Thermophysical Property Measurements of Indium Iodide Crystals

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Introduction

Indium(I) iodide (InI, indium monoiodide) Applications

- Room temperature γ-ray and X-ray detectors
  - Z number of 51, 2 eV bandgap
- IR optical and acousto-optical material
- Gas sensor
- Photovoltaic material

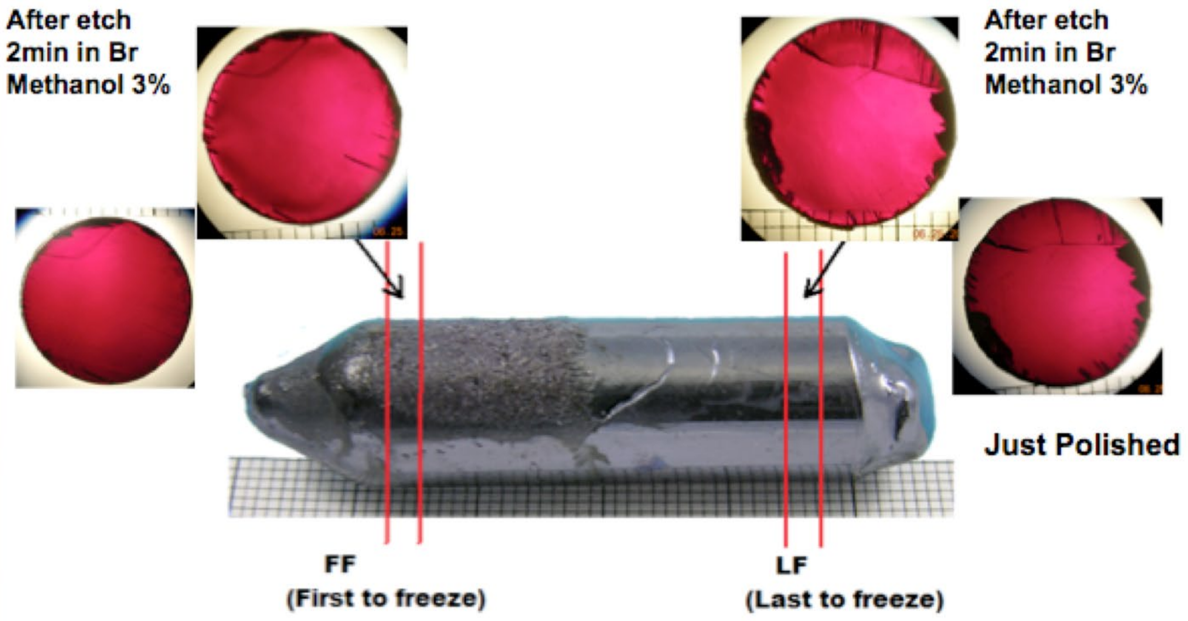
InI Advantages

- Not poisonous (as opposed to HgI_2, PbI_2, $TlPbI_3$)
- No deleterious solid-state phase changes (such as HgI_2)
- No tendency to form polytypes (like PbI_2, BiI_3)
- Has been grown by Bridgman-Stockbarger, Czochralski, and from the vapor

InI crystal grown from the vapor phase

Motivation

- NASA flight project "Detached Melt and Vapor Growth of InI in SUBSA Hardware", PI: Aleks Ostrogorsky.
- 4 melt growth, 2 vapor growth experiments
- Flight experiments conducted 2019-2021 on the International Space Station (ISS)
- Results of flight experiments presented on Monday, August 14, 4:40 in the Reduced gravity crystal growth symposium



InI crystal growth by the Bridgman process and sections used for device fabrication

Thermophysical properties needed for development of accurate numerical models

InI Properties

- 2 eV bandgap
- Orthorhombic, space group *Cmcm* - D_{2h}^{17}
- Density: 5320 Kg m^3
- Melt point: 637 K – 638 K

Thermal expansion measurements

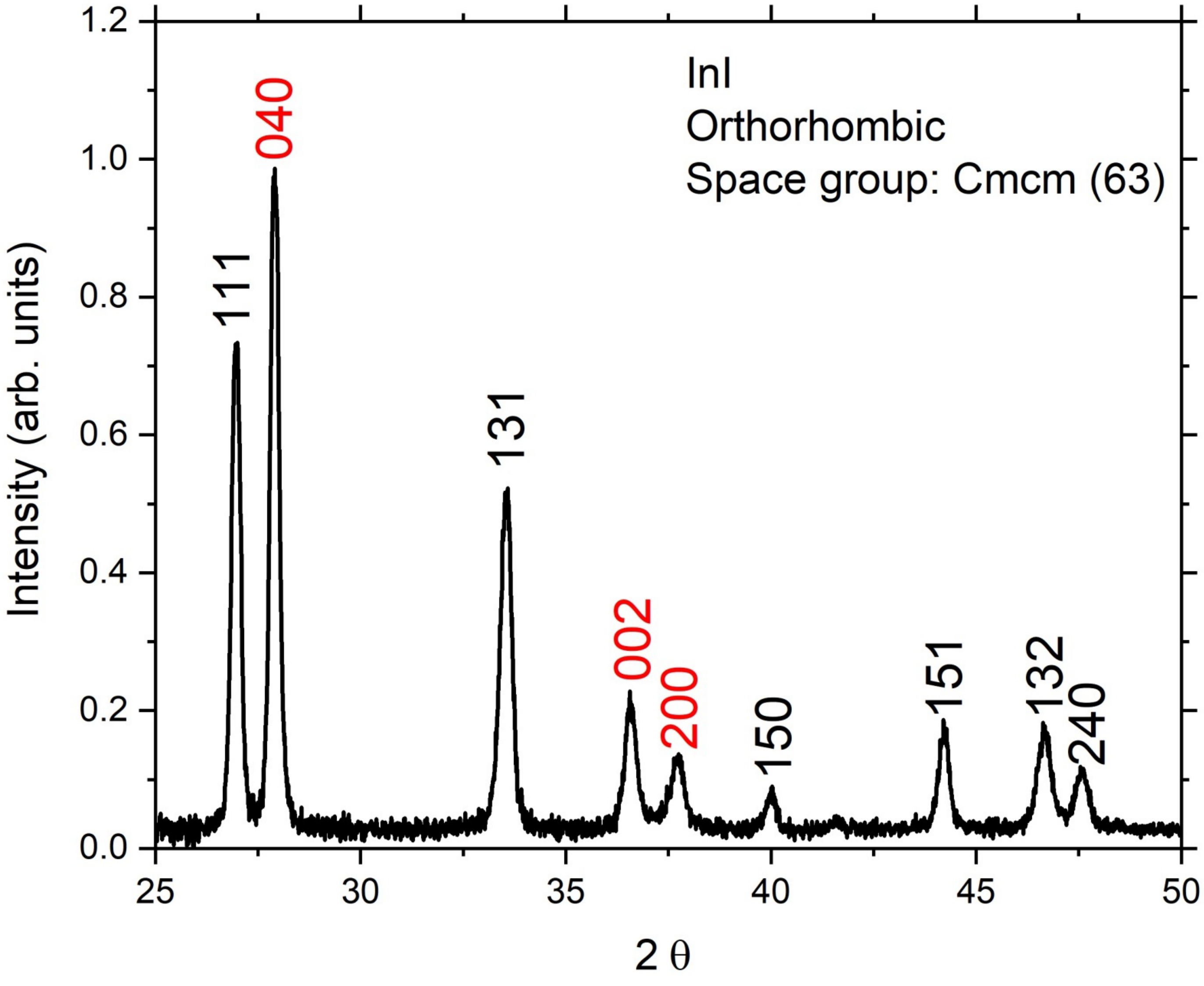
- InI is orthorhombic, with a layer structure (layers are perpendicular to the *b* direction)
- Thermal expansion is a symmetric 2nd rank tensor with the components α_{11}, α_{22} and α_{33} in the *a*, *b*, and *c* directions
- Thermal expansion coefficients determined between 298 K and 498 K
- X-ray powder diffraction measurements of the 200, 040, 080, 002, and 004 diffraction peaks made using a Malvern Panalytical X´Pert Pro diffractometer with a Cu-Kα source and an Anton Paar DHS 1100 heating stage.
- Measurements made by 2 methods:
  - Sample inside a graphite dome in a vacuum (0.4 mbar)
  - Sample covered by Kapton tape in air
- Sample temperature measured by thermocouple at back of sample and by IR thermometer at front of sample
- XRD volumetric expansion measurements compared to capillary measurements

X-ray diffraction

Lattice constants determined from Bragg's Law:

$$2\boldsymbol{d}\sin\theta = \boldsymbol{n}\lambda,$$

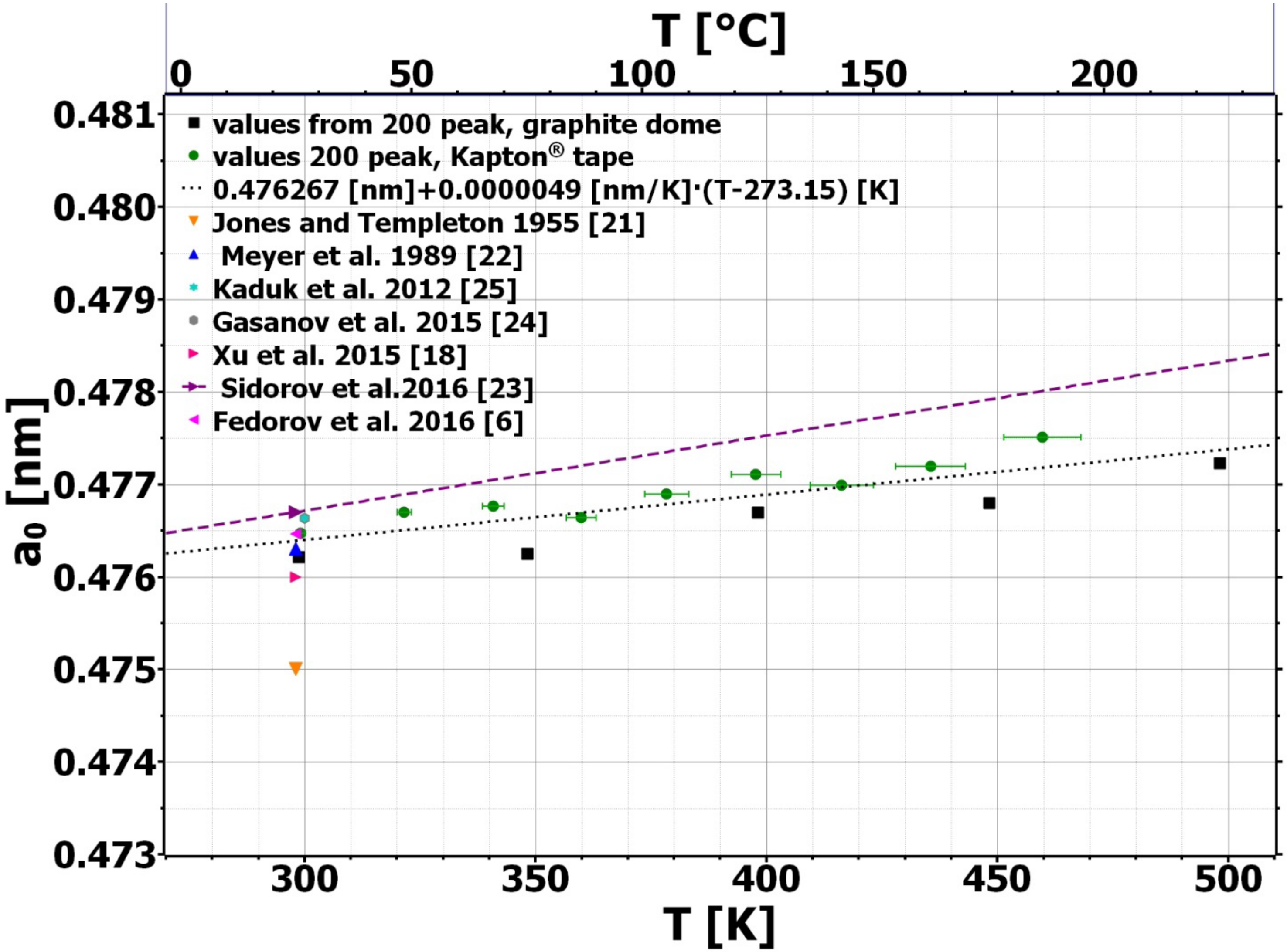
- λ: X-ray wavelength
- ***d***: spacing of crystal layers
- θ: incident angle
- ***n***: integer



Lattice constants a_0 from 200 peaks vs. temperature

a_0 lattice constants determined from position of 200 diffraction peak

Horizontal bars (green data) represent the temperature difference between the heater thermocouple at the back of the sample and the front of the sample measured by an IR thermometer



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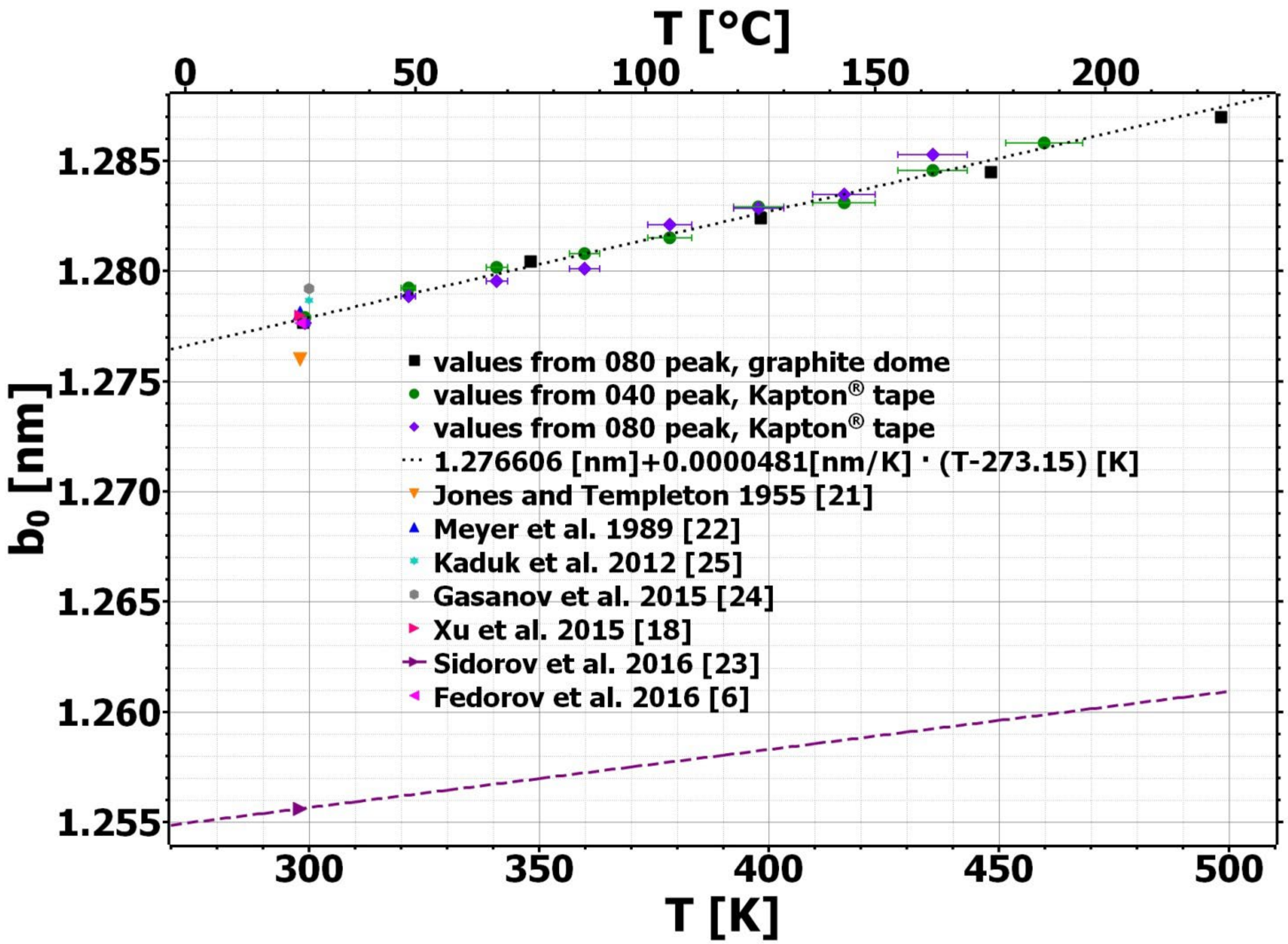
Lattice constants b_0 from 040 and 080 peaks vs. temperature

b_0 lattice constants determined from positions of 040 and 080 diffraction peaks

Horizontal bars (green and purple data) represent the temperature difference between the heater thermocouple at the back of the sample and the front of the sample measured by an IR thermometer



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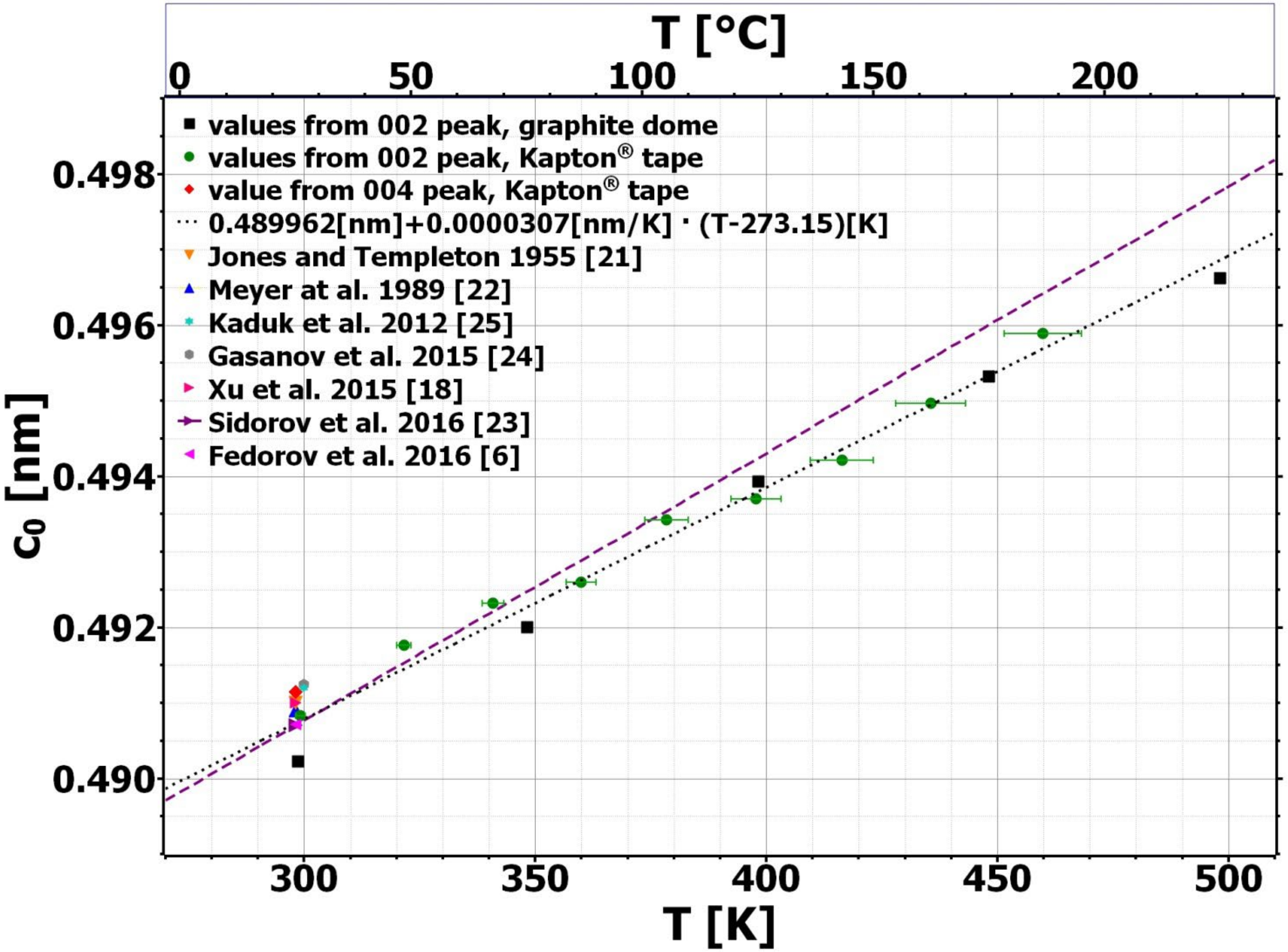
Lattice constants c_0 from 002 and 004 peaks vs. temperature

c_0 lattice constants determined from positions of 002 and 004 diffraction peaks

Horizontal bars (green data) represent the temperature difference between the heater thermocouple at the back of the sample and the front of the sample measured by an IR thermometer



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Thermal expansion coefficient results

XRD Results

Thermal expansion coefficients; 298-498 K [K^{-1}]

$\alpha_{11} = 1.03 \times 10^{-5}$

$\alpha_{22} = 3.77 \times 10^{-5}$

$\alpha_{33} = 6.26 \times 10^{-5}$

$\alpha_{avg} = 3.69 \times 10^{-5}$

$\alpha_{vol} = 1.106 \times 10^{-4}$

Capillary Measurements

- Bridgman growth ampoule
- 10 mm ID
- Melt point (638 K) up to 1000 K
- Observed volume expansion upon melting ($\Delta V_{melt}/V_{solid}$)

Capillary Measurement Results

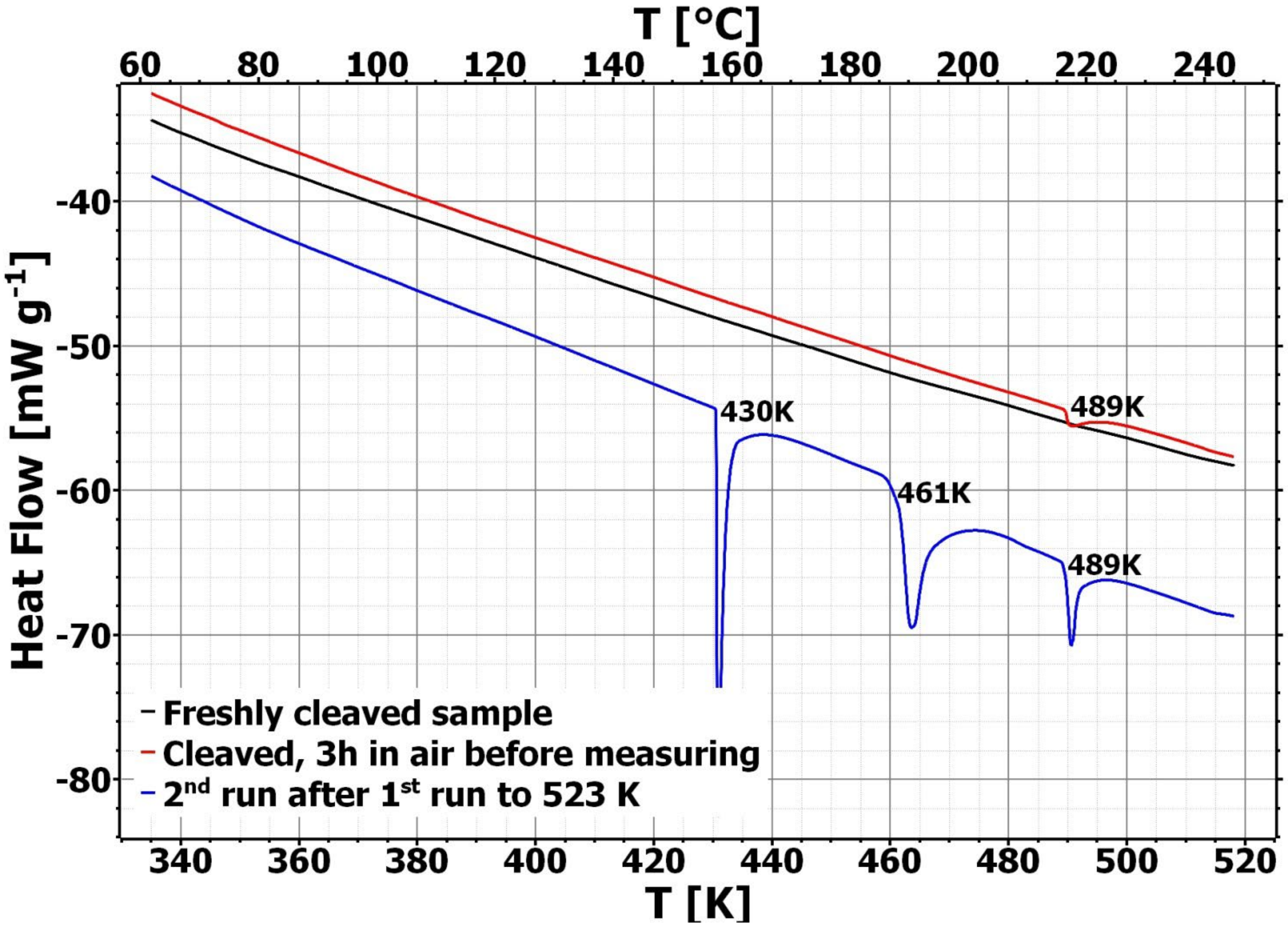
$\alpha_{avg,\ capillary} = 3.35 \times 10^{-4}$ (measured up to the melt point)
(*within 10% of XRD results*)

$\beta = 2.785 \times 10^{-4}$ (volumetric expansion in melt from 638 K to 1000 K)

$\Delta V_{melt}/V_{solid} = 9.57$ %

Specific heat measurements

- Measured by Differential Scanning Calorimetry (DSC) between 335 K and 520 K
- Instrument used was a model DSC Q20 by TA instruments
- Sample masses: 26 mg to 114 mg
- Measurements conducted in flowing argon
- Peaks observed at 430 K, 461 K, and 489 K are attributed to oxygen products after extended sample exposure



Specific heat peaks attributed to oxygen

Peak at 431 K

Possible solid state phase change to InI_2

$$4\,InI + 3\,O_2 \rightleftharpoons 2\,In_2O_3 + 2\,I_2$$

$$4\,InI + 2\,I_2 \rightleftharpoons 2\,In^{+}In^{3+}I_4 = 2\,In_2I_4 = 4\,InI_2$$

Peak at 461 K

Possible solid state phase change to InI_3

$$4\,InI + 3\,O_2 \rightleftharpoons 2\,In_2O_3 + 2\,I_2$$

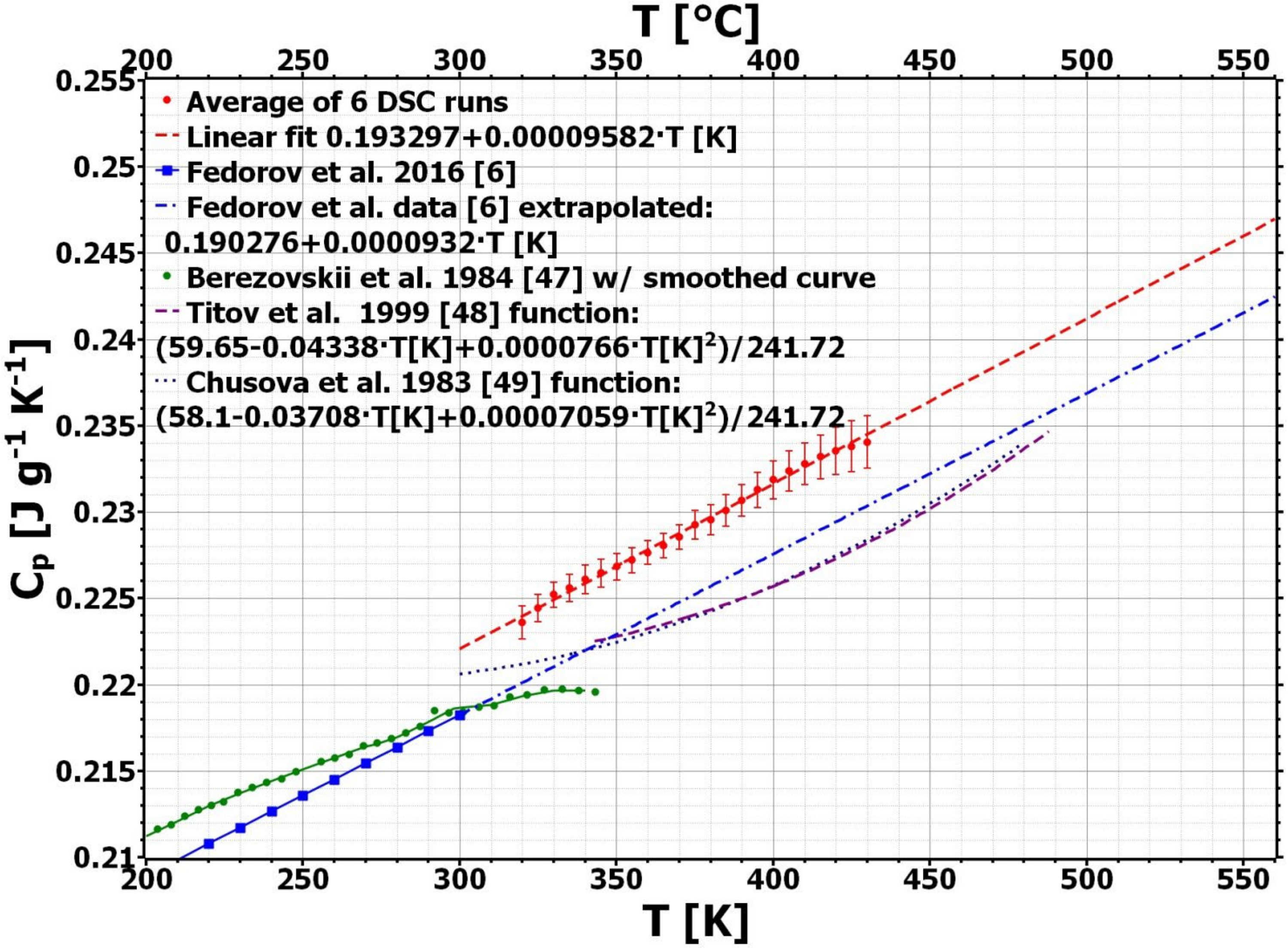
$$2\,InI + 2\,I_2 \rightleftharpoons 2\,InI_3$$

Peak at 489 K

Ascribed to oxidation of InI, likely to $In(OH)_3$, on the surface in humid air

Specific heat data

Measured values (red data) are within 2% of the previous measurements of Federov *et. al*. and Berezovskii *et al*. (blue and green data) at 300 K.



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G. A. Berezovskii, K. S. Sukhovei, T. P. Chusova, I. E. Paukov, *Russ. J. Phys. Chem*. **58** (1984), 1563-1564.

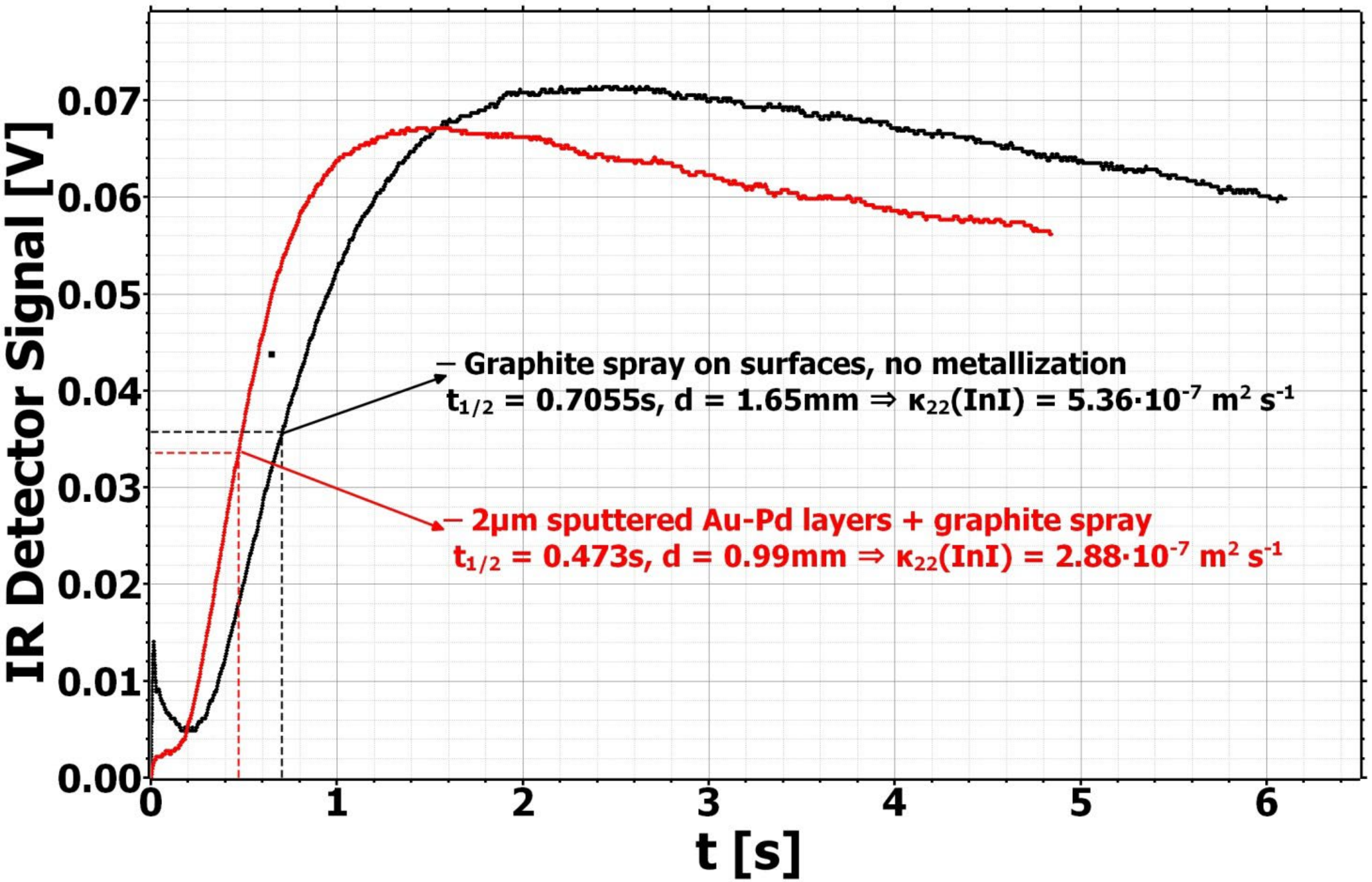
A. Cröll, M. Volz, V. Riabov, A. Ostrogorsky, *Int. J. Thermophysics*,**44** 53 (2023).

Thermal diffusivity and conductivity measurements

- Thermal diffusivity measured in *b* direction (κ_{22}) by Xenon flash method
- Instrument was ANTER (now TA Instruments) Flashline 3050
- Single crystal wafers, grown by Bridgman method, cut parallel to (010) plane
- Wafers sputter-coated with 2 μm of gold-palladium
- Atmosphere: argon
- Power: 600W

$$\kappa = 0.1388 \cdot \frac{d^2}{t_{1/2}}$$

Thermal response curves for InI (010)-oriented samples



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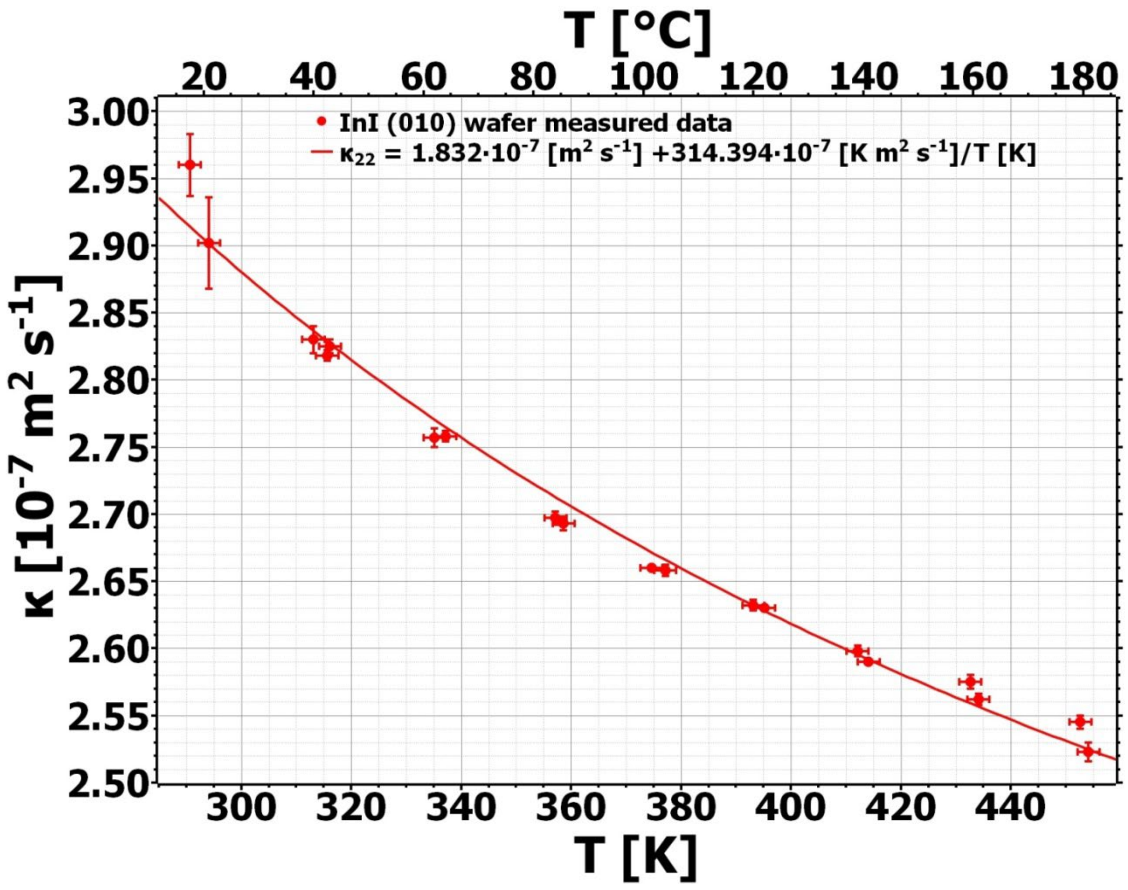
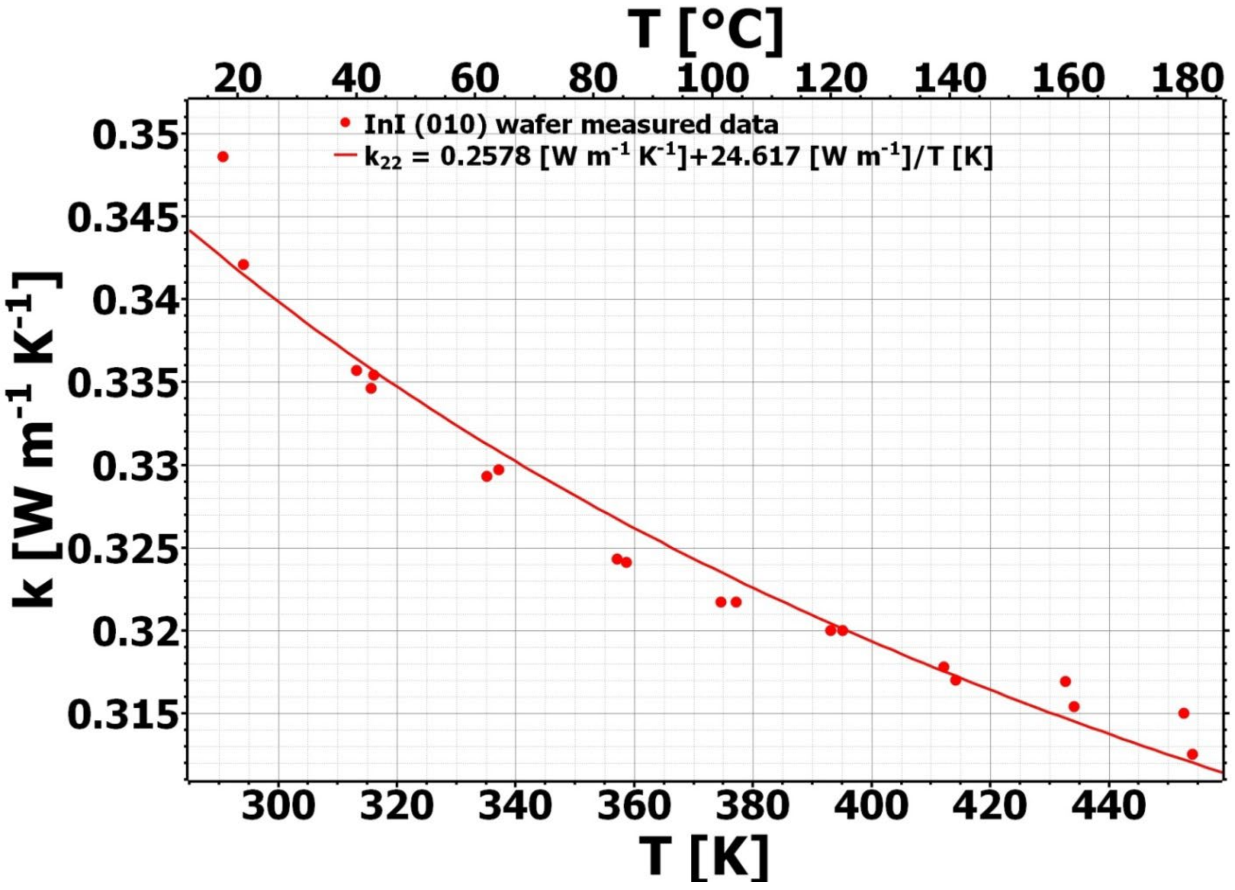
Thermal diffusivity and conductivity results

Thermal diffusivity κ_{22} of InI vs. temperature



Thermal conductivity k_{22} of InI vs. temperature



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Conclusions

- First measurements of thermal expansion coefficients above ambient temperatures
  - α_{11} = 1.03 x 10^{-5} K^{-1}; α_{22} = 3.77 x 10^{-5} K^{-1} ; α_{33} = 6.26 x 10^{-5} K^{-1}
  - Volumetric change upon melting ($\Delta V_{melt}/V_{solid}$ = 9.57 %) must be considered in crystal growth designs in sealed ampoules
- Several proposed and disputed solid-state phase changes in InI do not exist, but rather can be explained by the formation of oxidation products of InI in air.
- C_p measurements showed a linear behavior within the measured temperature range with a value of 0.226 J g^{-1} K^{-1} at 335 K and a slope of $9.582 \cdot 10^{-5}$ J g^{-1} K^{-2}, within 2% of previously reported values.
- The thermal diffusivity κ_{22} in the *b* direction, i.e. the direction of the layer stacking, was determined as $0.288 \cdot 10^{-6}$ m^2 s^{-1} at RT resulting in a thermal conductivity of k_{22} = 0.340 W m^{-1} K^{-1}.
- Lower value of thermal conductivity compared to previous results attributed to relatively high IR transparency of InI and previous lack of metal sample coating.