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ABSTRACT

The infrared-active phonon modes, in single-crystal samples of thorium dioxide (ThO_2) and uranium dioxide (UO_2), were investigated using spectroscopic ellipsometry and compared with density functional theory. Both ThO_2 and UO_2 are found to have one infrared-active phonon mode pair [consisting of one transverse optic (TO) and one associated longitudinal optic (LO) mode], which is responsible for the dominant features in the ellipsometric data. At room temperature, our results for the mode pair's resonant frequencies and broadening parameters are comparable with previous reflectance spectroscopy characterizations and density functional theory predictions. For ThO_2, our ellipsometry and density function theory results both show that the LO mode broadening parameter is larger than the TO mode broadening. This signifies mode anharmonicity, which can be attributed to the intrinsic phonon–phonon interaction. In addition to the main mode pair, a broad low-amplitude impurity-like vibrational mode pair is detected within the reststrahlen band for both ThO_2 and UO_2. Elevated temperature measurements were performed for ThO_2 in order to study the mechanisms by which the phonon parameters evolve with increased heat. The observed change in the TO resonant frequency is in excellent agreement with previous density functional calculations, which only consider volume expansion of the crystal lattice. This suggests that the temperature-dependent change in the TO frequency is primarily due to volume expansion. The change in the main mode pair's broadening parameters is nearly linear within the temperature range of this study, which indicates the intrinsic anharmonic scattering (via cubic anharmonicities) as the main decay mechanism.

I. INTRODUCTION

Due to their importance to nuclear fuel rods, thorium dioxide (ThO_2) and uranium dioxide (UO_2) have been the subject of many scientific investigations.[1,2] Heat transfer, fuel expansion, and related physical properties are of particular interest for fuel rods used in nuclear power plants,[3] where heat must be transferred from the core of the fuel rod to the outer surface. Because ThO_2 and UO_2 have low thermal conductivity, a better microscopic understanding of lattice vibrations may help with designing improved thermal

conductivity properties. This is all the more important because there are conflicting reports on whether the infrared-active (IR) phonon modes significantly contribute to heat transfer.[3,4] ThO_2 may be blended with UO_2 to improve fuel rod efficiencies.[5] Therefore, accurate measurement of the IR-active phonon modes of ThO_2 and UO_2 is a prerequisite for improvement of heat transport properties.

In order to fully characterize the IR-active modes, the complex-valued IR dielectric function $\varepsilon(\omega)$ must be determined from optical measurements. From the spectral behaviors of Re$\{\varepsilon(\omega)\}$ and

Im{$\varepsilon(\omega)$}, physically meaningful parameters can be extracted, such as phonon mode frequency, amplitude, and broadening parameters.[6] So far, only IR reflectance (intensity) spectroscopy has been used to optically characterize IR-active phonon modes in ThO_2 and UO_2.[7–10] This approach relies either on Kramers–Kronig transforms to obtain both Re{$\varepsilon(\omega)$} and Im{$\varepsilon(\omega)$} or relies on best-match model calculations using reflectance data as a model target with a predetermined parameterized model for $\varepsilon(\omega)$. In contrast to reflectance spectroscopy, spectroscopic ellipsometry (SE) measures two quantities (relative amplitude and relative phase shift between s- and p-polarized light after reflection) instead of just one quantity (reflectivity). This additional information allows Re{$\varepsilon(\omega)$} and Im{$\varepsilon(\omega)$} to be extracted independently from each other or can facilitate more accurate best-match model calculations targeting two independent spectra of the ellipsometric data using a predetermined parameterized model.

In this work, we employed IR spectroscopic ellipsometry (IRSE) to extract the dielectric functions of ThO_2 and UO_2. Our approach allows us to characterize their IR phonon modes. We compare our results with density functional theory (DFT) calculations and previous reflectance spectroscopy. The existence of an IR-active impurity-like vibrational mode pair is discussed, as well as its possible anharmonic coupling to other phonon modes. For ThO_2, variable temperature measurements were performed in order to investigate the variation of the phonon mode parameters with the increase in the sample volume at elevated temperatures.

II. THEORY

A. Spectroscopic ellipsometry

Spectroscopic ellipsometry is a measurement technique, which quantifies the change in the polarization of light $\tilde{\rho}$ after interaction with a sample.[6,11,12] In the case of reflection, the change in polarization can be written as

$$\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan(\Psi)e^{i\Delta}, \quad (1)$$

where $\tilde{r}_p$ and $\tilde{r}_s$ are the complex-valued Fresnel reflection coefficients for light polarized parallel (p) and perpendicular (s) to the plane of incidence. At each frequency, a (Ψ, Δ) pair is measured, where Ψ is rotation of the light's polarization state (about its axis of propagation) and Δ is the relative phase shift between the p and s components.

B. Optical model approach

To extract physically meaningful quantities from SE data (Ψ, Δ), an appropriate optical model must be implemented. The optical model used here consists of ambient air, a surface roughness layer, and bulk single-crystal ThO_2 or UO_2, where all constituents meet at plane parallel interfaces. The dielectric function for the surface roughness layer (ε_{rough}) is calculated by averaging the ambient air ($\varepsilon_{air} = 1$) and bulk (ε_{bulk}) dielectric functions, via $\varepsilon_{rough} = (1 + \varepsilon_{bulk})/2$. For the ThO_2 sample, a small silver contact (1% surface area coverage) must be included in the optical model to account for the metallic

reflectivity of a small electric contact, which was furbished onto the sample.

For the temperature and spectral range investigated here, the dominant contributions to $\varepsilon(\omega)$ come from IR-active phonon modes. The optical response of IR-active phonon modes can be modeled using anharmonic broadened Lorentz oscillators,[6] which can be cast into the so-called four-parameter semi-quantum (FPSQ) model.[13] The FPSQ model was motivated by Gervais and Piriou permitting for different phonon decay times of LO and TO modes in crystals with multiple branches of phonon modes. By allowing for independent damping parameters of TO and LO modes, anharmonic effects in multiple (polar) phonon-mode materials can be modeled.[13–16] We used the following model dielectric function to describe ε:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{i=1}^{N} \frac{\omega_{LO,i}^2 - \omega^2 - i\omega\gamma_{LO,i}}{\omega_{TO,i}^2 - \omega^2 - i\omega\gamma_{TO,i}}. \quad (2)$$

Here, index i specifies the phonon mode pair number and N is the total number of mode pairs. Corresponding to every phonon mode pair is a lattice resonance with transverse optic (TO) and longitudinal optic (LO) character. To avoid confusion, we refer to each term in Eq. (2) as "mode pairs" ($i = 1, 2, \ldots$) and their corresponding TO and LO components as just "modes." The parameters ω_{TO}, γ_{TO}, ω_{LO}, γ_{LO}, and ε_∞ are the resonant frequency and broadening of the TO resonance, resonant frequency and broadening of the LO resonance, and high frequency dielectric constant, respectively. Anharmonic phonon interactions may comprise, for example, optical phonon decays into acoustic phonons (by cubic or quartic anharmonicities).[17]
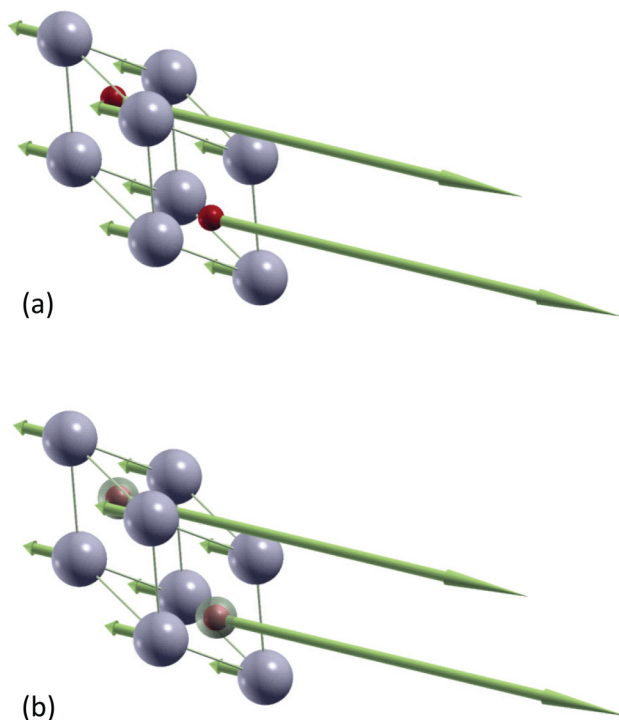
C. Density functional theory calculations

Theoretical calculations of long wavelength active Γ-point phonon frequencies were performed by plane wave density functional theory (DFT) using Quantum ESPRESSO (QE).[18] We used the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)[19] and ultrasoft pseudopotentials from the PSLibrary version 1.0.[20] The valence configuration for thorium used here is [Rn] $5f^{0.5} 6d^{1.5} 7s^2$. The standard fcc fluorite structures were first relaxed to force levels less than 10^{-5} Ry bohr^{-1}. A regular shifted $8 \times 8 \times 8$ Monkhorst–Pack grid was used for sampling of the Brillouin zone.[21] A convergence threshold of 10^{-12} Ry was used to reach self consistency with large electronic cutoffs of 110 Ry for the wavefunction and 1000 Ry for the charge density. The structural relaxation yielded lattice constants of 5.61 Å for ThO_2 and 5.37 Å for UO_2. The fully relaxed cells were used for subsequent DFT phonon calculations.[22]

According to Born and Huang,[24] the lattice dynamic properties in crystals are categorized under different electric field **E** and dielectric displacement **D** conditions.[25] Specifically, **E** = 0 and **D** = 0 define the transverse optical (TO) modes, associated with the dipole moment. **E** $\neq$ 0 but **D** = 0 define the longitudinal optical (LO) modes. The latter can be obtained using Born effective charges calculated by the QE's phonon code.[26] Thus, the parameters of the TO modes are obtained as eigenvalues and eigenvectors of the dynamic matrix without the electric-field effects. The parameters of the LO

modes were obtained by adding so-called non-analytical terms to the dynamic matrix in appropriate crystal directions. In cubic crystals, the tensors of Born effective charges are isotropic, which leads to the same eigenvector being the solution for both the TO and LO mode as shown in Fig. 1. From the point of view of DFT, a low bandgap UO_2 is a semimetal, which makes the calculations of Born effective charges (and any other electric-field-related properties) problematic at this particular level of theory. Therefore, we focused on calculations of phonon properties of ThO_2. It is worth noting, however, that due to the similarity of the crystal structure and the atomic mass, the lattice dynamical properties of ThO_2 are expected to be qualitatively valid for UO_2 as well. In addition to the Γ-point phonons, the dynamical matrices were calculated over a regular $8 \times 8 \times 8$ grid in the first Brillouin zone. They were used to produce real-space interatomic force constants, which in turn were used to plot the complete phonon dispersion along a high symmetry path through the first Brillouin zone, shown in Fig. 2.

The fluorite crystal structure with three atoms in the primitive cell possesses nine phonon modes, three acoustic modes, and six optical modes. The optical phonon modes further divide into three

FIG. 2. The phonon dispersion along a high symmetry path in the Brillouin zone for ThO_2. Labeling of high symmetry points as in Ref. 23.

FIG. 1. Examples of TO (a) and the corresponding LO (b) modes for ThO_2 are shown for the primitive unit cell. Please note that the modes, i.e., the atomic displacement patterns, are exactly the same for these two modes. As described in the text, the TO mode is an eigenvector of the dynamic matrix of interatomic force constants. The LO mode was obtained by adding the non-analytical terms to the dynamic matrix in the direction of the transition dipole of the TO. Semi-transparent isosurfaces of the electron charge density are shown around the oxygen atoms in (b).

triply degenerated IR-active modes and three triply degenerated Raman-active modes. Partial charges on the atoms are quantified in terms of the Born effective-charge tensors, i.e., mixed second-order derivatives with respect to atomic displacement and electric field.[26] For ThO_2, the Born effective-charge tensors are isotropic, and the positive charge on thorium equals the sum of negative charges on both oxygen atoms. Thus, the electric field adds to the restoring force of the mode, which results in the higher frequency of the LO mode, while the eigenvector direction of the dynamic matrix does not change. The LO mode is the highest frequency branch in the phonon dispersion plot (between 500 and 600 cm^{-1}). Figure 1 shows renderings of atomic displacements for TO and LO modes as examples prepared using XCrysDen[27] running under Silicon Graphics Irix 6.5.

In order to verify the general trends of energy and broadening of the TO and LO phonon modes, we performed anharmonic calculations using the D3Q code integrated with the QE distribution.[28–30] Due to the limitations of the code (only implemented for norm-conserving pseudopotentials) for these calculations, we used Hamann–Schlüter–Chiang–Vanderbilt (HSCV)[31] pseudopotentials and the Perdew–Zunger (PZ)[32] local density approximation exchange-correlation functional. The calculations were performed on a regular shifted $6 \times 6 \times 6$ Monkhorst–Pack grid with a large cutoff of 200 Ry for the wavefunction. These parameters were tested and seen to provide convergence of the harmonic phonon frequencies to the level of 0.1 cm^{-1}. The structure was again fully relaxed using the same criteria as for the GGA calculations described above, and the subsequent phonon calculations (second-order harmonic and third order anharmonic) were performed on a regular $8 \times 8 \times 8$ grid in the first Brillouin zone. The resulting anharmonic dynamical matrices were used to compute the intrinsic phonon–phonon interactions, i.e., widths and energies of phonon modes as a function of temperature in the temperature range of 0 K–800 K. The calculations were performed at a small displacement (1×10^{-5} of the reciprocal lattice vector) from the Γ point, on a $200 \times 200 \times 200$ regular
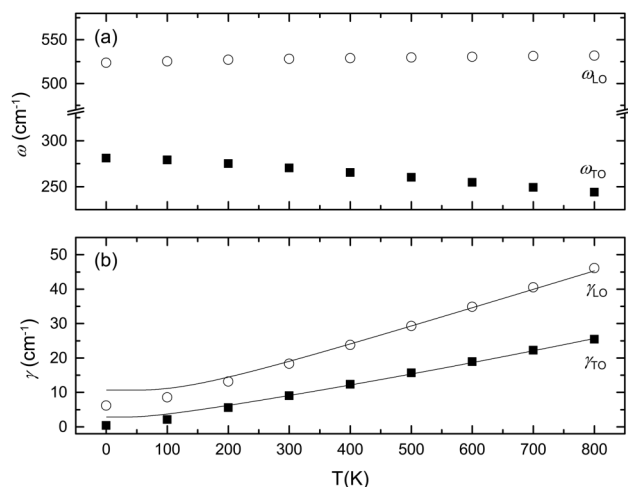
FIG. 3. Results of the anharmonic DFT calculations for energy (a) and broadening parameters (b) of TO and LO phonon modes as a function of temperature. Solid lines in (b) are fits to Eq. (4). The resulting best-match model fit parameters are given in the text.

unshifted grid, and with the Gaussian smearing parameter of $10 \, \text{cm}^{-1}$. The results are presented in Fig. 3.

III. EXPERIMENT

A. Crystal growth

Hydrothermal synthesis was used to grow the ThO_2 and UO_2 single-crystals investigated in this work.[33,34] Similar growth procedures were implemented for both ThO_2 and UO_2. The mineralizer solution for both growth reactions was a 6M cesium fluoride solution (Alfa Aesar, 99.99%). Growth reactions were contained in sealed silver ampoules (99.95% Ag, Refining Systems, Inc.).

For the ThO_2 single-crystal, a ThO_2 seed crystal was suspended in the upper end of the silver ampoule on a silver seed rack. A charge of ThO_2 nutrient/feedstock (99.99% thorium oxide, International Bio-analytical Laboratories) was placed into the lower end of the tube, with a porous silver baffle separating the feedstock and the seed crystal. The silver tubes were then placed in a 250 ml Inconel autoclave. Band heaters were installed on the autoclave to form two temperature zones (feedstock and seed crystal zones). The dissolution zone temperature was $650\,^{\circ}\text{C}$ and the crystallization zone was $600\,^{\circ}\text{C}$. This generated a pressure of 172 MPa. These conditions were maintained for 90 days.

The UO_2 single-crystal was also grown on a ThO_2 seed crystal. The mineralizer solution, temperatures, and pressures were the same for the UO_2 (99.998% uranium oxide, International Bio-analytical Laboratories) growth procedure. However, the growth was only maintained for 50 days.

Both crystals were ground down to the (100) surface (3000 grit, Ultra Tec V5 faceting machine) and polished ($0.10 \, \mu\text{m}$ diamond slurry applied to a ceramic lap). The final dimensions of the ThO_2

single-crystal are $12 \times 6 \times 1 \, \text{mm}^3$. The dimensions of the UO_2 single-crystal are $5 \times 5 \times 1 \, \text{mm}^3$.

B. Ellipsometric measurements

Spectroscopic ellipsometry, in the reflection mode, was the measurement technique employed here. For the room temperature measurements on ThO_2 and UO_2, the ellipsometric parameters Ψ and Δ were measured from $100 \, \text{cm}^{-1}$ to $7000 \, \text{cm}^{-1}$ with a resolution of $2 \, \text{cm}^{-1}$. Data from $100 \, \text{cm}^{-1}$ to $400 \, \text{cm}^{-1}$ were acquired using a home-built Fourier transform-based far-infrared ellipsometer.[35] Data from $400 \, \text{cm}^{-1}$ to $7000 \, \text{cm}^{-1}$ were acquired using a commercially available Fourier transform-based mid-infrared ellipsometer (IR-VASE, J.A. Woollam Co., Inc.). These measurements were performed at three angles of incidence ($\Phi_a = 50°$, $60°$, and $70°$). The WVASE software (J.A. Woollam Co., Inc.) was used to acquire and analyze all data. All measurements were performed in an open air environment.

For ThO_2, additional variable temperature measurements were taken from 293 K to 648 K in increments of 25 K. These were performed using only the far-infrared ellipsometer.[35] Ψ and Δ were measured from $100 \, \text{cm}^{-1}$ to $650 \, \text{cm}^{-1}$ with a resolution of $2 \, \text{cm}^{-1}$. These measurements were performed at a single angle of incidence ($\Phi_a = 70°$).

To perform the variable temperature measurements, the ThO_2 crystal was mounted to an aluminum plate via vacuum seal. To elevate the temperature, the aluminum plate was heated by a pyrolytic boron nitride/pyrolytic graphite resistive heater. The temperature was read before and after each ellipsometric measurement by probing the sample surface with a k-type thermocouple. During the measurement, the thermocouple was removed from the surface.

IV. RESULTS AND DISCUSSION

A. ThO_2 and UO_2 room temperature characterization

In order to characterize the IR-active phonon modes in ThO_2 and UO_2, we implemented the following three-step approach. (i) We apply our optical model and a model dielectric function approach to compare experimental data with best-match model calculated data to obtain the thickness of the surface roughness layer and to identify all IR-active modes. (ii) We extract $\text{Re}\{\varepsilon(\omega)\}$ and $\text{Im}\{\varepsilon(\omega)\}$ for ThO_2 and UO_2 for each measured wavelength separately by holding all other optical model parameters constant (surface roughness thickness and ThO_2 silver contact diameter). (iii) We perform a best-match model calculation using the FPSQ model and by directly comparing the result of the FPSQ model with the wavelength-by-wavelength obtained dielectric function obtained in the second step. In this best-match model calculation, we included evaluations of the match in $\varepsilon(\omega)$ as well as the match in $\varepsilon^{-1}(\omega)$ between the model and wavelength-by-wavelength obtained dielectric function.

Step (i): shown in Fig. 4 is the best-match model calculated ellipsometry data (black solid lines) to the experimental data (dashed lines) for ThO_2 [panel (a)] and UO_2 [panel (b)]. The analysis yields a surface roughness layer thickness of $(34 \pm 1) \, \text{nm}$ for ThO_2 and $(22 \pm 1) \, \text{nm}$ for UO_2. In addition to the main mode pair, a small IR-active impurity-like mode pair is detected for both crystals within the reststrahlen band (band of high reflectivity).
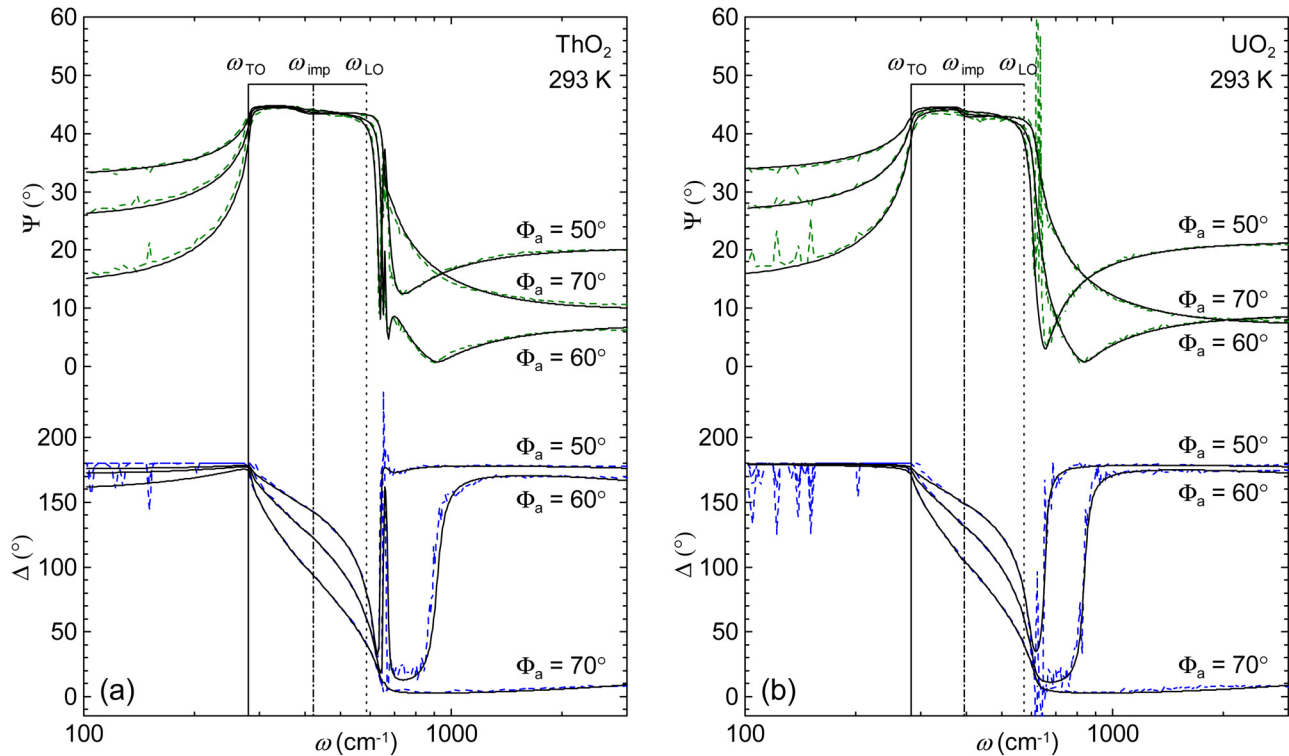
FIG. 4. Experimental (dashed lines) and best-match model calculated (black solid lines) ellipsometric data (Ψ, Δ) for single-crystal ThO$_2$ [panel (a)] and UO$_2$ [panel (b)]. The optical model parameters ω_{TO} (solid vertical lines) and ω_{LO} (dashed vertical lines) are the TO and LO frequencies, respectively, that correspond to the main IR-active phonon modes. The parameter ω_{imp} ($= \omega_{TO,imp} = \omega_{LO,imp}$) (dashed-dotted vertical lines) corresponds to the small-amplitude IR-active impurity-like mode pair within the reststrahlen band. Data are taken at three angles of incidence ($\Phi_a = 50°$, $60°$, and $70°$) and at room temperature.

Because only two mode pairs are observed, we designate the impurity mode pair index as $i =$ "imp" and the main mode pair index as null ($i =$ ""). We find that there is limited sensitivity to the parameters $\omega_{TO,imp}$ and $\omega_{LO,imp}$; therefore, they were set equal in the model analysis ($\omega_{imp} = \omega_{TO,imp} = \omega_{LO,imp}$), as was done in Ref. 36 for impurity-like modes detected in α-GaN thin films. In Fig. 4, the impurity mode resonant frequency is labeled as ω_{imp} and the main mode as ω_{TO} and ω_{LO}. The occasional spike-like features in Ψ and Δ (Fig. 4) are due to noise in low-reflectivity spectral ranges. For the ThO$_2$, the small silver contact area was found to be approximately 1% surface coverage of the sample. The analysis verifies that both crystals are optically isotropic for the given temperature and spectral range. No significant contribution from free charge carriers is detected.

Step (ii): shown in Fig. 5 is the wavelength-by-wavelength extracted Im$\{\varepsilon(\omega)\}$ [panel (a)] and Im$\{\varepsilon^{-1}(\omega)\}$ [panel (b)] for ThO$_2$ (green dashed lines) and UO$_2$ (blue dotted lines). The resulting best-match calculated ellipsometry data are virtually indistinguishable from the measured data and are, therefore, not included in Fig. 4.

Step (iii): shown in Fig. 5 is the best-match model dielectric function obtained using the FPSQ model (black solid lines), obtained by direct comparison with the wavelength-by-wavelength

extracted dielectric function. Shown in Table I are the resulting fit parameters for the main mode pair, DFT calculated parameters, and previous results from reflectance spectroscopy. Our results are similar to previous characterizations and our DFT calculations (Fig. 6). For the experiments that report values of γ_{TO} and γ_{LO}, it holds true that $\gamma_{TO} < \gamma_{LO}$. The anharmonicity indicated by $\gamma_{TO} \neq \gamma_{LO}$ is thought to arise from anharmonic coupling between different phonon modes.[13,14,37] The impurity mode pair also exhibits anharmonicity since $\gamma_{TO,imp} > \gamma_{LO,imp}$. Best-match model results for the impurity mode parameters in both crystals are given in Table II. The anharmonic DFT calculations on ThO$_2$ show $\gamma_{TO} < \gamma_{LO}$ as well (Fig. 3). Since our DFT calculations do not consider any impurity modes, this establishes that the anharmonicity in the main phonon mode pair in ThO$_2$ is intrinsic to the material and does not depend on the existence of an impurity-like mode pair. However, the existence of impurities could of course influence the phonon properties.

B. ThO$_2$ variable temperature characterization

To further investigate ThO$_2$, we performed ellipsometric measurements as a function of temperature from 294 K to 648 K. The spectra acquired at each temperature increment are analyzed
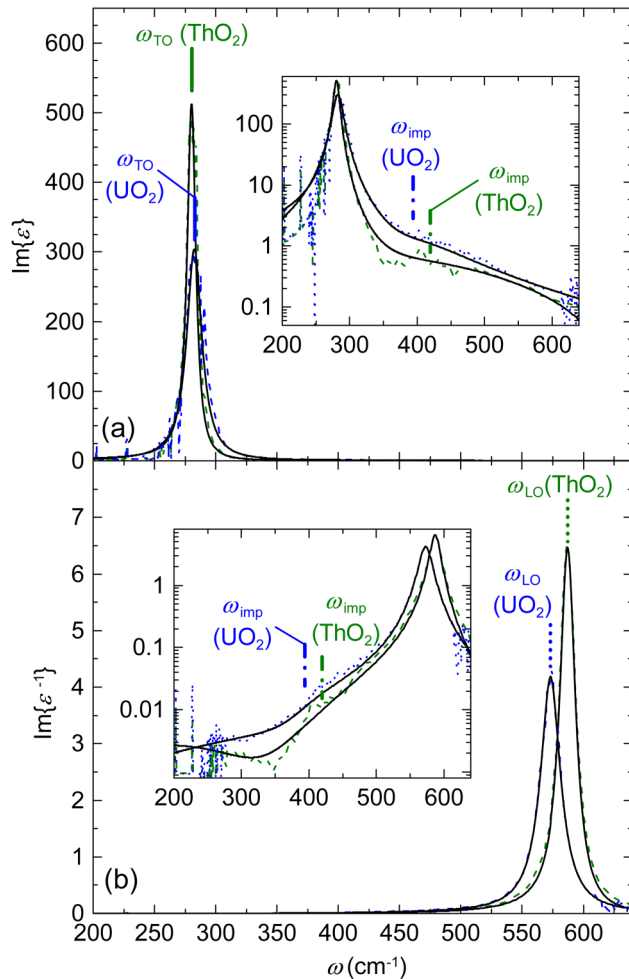
FIG. 5. Wavelength-by-wavelength extracted (broken lines) and best-match model calculated (solid black lines) $Im\{\varepsilon(\omega)\}$ [panel (a)] and $Im\{\varepsilon^{-1}(\omega)\}$ [panel (b)] for single-crystal ThO_2 (green) and UO_2 (blue). The solid black lines show the best-match model calculation using Eq. (2) to the wavelength-by-wavelength extracted $Im\{\varepsilon(\omega)\}$ and $Im\{\varepsilon^{-1}(\omega)\}$. The resulting best-match model parameters are shown in Tables I and II. The TO and LO resonant frequencies are labeled as ω_{TO} and ω_{LO} for the main phonon mode pair and ω_{imp} ($= \omega_{TO,imp} = \omega_{LO,imp}$) for the impurity-like mode pair. To make the impurity mode features visible, $Im\{\varepsilon(\omega)\}$ and $Im\{\varepsilon^{-1}(\omega)\}$ are also shown on a logarithmic scale (inset plots). Note, ω_{imp} does not exactly coincide with the corresponding peak in $Im\{\varepsilon(\omega)\}$ because the impurity mode broadening is comparable to ω_{imp}.

independently and using the model approach described at room temperature. To examine the influence of heat on the surface roughness layer, a separate, variable temperature experiment was performed in the visible spectral range (1.0 eV–6.5 eV, RC2, J.A. Woollam Co., Inc.). No significant change in the roughness layer's thickness or dielectric function was observed. We further assume that the IR optical properties of the small silver contact area remain temperature independent. Therefore, we held these optical model parameters constant as a function of temperature.

Using the approach described previously, we performed a wavelength-by-wavelength fit to extract $Re\{\varepsilon(\omega)\}$ and $Im\{\varepsilon(\omega)\}$ for each measured temperature. The FPSQ model is then fit to the wavelength-by-wavelength extracted $\varepsilon(\omega)$ and $\varepsilon^{-1}(\omega)$ (Fig. 7). The resulting main mode pair and impurity mode pair parameters are shown in Fig. 7. For the main mode pair, the resonant frequency parameters (ω_{TO} and ω_{LO}) decrease with increasing temperature, whereas the broadening parameters (γ_{TO} and γ_{LO}) increase with increasing temperature, which is a typical behavior for IR-active phonon modes.[40] For the impurity-like mode pair, ω_{imp} decreases with increasing temperature, but interestingly, $\gamma_{TO,imp}$ and $\gamma_{LO,imp}$ decrease with increasing temperature. This anomalous behavior is discussed in more detail below.

To model the temperature-dependence of the resonant frequencies and broadening parameters, we followed the same approach as in Ref. 16. Similar to Ref. 16, we find that the change in our resonant frequencies is directly proportional to the change in volume of the crystal lattice. The change in resonant frequencies for a given change in volume can be quantified by the mode Grüneisen parameter g_j, where the index j specifies the particular lattice resonance (here, j=TO, LO, or imp). Assuming a temperature-independent g_j, the change in the jth resonant frequency can be written as $\Delta\omega_j(T) = -\omega_j g_j(\Delta V(T)/V)$, where ω_j is the initial resonant frequency and V is the lattice volume.[16] This form also assumes that the only change in $\omega_j(T)$ is due to the lattice expansion. Other temperature-dependent contributions, such as anharmonicity (i.e., the real part of the phonon self-energy), electron–phonon coupling, spin–phonon coupling, etc., were not considered.[13,41] If this model is unable to fit $\Delta\omega_j(T)$, this is indicative of other contributions to the frequency shift. To express $\Delta V(T)/V$ in terms of the linear expansion coefficient α_L and change in the temperature ΔT, we write $\Delta V(T)/V = 3\alpha_L\Delta T$, where the volume expansion coefficient $\alpha_V = 3\alpha_L$ (assuming small differential changes in an isotropic material). Rearranging the prior equation for $\Delta\omega_j(T)$ to only fit for g_j yields

$$\omega_j(T) = -\omega_{j,init}(g_j 3\alpha_L)(T - T_{init}) + \omega_{j,init}. \tag{3}$$

Here, $\omega_{j,init}$ and T_{init} are the initial resonant frequency and temperature [$\omega_{j,init} = \omega_j(T_{init})$, $T_{init} = 293$ K]. For ThO_2, we find that the average linear expansion coefficient in our temperature range is $\alpha_L = 9.9 \times 10^{-6}$ K^{-1}.[42] Fitting Eq. (3) to our results for $\omega_{TO}(T)$, $\omega_{LO}(T)$, and $\omega_{imp}(T)$ gives $g_{TO} = 3.3 \pm 0.1$, $g_{LO} = 0.8 \pm 0.02$, and $g_{imp} = 17.1 \pm 1.0$ [Fig. 7(c)]. The results for g_{TO} are in excellent agreement with previous DFT calculations, which predict $g_{TO} \approx 3.2$, only considering volume change effects on the harmonic mode frequency.[5] This suggests that the temperature-induced change in ω_{TO} is primarily due to volume expansion of the crystal lattice, and other temperature-dependent contributions are not significant or perhaps counterbalance each other.[16] However, the g_{LO} parameter calculated in Ref. 5 is larger than our experimentally determined value. This could mean that the change in ω_{LO} is due to other temperature-dependent contributions besides a pure volume change. In our anharmonic DFT calculations, performed at a fixed cell volume, i.e., only including the effect of phonon self-energy, the frequency shift of the LO mode has a positive slope (Fig. 3), possibly compensating the effect of the lattice expansion. It is worth noting though that our

TABLE I. Best-match model results for the room temperature IR-active phonon mode parameters in single-crystal ThO$_2$ and UO$_2$. Error bars shown for this work correspond to the 90% confidence interval within the best-match model data analysis. The low-frequency (static) dielectric constant ε_{DC} is calculated using the Lyddane–Sachs–Teller (LST) relation.[38]

Parameter	DFT (this work) ThO$_2$	Ellipsometry (this work) UO$_2$	Ellipsometry (this work) ThO$_2$	Axe and Pettit[a] UO$_2$	Axe and Pettit[a] ThO$_2$	Chernia[b] UO$_2$	Schoenes[c] UO$_2$	DeVetter et al.[d] UO$_2$	Dolling et al.[e] UO$_2$
ω_{TO} (cm^{-1})	260	(282.8 ± 0.2)	(280.5 ± 0.1)	(278 ± 2)	(279 ± 2)	283.4	(280 ± 2)	(277 ± 3)	(284 ± 4)
ω_{LO} (cm^{-1})	554.8	(573.3 ± 0.5)	(587.5 ± 0.2)	(556 ± 4)	(568 ± 4)	574.0	(578 ± 2)	(571 ± 1)	(557 ± 20)
γ_{TO} (cm^{-1})	9.0[f]	(14.8 ± 0.5)	(8.2 ± 0.2)	18.5	16.2	29.4	7.5	…	…
γ_{LO} (cm^{-1})	18.4[f]	(20.1 ± 1.1)	(16.1 ± 0.5)	…	…	30.4	14	…	…
ε_∞	4.79	(5.2 ± 0.2)	(4.7 ± 0.1)	5.51	4.86	5.46	5.0	…	…
ε_{DC}	21.9	21.1	20.4	21.31	19.71	22.36	21.5	…	…

[a]Reference 7: ω_{TO} and ω_{LO} from Kramers–Kronig analysis. γ_{TO}, ε_∞, and ε_{DC} from best-match model parameter results using a Lorentz oscillator to render the dielectric function behavior.
[b]Reference 8.
[c]Reference 9.
[d]Reference 10.
[e]Reference 39.
[f]From the anharmonic calculation at 300 K.

calculations only include third order anharmonicity, while fourth order contributions, if present, can in principle be of the same order of magnitude as the third order one, and not necessarily with the same sign, further complicating the picture. For $\omega_{imp}(T)$, the trend is not perfectly linear, contrary to what Eq. (3) predicts. This also indicates other mechanisms besides the volume change (Fig. 8).

To investigate the mechanism of anharmonic phonon–phonon scattering, we implement the Bose–Einstein based model for $\gamma_j(T)$ employed in Ref. 13. Since $\gamma_{TO}(T)$ and $\gamma_{LO}(T)$ are reasonably linear within our temperature range, the only term in the equation needed is the one that corresponds to decay via cubic anharmonicities,[16]

$$\gamma_j(T) = a_j \left[n\left(\frac{\omega_j(T)}{2} \right) + \frac{1}{2} \right], \quad (4)$$

where $n(\tilde{\omega}) = (e^{\hbar\tilde{\omega}/k_B T} - 1)^{-1}$ is the phonon occupation number evaluated at the average frequency $\tilde{\omega} = (\omega_j(T)/2)$. The parameters $\hbar$, k_B, and a_j are the reduced Planck constant, the Boltzmann constant, and the cubic anharmonic parameter, respectively.

TABLE II. Best-match model results for the room temperature IR-active impurity-like phonon mode parameters in single-crystal ThO$_2$ and UO$_2$. Error bars shown correspond to the 90% confidence interval within the best-match model data analysis.

Parameter	Ellipsometry (this work) UO$_2$	Ellipsometry (this work) ThO$_2$
ω_{imp} (cm^{-1})	(394.3 ± 20.3)	(419.6 ± 11.4)
$\gamma_{TO,imp}$ (cm^{-1})	(143.5 ± 85.5)	(511.9 ± 68.6)
$\gamma_{LO,imp}$ (cm^{-1})	(133.8 ± 80.2)	(443.7 ± 59.5)
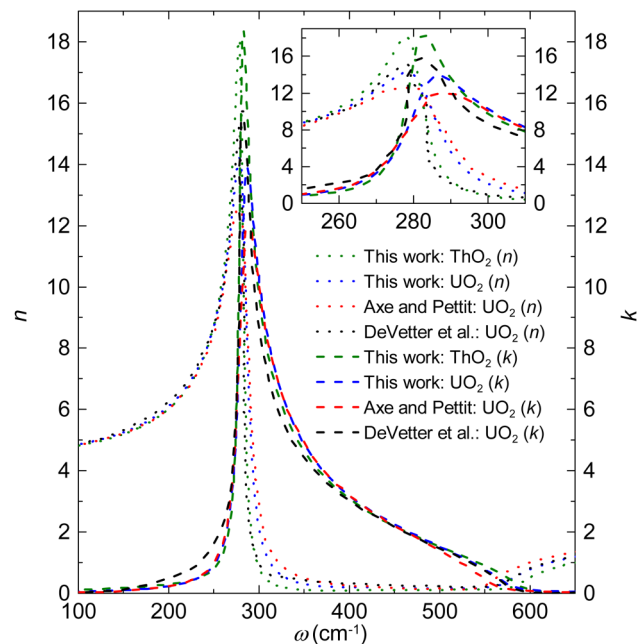
FIG. 6. Resulting optical constants n and k for the room temperature analysis of ThO$_2$ and UO$_2$ compared with other n and k values from previous UO$_2$ characterizations. Optical constants determined in this work [ThO$_2$ (green lines) and UO$_2$ (blue lines)] were converted from the best-match model calculated dielectric function shown in Fig. 5. For comparison, dispersion model-calculated optical constants from Axe and Pettit[7] (red lines) were included, as well as values calculated from experimental reflectance spectra by DeVetter et al.[10] (black lines). Dotted lines were chosen for n and dashed lines for k.
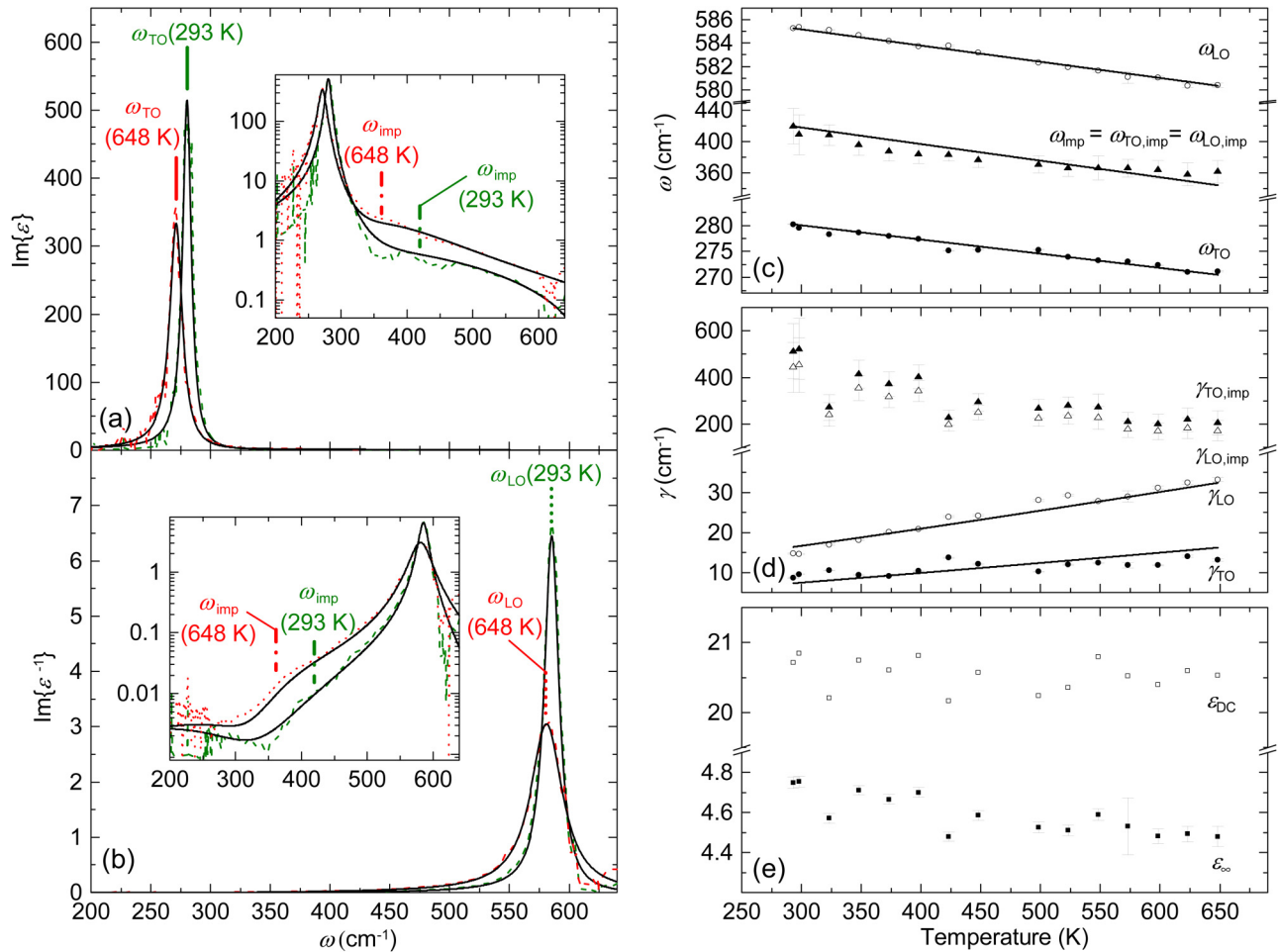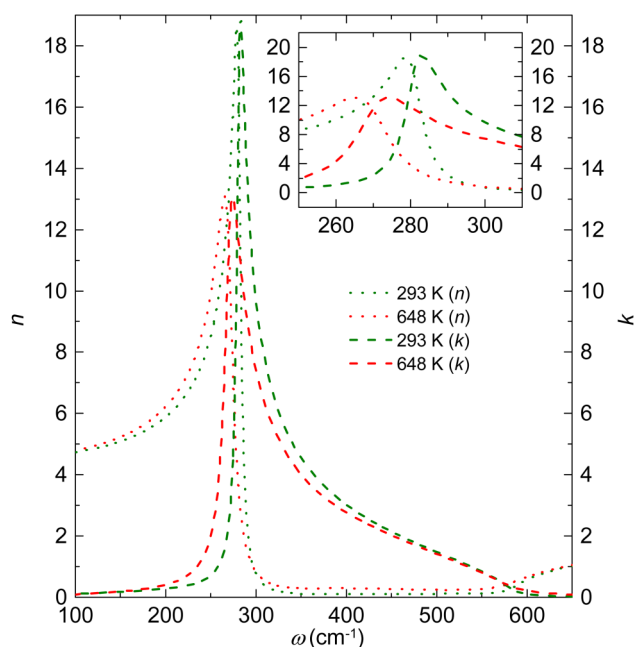
FIG. 7. Results for ThO$_2$ variable temperature characterization. Wavelength-by-wavelength extracted (broken lines) and best-match model calculated (solid black lines) Im$\{\varepsilon(\omega)\}$ [panel (a)] and Im$\{\varepsilon^{-1}(\omega)\}$ [panel (b)] for single-crystal ThO$_2$ at 293 K (green) and 648 K (red). To make the impurity mode features visible, Im$\{\varepsilon(\omega)\}$ and Im$\{\varepsilon^{-1}(\omega)\}$ are also shown on a logarithmic scale [inset plots in panels (a) and (b)]. The solid black lines in panels (a) and (b) show the best-match model results of Eq. (2) to the wavelength-by-wavelength extracted Im$\{\varepsilon(\omega)\}$ and Im$\{\varepsilon^{-1}(\omega)\}$. The resulting FPSQ model parameters for all measured temperatures are shown in panels (c)–(e). The low-frequency (static) dielectric constant ε_{DC} is calculated using the Lyddane–Sachs–Teller (LST) relation.[38] The solid black lines in panel (c) show the best-match model results using Eq. (3) to match $\omega_j(T)$. The solid black lines in panel (d) show the best-match model using Eq. (4) for $\gamma_j(T)$.

Fitting Eq. (4) to $\gamma_{TO}(T)$ and $\gamma_{LO}(T)$ gives $a_{TO} = (4.8 \pm 0.2)\,\mathrm{cm}^{-1}$ and $a_{LO} = (20.2 \pm 0.4)\,\mathrm{cm}^{-1}$. Our anharmonic DFT calculated results for $\gamma_{TO}(T)$ and $\gamma_{LO}(T)$ (Fig. 3) give similar fit parameter results of $a_{TO} = (5.7 \pm 0.1)\,\mathrm{cm}^{-1}$ and $a_{LO} = (21.3 \pm 0.6)\,\mathrm{cm}^{-1}$. A larger temperature range is used when fitting the DFT results (0 K–800 K) than for our ellipsometry results (293 K–648 K). However, the a_{TO} and a_{LO} for DFT are nearly identical when only including data within the range of 293 K–648 K. We can then conclude that the dominant decay mechanism can be described as phonon–phonon interactions via cubic anharmoncities.[17] It is worth noting that Eq. (4) was introduced in Ref. 13 to describe the decay of optical phonons into pairs of acoustic phonons via cubic anharmonicities, while the anharmonic DFT code considers a more complex decay mechanism involving triplets of phonons at arbitrary wavevectors over a fine grid of q-points within the Brillouin zone (in our case on a grid of $200 \times 200 \times 200$ points). Equation (4), however, describes thermal occupations of phonon states within the Bose–Einstein statistics and hence should be applicable in either case.

Interestingly, $\gamma_{TO,imp}(T)$ and $\gamma_{LO,imp}(T)$ decrease with increasing temperature. This dependence cannot be fit by the model in Ref. 13 and is not typical for IR-active phonon modes in pure crystals.[40] However, the temperature-dependence of impurity-like modes is not well understood. While the exact nature of the impurity mode is unclear, it may be a result of subtle anharmonic phonon–phonon interactions, as reported for MgO.[43] This, however, falls outside the scope of our current study.

FIG. 8. Resulting optical constants n and k for the variable temperature characterization of ThO_2. Optical constants (green for 293 K and red for 648 K) were determined by converting the best-match model calculated dielectric function shown in Fig. 7. Dotted lines are chosen for n and dashed lines for k.

V. CONCLUSION

In summary, IRSE experiments and DFT calculations were used to study the IR-active phonon modes in ThO_2 and UO_2. Their dielectric functions are extracted from the ellipsometric data in order to determine the phonon mode resonant frequency and broadening parameters. In agreement with previous results, we find $\gamma_{TO} < \gamma_{LO}$ for both crystals, which is indicative of lattice anharmonicity due to anharmonic interactions between phonon modes. For ThO_2, additional ellipsometric measurements were performed at elevated temperatures. For the main TO resonance, our experimentally determined results for the mode Grüneisen parameter are in excellent agreement with previous DFT calculations, which suggests that the temperature-induced change in the TO resonant frequency is due to volume expansion of the crystal lattice. However, the mode Grüneisen parameter for the main LO resonance does not exactly match the DFT predictions. This indicates that the temperature-dependence of the LO resonant frequency is determined by additional factors besides just a volume change. By implementing the Bose–Einstein based model in Ref. 13 to describe the broadening's temperature-dependence, we find that the decay mechanism of the main mode's IR-active phonons can be described as cubic anharmonicity. For the detected impurity-like mode pair, the broadening parameters decrease with increasing temperature. This behavior is not predicted by the Bose–Einstein model, and more investigation is needed to understand temperature-dependence of the impurity-like modes.

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