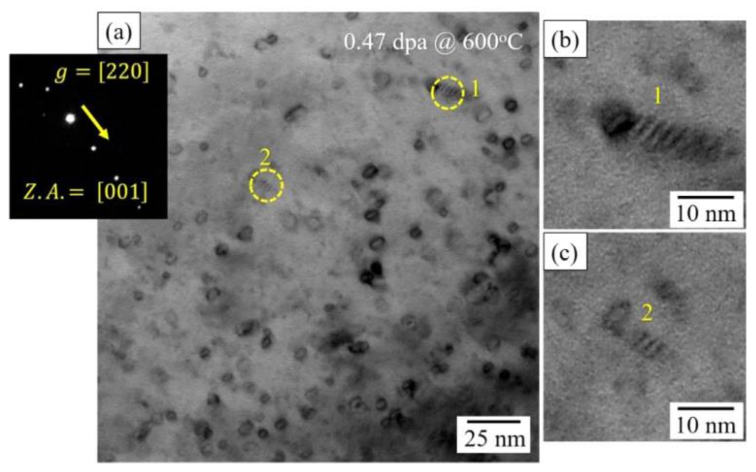


- Irradiation at 20°C and 600°C
- 'Plateau' damage dose ranged from 0.001 dpa to 0.79 dpa



Colorless and transparent pristine thoria before irradiation developed a deep blue color following proton irradiation

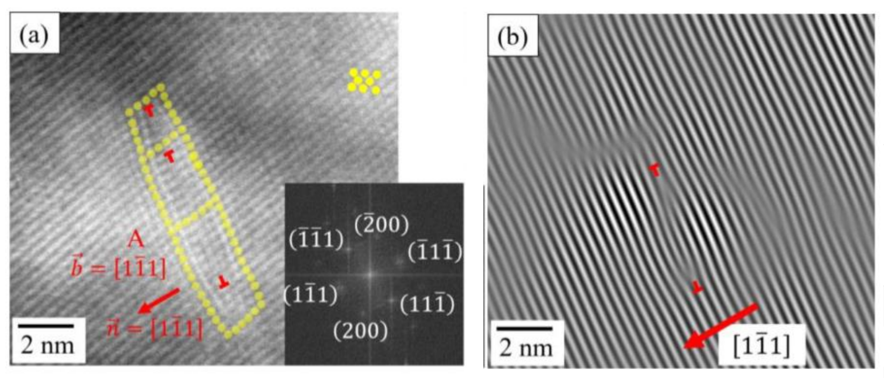
Characterization of faulted dislocation loops in irradiated ThO_2 using transmission electron microscopy (TEM)



(a) Kinematic bright field TEM image of ThO_2 with g = [220] strongly excited near [001] zone after 0.47 dpa proton irradiation at 600°C; (b), (c) enlarged images at location 1 and 2, respectively.

Burgers vector analysis using $\vec{g}.\vec{b} = 0$ invisibility criterion.

Loops	$\vec{g}$ [02$\bar{2}$]	[11$\bar{1}$]	[200]	[1$\bar{1}$1]	[$\bar{2}$20]	[020]	[220]	$\vec{b}$
A	V	V	V	V	V	V	I	[1$\bar{1}$1]
B	V	V	V	V	I	V	V	[$\bar{1}\bar{1}$1]
C	I	V	V	V	V	V	I	[11$\bar{1}$]



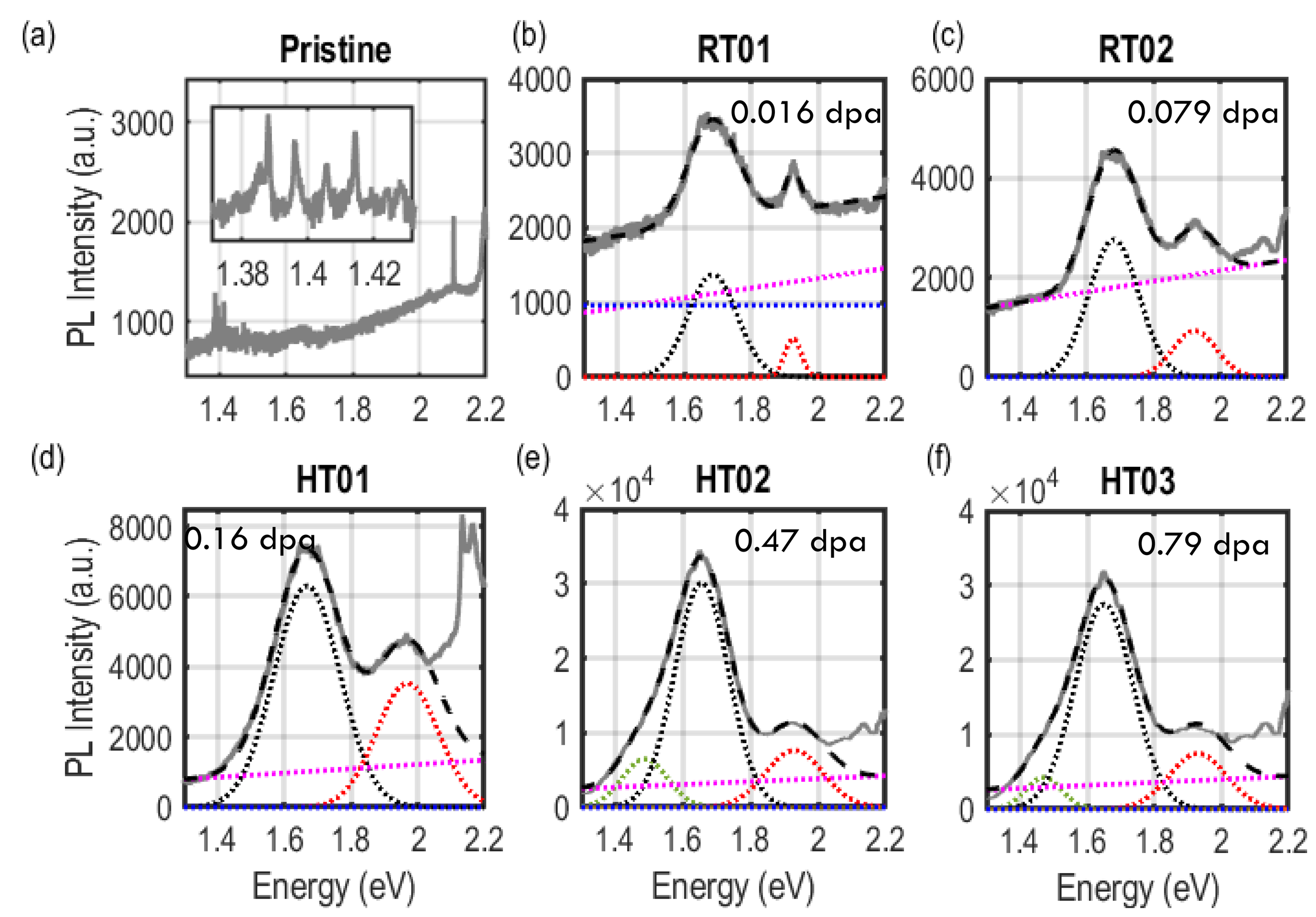
(a) On-zone atomic resolution STEM-HAADF image of a dislocation loop obtained using [011] zone with the FFT pattern at inset; (b) corresponding inverse FFT image from the (1$\bar{1}$1) and ($\bar{1}$1$\bar{1}$) spots.

Average size and density of dislocation loops from TEM image analysis

Irradio-tion Temp.	Dose (dpa)	Loop Radius (nm)	Loop Density (x 10^{22} m^{-3})
600°C	0.01	1.32 ± 0.41	2.35 ± 0.35
600°C	0.03	1.53 ± 0.59	3.13 ± 0.08
600°C	0.1	1.93 ± 0.98	3.21 ± 0.13
600°C	0.16	2.2 ± 0.4	2.6 ± 0.5
600°C	0.47	3.1 ± 0.9	3.5 ± 0.7
600°C	0.79	2.6 ± 0.6	5.2 ± 0.8

Photoluminescence (PL) measurements in proton-irradiated thoria (ThO_2) single crystals

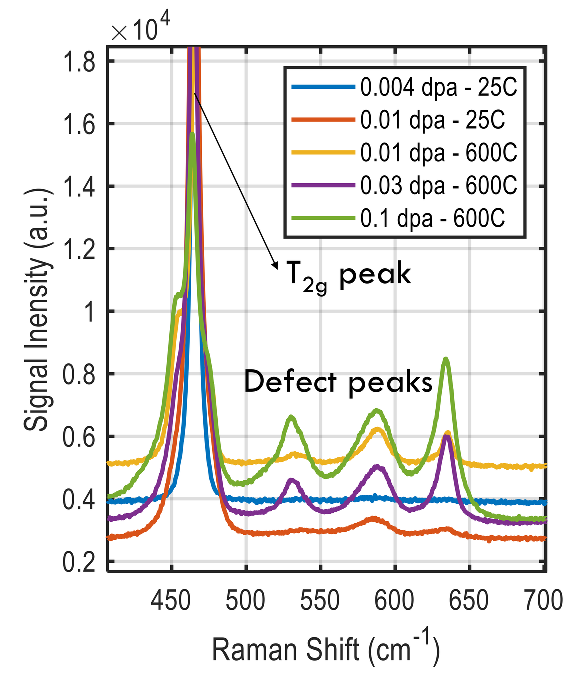
Dose-dependent photoluminescence emission intensity



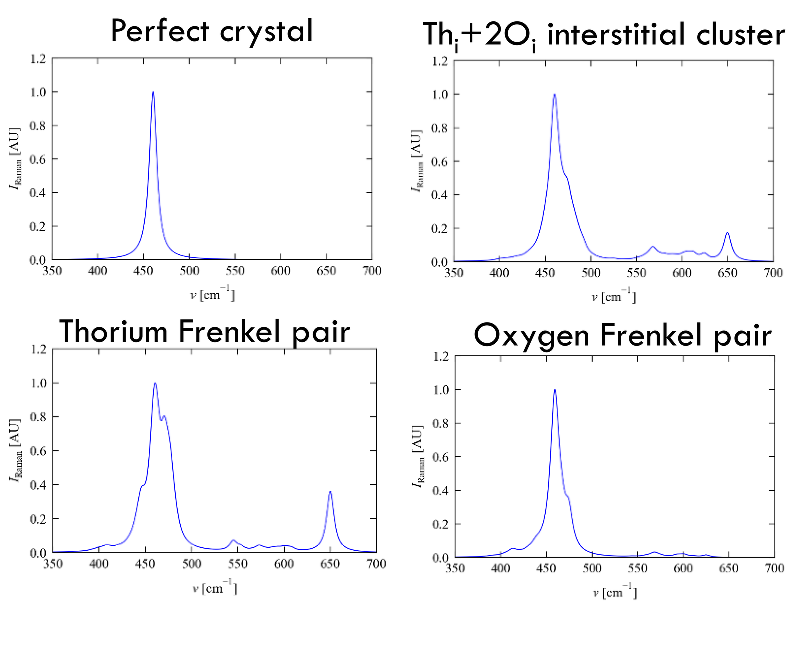
- Photoluminescence (PL) spectra reveal two broad peaks at ~1.67 eV and ~1.92 eV, whose intensity increases with irradiation dose, and is attributed to electronic transitions following photoexcitation of electrons trapped in neutral or charged oxygen vacancies (***'F-centers'***).

Raman spectroscopy for characterizing small-scale defect clusters in proton-irradiated thoria (ThO_2) single crystals

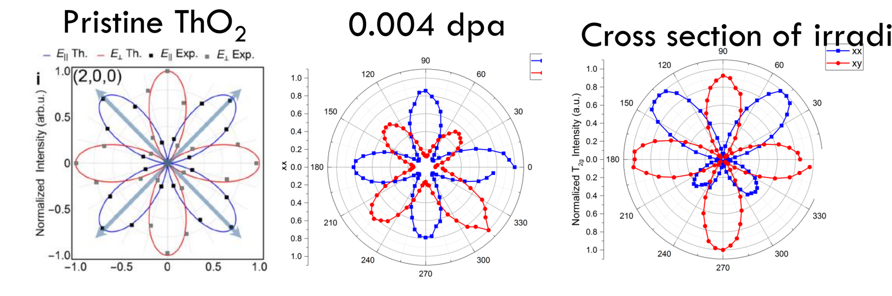
Measured 'defect peaks' in top-down Raman spectra



Density Functional Theory predictions of Raman spectra



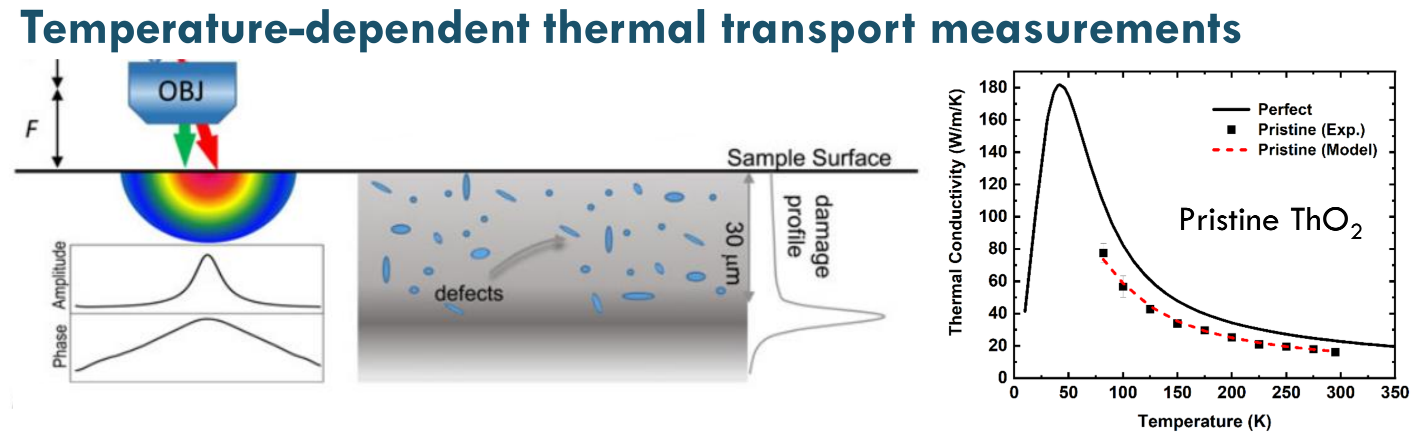
Polarized rotational Raman – Intensity of T_{2g} peak



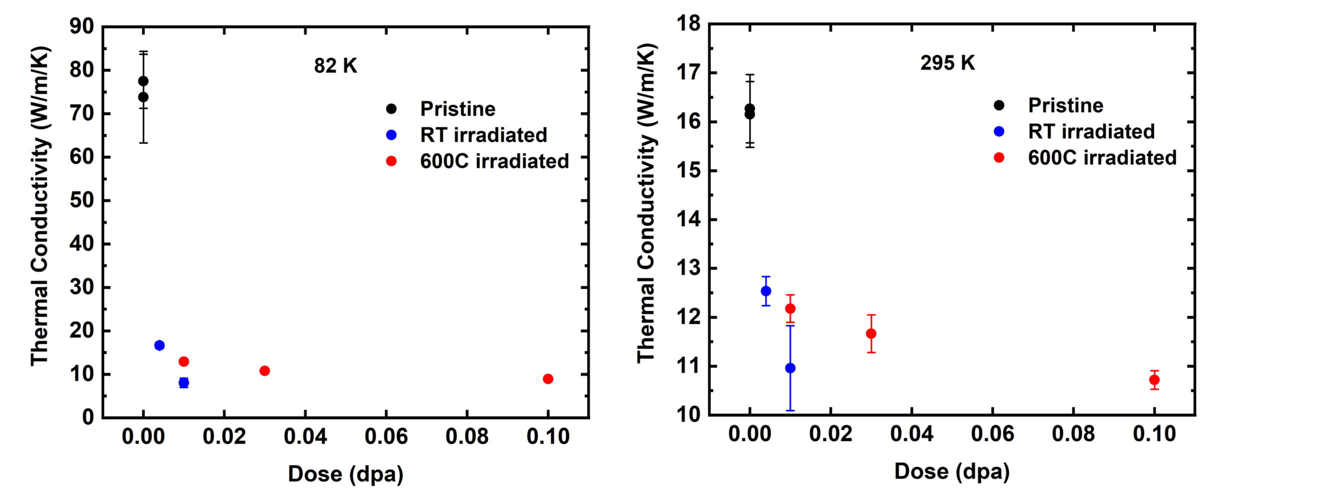
- Measured intensity of fluorite T_{2g} peak in good agreement with theory
- Distortion of T_{2g} intensity from pristine in irradiated ThO_2 crystal indicates a possible loss of symmetry (i.e., Jahn-Teller distortion).

Mesoscale thermal transport measurements in the irradiated region using modulated thermoreflectance

Temperature-dependent thermal transport measurements



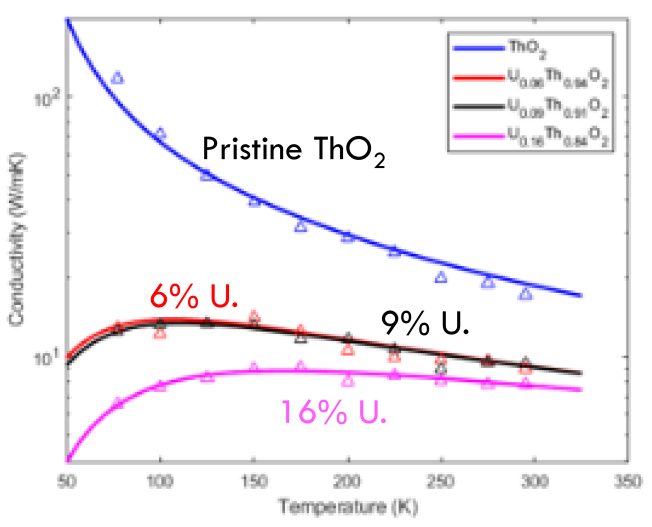
Reduction in thermal conductivity with irradiation dose



- Our measurements capture the displacement damage regime where monotonic reduction in thermal conductivity with dose is observed.
- Recovery in thermal conductivity in 600°C irradiated crystals is a result of lower phonon scattering cross section of dislocation loops that form due to the increased mobility of point defects at elevated temperatures that cluster into extended defects.

Light uranium doping in ThO_2 leads to rapid reduction in thermal conductivity

Resonant scattering from 5f electrons introduced by U-doping



- Large reduction in thermal conductivity with low doping levels of U-atoms
- Temperature-dependent measurements of thermal conductivity fitted to a Klemens-Callaway model that considers phonon scattering from point defects as well as *resonant scattering*
- *Phonon scattering rate:*

$$\tau^{-1} = \boldsymbol{B}\,T\exp\left(-\frac{T_D}{3T}\right)\omega^2 + \frac{V_0}{4\pi N v^3}\boldsymbol{\Gamma}\,\omega^4 + \boldsymbol{A_0}\frac{\omega^4 F(T)}{(\omega^2-\omega_0^2)^2};$$

Relevant TETI-supported publications

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- Bawane, K., Liu, X., Yao, T., Khafizov, M., French, A., Mann, J.M., Shao, L., Gan, J., Hurley, D.H. and He, L., 2021. TEM characterization of dislocation loops in proton irradiated single crystal ThO2. Journal of Nuclear Materials, 552, p.152998.
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- Jin, M., Dennett, C.A., Hurley, D.H. and Khafizov, M., 2022. Impact of small defects and dislocation loops on phonon scattering and thermal transport in ThO2. Journal of Nuclear Materials, p.153758.

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