

LONG-TERM STABILITY, VIBRATIONAL AND OPTICAL PROPERTIES OF
 β -ZnTe(en)_{0.5} AND RELATED ORGANIC-INORGANIC HYBRID SUPERLATTICES

by

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ABSTRACT

TANG YE. Long-term stability, vibrational and optical properties of β -ZnTe(en)_{0.5} and related organic-inorganic hybrid superlattices
(Under the direction of DR. YONG ZHANG)

Organic-inorganic hybrids may offer material properties enhanced compared to or not available from their inorganic and organic components. However, they are typically less stable and disordered. A group of highly ordered II-VI based hybrid structures has been shown to possess various unusual properties and potential applications. As a prototype, β -ZnTe(en)_{0.5} can be viewed as a superlattice with alternating layers of two-monolayer thick (110) ZnTe and single-molecule length ethylenediamine. In contrast to all the known inorganic superlattices where interfacial diffusion is inevitable, we demonstrate in this thesis that β -ZnTe(en)_{0.5} exhibits an unusually high degree of crystallinity, as is evidenced by $< 25''$ x-ray diffraction (XRD) rocking curve linewidth and $< 1 \text{ cm}^{-1}$ Raman linewidth, which are comparable to many high-quality binaries. Besides manifesting in the macroscopic scale crystallinity characterization, it also shows an exceptionally low level of microscopic scale defects, as suggested by the observed linear dependence of photoluminescence (PL) intensity on the excitation density over 6 orders of magnitude, which has not been possible even for the very high-quality CdTe, GaAs, and hybrid perovskite MAPbI₃.

β -ZnTe(en)_{0.5}'s exceptionally high crystallinity enables a systematic investigation of its vibrational property, which makes it possible to compare the experimental results with theoretical predictions without the extrinsic interferences that inevitably exist in other superlattices. We perform on-axis and angle-resolved polarization selective Raman

measurements to study $\beta\text{-ZnTe(en)}_{0.5}$'s vibrational modes. A set of on-axis polarization configurations are used to identify and analyze the vibration modes according to their symmetries. A mode-by-mode analysis allows for unambiguous assignments of the Raman-active modes. With the assignments, the Raman tensors can be estimated from both the on-axis and the angle-resolved measurement. The two independent measurements yield consistent estimations. In addition, it has been shown that the angle-resolved polarization measurement enables unambiguous determination of the crystal orientations. A few exceptions and additional features are discussed.

A distinction of $\beta\text{-ZnTe(en)}_{0.5}$ among the hybrid materials is its unprecedented ambient long-term stability over 15 years, which is still limited by extrinsic mechanisms but is already the longest documented hybrid semiconductor. In this work, we used Raman spectroscopy to investigate its degradation in air and a protected condition and framed the factors contributing to its long-term stability into (1) intrinsic effect such as large formation energy and large kinetic barrier in excess of the formation energy; (2) extrinsic factors, including surface or edge effect, where degradation can initiate through processes such as oxidation, and the structural defects, which may provide more accessible paths for degradation. Based on this approach, we estimate the room-temperature lifetime of $\beta\text{-ZnTe(en)}_{0.5}$ in a protected environment can be as long as 1.9×10^8 years, while in the ambient air, its lifetime is on the order of 10 years.

DEDICATION

To my grandmother, in loving memory.

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Chapter 1: Introduction

Section 1.1 introduces semiconductor superlattice and the pursuit of a perfectly ordered structure.

Section 1.2 focuses on crystalline organic-inorganic hybrid materials, e.g., hybrid perovskite, with promising application performance but lack short-range order and inadequate stability.

Section 1.3 introduces β -ZnTe(en)_{0.5}, a member of the II-VI hybrid nanostructure family. β -ZnTe(en)_{0.5} retains the advantage of hybrids while demonstrating perfectly ordered structure and long-term stability. Many of its other interesting properties will be noted. Section 1.4 presents the motives and objectives of the thesis.

1.1. Semiconductor superlattices

In 1970, Esaki and Tsu advocated using advanced thin film growth techniques to realize one-dimensional semiconductor superlattices [1]. Only two years later, the basic electronic properties of such structures were demonstrated in double-barrier structures having a thin GaAs sandwiched between two GaAlAs barriers, grown by MBE (molecular beam epitaxy) [2]. The pioneering experiments triggered a broad spectrum of experimental and theoretical investigations on superlattices over the following few decades. Investigation on their electronic [3] and optical properties [4,5] materialized in real-world applications such as infrared detectors [6], LASER [7], LED [8–10]. To achieve better performance on the device level, efforts are being made to improve the quality of the superlattices, manifested as fewer defects, uniform vertical and lateral composition profiles, etc. [11]. However, achieving a structure without inter-diffusion between the adjacent monolayers of the constituents remains elusive, even for the best-studied examples (GaAs)_n/(AlAs)_m and (GaP)_n/(InP)_m [12–14]. Although disordering could be even beneficial for some applications [15,16], it diminishes quantum coherence, which is required for various

advanced applications, such as quantum optics [17], and negatively affects many basic material properties, such as exciton dynamics and electronic conductivity [18]. Therefore, a synthesis approach that can yield a perfectly ordered nanostructure array will be of both fundamental and practical interest.

1.2. IV-VII₂ based organic-inorganic hybrid materials – hybrid perovskites

Organic-inorganic hybrid materials may offer properties not available from their inorganic components alone [19–21]. Most hybrids are less stable and disordered because of the weak coupling between the organic and inorganic parts. This work focuses on a subset of the hybrid materials having periodic microstructures – crystalline hybrids. One well-known example of a crystalline hybrid is hybrid perovskites, e.g., MAPbI₃. Although known since the 1980s [22–24], in the past 10+ years, in addition to fundamental research [25], hybrid perovskites have received extraordinary research attention in electronic, optical, and energy-based applications [26] for its versatile and scalable processibility [27–29].

The structure of hybrid perovskites can be viewed as organic molecules sitting in the void of an octahedral inorganic framework (Figure 1-1). Although having long-range order, hybrid perovskites are structurally disordered in short-range in their room temperature phases [16,30]. In addition, hybrid perovskites are known to have relatively poor long-term stability, both under ambient conditions [31] and illumination [32], which limits the scope of their applications. Long-term means a time scale of one or two decades that is typically expected for (opto-)electronic applications. Despite the major improvement in stability from hours just a few years ago [32] to currently up to a couple of months, benefiting from the reduction in structural defects and surface

passivation [33–36], and some 2D versions show moderately better stability [37–39], there is still a long way to go for practical applications.

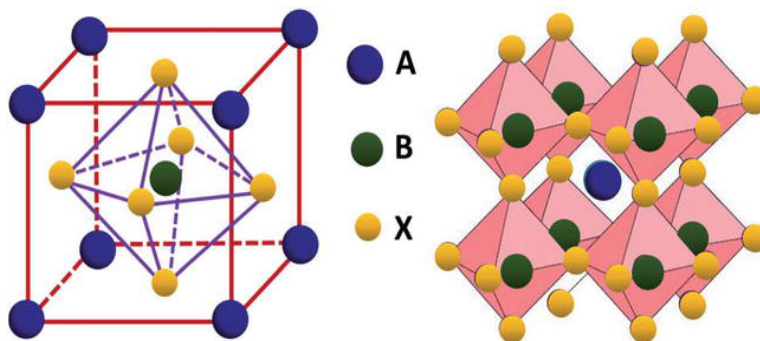


Figure 1-1. Schematic representation of the typical ABX_3 crystal structure of halide perovskites. (reproduced from ref. [40])

1.3. II-VI based hybrid nanostructures – $\beta\text{-ZnTe(en)}_{0.5}$

The II-VI based organic-inorganic hybrid materials, first reported in 2000 [41], is another family of crystalline hybrids. They can be viewed as a hybrid superstructures with the organic molecules serving as electronic barriers as well as dielectric confinement layers [42]. The II-VI based organic-inorganic hybrid family includes a large number of combinations of II-VI compounds (ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, MnSe) and aliphatic alkyl diamines as well as distinctly different structure types [43]. In addition to aliphatic alkyl diamines, a group of monoamines with different aromatic or heterocyclic aliphatic rings has been assembled with ZnS to synthesize a 2D version of the hybrid materials [44]. Those hybrids exhibit smaller bandgaps compared to hybrids assembled by a similar length of aliphatic alkyl amines.

Most II-VI hybrids show strong quantum confinement effects (QCE) [43]. Their bandgaps, typically exceeding 3 eV, are tunable via altering the inorganic layer thickness or length of the

aliphatic organic ligands [45]. Surprisingly, one member of the family, 2D-[Cd₂S₂(ba)], emits directly white light with an IQY ~4-5% [46]. A prototype WLED bulb was built by coating it onto a UV LED chip [46].

β -ZnTe(en)_{0.5} (en = C₂N₂H₈, ethylenediamine) is one of the II-VI based organic-inorganic hybrids consisting of two-monolayer thick ZnTe (110) slabs interconnected by en molecules forming covalent-like bonding through Zn and N atoms [41](Figure 1-2). In contrast to the inorganic superlattices, this hybrid superlattice is a perfectly ordered structure microscopically. It has both long and short-range order because the organic molecules all stay in well-defined configurations. The inter-diffusion between the inorganic and organic layers is impossible due to their vastly different structures.

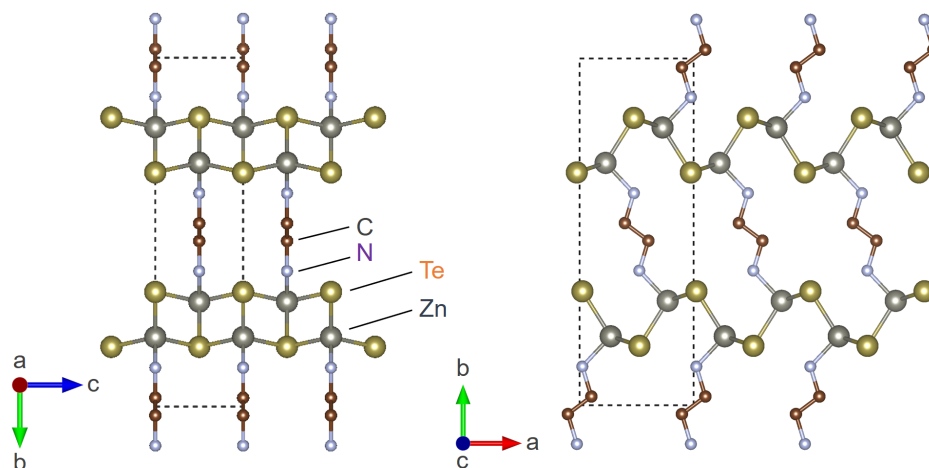


Figure 1-2. Crystal structure of β -ZnTe(en)_{0.5} viewed along *a*-axis and *c*-axis

β -ZnTe(en)_{0.5} has been shown to have crystallinity comparable to most high-quality elemental and binary semiconductors, e.g., low-temperature Raman linewidth below 1 cm⁻¹ [43,47]. More interestingly, it exhibits various desirable properties, e.g., room temperature excitonic emission

due to a large exciton binding energy estimated to be over 200 meV, strongly enhanced optical absorption as high as 10^6 cm^{-1} [42], broad-range zero-thermal expansion [47], much-reduced density and dielectric constants [42], and significantly reduced thermal conductivity [48,49]. It has recently been demonstrated that one could even exfoliate the thin inorganic slabs individually from these II-VI hybrids [50]. Because of its large bandgap ($3.562 \pm 0.006 \text{ eV}$), it can be explored for applications in UV detection and emitting devices, transparent transistors, sensors, conductive layers, and electronic or hole transport layers in optoelectronic devices. It is also a promising candidate for room temperature exciton-polariton condensation and related quantum effects. These attributes make $\beta\text{-ZnTe(en)}_{0.5}$ an attractive prototype system for revealing the pertinent mechanisms dictating the long-term stability of hybrid materials and general design principles to achieve highly ordered hybrid structures.

1.4. Motives and objectives of the thesis

This work was motivated by $\beta\text{-ZnTe(en)}_{0.5}$'s perfect crystalline structure. Defects such as interlayer diffusions in traditional semiconductor superlattices introduce extra layers of complexities into their Raman spectra. $\beta\text{-ZnTe(en)}_{0.5}$'s perfect crystalline structure, on the other hand, allows for a study of its vibrational properties arising from the pristine structures alone. This work uses Raman spectroscopy to study $\beta\text{-ZnTe(en)}_{0.5}$'s vibrational modes and pursue a systematic understanding of $\beta\text{-ZnTe(en)}_{0.5}$'s Raman modes (Chapter 5).

While carrying out the study, a surprising observation arose that most of the 15+-year-old samples retain their original pristine structure (Chapter 3). The observation begs one to ask the following questions. Can we estimate $\beta\text{-ZnTe(en)}_{0.5}$'s lifetime? What factors contribute to $\beta\text{-ZnTe(en)}_{0.5}$'s much longer lifetime than hybrid perovskites? Is there a factor posing the limit of

an achievable lifetime of a hybrid? Insights to these questions would be unique contributions to the literature because there is neither a reliable theoretical method to predict the long-term stability of a hybrid material nor a hybrid material like $\beta\text{-ZnTe(en)}_{0.5}$ with demonstrated long-term stability that can serve as an example to show the necessary characteristics.

In order to answer the questions, Chapter 4 of this thesis presents a systematic long-term stability study of hybrid materials, identifies $\beta\text{-ZnTe(en)}_{0.5}$'s two key degradation pathways, and proposes their possible mechanisms. This is the first-ever effort on the family of II-VI hybrids. Note that the degradation mechanisms of hybrid perovskites are not completely understood and itself is a popular ongoing research topic [51–53].

Chapter 2: Materials and experiment methods

Section 2.1–2.5 describes materials and experimental techniques and conditions used in this work. Because Raman spectroscopy will be used all along with the thesis, in particular, polarized Raman spectroscopy and Raman selection rule will be the key tool in *Chapter 5: Identification and analysis of Raman modes and their selection rules in β -ZnTe(en)_{0.5}*, section 2.6 is dedicated to lay down the necessary framework of Raman scattering/spectroscopy that future chapters will build upon.

2.1. Materials

New samples of β -ZnTe(en)_{0.5} in this work was synthesized by Andrei Nesmolov and Margaret Kochergain¹ following slight modifications of previously reported literature procedures [43]. ZnCl₂ (333 mg, 2 mmol), Te (128 mg, 1 mmol), and ethylenediamine (4 mL) were placed in a Teflon-lined stainless steel high-pressure acid digestion vessel (Parr model 4746). The vessel was placed in a muffle furnace set at 200°C for 10 days. After slow cooling to room temperature, the resulting product mixture was filtered and washed with distilled water, 95% ethanol, and diethyl ether, then dried in air to produce colorless plate-like crystals. The samples used in this work are labeled as Sxx-y, where xx indicates the year of synthesis (e.g., 03 for 2003), and y indicates the degradation status (e.g., p for pristine, d for degraded). Samples labeled as S19-p were from one newly synthesized batch. The oldest samples (2006 or earlier) were the same pieces mounted on their sample holders used in previous studies [42,43,47,54], and the 2007

¹ Margaret and Andrei were graduate students then working in Dr. Thomas A. Schmedake's research group.

samples were from one synthesis batch and were not studied previously. Majority of S07 showed no sign of degradation, with few exceptions (e.g., S07-pd). The aged samples were stored under ambient condition until they were (re-)measured recently.

2.2. Optical characterization

Raman and PL measurements were carried out on a Horiba LabRam HR800 confocal Raman microscope with a 1200g/mm grating. For Raman, a 532 nm laser beam was focused on the sample surface using a long working distance 50x microscope lens with NA = 0.5. Unless otherwise stated, the laser power focused on the sample was at D-2 level: $125 \pm 10 \mu\text{W}$ ($9.4 \times 10^3 \text{ W/cm}^2$). A shutter was placed in the incident light path. Fed by the CCD clock, the shutter regulates the time sequence of the incident beam such that it was directed to the sample surface only during active data collection. An integration time of 20 seconds was used unless otherwise stated. Although higher laser powers may provide a larger signal-to-noise ratio, our experience indicates that using those power levels significantly increases the risks of damaging the sample surface through the heating effect.

For PL, the sample was excited by a 325 nm laser beam, which was focused through a 40x UV microscope lens with NA = 0.5. The laser power delivered to the sample was $15.5 \mu\text{W}$ ($3.1 \times 10^3 \text{ W/cm}^2$). The same shutter control scheme was applied. An integration time of 1 second was used. In the study of PL's dependence of excitation power, smaller exposure times were applied for excitations with higher powers. Compared to the Raman characterization, a weaker power was used because the hybrids are more prone to degradation under the above bandgap UV excitation.

2.3. Structural characterization

High-resolution X-ray diffraction (HRXRD) measurements were performed at room temperature on an XRD diffractometer (PANalytical's X'Pert PRO) with triple-axis configuration using monochromatized Cu K α radiation (1.5418 Å). To compare the line shape of 2θ - ω coupled scans and rocking curves, peak intensities were normalized, and the peak positions were centered at zero.

2.4. Surface analysis

The hybrid samples' morphology was investigated using a scanning electron microscope (JEOL JSM-6480) equipped with x-ray energy dispersive spectrometry (EDX). EDX spectra were obtained with 10 keV beam energy. X-ray photoelectron spectroscopy (XPS; Thermo Scientific ESCALAB XI+) was carried out using a 200 μ m diameter monochromatized Al source ($h\nu$ = 1486.6 eV). For depth profiling, sample surface was repeatedly sputtered with an argon beam (3000 eV, 500 μ m diameter) and analyzed by XPS. The etch rate was estimated to be 10 nm/s. Binding energies were calibrated relative to the C 1s peak at 284.8 eV.

2.5. Thermal study

Temperature-dependent Raman measurements shown in Chapter 3 were carried out with a heating system Linkam TS1500. At each temperature step, five minutes were allowed for thermal stabilization of the sample before the Raman spectrum was measured. A 10°C/minute ramping rate was used to heat the sample to the next temperature step. N₂ protected condition was achieved by a mild sustained N₂ flow into the chamber during the entire temperature profile [55]. Thermogravimetric analysis was performed using the Mettler Toledo TGA/SDTA851

instrument (Mettler-Toledo AG Analytical, Schwensenbach, Switzerland) in both air and N₂ surroundings. Blanks were run under identical conditions for each gas and subtracted from the respective TGA curves to correct for buoyancy. Ramping rate was 5°C/minute.

Thermal degradation results shown in Chapter 4 were obtained in the same way under the N₂ condition and in air with a ramping rate of 20°C/minute to reach the targeted temperature and by taking a Raman spectrum every 5 minutes.

2.6. Raman scattering and Raman selection rules

2.6.1. Raman scattering - an inelastic process

When a traveling monochromatic light beam reaches a specimen, the beam will be scattered in all different directions. While most of the scattered beams retain the frequency of the original light, a fraction (10^{-6} – 10^{-7}) of them acquire additional frequencies. Rayleigh scattering describes the elastic scattering process at the same frequency as the incoming beam. Raman scattering refers to the inelastic scattering process that yields additional frequencies. Because Raman scattering is a higher-order process compared to Rayleigh scattering, the much weaker signal from Raman scattering was only discovered in 1928 by Sir Chandrasekhara Venkata Raman.

In modern Raman spectroscopy, a LASER light is directed onto the specimen. The scattered light is then analyzed through a grating and collected by an image sensor. One observes the spectrum registered on the image sensor and identifies Raman signals to learn the vibrational properties of the specimen. The following section aims to illustrate the idea of Raman scattering to the extent that we will apply it to the β -ZnTe(en)_{0.5} system. In particular, we will focus on a classical treatment that sees the Raman signal as an incident light wave modulated by the system's

vibration under study. Although we will touch on the quantum picture to describe the energy exchange during Raman scattering, it will be sufficient to use the classical treatment to explain that Raman spectrum contains frequencies and symmetries of the specimen's vibration modes. In future sections, we will use the classical picture to examine $\beta\text{-ZnTe(en)}_{0.5}$'s Raman spectra.

2.6.2. Raman mode frequencies

To illustrate that Raman spectrum contains information of vibrational modes, let's begin with H_2^+ molecule [56], a system of two hydrogen ions and one electron (Figure 2-1). Under adiabatic approximation, the electron adjusts its configuration instantaneously as the ions' configuration changes, which enables our approximation to ignore the electron when discussing ions' vibrations, and vice versa. With two ions, the H_2^+ molecule has only one possible vibrational mode. We can describe the atom displacement of this mode using a scalar function $q(t)$.

$$q(t) = q_0 \cos(\omega_m t) \quad (2-1)$$

The scalar q can be read as the deviation from the optimal interatomic distance with the lowest potential. q_0 is the vibration amplitude. ω_m is the vibration frequency of the normal mode.

Now let's illuminate the molecule with monochromatic light, with frequency ω_0 and amplitude E_0 . Because the wavelength of the light (on the order of 10^2 nm) is much larger than the length scale of a small molecule (on the order of 10^{-1} nm), it would be convenient to ignore the spatial variation when describing the oscillating electric field at the molecule. The oscillating electric field illuminating on the molecule can be described using the following equation.

$$E = E_0 \cos(\omega_0 t) \quad (2-2)$$

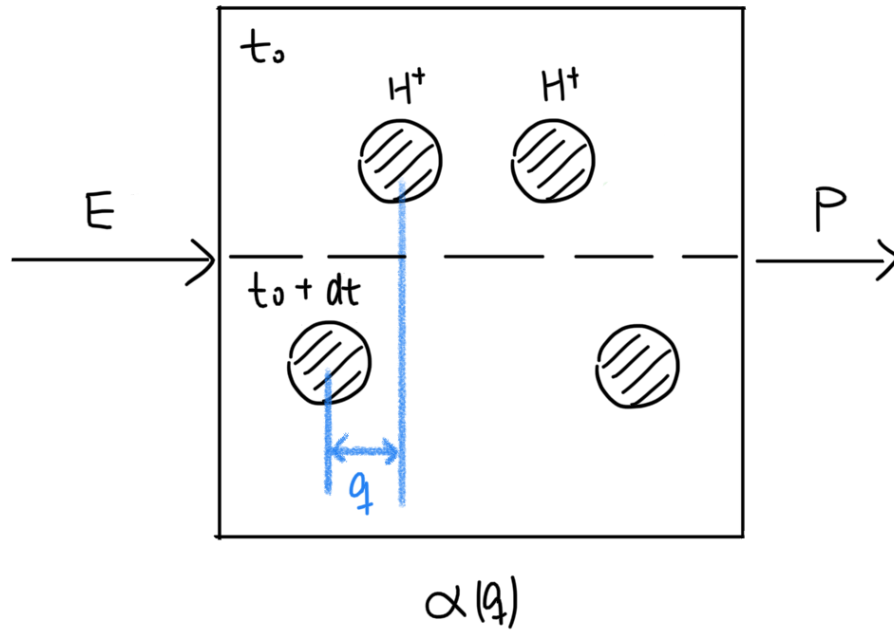


Figure 2-1. A diagram for the classical picture of Raman scattering arises from the vibration of a simple system – H_2^+ molecule. In the system, the vibration of the H_2^+ molecule is characterized by the interatomic distance d . At $t=t_0$, the molecule has the optimal interatomic distance $d(t_0) = d_0$ determined by the lowest potential. At $t=t_0+dt$, the interatomic distance changes to $d(t_0+dt) = d_0+q$. The external variable E is the electric field of the incident light illuminated on the molecule. P is the dipole moment from the molecule, which is responsible for the scattering signal. The system response can be characterized using the polarizability – α , which itself is a vibration-dependent variable.

Affected by an oscillating electric field, the electron oscillates accordingly and induces an oscillating dipole moment. The intensity of the dipole moment P is:

$$P = \alpha E \quad (2-3)$$

α is polarizability, which describes the proportionality between the induced dipole moment and the external electric field of light. Because polarizability is affected by the ion configuration, we should treat α as a parameter of q . Equation 2-3 becomes:

$$P = \alpha(q)E \quad (2-4)$$

Expand $\alpha(q)$, and ignore the terms higher than the first order of q . We have

$$\begin{aligned} P &= \left[\alpha_0 + \left(\frac{d\alpha}{dq} \right)_0 q + \dots \right] E_0 \cos(\omega_0 t) \\ &= \alpha_0 E_0 \cos(\omega_0 t) + \frac{1}{2} \left(\frac{d\alpha}{dq} \right)_0 q_0 E_0 \{ \cos[(\omega_0 + \omega_m)t] + \cos[(\omega_0 - \omega_m)t] \} \end{aligned} \quad (2-5)$$

In the equation, $\alpha_0 = \alpha(q=0)$. According to Equation 2-5, the scattered lights from the induced dipole will have three frequencies: (1) A frequency of ω_0 , the same as the incident light, corresponds to Rayleigh scattering. (2) A frequency of $\omega_0 - \omega_m$ (Stokes Raman signal) is lower than the incident light. (3) A frequency of $\omega_0 + \omega_m$ (anti-Stokes Raman signal) is higher than the incident light. In Raman spectroscopy, the Raman-active modes will register their frequencies (ω_m 's in Equation 2-5) on the Raman spectrum.

Equation 2-5, and the discussion after that is derived by treating light and molecule vibrations as waves. Although the approach explains Raman signal arises from molecule vibrations, it provides few insights from the perspective of energy exchange during Raman scattering. A quantum mechanics approach sees the light and molecule vibrations as particles containing wave packets of energy and models them as photons and phonons, respectively. In the Stokes Raman scattering process (Figure 2-2a), an incoming photon with energy $\hbar\omega_0$, is absorbed in the system

and excites the system from a lower-energy electronic state $|0\rangle$ into a higher-energy electronic state $|1\rangle$. When the system relaxes, it arrives at an intermediate vibrational state $|0,m\rangle$ and emits a photon with energy $\hbar(\omega_0 - \omega_m)$. Note that during the process, a phonon with energy $\hbar\omega_m$ is created. The Anti-Stoke Raman scattering process (Figure 2-2b) starts at the state $|0,m\rangle$, after being excited with an incoming photon with energy $\hbar\omega_0$, the system relaxes to $|0\rangle$ and emits a photon with energy $\hbar(\omega_0 + \omega_m)$. Note that during the process, a phonon with energy $\hbar\omega_m$ is annihilated. Therefore, Raman scattering is an inelastic scattering where a net energy exchange happens between photon and phonon. The energy difference between the incoming and the emitting photon is observed in the Raman spectroscopy as they reveal the energy of phonons in the system.

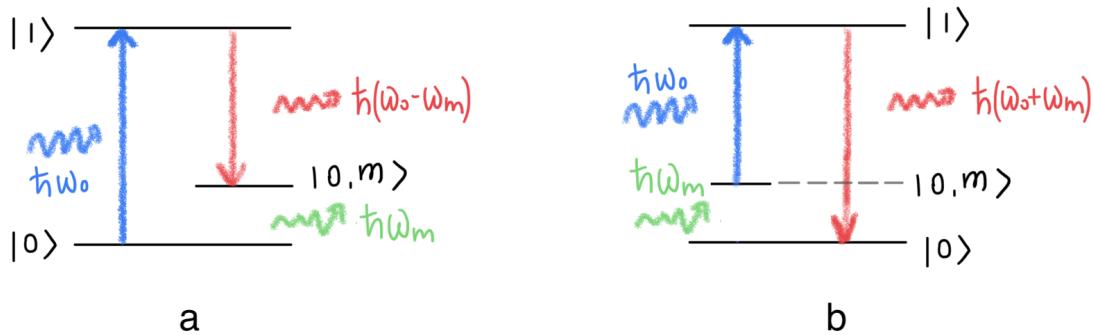


Figure 2-2. A diagram for the quantum picture of Raman scattering. (a) Stock process – an incoming photon (in blue) is absorbed, and a new photon (in red) with lower energy is emitted. A phonon (in green) is created during the process. (b) Anti-Stock process – an incoming photon is absorbed, and a new photon with higher energy is emitted. A phonon is annihilated during the process.

2.6.3. Raman-selection rules

Not all vibration modes can be observed by Raman spectroscopy. Equation 2-5 illustrate the idea that for a normal mode to be Raman-active, $d\alpha/dq$ must not equal zero. Such criterion is called the Raman-selection rule. However, the selection rule entailed by the equation is only applicable when electric field and atom movement are limited in 1D. In the laboratory setting, both electric field and atom movement have three independent directions, and the vibration of the system, q , typically has $3N$ degrees of freedom, with N the number of atoms in the system. Expanding Equation 2-5 from 1D to 3D yields the following form.

$$P_i = \alpha_{ij}(q) E_j \quad (2-6)$$

$\alpha_{ij}(q)$ describes E_j 's contribution to P_i as a function of vibration. A necessary condition for a vibration mode to be Raman-active is that at least one of the matrix elements in $\alpha(q)$ shall have a dependence on q . While this criterion can be used to determine whether a normal mode is allowed for Raman scattering, it becomes non-practical beyond the cases of very simple molecules. In order to derive the selection rules for $\beta\text{-ZnTe(en)}_{0.5}$, we apply the work of Loudon, who not only summarized the Raman selection rules for systems belonging to different symmetry groups [57] but developed the expression for Raman tensors to predict the first-order Raman scattering rates. With the Raman tensor, the Raman cross-section can be calculated using the following relationship.

$$RC = |\mathbf{r}_i \cdot \mathbf{R} \cdot \mathbf{r}_e|^2 \quad (2-7)$$

In the equation, RC is the Raman cross-section. $\mathbf{R}$ is a 3×3 Raman tensor of the normal mode under consideration. The tensor reflects both the optoelectronic interaction and the electronic-phonon interaction. Raman selection rules are imposed by the non-zero components in the

Raman tensor, which themselves are dictated by the symmetry of the normal mode. $\mathbf{r}_i$ and $\mathbf{r}_e$ represent the incident and scattered beam polarization, respectively. Note that because $\mathbf{r}_i$, $\mathbf{R}$, $\mathbf{r}_e$ are coordinates, their values depend on the basis being chosen.

Chapter 3: Observation of β -ZnTe(en)_{0.5}'s crystallinity and long-term stability

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In this chapter, we use optical spectroscopy and x-ray diffraction to demonstrate that β -ZnTe(en)_{0.5} has a high degree of crystallinity and can maintain its crystallinity in the course of more than 15 years in ambient air. The degradation product, metallic tellurium, is often limited to the top ~2 μm even for the most degraded samples. Surface analysis confirms the oxygen resides on the top few micrometers and is absent in the bulk, suggesting the degradation begins at the sample surface with the ambient air and gradually penetrates into the bulk as the reaction progresses. Thermal study shows different temperature profiles and degradation products in nitrogen-protected and ambient air conditions, suggesting two different degradation pathways. The thermal study also eludes a practical temperature window to study the kinetics of the two different degradations, which would be the subject of Chapter 4.

3.1. Structural ordering, optical properties, and stability probed by optical spectroscopy

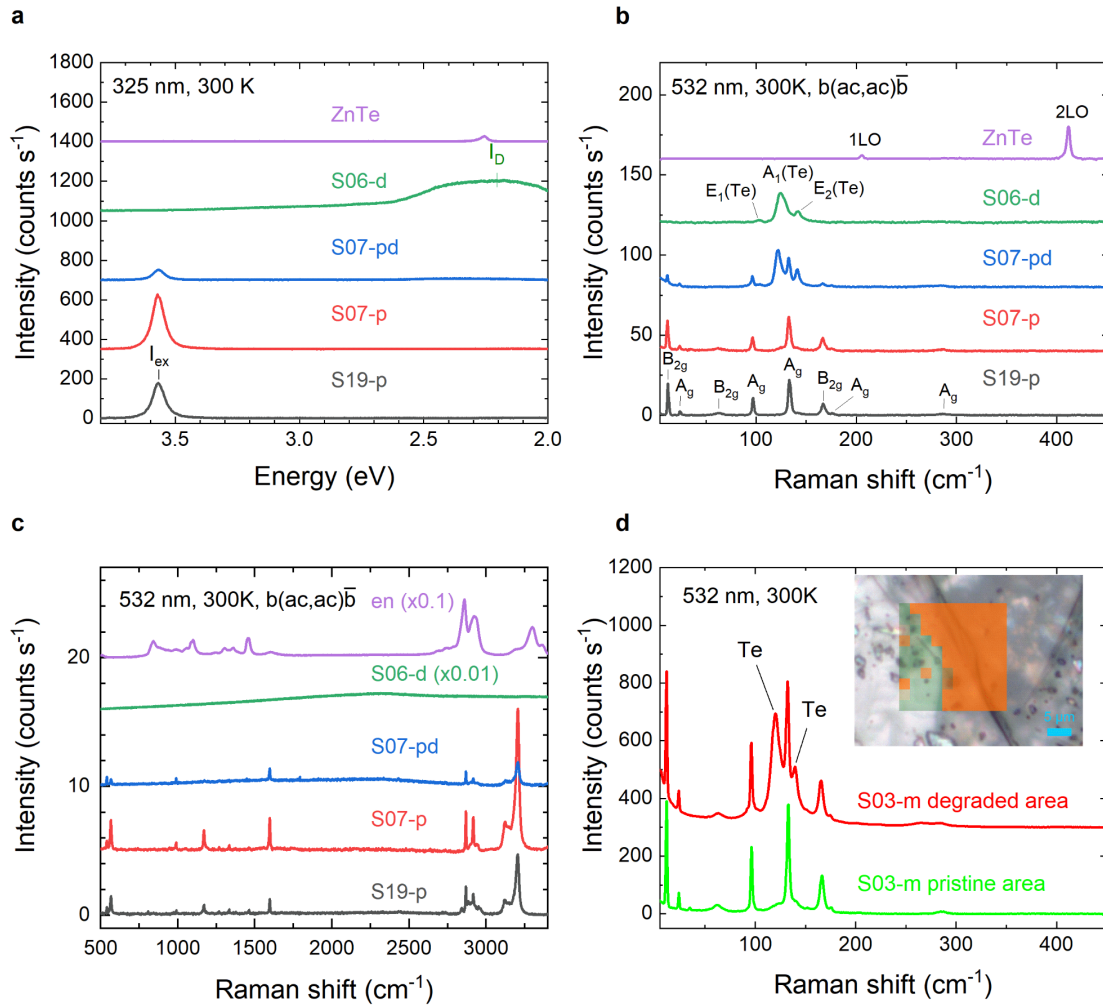


Figure 3-1. Optical spectroscopy signatures of β -ZnTe(en)_{0.5} at different degradation stages. (a) Photoluminescence spectra. (b) Raman spectra of the low wavenumber region. (c) Raman spectra of a large wavenumber region. (d) Raman spectra of pristine and partially degraded areas adjacent to each other (inset: Raman mapping of the Te mode showing no sign of degradation in the green area but partial degradation in the red area).

β -ZnTe(en)_{0.5} exhibits distinctly different optical properties from those of ZnTe. Figure 3-1(a)–(d), respectively, compare the spectra of photoluminescence (PL) excited at 325 nm and Raman

excited at 532 nm (in small and large frequency regions) of the hybrid samples in pristine and varying degrees of degradation states, with comparison to those of ZnTe. In Figure 3-1(a), the PL spectrum of a fresh-made sample S19-p (“19” stands for the year of synthesis 2019, “p” for pristine) shows only a single peak (I_{ex}) at 3.569 eV of free exciton emission [42]. This hybrid crystal is free of below bandgap defect emission, which is in stark contrast to most high bandgap inorganic semiconductors such as GaN and ZnO, where below bandgap defect emission is almost inevitable [58,59].

In Figure 3-1(b), the Raman spectrum of S19-p, measured in a backscattering geometry along the *b*-axis and parallel polarization configuration of 45° between *a* and *c* axes to reveal a maximum number of Raman modes intrinsic to the hybrid structure, exhibits multiple sharp peaks similar to those reported previously [47] but with two additional lower frequency modes.² Despite being a much more complex structure (32 atoms/unit cell), the Raman linewidths (measured by full width at half maximum, FWHM) of the hybrid is comparable to that of ZnTe: e.g., 3.2 vs. 3.7 cm^{-1} between the strongest hybrid mode at 133.2 cm^{-1} and ZnTe 1LO at 205.8 cm^{-1} , indicating a high degree of structural ordering in the hybrid. The Raman spectrum of S19-p in the higher frequency region is shown in Figure 3-1(d). Because of the strong bonding between the ZnTe sheets and en molecules, the ordering also reflects on the en derived Raman modes, where the en modes are typically shifted in frequency but substantially narrower, compared to those of free-standing en [60–62], for instance, 2869 (FWHM = 5) vs. 2860 (FWHM = 36) cm^{-1} . It is worth noting that $\beta\text{-ZnTe(en)}_{0.5}$ studied here has fewer Raman modes in the high-frequency region than

² Chapter 5 examines all Raman-active modes in $\beta\text{-ZnTe(en)}_{0.5}$ and offers more detailed discussions.

α -ZnS(en)_{0.5} measured previously [63] because the α phase has twice as many atoms in the unit cell.

A number of aged samples were measured under the same conditions. Quite remarkably, the same intrinsic PL and Raman spectra were observed in some samples that were more than a decade old, although the aged samples often exhibited varying degrees of degradation, manifested as changes in both PL and Raman spectrum. They fall into three groups: (1) pristine: showing practically identical optical spectra as S19-p, (2) degraded: showing no intrinsic hybrid spectroscopy features but those of the degradation products, (3) partially degraded: showing the spectroscopy features of both (1) and (2). Representative results are shown in Figure 3-1. For example, S07-p, typical from a batch of crystals, exhibits nearly identical spectroscopy signatures of S19-p, as shown in Figure 3-1(a) for PL, Figure 3-1(b), and 3-1(c) for Raman. Typical PL and Raman spectra for a partially degraded sample (S07-pd) and severely degraded sample (S06-d) are shown in Figure 3-1(a), 3-1(b), and 3-1(c), respectively. They show in PL the weakening or disappearance of the band edge emission peak and appearance of a broad below bandgap emission band (I_D), whereas in Raman, the weakening or disappearance of the hybrid Raman modes, and most noticeably the appearance of Raman modes related to metallic Te at ~ 124 and 142 cm^{-1} [64]. Degradation is often non-uniform over the surface area of a crystal. For instance, the intrinsic Raman features were observed in some even older samples, such as S03-m (“m” for mixed states of degradation), where adjacent pristine and partially degraded regions co-existed, as shown in Figure 3-1(d). Similar spatial variation was also observed in a bulk hybrid perovskite crystal [32], but the overall degradation occurred in a totally different time scale. Although β -ZnTe(en)_{0.5} is still not as stable as inorganic semiconductors like Si and GaAs, it is far more stable than most known hybrid materials, and some of them even have a shelf life of

over one and half decades! More significantly, these findings indicate that the observed structural degradation may not even be intrinsic in nature rather due to some extrinsic mechanisms because of the variation in shelf life and the non-uniform degradation.

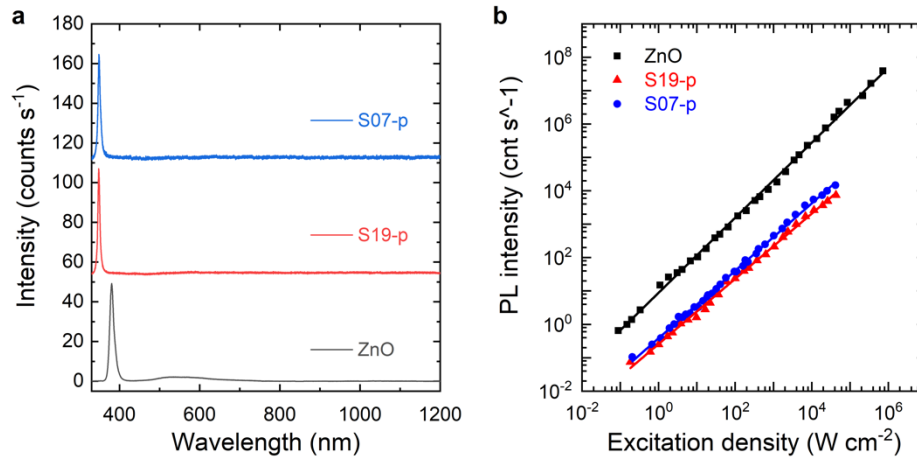


Figure 3-2. Comparison between recently synthesized (S19-p), aged (S07-p) samples, and a single crystalline ZnO in PL. (a) Large range PL (spectra are vertically displaced for clarity), (b) PL intensity vs. excitation density

To further examine the microscopic scale crystallinity and how it might be affected by aging, a more detailed comparison in PL between S19, S07, and top quality single crystalline ZnO is provided in Figure 3-2. Figure 3-2(a) depicts their PL spectra in a larger range up to 1200 nm. Comparing with ZnO showing weak but visible below bandgap emission, S19 and S07 show minimal below bandgap PL emission over the entire range, which indicates that there are very few radiative defect centers in the materials. The influence of the potential non-radiative defect centers can be effectively probed by the excitation density dependence of PL intensity over a large range of excitation density [16,65]. Indeed, as shown in Figure 3-2(b), when the excitation density (p) is varied by six orders, both S19 and S07 exhibit a very close to linear dependence ($I \propto p^n$, $n = 0.98 \pm 0.01$ for S19 and 1.01 ± 0.01 for S07), implying a near 100% internal quantum

efficiency, superior to the best reported CdTe, GaAs and hybrid perovskite [16]. In comparison, the $n = 1.12$ is found for the ZnO sample, reflecting some nonradiative recombination loss. These results further confirm that the materials have very few either radiative or nonradiative defect centers, thus, very high degree crystallinity on a microscopic scale, and may retain the high crystallinity well over a decade.

We also note that β -ZnTe(en)_{0.5} exhibits considerably better photo-stability than MAPbI₃. In the air with prolonged exposure to above bandgap excitation, the former has a degradation threshold 300 W/cm², and the latter 10 W/cm² [16], compared to CZTSe 3x10⁴ W/cm² and Si above 10⁶ W/cm² [66].

3.2. Crystallinity and stability probed by X-ray diffraction

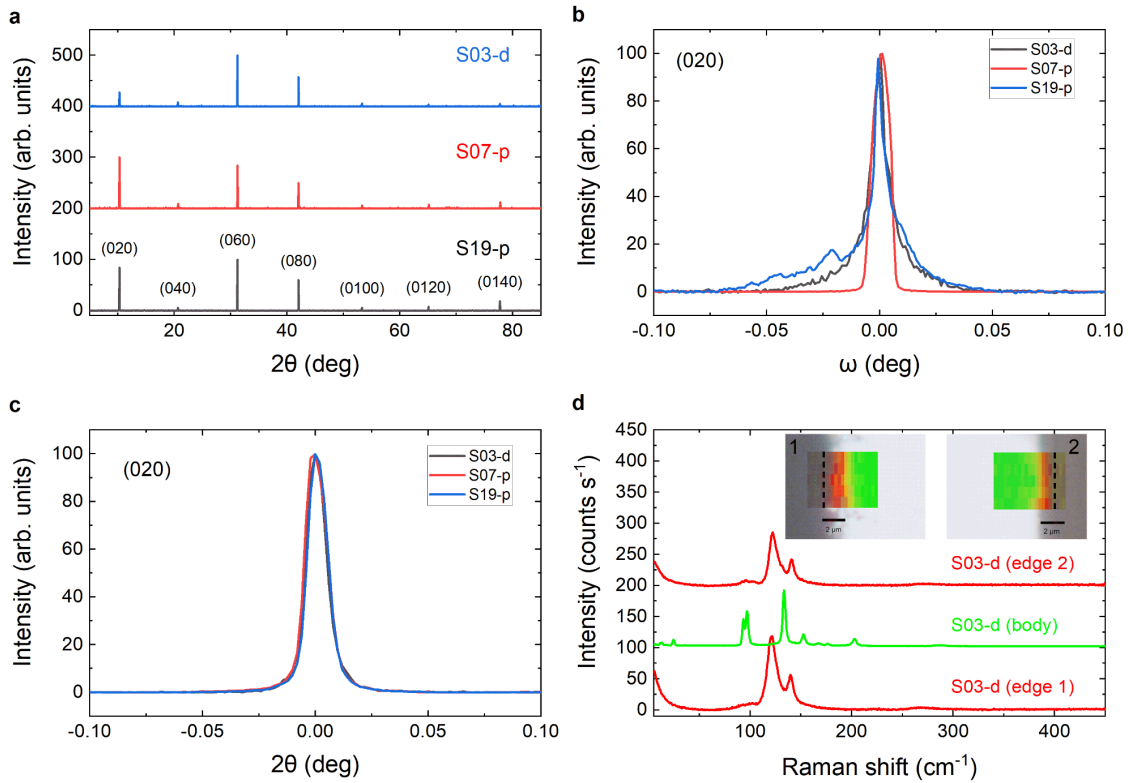


Figure 3-3. XRD and Raman characterization of pristine and seemingly degraded samples. (a) b -axis XRD 2θ scans for S19-p, S07-p, and S03-d. (b) and (c), High-resolution XRD rocking curves or ω scans and 2θ scans, respectively, at (0,2,0) reflection for the three samples. (d) Raman spectra of S03-d measured from the cleaved edge at locations close and away from the surfaces (insets: Raman mapping of the Te mode, overlaid with the optical image, on the cleaved edge near the upper and lower surface of the crystal, where the dashed lines indicate the sample surfaces).

Samples like S06-d were severely degraded, but visually they remained intact. Thus, we performed HRXRD measurements on selected pristine and “degraded” samples. Figure 3-3(a) shows very similar (0n0) single crystal diffraction peaks between S19-p, S07-p, and S03-d,

except for the (020) peak of S03-d being significantly weaker. They all exhibit a very high degree of macroscopic crystallinity, as indicated by the single-crystal XRD results of rocking curve or ω scan linewidths (W_{RC}) and ω - 2θ coupled scan linewidths ($W_{2\theta}$). Roughly speaking, W_{RC} measures the lateral uniformity of the crystalline structure, and $W_{2\theta}$ reflects the uniformity of lattice spacing along the stacking direction. For the (020) diffraction, $W_{RC} = 22''$ and $W_{2\theta} = 38''$ for S19-p, as shown in Figure 3-3(b) and 3-3(c), respectively, compared to the results of a high quality ZnTe single crystal with $W_{RC} = 19''$ and $W_{2\theta} = 16.5''$ for the (002) diffraction [67]. For comparison, the best reported W_{RC} is $35''$ for bulk MAPbI₃ [68] and $30''$ for epitaxially grown GaN [69]. Interestingly, the W_{RC} results of S07-p and S03-d are very similar, $35''$ and $31''$, respectively. The XRD results of S03-d suggest that despite the signs of degradation in optical spectroscopy, the hybrid samples retained the same crystal structure as a whole. Keep in mind that the mm size X-ray beam not only averaged over the entire sample area (typically a few hundred μm) but also the entire thickness (typically 10-20 μm), whereas the spectroscopy measurements were performed with a confocal optical system that only probed a small volume near the sample surface (on the scale of one μm). Raman depth profiling was conducted for the degraded sample using 532 nm laser that is supposed to be transparent to the pristine material, but the Raman signal decayed quickly into the sample, suggesting the surface region of the degraded sample was highly absorptive to this below bandgap wavelength.

We then cleaved a severely degraded crystal S03-d and performed Raman mapping on the newly exposed edge, shown as an inset in Figure 3-3(d). It turned out that the body of the about 20 μm thick crystal exhibited the same Raman modes as a pristine sample, and only the regions approximately 2 μm thick from the top and bottom surface were degraded, as shown in Figure 3-3(d). The results explain the puzzling “inconsistency” between the optical and XRD results,

including the weakened (020) peak of S03-d, corresponding to the largest incidence angle at which more surface region was probed. The observation of the Te modes from the surface region of the “degraded” hybrid is similar to thermally oxidized ZnTe, where the top layer consists of amorphous ZnO and nanoscale Te domains [70]. The observations suggest that the hybrid's degradation is caused by surface oxidation, as to be confirmed next, that occurs in most non-oxide semiconductors. We may further speculate that a terminating layer of en molecules might prevent the surface from oxidation, a self-passivation effect. However, the oxidation process might initiate at a defective surface or a region with structural defects. This understanding is consistent with the observed variation in shelf life and degradation inhomogeneity. We have also noticed that the edges of a newly synthesized crystal tend to degrade faster than the top surface because the edges are not terminated by en molecules.

3.3. Stability probed by surface analyses

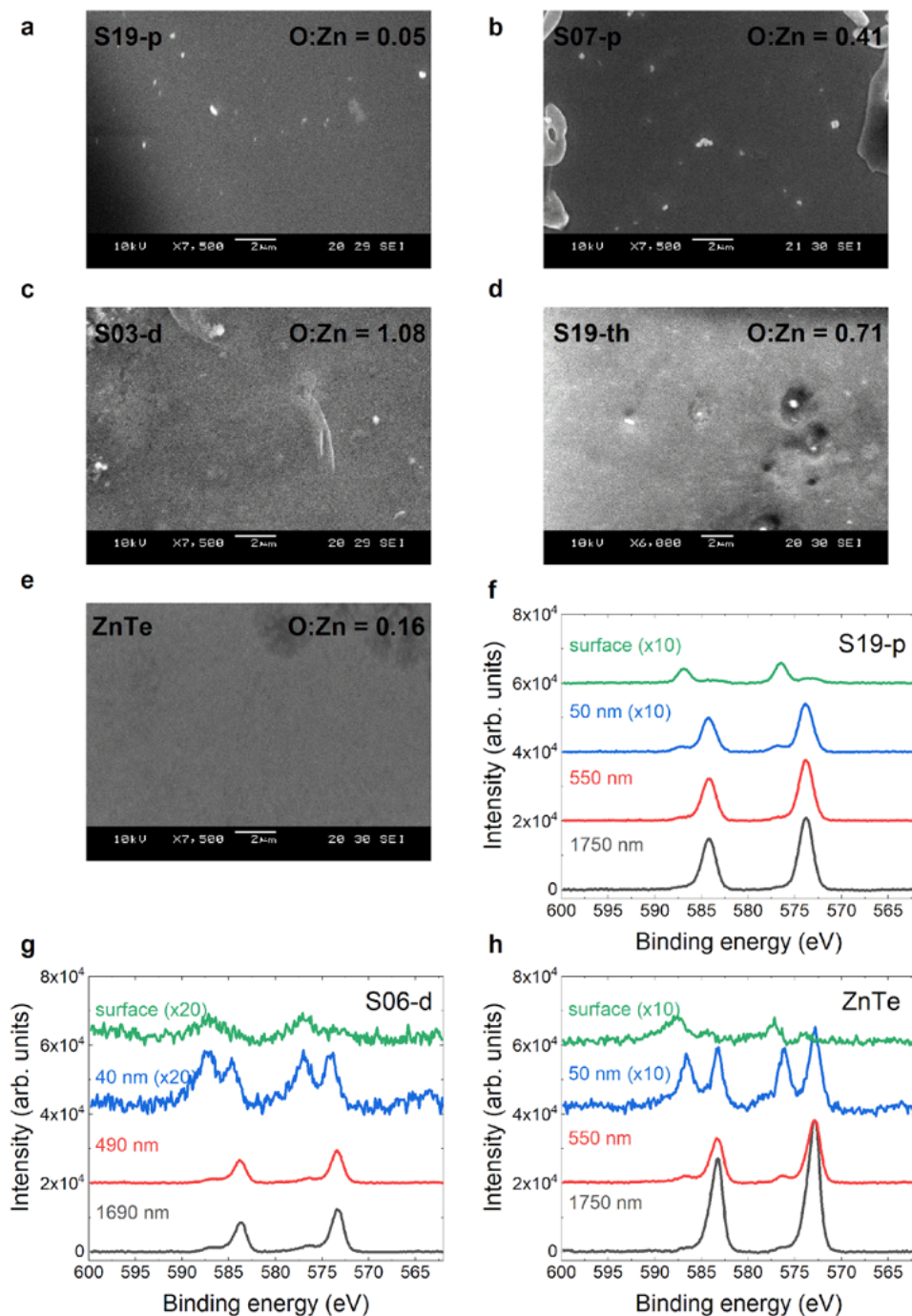


Figure 3-4. SEM and XPS surface characterization and analyses. (a–e) SEM images of a fresh sample (S19-p) (a), an aged sample showing very little degradation optically (S07-p) (b), an aged sample optically showing severe degradation (S03-d) (c), a thermally

degraded fresh sample (S19-th) (d) and single-crystalline ZnTe (e). (f–h) XPS spectra at different etching times or depths of sample S19-p (f), sample S06-d (g), and ZnTe (h).

To verify the oxidation process and degradation mechanism, we performed surface analyses using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, and X-ray photoelectron spectroscopy (XPS) on multiple pristine and “degraded” samples.

Figure 3-4(a)–(e) shows the SEM images obtained for S19-p, S07-p, S03-d, and S19-th (thermally oxidized at 190°C for 20 minutes), and ZnTe, respectively, taken from smooth and clean areas of the samples where optical measurements were conducted. The O:Zn ratio obtained from the EDX analysis is shown with each SEM image³. The comparison reveals a steady increase in oxygen content on the surface with an increasing level of degradation, for instance, O:Zn = 0.05 for S19-p and 1.08 for S03-d. These results qualitatively support the proposed degradation mechanism of surface oxidation.

XPS data further corroborate the above results. We measured depth-resolved XPS spectra for S19-p, S06-d, and ZnTe by applying in-situ Ar etching, with the results shown, respectively, in Figures 3-4(f)–(h) near the energies of two Te 3d transitions.⁴ For S19-p, on the non-etched surface, two peaks were at 576.5 eV (3d_{5/2}) and 586.9 eV (3d_{3/2}), similar to a naturally oxidized ZnTe in the air as reported in the literature [71]; after etching, two new peaks emerged on the lower energy sides respectively at 573.8 eV ($\delta E = - 2.7$ eV) and 584.2 eV ($\delta E = - 2.7$ eV), and after about 15-second etching (or removal of around 150 nm top layer), the high energy peaks

³ The original EDX spectra can be found in Appendix A.

⁴ Additional XPS scans of a broader energy range and finer depth resolutions can be found in Appendix B.

disappeared and the new peaks reached saturated intensities. Similar shifts were observed in ZnTe, but the transition energies for pure ZnTe are slightly lower than in the hybrid, by about 0.8 eV. The difference can be understood by the fact that the Te bonding situations are different in the two structures: with each Te bonding to only three Zn in the hybrid and four Zn in ZnTe. For the severely degraded sample, a similar trend was observed, but a much longer etching time (170 s, approximately corresponding to 1.7 μm in depth) was required to reach a steady-state, which suggests a thicker oxidized layer on this severely degraded sample and is consistent with the cleaved edge Raman results (Figure 3-3d). The remaining weak oxidation peaks after etching indicate that oxidation might have somewhat penetrated into the deeper volume of the crystal. Note that similar to XRD, XPS probes a large area due to its macroscopic beam size. Therefore, the results could be affected by the embedded extended defects and surface contamination, whereas micro-Raman and EDX are able to analyze visually perfect regions. We note that even the new sample S19-p had a thin oxide layer, although showing no effect in optical spectroscopy after being kept in air for one year. The existence of the pristine area in S03-m seems to suggest that the oxidation process is self-limiting, if no structural defects, as in most non-oxide inorganic semiconductors.

3.4. Thermal stability in different environments

Thermal stability is important for device application because of a self-heating effect under the operation condition. Thermal stability study was performed in both air and N_2 protected condition on newly made crystals (S19-p) in two ways: (1) By heating one single piece of the crystal using a heating stage with a small heating chamber from 40 to 500°C while monitoring with Raman spectroscopy in-situ. (2) By performing the thermogravimetric analysis (TGA) to a

collection of small crystals. These two experiments are similar in the sense that in both cases, the material property is probed when the sample temperature is raised in a small step and held steady briefly at each step to take the measurement, but in the former case, a Raman spectrum is measured versus the weight in the latter case.

In Raman, a significant difference in thermal degradation was observed between heating in air or N_2 until approximately 150°C . Figure 3-5(a) shows the evolution of the Raman spectra while heated in air⁵, where the Te peaks start to grow at around 160°C , and the hybrid peaks vanish above 210°C , mimicking an accelerated degradation process in ambient condition. Figure 3-5(b) shows the results under N_2 protection. In this case, no or very little Te-related Raman signal can be observed for temperature up to 300°C ; but at around 230°C , ZnTe LO phonon starts to emerge. When brought back to room temperature after heated up to 500°C , the sample exhibits the characteristic multiple LO phonon resonant Raman modes of a somewhat defective ZnTe [67] (Figure 3-5c), which is similar to the report where thermal annealing of $\text{ZnS}(\text{en})_{0.5}$ at 600°C in vacuum yielded ZnS [72]. However, if heated in air, no ZnTe is found in the degradation product either at high temperature (up to 400°C , Figure 3-5a) or after returning to room temperature (Figure 3-5c) where instead either a mixture of Te and TeO_2 [73], or sometimes ZnO [74] (inset of Figure 3-5c) is seen. Thus, N_2 , to a large extent, prevents the oxidation process, and the process reflects the Intrinsic-degradation path: evaporation of en molecules. The finding provides guidance to the acceptable operating temperature of a potential device using this material with proper encapsulation to minimize oxidation.

⁵ Spectra at more temperature points can be found in Appendix C.

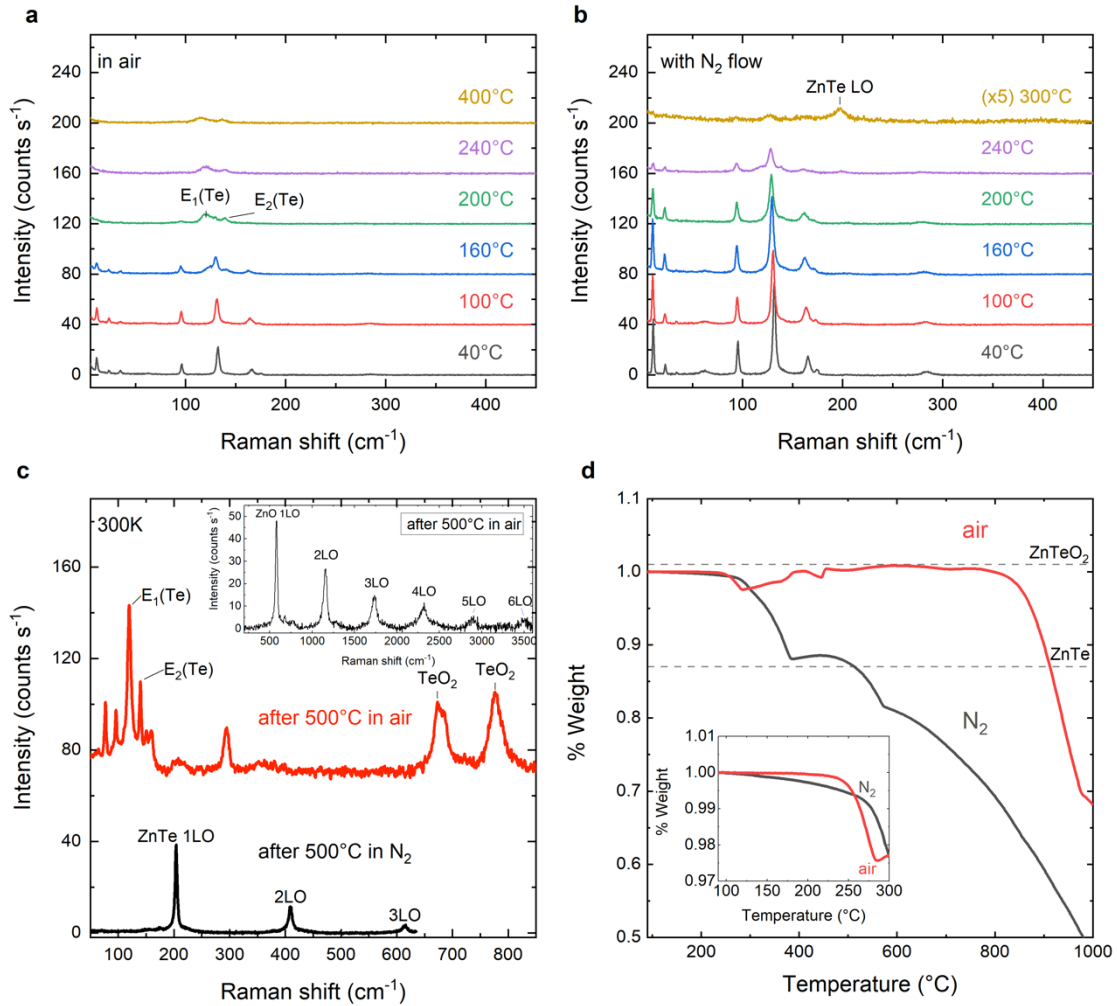


Figure 3-5. Thermal degradation of a freshly made sample (S19-p) in air and N₂ environment probed by Raman and thermogravimetric analysis (TGA). (a) In-situ Raman spectroscopy in air. (b) In-situ Raman spectroscopy in N₂. (c) Raman spectra (with the 532 nm excitation) at room temperature after the sample being heated to 500°C in air and N₂ then returning to room temperature (Inset: a Raman spectrum with the 325 nm excitation showing ZnO nLO resonant Raman peaks). (d) TGA in air and N₂ (inset: low-temperature region).

The TGA results⁶, shown in Figure 3-5(d), are qualitatively consistent with the spectroscopy results but offer more insight. Initially, till around 230°C, both curves show a slow mass reduction, but the curve in N₂ is slightly faster (inset of Figure 3-5d), which can be explained by that while ligand evaporation or calcination occurs due to heating in both cases, in the air the mass loss is made up partially by oxidation. The TGA curve in N₂ shows continual decrease but accelerated near 290°C, reaching a plateau before 400°C, corresponding to the complete conversion into ZnTe, which matches the mass loss of the molecules (about 13% in weight). In contrast, in air, a significant mass loss does not occur until around 200°C, and at about 290°C, the curve actually begins to increase, reflecting the oxidation process is accelerated; and the mass gain saturates at around 600°C. We may understand the intriguing curve as a convoluted effect of multiple competing oxidation processes: $\text{ZnTe(en)}_{0.5} \rightarrow \text{ZnTeO}_2$, where ZnTeO₂ is predominantly a mixture of $\text{ZnO} + x\text{Te} + y\text{TeO} + z\text{TeO}_2$ ($x + y + z = 1$), where the highest point matches $\text{ZnO} + 0.5\text{Te} + 0.5\text{TeO}_2$.

We may have a unified picture for the thermal degradation: following the initial loss of en near the surface, the molecules in the body start to leave at around 290°C, and at close to 400°C, the hybrid is fully degraded, resulting in different products in different environments.

Although naturally occurring slow degradation can be mimicked to some extent by an accelerated process – heating in air, the heating process is not able to reveal some subtle, often extrinsic effects that actually happened in the real process, such as the region to region or sample to sample variations. It is also non-trivial to establish a reliable quantitative correlation of the

⁶ TGA experiment was performed by Margaret Kocherga and Andrei Nesmolov.

thermal degradation temperature with the shelf life of the material other than the qualitative correlation.

3.5. Summary

We have demonstrated that despite the complex structure, β -ZnTe(en)_{0.5} can have an exceptionally high degree of both macroscopic and microscopic scale structural perfectness, manifesting as small XRD and Raman linewidths comparable to the high-quality ZnTe and near 100 % internal PL quantum efficiency superior to most known inorganic semiconductors such as GaAs, CdTe, ZnO and GaN.

Using a comparative study on newly-synthesized and aged samples, we have demonstrated that aged samples retain their pristine structures over the course of more than 15 years. Although surface degradation was noted on a few aged samples, its nonuniform distribution on sample surface suggests that faster degradation can arise from higher defect levels, and longer life can be achieved if it were made with fewer defects.

The long-term stability of the hybrid begs one to ask why, specifically, what factors contribute to β -ZnTe(en)_{0.5}'s much longer lifetime than hybrid perovskites? How much longer those pristine crystals can “live”? To address those questions, we have identified two degradation reactions – the intrinsic degradation, where the hybrid decouples into free en molecules, leaving the ZnTe slabs transformed into bulk ZnTe; and the natural degradation, where the hybrid is transformed into a spectrum of oxidized products – Te, TeO₂, ZnO, etc., with the oxidation agents in ambient air. In Chapter 4, we will proceed with a kinetic study on the two identified reactions.

Chapter 4: Prediction of lifetime of β -ZnTe(en)_{0.5} under-protected and ambient condition

The quest for this chapter is to look into β -ZnTe(en)_{0.5}'s long-term stability and ask what factors contribute to its stability. We will begin with the discussion of β -ZnTe(en)_{0.5}'s intrinsic degradation, which is the key reaction we want to study because: (1) it is simpler. The simplicity of Intrinsic-degradation has been manifested in Chapter 3, where we identified its reactant (β -ZnTe(en)_{0.5}) and products (bulk ZnTe and en molecules). Further, as we will see in section 4.2, the in-situ Raman measurements suggest β -ZnTe(en)_{0.5}'s Intrinsic-degradation behaves like a one-step reaction. The simplicity of the reaction allows us to propose a transition state and clarify different contributions to the kinetic barrier. (2) Studying Intrinsic-degradation has application value. We will estimate the room temperature lifetime of intrinsic degradation, which is a good estimate of the lifetime of operating material in an encapsulated condition. The second reaction of our focus is the β -ZnTe(en)_{0.5}'s oxidation in ambient air. Because the overall oxidation can have a much more complex mechanism, we aim to use in-situ Raman measurement to estimate its activation barrier and lifetime at room temperature.

4.1. Formation energy and kinetic energy barrier

The formation energy (E_F) of β -ZnTe(en)_{0.5} can be defined as the total energy difference between the two states: (1) the state of β -ZnTe(en)_{0.5}, and (2) the state of free en molecules and bulk ZnTe. As shown in the energy landscape (Figure 4-1), E_F sets the lower bound for the energy barrier (E_A) of the degradation reaction. β -ZnTe(en)_{0.5}'s formation energy (per formula unit) can be calculated using the definition.

$$\begin{aligned}
E_F &= (E[\text{ZnTe}] + \frac{1}{2}E[\text{C}_2\text{N}_2\text{H}_8]) - E[\text{ZnTe}(\text{en})_{0.5}] \\
&= [(-64.803 \text{ eV/en} \times 0.5 \text{ en}) + (-5.912 \text{ eV})] - (-155.399 \text{ eV/cell} \times \frac{1}{4} \text{ cell}) \\
&= 0.536 \text{ eV}
\end{aligned}$$

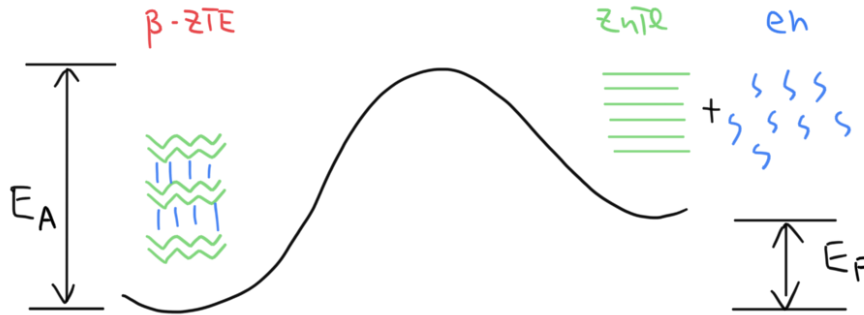


Figure 4-1. Energy landscape for β -ZnTe(en)_{0.5}'s intrinsic degradation, progressing from left to right in the diagram. E_F is the formation energy of β -ZnTe(en)_{0.5}. E_A is the activation barrier of the degradation reaction.

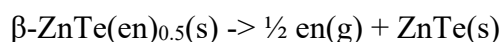
where $E[\text{ZnTe}(\text{en})_{0.5}]$ is the total energy per formula unit of ZnTe(en)_{0.5}, $E[\text{ZnTe}]$ is the total energy per formula unit of ZnTe in zinc-blende structure and $E[\text{C}_2\text{N}_2\text{H}_8]$ is the total energy of the en molecule⁷. The calculated formation energy (0.536 eV per formula) has a smaller magnitude compared to ZnTe (0.80 eV, typical for II-VI compounds). But it is much larger than that of the hybrid perovskite (CH₃NH₃)PbI₃, which is in the range of ± 0.1 eV [75,76]. It should not be surprising that β -ZnTe(en)_{0.5}'s long lifetime relates to its large formation energy.

⁷ Total energy calculation was performed by Dr. Yi-yang Sun.

4.2. Intrinsic-degradation in protected condition

Large formation energy contributes to $\beta\text{-ZnTe(en)}_{0.5}$'s stability. But this is only part of the story. To further understand $\beta\text{-ZnTe(en)}_{0.5}$'s stability, we need to delve into the energy barrier E_A . In fact, as we will see shortly, E_A of intrinsic-degradation is 3x higher than the formation energy E_F .

Thermal study in chapter 3 suggests a nitrogen-protected environment allows us to isolate and study the intrinsic degradation, where the en molecules leave the hybrid structure, and the inorganic slabs, left behind, crystallize into zincblende ZnTe crystals. The reaction can be described using the formula.



In this work, in order to estimate the activation energy, we use Raman mode intensities to monitor the reaction progress (Figure 4-2) under multiple elevated target temperatures. In each experiment, a piece of $\beta\text{-ZnTe(en)}_{0.5}$ crystal is heated from room temperature directly to a target temperature. While being kept at the target temperature, the Raman signal from a fixed volume near the crystal surface is recorded as a function of time. At the very beginning ($t=0$), because the crystal structure is intact, the Raman peaks $A(t=0)$ are at their highest intensities. As en molecules leave the structure, the amount of crystal in the probed volume diminishes. Hence the Raman peaks decay. Eventually, when there is almost no hybrid structure in the probed volume, Raman modes become non-observable. We may normalize $A(t)$ to $A(t=0)=1$, and use the normalized $A(t)$ to quantify the reaction progress.



Figure 4-2. Using Raman intensities to monitor the reaction progress of $\beta\text{-ZnTe(en)}_{0.5}$'s thermal degradation. Peak height vs Time, $A(t)$, exhibit a decay function as the hybrid structure degrades into en and ZnTe in the probed volume. $A(t)$ is normalized to $A(t=0)=1$

Figure 4-3 shows the measured Raman peak height as a function of time $A(t)$ exhibits exponential decays under multiple elevated temperatures, at a target temperature range within 210–270°C. The exponential decays suggest the thermal degradation can be described using a simple first-order kinetic model:

$$A(t) = \exp[-kt] \quad (4-1)$$

$$k = k(T) \propto \exp(-E_A/k_B T) \quad (4-2)$$

Figure 4-4 shows the results using the Arrhenius relationship to estimate activation energy E_A of thermal degradation. The estimated $E_A = 1.62 \pm 0.09$ eV. Extending the fitted exponential relationship $k(T)$ to $T = 300\text{K}$, we may get an estimate of the room temperature lifetime $t_{1/2}(T=300\text{K}) = 1.9 \times 10^8$ years.

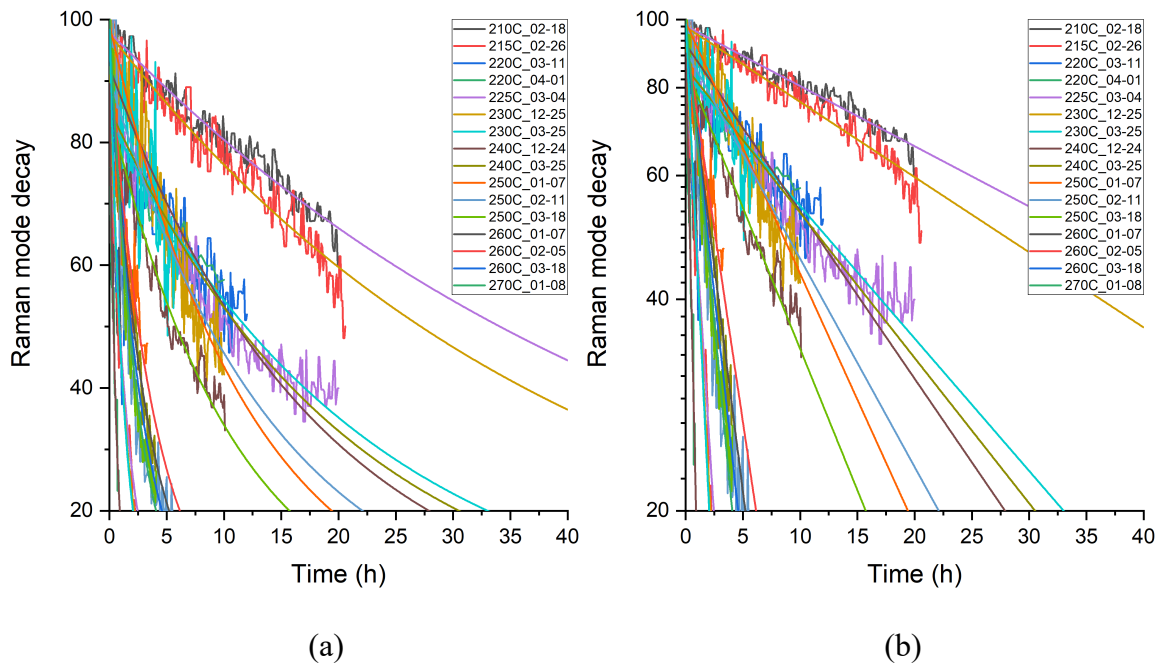


Figure 4-3. Raman peak intensity vs. time at different elevated temperatures ranging from 210 to 270°C, in N₂. Raman mode #20 (133 cm⁻¹) is used. A(t) is plotted in linear scale (a) and log scale (b). Solid line: peak intensity in acquired Raman spectra (not shown) at different times, in intervals of 30 minutes, overlapped with fitted exponential function: $A(t)=A \exp(kt)$. The measured A(t)s show a good fit with exponential decays, except the tails of 220C_03-11 and 225C_03-04, which deviate from exponential decay after ~20th hour, possibly affected by the experiment set up.

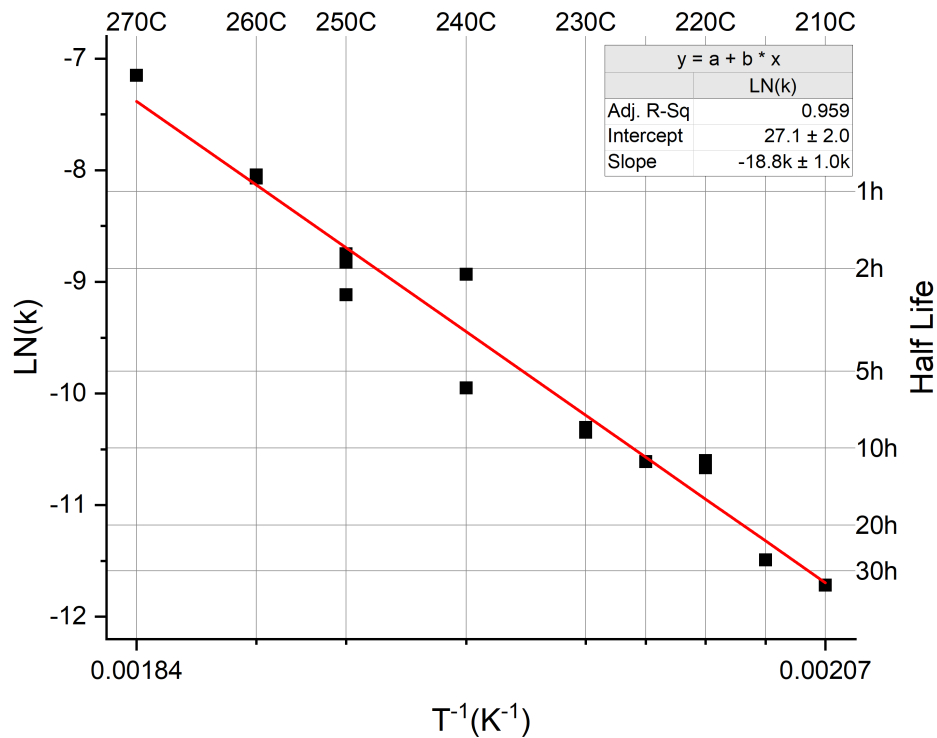


Figure 4-4. Using Arrhenius relationship $k \propto \exp(-E_A/kT)$ to estimate activation energy E_A of thermal degradation. Right axis labels the half-life corresponding to different values of $LN(k)$. Line: Linear fit of $LN(k)$ vs. $1/T$. The rate constant k at each temperature is determined by $1/t_{1/2}$, where $t_{1/2}$ is the intensity decay time of the Raman mode #20 (133 cm^{-1}) reaching 50% of the $t = 0$ intensity. The fitting yielded a slope of $-18800 \pm 959 \text{ K}$, corresponding to an estimated $E_A = 1.62 \pm 0.09 \text{ eV}$.

The measured E_A (1.62 eV) is about 3x E_F (0.53 eV). This signifies factors other than the formation energy, measured by the energy barrier in excess of the formation energy ($E_B = E_A - E_F$), contribute $\frac{2}{3} E_A$. Clarifying the source of E_B will offer further understanding of β -ZnTe(en)_{0.5}'s stability.

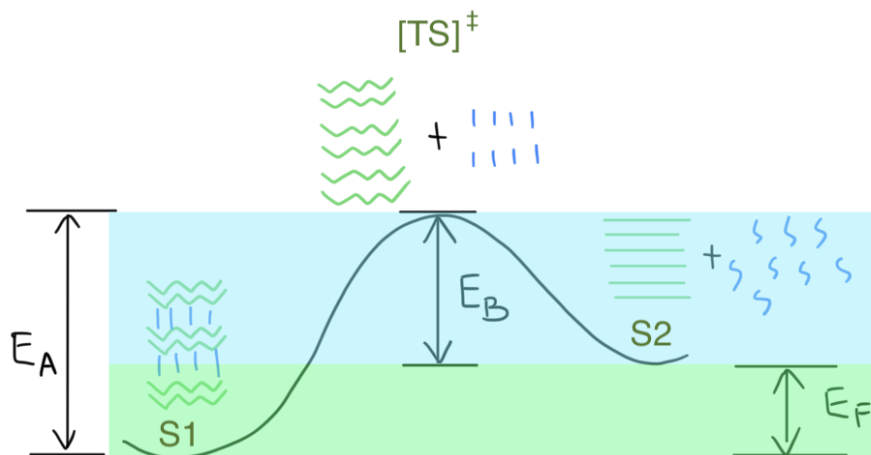


Figure 4-5. The energy landscape of $\beta\text{-ZnTe}(\text{en})_{0.5}$'s thermal degradation. The vertical axis is the total energy. The horizontal axis depicts possible states in the reaction progress. The key states of our concern are: S1, refers to the state of hybrid structure; S2 refers to the state of bulk ZnTe and free en molecules; TS refers to the transition state that either state (S1 or S2) must overcome to be transformed to the other. In the energy landscape, formation energy (E_F) is highlighted in green, and the barrier in excess of the formation energy (E_B) is highlighted in blue.

In the depicted energy landscape (Figure 4-5), the energy barrier in excess of the formation energy equals the difference of the energy levels of TS and S2:

$$E_B = E_{TS} - E_{S2} \quad (4-3)$$

Therefore, one strategy to identify the source of E_B is to compare TS and S2. Note that traveling from S2 to TS, there is no interaction yet between inorganic layers and organic molecules, so we may separately discuss ZnTe and en molecules. In particular, we ask (1) what changes must

happen for ZnTe and en molecules to transform from S2 to TS, and (2) how much energy input is needed for those changes?

First, from S2 to TS, bulk ZnTe needs energy input to break into thin slabs. Second, because ZnTe slabs in hybrid (S1) are in different conformation compared to ZnTe layers in ZnTe crystals (S2), for S2 to become S1, ZnTe layers must be able to adopt the new conformation. We define such a state as ZnTe's transition state (TS). The transformation from S2 to TS needs energy input. Third, the same can be said to the en molecules, that en molecules in S2 adopt different conformations than they are in S1. Going from S2 to S1, there must be a transition state (TS) for en molecules where they adopt S1 confirmation. Traveling to this TS needs energy input. Table 4-1 summarizes the changes from S2 to TS that require energy input.

Table 4-1. Energy input from S2 (defined) to TS (defined) in β -ZnTe(en)_{0.5}'s thermal degradation

Energy input	Substrate	Transformation
E ₁	bulk ZnTe	break into thin slabs between (110) planes
E ₂	ZnTe layers	adopt new conformation
E ₃	en molecules	adopt new conformation

A DFT calculation of the total energy of β -ZnTe(en)_{0.5} (S1), transition state (TS), transition state of relaxed conformation (TS'), and en molecules plus bulk ZnTe (S2) further clarifies the energy contribution from each of the above factors.

Table 4-2. Calculated total energy of β -ZnTe(en)_{0.5} (S1), transition state (TS), transition state after relaxation (TS'), and en molecules plus bulk ZnTe (S2)

	S1(hybrid)	TS	TS' (after relaxation)	S2
en (per molecule)	-38.849 eV/f.u.	-63.837 eV	-64.803 eV	
en (per hybrid f.u.)		-31.919 eV	-32.402 eV	
ZnTe slab (per layer)		-10.462 eV/layer	-11.246 eV/layer	-5.912 eV/f.u. (bulk ZnTe)
ZnTe slab (per f.u).		-5.231 eV	-5.623 eV	

From the total energies (Table 4-2), one can derive the magnitude of E_1 , E_2 , E_3 , and E_A . First, by comparing the total energy of bulk ZnTe to TS' ZnTe, we can get the energy needed for bond breaking between (110) ZnTe planes.

$$\begin{aligned}
 E_1 &= E_{TS'}(\text{ZnTe}) - E_{S2}(\text{ZnTe}) \\
 &= -5.623 \text{ eV} - (-5.912 \text{ eV}) = 0.289 \text{ eV per f.u.}
 \end{aligned}$$

Second, the energy cost for adopting the transition state ZnTe (layer) conformation can be acquired by:

$$\begin{aligned}
 E_2 &= E_{\text{TS}}(\text{ZnTe}) - E_{\text{TS}}'(\text{ZnTe}) \\
 &= -5.231 \text{ eV} - (-5.623 \text{ eV}) \\
 &= 0.392 \text{ eV per f.u.}
 \end{aligned}$$

Third, for en molecules, the energy cost to adopt the transition state conformation is:

$$\begin{aligned}
 E_3 &= E_{\text{TS}}(\text{en}) - E_{\text{TS}}'(\text{en}) \\
 &= -31.919 \text{ eV} - (-32.402 \text{ eV}) \\
 &= 0.483 \text{ eV per f.u.}
 \end{aligned}$$

The activation barrier:

$$\begin{aligned}
 E_A &= E_{\text{TS}}(\text{en}) + E_{\text{TS}}(\text{ZnTe}) - E_{\text{S1}} \\
 &= -31.919 \text{ eV} + (-5.231 \text{ eV}) - (-38.849 \text{ eV}) \\
 &= 1.699 \text{ eV per f.u}
 \end{aligned}$$

The calculated activation energy barrier (1.699 eV) is within the uncertainty of the measurement (1.62 ± 0.09 eV). We now have decoupled the activation barrier into four different factors: $E_A = E_F + (E_1 + E_2 + E_3)$, and can compare their shares of contribution to the activation barrier (Figure 4-6). The formation energy accounts for $\sim \frac{1}{3} E_A$, while the energy input needed to reach TS from S2 (EB) accounts for an additional $\frac{2}{3} E_A$.

The discussion can be extended to other hybrid materials to help us understand and improve their stability. For example, hybrid perovskite, in general, has inadequate stability, not only because they have smaller formation energy, but because the organic molecules within the hybrid

perovskite, such as MeNH_3 in MAPbI_3 , can freely rotate. The two factors both contribute to a smaller energy barrier. This work enables a vision that hybrid perovskite may capture additional stability if one can engineer a transition state with a higher barrier, perhaps via choosing an organic molecule such that the inorganic part will have the “right” bonding with the organic molecule and lock it in a conformation that would be unfavored outside the inorganic framework.

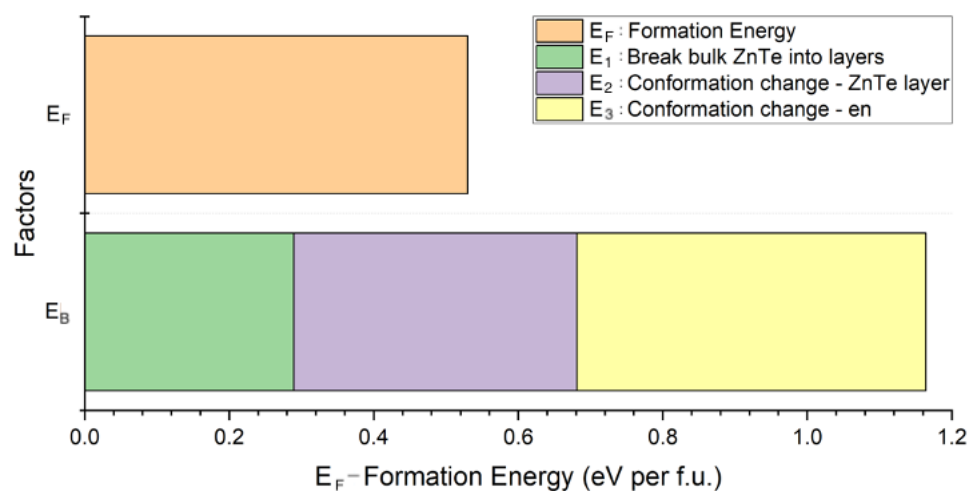


Figure 4-6. Factors and their contributions to $\beta\text{-ZnTe}(\text{en})_{0.5}$'s thermal degradation barrier. The total barrier E_A can be decoupled into E_F , the formation energy, and E_B , the barrier in excess of the formation energy. E_B can be further decoupled into E_1 (break bulk ZnTe into ZnTe layers), E_2 (ZnTe layer conformation change), and E_3 (en conformation change).

4.3. Oxidation in ambient condition

$\beta\text{-ZnTe}(\text{en})_{0.5}$ has a large energy barrier toward thermal degradation. However, a thermodynamically stable structure may still be environmentally unstable because molecules in ambient air can enable alternate pathways with lower energy barriers. For example, silicene is

stable in a vacuum but is usually oxidized very quickly in the air [77]. In this section, we discuss β -ZnTe(en)_{0.5}'s degradation barrier in ambient air. We choose ambient air degradation because it has a lower barrier compared to the intrinsic degradation. Usually, it's the pathway with the lowest barrier that determines the lifetime of the starting material. Studying ambient air degradation allows an estimate of β -ZnTe(en)_{0.5}'s lifetime in typical operating conditions.

The thermal study in chapter 3 demonstrates that β -ZnTe(en)_{0.5}'s degradation in ambient air involves oxidation. Provided with enough energy, en molecule leaves the structure, and ZnTe slabs are oxidized to ZnO, Te, and TeOx. The overall oxidation process is much more complex than thermal degradation. Nevertheless, we can expect it has a smaller E_A than intrinsic-degradation because, within similar time durations, tellurium (the degradation product in ambient air) becomes observable at 160°C, whereas ZnTe (the product from the intrinsic degradation) only becomes observable when the temperature is greater than 230°C.

Similar to the measurement in the nitrogen-protected environment, here, we use Raman decay, denoted as $A(t)$ to monitor reaction progress in multiple elevated temperatures. Then, by fitting the measured Raman decays, we extract the effective rate constant $k(T)$, which will be used to estimate the overall kinetic barrier. Note that because tellurium has a much higher absorption than ZnTe in the relevant wavelength, the Raman intensity decay of a hybrid mode in oxidation is caused by the growing tellurium thickness (the end state of the oxidation experiment coincides with a tellurium depth $\sim 10^{-2}$ μm), while in intrinsic degradation, both en evaporation and ZnTe formation contribute to the Raman decay.

Unlike the case of intrinsic degradation, in which the observed Raman intensity $A_{\text{nitrogen}}(t)$ exhibits exponential decay, fitting the ambient air curves $A_{\text{air}}(t)$ with exponential (Equation 4-1)

results in large systematic residues, suggesting a single exponential decay may not adequately describe the oxidation process. To improve the fitting quality, in addition to simple exponential, we use the stretched-exponential to describe the reaction process in ambient air.

$$A(t) = \exp[-(kt)^b], \quad \text{with } 0 < b < 1 \text{ and } k = k(T) \quad (4-4)$$

In contrast to the simple exponential decay where a global rate (k) is assumed, the stretched-exponential view the process as a linear combination of different rates, whose weights can be described using a continuous distribution [78,79]. In the expression of the stretched exponential decay (Equation 4-4), there are two parameters: (1) k – determining the position of effective rate, and (2) b – controlling the width of the distribution.

The stretched-exponential model considers that the reaction rates, corresponding to different sample depths, are different in a solid. In our case, accumulation of the tellurium products from the early stage will remain on the sample, which affects the decay of the underneath material. From the perspective of the oxidation agent, such as O_2 , H_2O molecules, tellurium layer becomes an obstacle for them to reach the hybrid surface underneath. Therefore, we expect a slower rate constant in a later stage compared to the early stage. We choose stretched-exponential because it captures the dispersive rate along the different stages of the reaction and thus is expected to give more accurate estimate of lifetime. Using a single exponential, on the other hand, may underestimate the lifetime. We note that the stretched-exponential does not provide much insight to resolve the explicit reaction mechanism. However, it does not hinder the quest to study the overall kinetic barrier of natural degradation and estimate the room temperature lifetime.

Figure 4-7 depicts the observed Raman decay, fitted with exponential and stretched exponential.

From each of the models, the activation barrier (E_A) and the half-life at room temperature $t_{1/2}(T=300K)$ are estimated. For the stretched exponential model, we got $b = 0.49 \pm 0.03$.

4.3.1. Exponential

In the exponential model, the observed $A(t,T)$ data are fitted with Equation 4-1, despite not every $A(t,T)$ curve exhibiting exponential decay within the observation time frame (20 hours), fitting $k(T)$ s with the Arrhenius relationship (Equation 4-2) gives an estimate of the activation energy of the oxidation process.

$$\begin{aligned} E_A &= -\text{slope} \times k_B \\ &= 9.9 \times 10^3 \text{ K} \times 8.617 \times 10^{-5} \text{ eV/K} \\ &= 0.85 \text{ eV} \end{aligned}$$

Extending the fitted exponential relationship $k(T)$ to $T = 300K$, we can calculate an estimate of the room temperature lifetime:

$$\begin{aligned} t_{1/2}(T=300K) &= 1/k(T=300K) \\ &= 1/\exp(\text{slope} \times 1/300 + Y_{\text{intercept}}) \\ &= 1/\exp(-9.9 \times 10^3 \times 1/300 + 13) \text{ seconds} \\ &= 19 \text{ years.} \end{aligned}$$

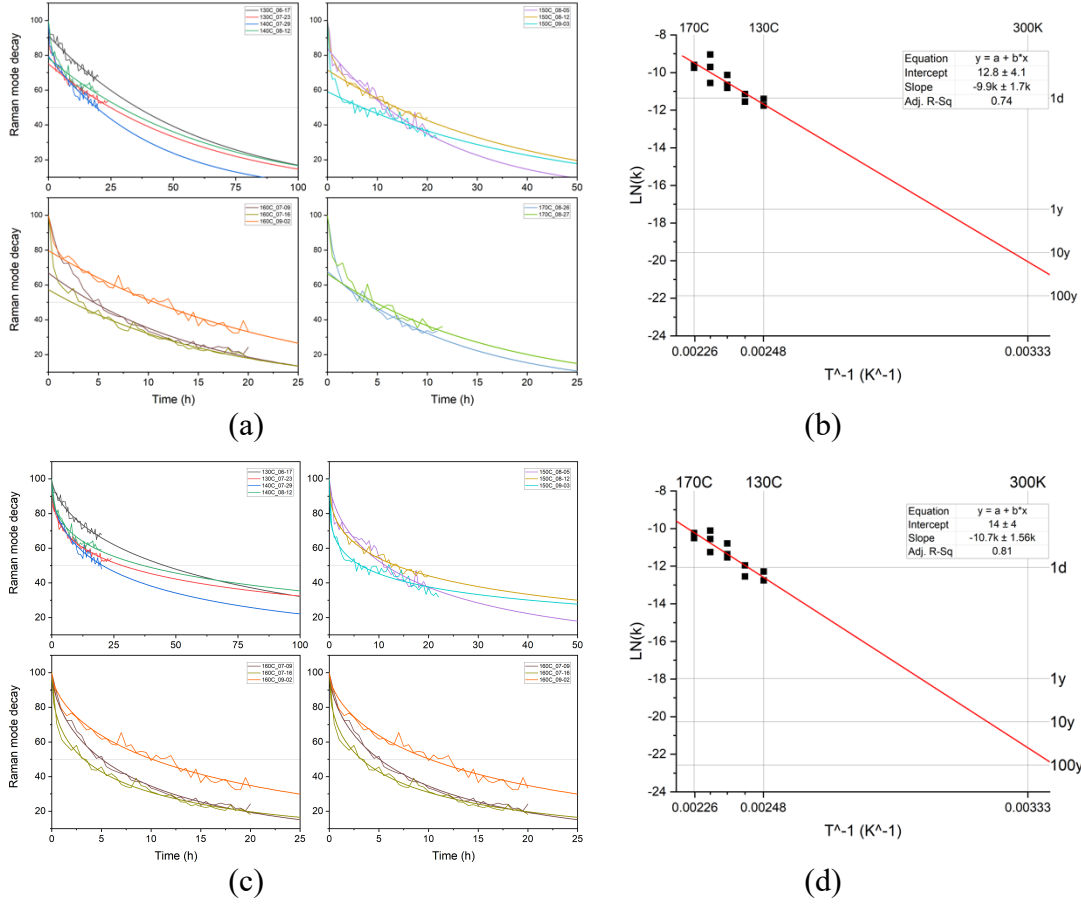


Figure 4-7. Observed Raman intensity vs Time $A(t)$, overlapped with the fitted $A(t)$ in an extended time scale using two different fitting models: exponential (a), stretched exponential (c), their corresponding Arrhenius relationship $k(T)$ is plotted in (b), (d), respectively, to yield an estimate of E_A and $t_{1/2}(T=300K)$.

4.3.2. Stretched exponential

Fitting the observed $A(t)$ with the stretched exponential (Equation 4-4) will give us $k(T)$. An estimate of E_A can be derived from the slope in the Arrhenius plot of $k(T)$.

$$\begin{aligned}
 E_A &= -\text{slope} \times k_B \\
 &= 10.7 \times 10^3 \text{ K} \times 8.617 \times 10^{-5} \text{ eV/K} = 0.92 \text{ eV}
 \end{aligned}$$

From Equation 4-4, the lifetime at room temperature can be estimated by:

$$\begin{aligned}
 t_{1/2}(T=300K) &= [1/k(T=300K)] \text{LN}[2]^{1/\bar{b}} \\
 &= [1/\exp(\text{slope} \times 1/300 + Y_{\text{intercept}})] \text{LN}(2)^{1/\bar{b}} \\
 &= [1/\exp(-10.7 \times 10^3 \times 1/300 + 14)] \text{LN}(2)^{(1/0.49)} \text{ seconds} \\
 &= 39 \text{ years}
 \end{aligned}$$

$\bar{b}$ is the average of the fitted $[b_i]$ from Raman decays $A_i(t)$.

Table 4-3. Estimated E_A and $t_{1/2}(T=300K)$ from exponential, and stretched exponential fit

	Equation	E_A (per f.u.)	$t_{1/2}(T=300K)$
Exponential	$A(t)=\exp(-kt)$, $k=k(T)$	0.85 eV	19 years
Stretched exponential	$A(t)=\exp[-(kt)^b]$, $k = k(T)$ $0 < b < 1$	0.92 eV	39 years

Table 4-3 summarizes the E_A and $t_{1/2}(T=300K)$ from the two models. The estimated E_A varies from 0.85 eV to 0.92 eV. The experiment suggests a lower bound of $\beta\text{-ZnTe(en)}_{0.5}$'s room temperature lifetime is in the order of 20 years. The prediction is in accord with the most aged sample (S03-m, 18-year-old) still showing areas with the pristine spectroscopic features.

4.4. Summary

In general, stability includes three key aspects:

- (1) Intrinsic effect, measured by the activation energy (E_A) of the degradation process in a protected environment. For $\beta\text{-ZnTe(en)}_{0.5}$, the measured E_A from the Arrhenius plot is 1.62 ± 0.09 eV. E_A represents the binding strength between the organic molecules and the inorganic layer. Using the transition state theory, E_A can be decoupled into E_F , the formation energy, and E_B , the barrier in excess of the formation energy. The calculated barrier from the proposed transition state is $E_F + E_B \approx 1.70$ eV, which is within the uncertainty of the measured E_A . The decoupling suggests one may raise E_B and improve the stability of a hybrid material via engineering a transition state with higher energy. The experiment shows the room-temperature lifetime of $\beta\text{-ZnTe(en)}_{0.5}$ in a protected environment can achieve 1.9×10^8 years.
- (2) The surface or edge effect, which is most relevant to the chemical stability of the material in different environments, where degradation can initiate through processes such as oxidation and/or evaporation of the terminating molecules. Alternative organic layers in $\beta\text{-ZnTe(en)}_{0.5}$, combined with their large binding strength (suggested by the large E_A in intrinsic degradation), hindered the surface effect because each organic layer underneath will serve as a new protective layer.
- (3) The structural defects may provide easier paths for degradation. The substantial variation in shelf life from sample to sample even between different regions within one sample indicates that the observed degradation might not be intrinsic in nature but is associated with a surface imperfection or structural defects.

The measured E_A for $\beta\text{-ZnTe(en)}_{0.5}$'s natural degradation in ambient air varies from 0.85 to 0.92 eV. Experiments also predict the $\beta\text{-ZnTe(en)}_{0.5}$'s room temperature lifetime in ambient air can exceed 20 years.

Chapter 5: Identification and analysis of Raman modes and their selection rules in $\beta\text{-ZnTe(en)}_{0.5}$

Heterostructures such as 1D superlattice typically have imperfect interfaces [12–14]. These defects modulate the ideal structure and bring an extra layer of complexities into the observed Raman spectrum. Interpretations of such spectrum are often lack precision if not with ambiguities, secluding one's intention to understand the vibration modes belonging to the unmodulated ideal structure. $\beta\text{-ZnTe(en)}_{0.5}$'s exceptionally high crystallinity, on the other hand, allows its Raman-active vibrational modes to be analyzed with fewer complications. A systematic understanding of $\beta\text{-ZnTe(en)}_{0.5}$'s Raman modes not only supports the degradation study in the earlier chapters but paves the roads for future applications.

In this chapter, we will follow the three steps to analyze $\beta\text{-ZnTe(en)}_{0.5}$'s Raman modes: (1) perform a first-principle calculation to derive a complete set of Γ -point phonon modes, with their frequencies and displacement patterns/symmetries; (2) examine Raman spectra measured from a pristine crystal under a set of on-axis polarization configurations and assign Raman peaks in the context of the Raman selection-rules and computation results of the phonon frequencies and symmetries; (3) estimate $\beta\text{-ZnTe(en)}_{0.5}$'s Raman tensors using two independent measurements - the on-axis polarizations and angle-resolved polarizations. In step (2) and (3), we will compare peak assignments and estimated tensor components with the results derived from the first-principle calculations. Their discrepancies between the computation results and the measurements will be discussed.

5.1. Vibrations in the $\beta\text{-ZnTe(en)}_{0.5}$ system

A classic treatment of vibrations in a superlattice assumes the knowledge of phonon dispersion of each component [80–83]. While this approach has been demonstrated for systems such as GaAs/AlAs [84,85], in $\beta\text{-ZnTe(en)}_{0.5}$, because the conformation of ZnTe slab and en molecules are highly distorted compared to their bulk counterparts, neither of their phonon spectrum is known to us. For this reason alone, we should seek an alternative approach to treat the vibrations in the $\beta\text{-ZnTe(en)}_{0.5}$ system. Other notable differences between $\beta\text{-ZnTe(en)}_{0.5}$ and traditional superlattice are: (1) $\beta\text{-ZnTe(en)}_{0.5}$'s two components - ZnTe slab and en molecule are drastically different in their structures; (2) the ZnTe slab in $\beta\text{-ZnTe(en)}_{0.5}$ is only two-monolayer thick. Those differences favor an alternate approach to studying $\beta\text{-ZnTe(en)}_{0.5}$'s vibration modes, i.e., treating it as a new crystal structure.

In this work, we use a spring-mass 3D network to model $\beta\text{-ZnTe(en)}_{0.5}$'s vibrations. The masses are the atomic mass of Zn, Te, N, C, H. Each spring in the network connects two atoms and is described by a spring constant, also known as the force constant. The spring constants capture the interatomic interactions, which can be further decomposed into the ion-ion interactions and the electron-ion interactions. While the former (ion-ion) is Coulomb interactions, the latter (electron-ion) is non-trivial - it involves electron densities of the system in disturbed ion configurations. We can derive the interatomic forces using a first-principle approach in the framework of density functional perturbation theory (DFPT). With the growth of computation power, such an approach is becoming not only practical but preferable in the case of a new superlattice system. The DFPT calculation in this work is performed by Dr. Yi-yang Sun's group.

Having known the masses and force constants, the spring-mass system can be solved using Newton's second law, resulting in a set of linear differential equations in their matrix form:

$$MX'' = -KX \quad (5-1)$$

M has the mass of atoms. X describes atom vibrations. K has interatomic force constants (derived from the DFPT calculation). To acquire normal modes, we decouple atom vibrations into a space-variant part and a time-variant part by letting X equals:

$$X = A e^{i\omega t} \quad (5-2)$$

A describes the displacement pattern of atoms in the normal mode. $e^{i\omega t}$ captures the coherent motion of the normal mode. Solving Equation 5-1, 5-2 gives:

$$M^{-1}K = \omega^2 A \quad (5-3)$$

The vibrational frequencies and displacement patterns can then be read from $M^{-1}K$'s eigenvalues and eigenvectors.

Table 5-1 presents the vibration frequency, atomic displacement/symmetry of each normal mode derived from Equation 5-3. The calculation was performed using the Phonopy open source project [86]. Note that only Γ -point phonons are considered in the calculation. The phonons away from Γ -point will not participate in the first-order Raman scattering process for the reason of momentum conservation. The calculated normal modes are labeled from #1 to #96 with ascending frequencies. Depending on the localization of the vibration, each normal mode is classified into one of the following types:

Inorganic:	mostly the motion of the inorganic slabs
Coupled:	involving both slabs and molecules
Molecule:	molecule backbone (N-C-C-N) movement, no motion of ZnTe slabs
NH/CH:	NH ₂ and CH ₂ groups move in phase
NH:	NH ₂ groups move in phase
CH:	CH ₂ groups move in phase

Note that because of the inorganic slab being very thin and the strong binding between the inorganic-organic component, there are very few modes involving only the inorganic part. Mode #4-7, #17 can be approximately viewed as the inorganic modes. Besides the coupled modes, the rest four types of modes are nearly confined within the en molecule layers, because the en molecule is much lighter than the inorganic component.

Table 5-1. β -ZnTe(en)_{0.5}'s vibrational modes – their frequencies, symmetries, and atom displacement patterns ⁸

Mode # (freq., cm ⁻¹)	Symmetry in (a,b,c)	Comments	type
4 (14.3)	B _{2g}	Relative motion of the two slabs along c	inorganic

⁸ Animated displacement pattern of each mode is available on the webpage: https://tye2.tk/phonon_b-zte/

5 (23.0)	A _g	Relative motion of the two slabs along a	inorganic
6 (49.5)	A _u	Relative motion within each slab along c; two slabs in phase.	inorganic
7 (53.0)	B _{3g}	Relative motion within each slab along c; two slabs out of phase.	inorganic
8 (55.0)	B _{1g}	Relative motion of each slab along b; two slabs out of phase.	coupled
9 (70.7)	B _{2u}	Relative motion within each slab along a; two slabs in phase.	coupled
10 (70.8)	B _{3u}	All moving along b; two slabs in phase.	coupled
11 (91.6)	B _{1g}	Mostly along a; two slabs out of phase along b	coupled
12 (95.5)	B _{1u}	Molecule bending in c, adjacent layers in phase	coupled
13 (95.9)	A _u	Molecule bending in c, adjacent layers out of phase	coupled
14 (95.9)	A _g	Relative motion within each slab along b; two slabs out of phase.	coupled
15 (98.5)	B _{2g}	C-C motion along c; adjacent molecules out of phase	coupled
16 (99.1)	B _{3g}	C-C motion along c; adjacent molecules in phase	coupled

17 (119.4)	B _{3u}	Relative motion within each slab along b; adjacent slabs out of phase	inorganic
18 (125.4)	B _{2u}	Molecular motion along b; adjacent ones in phase	coupled
19 (133.3)	B _{3u}	Molecular motion along b; adjacent ones out of phase	coupled
20 (137.1)	A _g	Relative motion of the two monolayers within the slab in the a-b plane; two slabs out-of-phase	coupled
21 (147.5)	B _{2u}	Mostly relative motion in each slab along a; adjacent slab in phase	coupled
22 (151.5)	B _{3g}	Relative motion in each slab along c; Te and Zn out of phase; N-C-C-N bending along c; adjacent molecules in phase	coupled
23 (152.3)	B _{2g}	Relative motion in each slab along c; Te and Zn out of phase; N-C-C-N bending along c; adjacent molecules out of phase	coupled
24 (153.4)	B _{1g}	Mostly relative motion in each slab along a; adjacent slab out of phase	coupled
25 (163.5)	B _{1u}	Relative motion in each slab along c; Te and Zn out of phase	coupled
26 (166.6)	A _u	Relative motion in each slab along c; Te and Zn out of phase	coupled
27 (172.6)	B _{2g}	Relative motion in each slab along c; Te and Zn out of phase	coupled
28 (175.8)	B _{3g}	Relative motion in each slab along c; Te and Zn out of phase	coupled

29 (179.1)	B _{3u}	Relative motion in each slab along a,b; adjacent slab in phase	coupled
30 (180.1)	A _g	Relative motion in each slab along a,b; adjacent slab out of phase	coupled
31 (190.7)	B _{1u}	N-C-C-N rocking around b; adjacent molecules in phase	coupled
32 (191.4)	A _u	N-C-C-N rocking around b; adjacent molecules out of phase	coupled
33 (192.8)	B _{2u}	Mostly relative motion within the slab along b; two slabs in phase. Zn,Te out of phase	coupled
34 (203.1)	B _{1g}	Mostly relative motion within the slab along b; two slabs out of phase. Zn,Te out of phase	coupled
35 (243.5)	B _{3u}	Coupled motion of slabs and molecule along a,b; adjacent molecules out of phase	coupled
36 (249.0)	B _{2u}	Coupled motion of slabs and molecule along a,b; adjacent molecules in phase	coupled
37 (289.7)	A _g	Coupled motion of slabs and molecule in the a-b plane, mostly molecular rotations, adjacent molecules out of phase	coupled
38 (289.9)	B _{1g}	Coupled motion of slabs and molecule along a,b; adjacent molecules out of phase	coupled
39 (453.1)	B _{3u}	Coupled motion of slabs and molecule along a,b; adjacent molecules out of phase	coupled
40 (454.6)	B _{2u}	Coupled motion of slabs and molecule along a,b; adjacent molecules in phase	coupled

41 (538.8)	A _g	N-C-C-N stretching along b; adjacent N-C in phase; adjacent molecules in phase	molecule
42 (540.6)	B _{1g}	N-C-C-N stretching along b; adjacent N-C in phase; adjacent molecules out of phase	molecule
43 (606.6)	B _{2g}	N-H rocking; C-H rocking; Ns within molecule out of phase; adjacent molecules in phase	NH, CH
44 (607.0)	B _{3g}	N-H rocking; C-H rocking; Ns within molecule out of phase; adjacent molecules out of phase	NH, CH
45 (608.4)	B _{1u}	N-H rocking; C-H rocking; Ns within molecule in phase; adjacent molecules in phase	NH, CH
46 (608.9)	A _u	N-H rocking; C-H rocking; Ns within molecule in phase; adjacent molecules out of phase	NH, CH
47 (751.9)	A _u	C-H rocking; N-H twisting; N-C-C-N bending along c; adjacent molecules out of phase	CH
48 (751.9)	B _{1u}	C-H rocking; N-H twisting; N-C-C-N bending along c; adjacent molecules in phase	CH
49 (949.5)	B _{2g}	N-H twisting; C-H rocking; C-C motion along c; adjacent molecules out of phase	NH, CH
50 (949.9)	B _{3g}	N-H twisting; C-H rocking; C-C motion along c; adjacent molecules in phase	NH, CH
51 (996.3)	A _g	C-C motion along a; N-H wagging; adjacent molecules in phase	molecule
52 (1002.4)	B _{1g}	C-C motion along a; N-H wagging; adjacent molecules out of phase	molecule

53 (1046.0)	B _{2u}	C-N stretching along b; N-H wagging; adjacent molecules in phase	molecule
54 (1054.0)	B _{3u}	C-N stretching along b; N-H wagging; adjacent molecules out of phase	molecule
55 (1060.0)	B _{1u}	N-H twisting; C-H twisting; (only Hs are moving); adjacent molecules out of phase	NH, CH
56 (1060.4)	A _u	N-H twisting; C-H twisting; (only Hs are moving); adjacent molecules in phase	NH, CH
57 (1068.0)	A _g	N-C-C-N stretching along b; adjacent N-C out of phase; adjacent molecules in phase	molecule
58 (1071.7)	B _{1g}	N-C-C-N stretching along b; adjacent N-C out of phase; adjacent molecules out of phase	molecule
59 (1104.3)	B _{3u}	N-H wagging; C-H wagging; C-N stretching along b; adjacent molecules out of phase	NH
60 (1105.9)	B _{2u}	N-H wagging; C-H wagging; C-N stretching along b; adjacent molecules in phase	NH
61 (1156.6)	A _g	N-H wagging; C-C motion along a; adjacent molecules in phase	NH
62 (1158.4)	B _{1g}	N-H wagging; C-C motion along a; adjacent molecules out of phase	NH
63 (1240.5)	B _{2g}	N-H twisting; C-H twisting; C-C motion along c; adjacent molecules out of phase	NH, CH
64 (1240.6)	B _{3g}	N-H twisting; C-H twisting; C-C motion along c; adjacent molecules in phase	NH, CH

65 (1286.4)	B _{3u}	C-H wagging; N-H wagging; C-N stretching along b; adjacent molecules out of phase	CH
66 (1287.1)	B _{2u}	C-H wagging; N-H wagging; C-N stretching along b; adjacent molecules in phase	CH
67 (1305.7)	B _{3g}	N-H twisting; C-H twisting; N-C-C-N bending along c; adjacent Cs out of phase; adjacent molecules in phase	NH, CH
68 (1305.7)	B _{2g}	N-H twisting; C-H twisting; N-C-C-N bending along c; adjacent Cs out of phase; adjacent molecules out of phase	NH, CH
69 (1330.5)	B _{1u}	N-H twisting; C-H twisting; N-C-C-N bending along c; adjacent Cs in phase; adjacent molecules in phase	NH, CH
70 (1330.6)	A _u	N-H twisting; C-H twisting; N-C-C-N bending along c; adjacent Cs in phase; adjacent molecules out of phase	NH, CH
71 (1340.4)	A _g	C-H wagging; C-C stretching along b; adjacent molecules in phase	CH
72 (1340.6)	B _{1g}	C-H wagging; C-C stretching along b; adjacent molecules out of phase	CH
73 (1432.7)	B _{1g}	C-H scissoring; Cs within molecule in phase; adjacent molecules in phase	CH
74 (1433.1)	A _g	C-H scissoring; Cs within molecule in phase; adjacent molecules out of phase	CH
75 (1443.7)	B _{3u}	C-H scissoring; Cs within molecule out of phase; adjacent molecules out of phase	CH

76 (1443.8)	B _{2u}	C-H scissoring; Cs within molecule out of phase; adjacent molecules in phase	CH
77 (1577.4)	B _{2u}	N-H scissoring; Ns within molecule out of phase; adjacent molecules in phase	NH
78 (1577.6)	B _{3u}	N-H scissoring; Ns within molecule out of phase; adjacent molecules out of phase	NH
79 (1578.6)	B _{1g}	N-H scissoring; Ns within molecule in phase; adjacent molecules out of phase	NH
80 (1579.4)	A _g	N-H scissoring; Ns within molecule in phase; adjacent molecules in phase	NH
81 (2928.4)	B _{1g}	C-H symmetric stretching; Cs within molecule in phase; adjacent molecules out of phase	CH
82 (2928.9)	A _g	C-H symmetric stretching; Cs within molecule in phase; adjacent molecules in phase	CH
83 (2941.2)	B _{2u}	C-H symmetric stretching; Cs within molecule out of phase; adjacent molecules out of phase	CH
84 (2942.1)	B _{3u}	C-H symmetric stretching; Cs within molecule out of phase; adjacent molecules in phase	CH
85 (2965.6)	B _{3g}	C-H anti-symmetric stretching; Cs within molecule out of phase; adjacent molecules in phase	CH
86 (2965.6)	B _{2g}	C-H anti-symmetric stretching; Cs within molecule out of phase; adjacent molecules out of phase	CH
87 (2990.5)	A _u	C-H anti-symmetric stretching; Cs within molecule in phase; adjacent molecules out of phase	CH

88 (2990.5)	B _{1u}	C-H anti-symmetric stretching; Cs within molecule in phase; adjacent molecules in phase	CH
89 (3175.6)	B _{2u}	N-H symmetric stretching; Ns within molecule out of phase; adjacent molecules in phase	NH
90 (3178.2)	B _{3u}	N-H symmetric stretching; Ns within molecule out of phase; adjacent molecules out of phase	NH
91 (3178.7)	B _{1g}	N-H symmetric stretching; Ns within molecule in phase; adjacent molecules out of phase	NH
92 (3179.3)	A _g	N-H symmetric stretching; Ns within molecule in phase; adjacent molecules in phase	NH
93 (3207.9)	A _g	N-H anti-symmetric stretching; Ns within molecule in phase; adjacent molecules out of phase	NH
94 (3207.9)	A _g	N-H anti-symmetric stretching; Ns within molecule in phase; adjacent molecules in phase	NH
95 (3208.2)	B _{3g}	N-H anti-symmetric stretching; Ns within molecule out of phase; adjacent molecules in phase	NH
96 (3208.3)	B _{2g}	N-H anti-symmetric stretching; Ns within molecule out of phase; adjacent molecules out of phase	NH

Comments

Completeness: The tabulated vibrational modes have zero crystal momentum and do not propagate in the lattice. For this reason, it is sufficient to use only one unit cell to describe the vibration of the entire crystal. β -ZnTe(en)_{0.5} has 32 atoms in each unit cell. Because each atom

has 3 degrees of freedom, the vibration has 96 degrees of freedom per unit cell, thus 96 normal modes including #1 - #3 with zero frequency.

Symmetry: Γ -point normal modes of the β -ZnTe(en)_{0.5} respect to the D_{2h} symmetry group, and can be further reduced to:

$$\Gamma = 14A_g(R) + 14B_{1g}(R) + 10B_{2g}(R) + 10B_{3g}(R) + 10A_u(IR) + 10B_{1u}(IR) + 14B_{2u}(IR) + 14B_{3u}(IR) \quad (5-4)$$

R means the Raman-active modes, IR means the IR-active modes. Note that in D_{2h}, each irreducible representation is either Raman-active or IR-active.

Frequency-dependent trend: At higher frequencies (#43-#96: above 600 cm⁻¹), vibrations are confined within the molecule layers and are driven mostly by the atoms within the same molecule. Note that a subset of the modes (#51-#96: above 995 cm⁻¹) can be assigned using the crystalline ethylenediamine vibrational modes [62]. Because one unit cell of β -ZnTe(en)_{0.5} has two ethylenediamine molecules, each mode of ethylenediamine splits into two modes in β -ZnTe(en)_{0.5} - symmetric and antisymmetric⁹. At lower frequencies (#8-#42: below 550 cm⁻¹), molecule vibrations are coupled with ZnTe slabs. The low-frequency modes contribute major heat transport under room temperature [48,49].

⁹ The correspondence between a subset of en modes and β -ZnTe(en)_{0.5} modes can be found in Appendix D.

5.2. Raman-selection rules for β -ZnTe(en)_{0.5}

The unit cell of β -ZnTe(en)_{0.5} has D_{2h} symmetry. In the D_{2h} point group, A_g, B_{1g}, B_{2g}, B_{3g} are the irreducible representations that are Raman-active. According to Loudon's work, when using the principle axes - [100], [010], and [001], Raman tensors of a D_{2h} system adopt the following forms:

$$A_g = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$
$$B_{1g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, B_{2g} = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, B_{3g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (5-5)$$

With Equation 2-7, 5-5, phonon modes belonging to a specific symmetry can be selected using an appropriate polarization configuration. For example, the Raman tensor for A_g modes has its non-zero components sitting on the diagonal positions. To select the diagonal components, one can illuminate the specimen with a beam polarized to one of the three principal axes and analyze the Raman signal using the same polarization. Raman tensors for the other three symmetries (B_{1g}/B_{2g}/B_{3g}) have non-diagonal components. Phonons having those symmetries yield Raman signal polarized perpendicular to the incident beam, assuming both the incident and scattered beams are propagating along on-axis directions.

In this work, we observe back-scattering Raman signals propagating along the crystal principal axes. Under backscattering configuration, it is possible to predict whether TO or LO modes will be observed given the propagating direction and the mode symmetry. Table 5-2 summarizes these selection rules.

Table 5-2. TO/LO dependence on mode symmetry and propagating direction. ‘A’ stands for allowed, ‘X’ stands for forbidden

symmetry	phonon polarization	photon propagating direction		
		a	b	c
A_g	a or b	No LO-TO splitting, A		
B_{1g}	a or b	X	X	TO, A
B_{2g}	c	TO, X	TO, A	LO, X
B_{3g}	c	TO, A	TO, X	LO, X

When limiting photon propagating direction in one of the three principal axes, twelve different configurations (3 propagating direction x 2 polarization for incident beam x 2 polarization for scattered beam) can be constructed to study the polarized Raman signals. Table 5-3 summarizes the twelve configurations and the selected symmetry under each of the configurations. In order to designate the polarization and direction of the incident and scattered light beam, Porto notation is used in this table. The first and last letter in the notation indicates propagation direction for the incident and scattered light, respectively. The first and last letter inside the parenthesis indicate polarization of the incident and scattered light, respectively. For example, $b(ac)\bar{b}$ would be an incident beam propagating along b, polarized in a, and the scattered beam propagating along -b, polarized in c.

Table 5-3. Raman selection rules for $\beta\text{-ZnTe(en)}_{0.5}$ calculated with Equation 2-7, 5-5

	A_g	B_{1g}	B_{2g}	B_{3g}
$b(aa)\bar{b}$ $c(aa)\bar{c}$	a^2	0	0	0
$b(cc)\bar{b}$ $a(cc)\bar{a}$	c^2	0	0	0
$a(bb)\bar{a}$ $c(bb)\bar{c}$	b^2	0	0	0
$b(ac)\bar{b}$ $b(ca)\bar{b}$	0	0	e^2	0
$a(bc)\bar{a}$ $a(cb)\bar{a}$	0	0	0	f^2
$c(ab)\bar{c}$ $c(ba)\bar{c}$	0	d^2	0	0

The twelve configurations are grouped into six pairs. Note that these configurations are sufficient to select the phonon modes with every possible symmetry. In particular, A_g modes can be selected in parallel configurations where incident light and scattered light have parallel polarizations. There are three pairs of parallel polarization configurations in total. Each of them selects one of the three diagonal components in the A_g Raman tensor. Although two configurations within each pair select the same component in the A_g Raman tensor, phonons of different propagating directions are selected under the two configurations. For example, $a(cc)\bar{a}$ and $b(cc)\bar{b}$ both can detect the c component of the Raman tensor for an A_g mode, but photon wave vectors are in the a and b direction, respectively, thus, in general the Raman tensor components are not the same. $B_{1g}/B_{2g}/B_{3g}$ can be selected in cross configurations, where incident light and scattered light have perpendicular polarizations. There are three pairs of cross

configurations in total. Each of them selects exactly one symmetry. Unlike parallel configurations, the two cross polarization configurations within each pair select phonons with the same propagating direction.

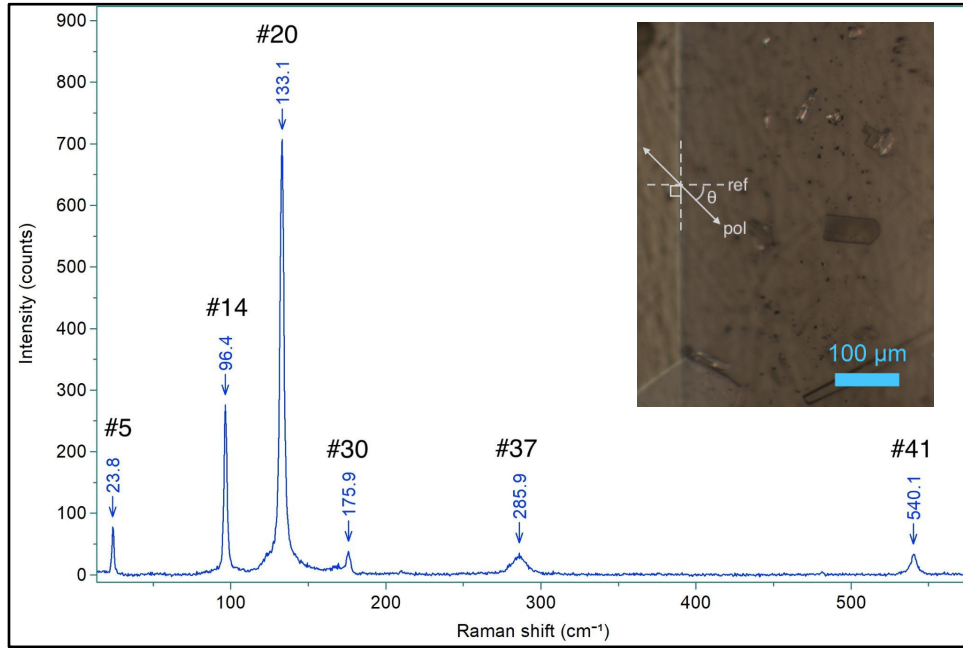
5.3. Polarized Raman spectra/Raman mode assignments for $\beta\text{-ZnTe(en)}_{0.5}$

The prior section has established the twelve polarization configurations enabling us to select phonon modes with any Raman-active symmetries belonging to $\beta\text{-ZnTe(en)}_{0.5}$. A critical assumption when implementing these configurations is the knowledge of the crystal orientation, namely, being able to identify the [100] (*a*-axis), [010] (*b*-axis), [001] (*c*-axis) directions of the $\beta\text{-ZnTe(en)}_{0.5}$ crystals. In this section, we first clarify the crystal orientation, followed by a close examination of the Raman spectra acquired under the twelve polarization configurations (Table 5-3).

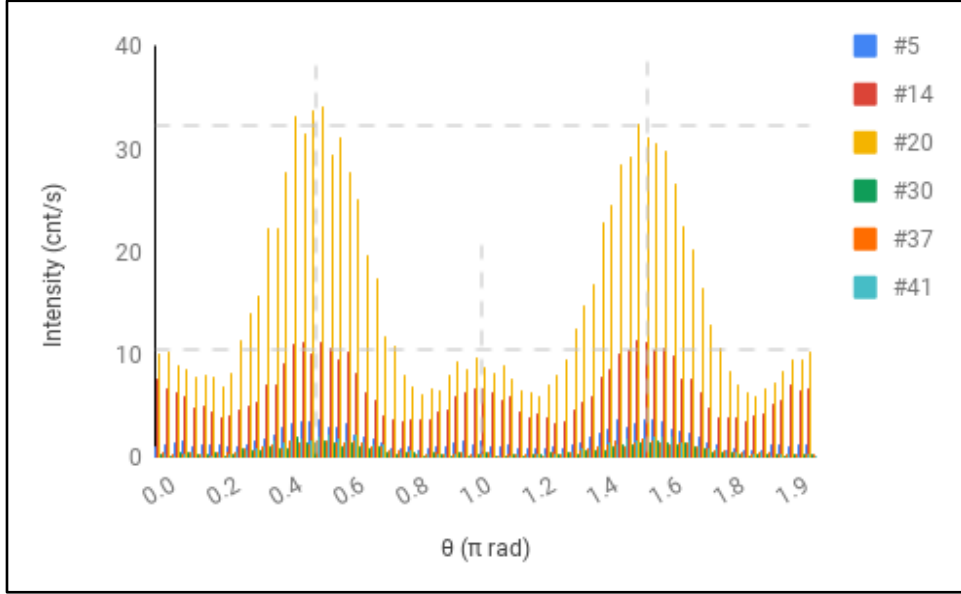
5.3.1. Identifying the crystal orientations of $\beta\text{-ZnTe(en)}_{0.5}$ crystal

$\beta\text{-ZnTe(en)}_{0.5}$ is typically found as a plate-like crystal with a rectangle shape. Typically, on the exposed plate-like surface, the longest edge is 2x–3x longer than the other edges. We name the longest edge the long edge and name the edge perpendicular to it the short edge. Identifying crystal orientation is usually accomplished with x-ray diffraction. Past experience has indicated that the *b* or [010] axis is always perpendicular to the exposed plate-like surface, and typically the long edge is parallel to the *c*-axis and the short edge is parallel to the *a*-axis. Knowing the direction of [010] reduces the 3D problem into a 2D problem, that is, to identify [100] (*a*-axis, in-plane direction) and [001] (*c*-axis, in-plane direction) on (010) surface. The 2D problem can be solved by conducting an angle-resolved polarization Raman study on the identified (010) surface without using the more time consuming XRD analysis.

In the experiment, incident light is propagated to the sample surface along $[010]$. The incident light is polarized, having an arbitrary direction in respect to the short edge of the crystal, the reference direction (Figure 5-1(a) inset). The back-scattered light with the same polarization is collected. Let θ be the angle between the polarized direction and reference direction, and φ be the offset between the chosen reference direction and a -axis ($\varphi = 0$, if the a -axis is indeed aligned with the short edge), then the angle between the a -axis and polarization is $\theta - \varphi$. When rotating the sample around its b -axis and varying θ from 0 to 2π , the Raman intensities for A_g modes as a function of $\theta - \varphi$ has the following form:



(a)



(b)

Figure 5-1. Using angle-resolved polarized Raman signal of a subset of A_g modes to solve crystal orientation. (a) a spectrum of the A_g modes. (b) Raman intensities of the A_g modes as a function of the angle θ , when the Raman signal is probed from the stacking direction (b -axis).

$$\begin{aligned}
 RC &= [\cos(\theta-\varphi), 0, \sin(\theta-\varphi)]^T R(A_g) [\cos(\theta-\varphi), 0, \sin(\theta-\varphi)] \\
 &= a^2 \cos(\theta-\varphi)^2 + c^2 \sin(\theta-\varphi)^2
 \end{aligned} \tag{5-6}$$

In the first step, we have used Equation 2-7. Figure 5-1(b) shows the Raman intensities of a few A_g modes when θ is varied from 0 to 2π . The shapes of the measured $RC(\theta)$ s suggest the phase offset φ in Equation 5-13 is either 0 or $\pi/2$, indicating the short edge of the crystal is either along a -axis or c -axis.

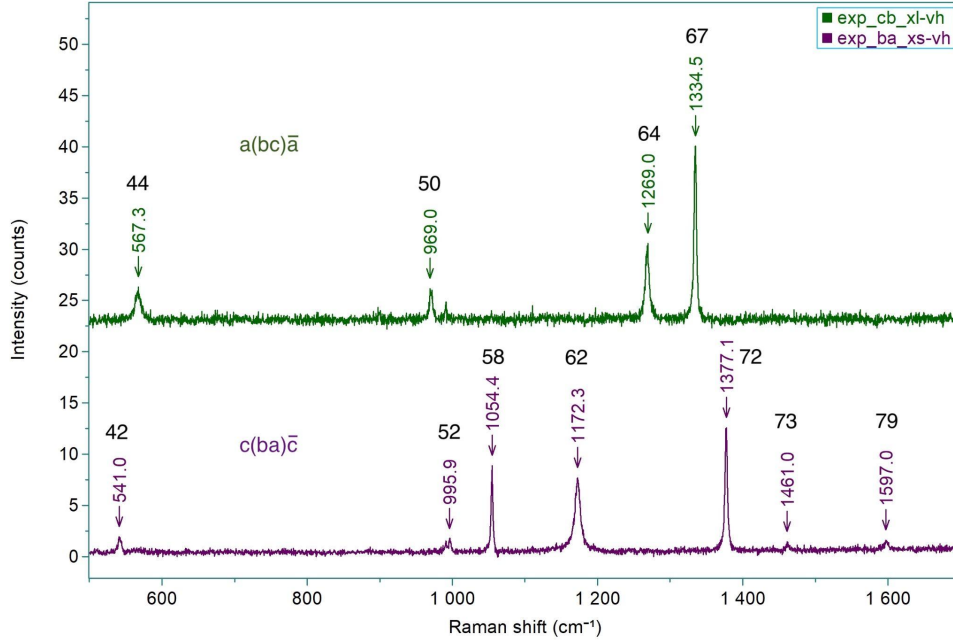


Figure 5-2. Using Raman signals from the $a(bc)\bar{a}$ (B_{3g} modes) and $c(ba)\bar{c}$ (B_{1g} modes) polarization configurations to determine the crystal orientations a and c . xl, xs designate the exposed cleavage is along the long edge, short edge, respectively. vh stands for the cross configuration.

We now demonstrate using the selection rule for B_{1g}/B_{3g} modes to further confirm the crystal orientations a and c from the cross configuration polarized Raman on the two perpendicular cleavages. Figure 5-2 shows Raman spectra of $\beta\text{-ZnTe}(\text{en})_{0.5}$ measured from the cleavage with the long edge (xl), and the cleavage with the short edge (xs). In the wavenumber range between 500 cm^{-1} and 1700 cm^{-1} , we have seen a set of 4 Raman peaks from the cleavage xl and another set of 7 Raman peaks from the cleavage xs. First, to identify the set of peaks belonging to B_{1g} , and confirm the other set belongs to B_{3g} , we refer to the results from the DFT calculation. The DFT calculation (Table 5-1) suggest 7 B_{1g} modes and 4 B_{3g} modes within the depicted wavenumber ranges. A close look at the frequency order and symmetry of those modes –

#42(B_{1g}), 44(B_{3g}), 50(B_{3g}), 52(B_{1g}), 58(B_{1g}), 62(B_{1g}), 64(B_{3g}), 67(B_{3g}), 72(B_{1g}), 73(B_{1g}), 79(B_{1g}), allows us to unambiguously label the 7 B_{1g} modes (#42,52,58,62,72,73,79) from the cleavage xs and 4 B_{3g} modes (#44,50,64,67) from the cleavage xl. Now, because B_{1g} modes exclusively register on $c(ab)\bar{c}$ or $c(ba)\bar{c}$ and from cleavage xs only B_{1g} modes are observed, we can come to the conclusion that the cleavage xs is parallel to ab, and the short edge of the crystal is along the *a-axis*. For the same reason, because B_{3g} exclusively register on $a(bc)\bar{a}$ or $a(cb)\bar{a}$, and from cleavage xl only B_{3g} modes are observed, we know the cleavage xl is parallel to ac, and the long edge is along the *c-axis*. These results are consistent with the angle-resolved measurement from the *b-axis* or *ac* plane.

5.3.2. Polarized Raman study under 12 configurations

Knowing the crystal orientation, it now becomes possible to implement the on-axis polarization measurement. This section examines the Raman spectra acquired under the twelve polarization configurations (Table 5-3) and accomplishes mode assignments.

Incident light with D-3 level power is used on the two perpendicular cleavages – (100) and (001). From the (010) direction, a D-2 level power incident light is used to get similar counts per second for the Raman signal, because the Raman signal from the (010) plane tend to be weaker than the other two planes.

For the on-axis polarizations, the selection rules can be used to determine whether a Raman mode can be observed given its symmetry and the polarization configuration being used. For example, #80 belongs to the A_g irreducible representation. According to the selection rule, A_g modes are allowed on the six parallel configurations. On the other hand, #72 belongs to the B_{1g} irreducible representation. B_{1g} modes are only allowed under $c(ba)\bar{c}$ or $c(ab)\bar{c}$.

Figure 5-3 shows the polarized Raman spectra between $1350 - 1650 \text{ cm}^{-1}$ under the six parallel configurations and three cross configurations. According to the calculation (Table 5-1), in this range, there are 3 A_g modes and 3 B_{1g} modes – #71(A_g), 72(B_{1g}), 73(B_{1g}), 74(A_g), 79(B_{1g}), 80(A_g). We assign the six modes to the corresponding Raman peaks in the spectra with the following observation: (1) The assigned peaks are in the same frequency order with the calculated modes. (2) The 3 A_g modes (#71, 74, 80) register on the parallel configuration per the selection rules. Note that #80(A_g) is observed in all the six parallel configurations, whereas #74(A_g) is absent in $b(aa)\bar{b}$ and $c(aa)\bar{c}$, illustrating that the selection rule is a necessary but not sufficient condition for a mode to be observed in a polarization configuration. The allowed mode can be silenced due to factors other than the selection rule. (3) Per the selection rules, the 3 B_{1g} modes (#72, 73, 79) is observed only in the cross-polarizations $c(ba)\bar{c}$ and $c(ab)\bar{c}$ (the latter is not shown but similar).

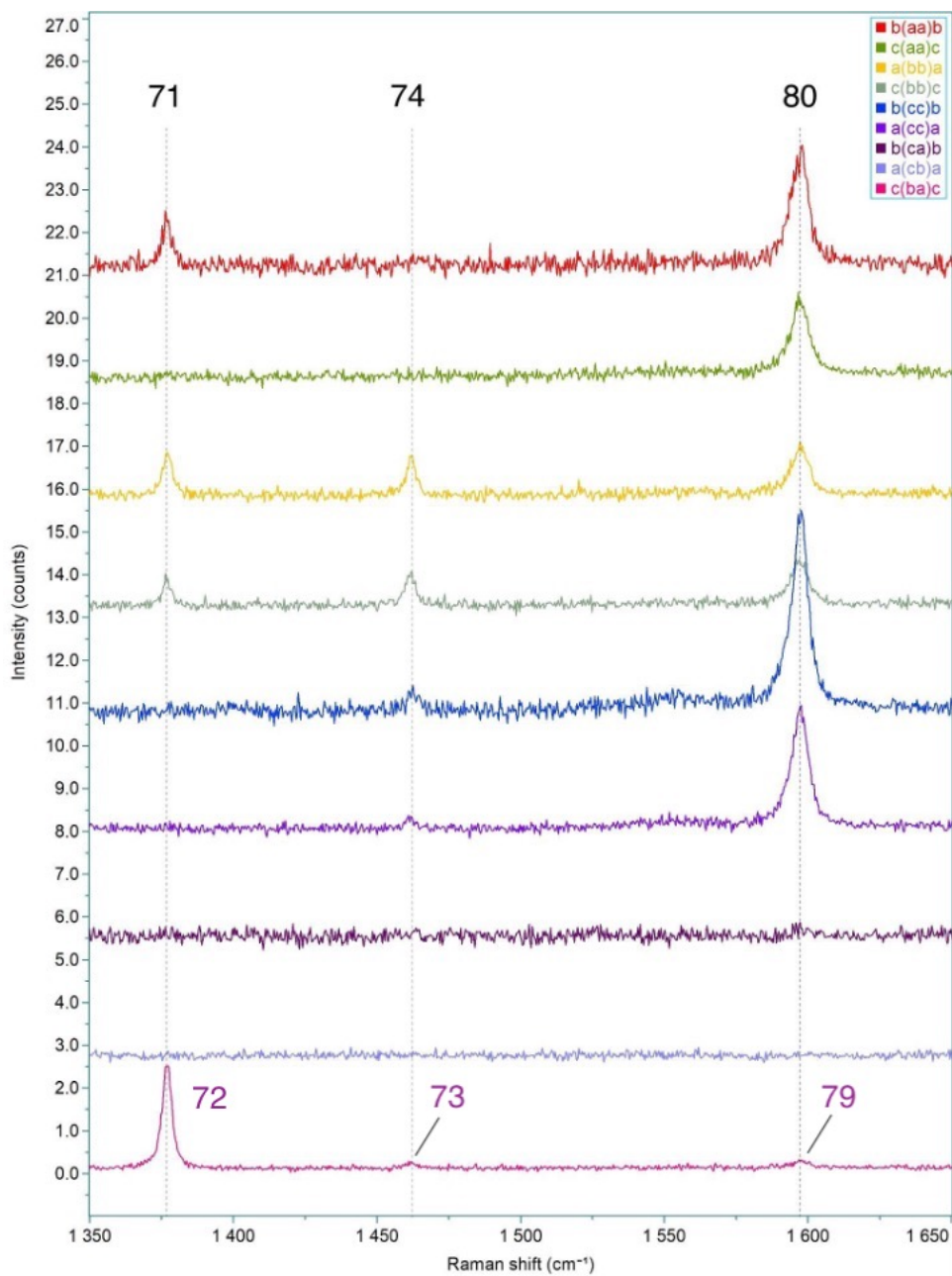


Figure 5-3. Polarized Raman spectra between 1350 – 1650 cm^{-1} under the six parallel configurations and three cross configurations. Because $b(ac)\bar{b}$ and $b(ca)\bar{b}$ yield effectively the same information, only one of them is shown in the figure. The same applies to $a(bc)\bar{a}$, $a(cb)\bar{a}$, and $c(ab)\bar{c}$, $c(ba)\bar{c}$.

To accomplish the Raman mode assignment, the same analysis is performed for each of the forty-eight calculated Raman modes (Table 5-1). Specifically, for every mode, we iterate the twelve polarization configurations and ask two questions: (1) Is the symmetry of the mode allowed in the configuration? and (2) Is this mode observed in the configuration? Table 5-4 summarizes the results, in which we have used ‘√’ to denote a mode is expected and observed; ‘X’ to denote expected but not observed; and ‘-’ to denote unexpected according to the selection rule but nevertheless observed.

Table 5-4. Summary of β -ZnTe(en)_{0.5} Raman modes measured in backscattering geometries

Mode #	Calculated Frequency ¹⁰ (cm ⁻¹)	Measured Frequency (cm ⁻¹)	Symmetry in (a,b,c)	Calculated Tensor Components ¹¹	(a,c) plane	(b,c) plane	(a,b) plane
4	14.34	11.44	B _{2g}	e=-0.214	-(a,a) √(a,c)	-(b,c)	-(b,a)
5	22.96	23.25	A _g	(a,b,c)= (0.113,-0.026,0.264)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
7	53.02	53.14	B _{3g}	f=-0.124		√(b,c)	-(b,b)
8	55.02		B _{1g}	d=0.005			X(b,a)

¹⁰ Reproduced from the frequencies in Table 5-1

¹¹ The Raman tensor calculation is performed by Dr. Yi-yang Sun.

Mode #	Calculated Frequency ¹⁰ (cm ⁻¹)	Measured Frequency (cm ⁻¹)	Symmetry in (a,b,c)	Calculated Tensor Components ¹¹	(a,c) plane	(b,c) plane	(a,b) plane
11	91.56	92.36	B _{1g}	d=-0.185			√(b,a)
14	95.92	95.74	A _g	(a,b,c)= (0.183,0.434,0.19)	√(a,a) √(c,c) -(a,c)	√(b,b) √(c,c) -(b,c)	√(b,b) √(a,a)
15	98.54		B _{2g}	e=-0.232	X(a,c)		
16	99.13		B _{3g}	f=-0.077		X(b,c)	
20	137.12	132.32	A _g	(a,b,c)= (-0.227,-0.323,-0.218)	√(a,a) √(c,c) -(a,c)	√(b,b) √(c,c)	√(b,b) √(a,a) -(b,a)
22	151.49		B _{3g}	f=-0.132		X(b,c)	
23	152.33		B _{2g}	e=0.291	X(a,c)		
24	153.44	151.38	B _{1g}	d=-0.095			√(b,a)
27	172.61	166.09	B _{2g}	e=0.082	√(a,c)		
28	175.82	168.68	B _{3g}	f=-0.029		√(b,c)	
30	180.05	175.25	A _g	(a,b,c)= (0.139,-0.298,-0.061)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
34	203.10	201.85	B _{1g}	d=-0.123			√(b,a)

Mode #	Calculated Frequency ¹⁰ (cm ⁻¹)	Measured Frequency (cm ⁻¹)	Symmetry in (a,b,c)	Calculated Tensor Components ¹¹	(a,c) plane	(b,c) plane	(a,b) plane
37	289.71	284.17	A _g	(a,b,c)= (0.389,0.145,0.056)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
38	289.90		B _{1g}	d=-0.149			X(b,a)
41	538.79	538.47	A _g	(a,b,c)= (0.031,0.047,-0.117)	X(a,a) √(c,c)	X(b,b) √(c,c)	X(b,b) X(a,a)
42	540.62	541.06	B _{1g}	d=0.113			√(b,a)
43	606.56	567.70	B _{2g}	e=-0.077	√(a,c)		
44	606.96	566.01	B _{3g}	f=0.019		√(b,c)	
49	949.48		B _{2g}	e=0.13	X(a,c)		
50	949.88	970.42	B _{3g}	f=0.02		√(b,c)	
51	996.32	990.50	A _g	(a,b,c)= (0.283,-0.238,0.155)	√(a,a) √(c,c)	√(b,b) √(c,c) -(b,c)	√(b,b) √(a,a)
52	1002.40	996.15	B _{1g}	d=-0.037			√(b,a)
57	1068.01	1053.91	A _g	(a,b,c)= (-0.146,0.179,-0.115)	√(a,a) X(c,c)	√(b,b) X(c,c)	√(b,b) X(a,a)
58	1071.68	1054.38	B _{1g}	d=0.016			√(b,a)

Mode #	Calculated Frequency ¹⁰ (cm ⁻¹)	Measured Frequency (cm ⁻¹)	Symmetry in (a,b,c)	Calculated Tensor Components ¹¹	(a,c) plane	(b,c) plane	(a,b) plane
61	1156.56	1171.22	A _g	(a,b,c)= (0.056,-0.048,0.145)	√(a,a) X(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
62	1158.41	1172.19	B _{1g}	d=0.269			√(b,a)
63	1240.53	1267.66	B _{2g}	e=-0.106	√(a,c)		
64	1240.64	1267.91	B _{3g}	f=-0.154		√(b,c)	-(b,b)
67	1305.70	1334.32	B _{3g}	f=0.083		√(b,c)	-(b,b)
68	1305.71	1334.22	B _{2g}	e=-0.12	√(a,c)		
71	1340.38	1376.42	A _g	(a,b,c)= (-0.055,-0.081,-0.004)	√(a,a) X(c,c)	√(b,b) X(c,c)	√(b,b) X(a,a)
72	1340.60	1376.82	B _{1g}	d=-0.21			√(b,a)
73	1432.70	1461.80	B _{1g}	d=0.048			√(b,a)
74	1433.07	1461.81	A _g	(a,b,c)= (0.018,-0.069,0.061)	X(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) X(a,a)
79	1578.59	1597.66	B _{1g}	d=0.083			√(b,a)
80	1579.37	1596.93	A _g	(a,b,c)= (-0.056,-0.108,0.279)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)

Mode #	Calculated Frequency ¹⁰ (cm ⁻¹)	Measured Frequency (cm ⁻¹)	Symmetry in (a,b,c)	Calculated Tensor Components ¹¹	(a,c) plane	(b,c) plane	(a,b) plane
81	2928.39		B _{1g}	d=0.014			X(b,a)
82	2928.87	2868.62	A _g	(a,b,c)= (-0.414,-0.468,-0.363)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
85	2965.58	2916.84	B _{3g}	f=-0.051		√(b,c)	
86	2965.59	2916.63	B _{2g}	e=0.349	√(a,c)		
91	3178.67	3201.46	B _{1g}	d=0.433			√(b,a)
92	3179.35	3199.46	A _g	(a,b,c)= (-1.109,-0.178,-0.544)	√(a,a) √(c,c)	√(b,b) √(c,c)	√(b,b) √(a,a)
95	3208.20	3209.62	B _{3g}	f=0.384		√(b,c)	
96	3208.25	3208.06	B _{2g}	e=1.004	√(a,c)		

When judging if a Raman mode is present, its peak intensity on the spectrum is examined and a 0.5 cps (count per second) is used as a key threshold. Figure 5-4 shows the Raman spectra acquired using polarization configurations from the *bc* plane (Figure 5-4a), the *ac* plane (Figure 5-4b) and the *ab* plane (Figure 5-4c), with simulated Raman intensities derived from the calculated Raman tensors. For each configuration, the correspondent Raman tensor component *x* (*x*=a,b,c,d,e,f, depending on the selection rules) is used to calculate the simulated Raman

intensity by αx^2 . α is the global coefficient ($\alpha=10^4$) applied across all configurations to achieve comparable simulated intensity level with the measured intensity level. The measured intensities in counts per second (cps) are multiplied by a factor of two before plotting in the log-scale. Therefore, any signal observed in the log-scale plot is greater than 0.5 cps. For the peaks less than 0.5 cps, they are either absent (mode # is marked in red), or they can still be recognized (mode # is marked in blue), in which case the signals in the vicinity of each mode are examined and a letter (A,B,C) is assigned to represent the quality of those peaks using the following criteria:

A - recognizable

B - barely recognizable

C - like noise but still stronger than noise

We note that when interpreting the presence of #15(B_{2g}), #16(B_{3g}), #22(B_{3g}), #23(B_{2g}), ambiguities may occur. In the inset with the green border in the first panel of Figure 5-4, we compare the spectra using two parallel configurations, $a(bb)\bar{a}$ and $a(cc)\bar{a}$, with the one using the cross configuration $a(cb)\bar{a}$. The peak at 96.3 cm⁻¹ in the cross configurations may either be interpreted as the presence of #16(B_{3g}), or the leakage from the high-intensity #14(A_g), at 95.9 cm⁻¹. In the inset with the green border in the second panel of Figure 5-4, we compare the spectra from three independent measurements using the cross configuration $b(ac)\bar{b}$ with the one from the parallel configuration $b(aa)\bar{b}$. The peak at 96.1 cm⁻¹ in the cross configurations may either be interpreted as the presence of #15(B_{2g}) or the leakage from the high-intensity #14(A_g). In both insets, the peak at 140 cm⁻¹ in the cross configuration may either be interpreted as #22(B_{3g}) (see the first panel), #23(B_{2g}) (see the second panel), or weak tellurium features, although in the

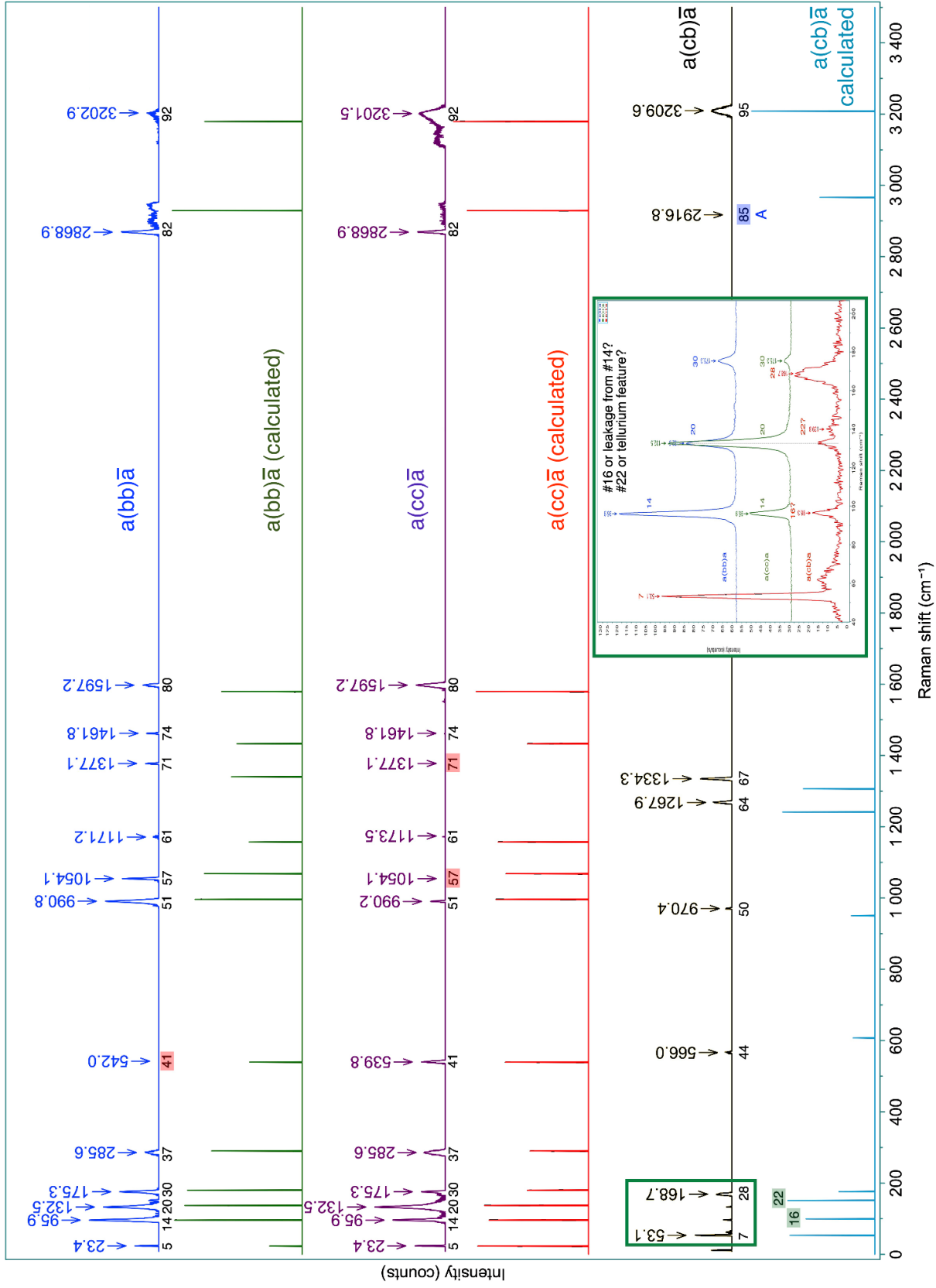
parallel configurations there are no signs of tellurium features. In the rest of the chapter, we assume the absence of the four modes.

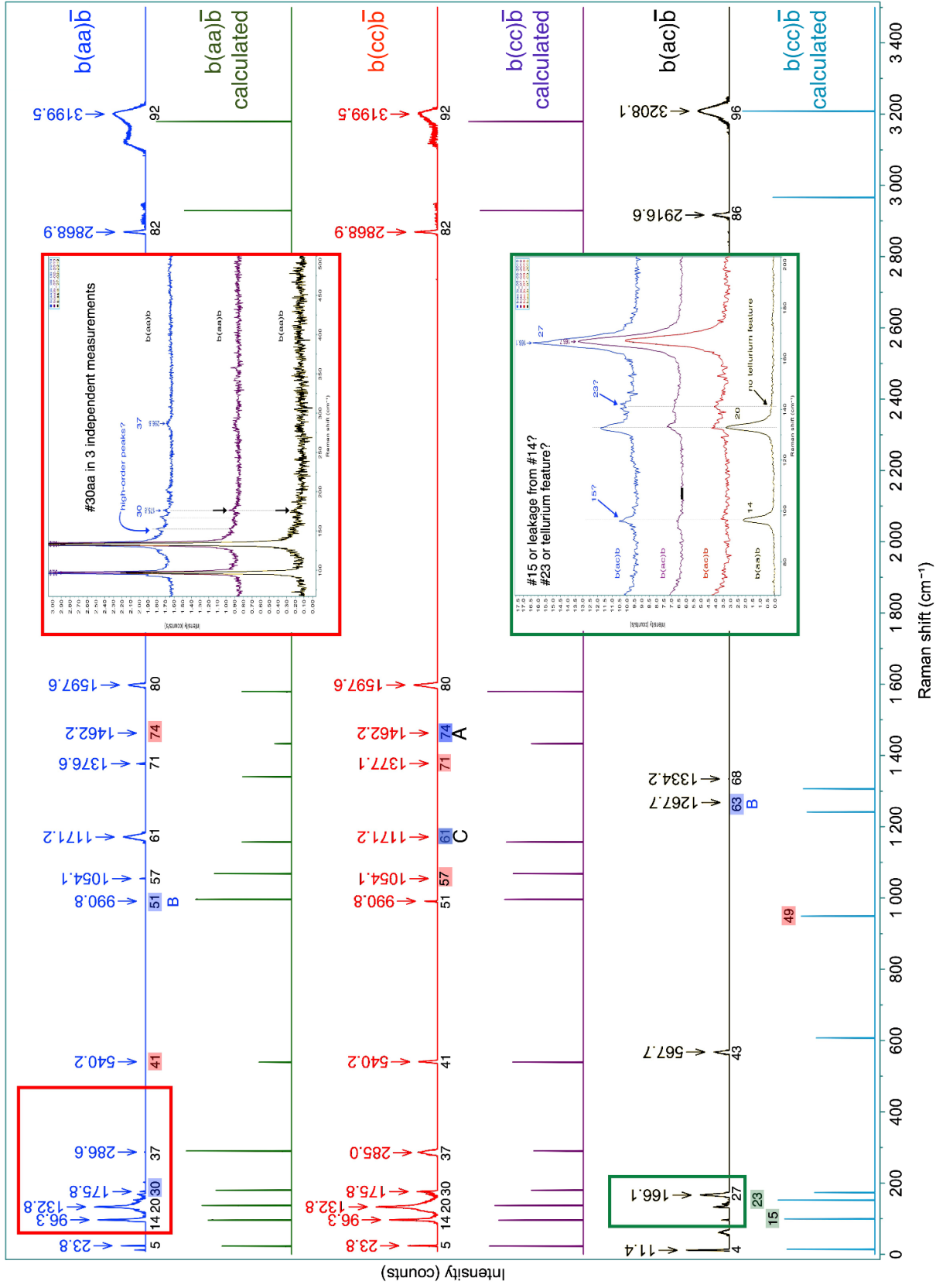
Figure 5-4. Raman spectra acquired using polarization configurations.

Each of the next three pages shows one panel. The first panel (a) plots the spectrum from the bc plane (propagating direction is a). The second panel (b) plots the spectrum from the ac plane (propagating direction is b). The third panel (c) plots the spectrum from the ab plane (propagating direction is c).

Insets are used to zoom into small wavenumber windows to resolve crowded features.

Below each spectrum is the simulated Raman intensity in that particular configuration derived from the calculated Raman tensor. The calculated Raman tensors are shown in Table 5-4 under the *computed tensor components* column.





Comments:

1. All 16 A_g modes have been observed in at least one of the six parallel polarization configurations, i.e., for each A_g mode, at least one component of the three diagonal components of the A_g Raman tensor has been measured.

- a. #5, #14, #20; #30, #37, #51; #80, #82, #92 have been observed in all six parallel polarization configurations.
- b. #57/aa and #71/aa have been observed in $b(aa)\bar{b}$ but not in $c(aa)\bar{c}$. #61/cc is observed in $a(cc)\bar{a}$ but not $b(cc)\bar{b}$.
- c. #41/aa, #41/bb, #57/cc, #71/cc, and #74/aa have not been observed in certain expected polarization configurations.

2. 10 B_{2g} modes: missing #15, #23 and #49.

3. 10 B_{3g} modes: missing #16, #22.

4. 14 B_{1g} modes: missing #8, #38, and #81.

The goal for the rest of this section is to discuss the absent modes (case 1b, 1c, 2–4) and other notable features in the spectra.

Case 1b: The a component of the Raman tensor of an A_g mode is observed in only one of the two allowed configurations, which are not equivalent, because photon wavevector $\mathbf{q}$ are not the same. Specifically, #57 and #71 are observed under $b(aa)\bar{b}$ but not $c(aa)\bar{c}$. To confirm their absence $c(aa)\bar{c}$, in Figure 5-5, we show the Raman spectra under the $c(aa)\bar{c}$ and $b(aa)\bar{b}$ configurations, in the wavenumber range of #37, #51, #57, #61, #71. The higher intensity of #61

in $b(aa)\bar{b}$ compared with $c(aa)\bar{c}$ suggests the system response of $b(aa)\bar{b}$ is stronger than $c(aa)\bar{c}$ within the depicted wavenumber ranges. In $b(aa)\bar{b}$, #37, #51 are the two modes having the weakest intensities, yet a trace amount of them can be recognized under $c(aa)\bar{c}$. The same cannot be said for #57 and #71, which have higher intensities in $b(aa)\bar{b}$, but not even a trace of them can be recognized under $c(aa)\bar{c}$.

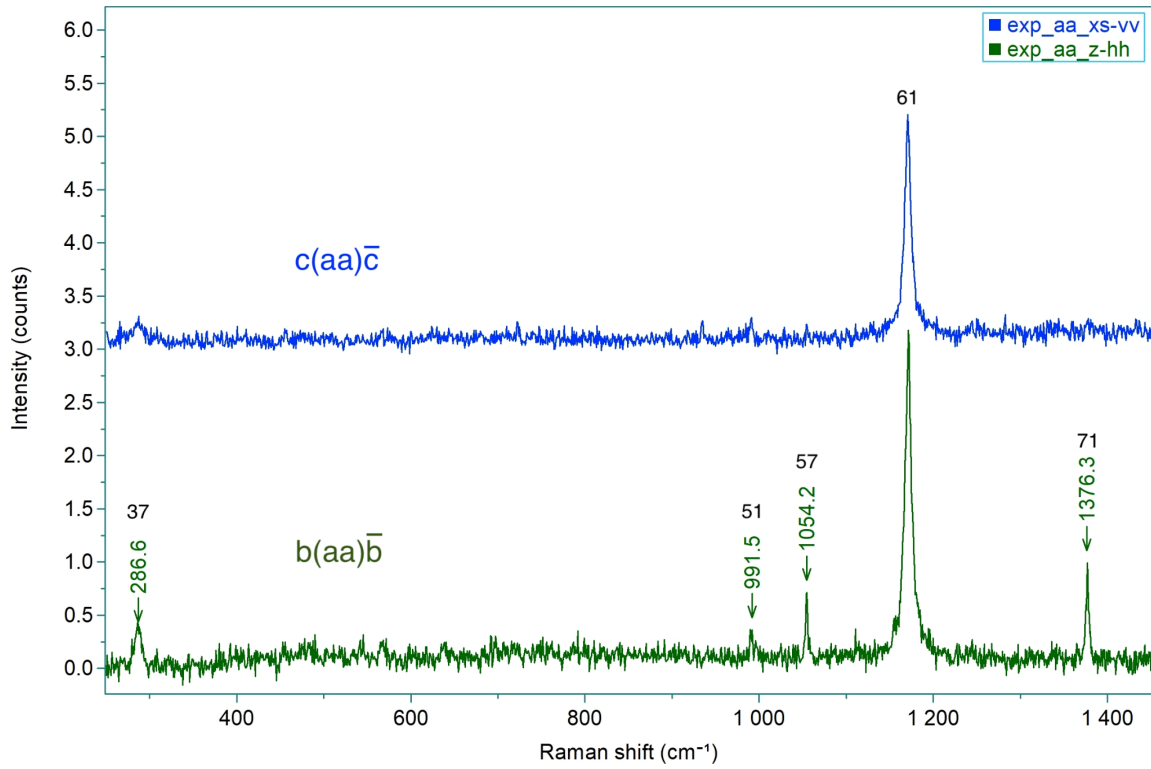


Figure 5-5. Raman spectra under the $c(aa)\bar{c}$ and $b(aa)\bar{b}$ configurations, in the wavenumber range of mode #37, #51, #57, #61, #71.

It remains unclear why #57, #71 are observed under $b(aa)\bar{b}$ but not $c(aa)\bar{c}$. However, we note an assumption being made in the calculation is that the phonons have zero crystal momentum. Raman measurement, on the other hand, probes phonons with a certain propagating direction with a small but non-zero crystal momentum. For example, although $b(aa)\bar{b}$ and $c(aa)\bar{c}$ are the

two parallel configurations selecting the same diagonal component in the A_g Raman tensors, the two configurations probe phonons with different propagating directions. $b(aa)\bar{b}$ probes the phonons propagating along the b -axis, while $c(aa)\bar{c}$ probes the phonons propagating along the c -axis. Since #57 and #71 are polarized along the b -axis, their absence under $c(aa)\bar{c}$ suggests that even for the A_g mode the Raman activity is sensitive to the relative direction of the phonon polarization and the propagation direction, i.e., LO vs. TO, despite no splitting at the zone center. In addition to #57 and #71, #61 is observed under $a(cc)\bar{a}$ but not $b(cc)\bar{b}$, which might be related to the fact that this mode is polarized along the a -axis.

Case 1c, 2–4: Table 5-5 organizes the absent Raman-active modes. When a polarization direction is followed by A_g modes, only at the specified polarization the A_g mode is not observed. A large energy span (from the low-energy coupling vibrations to the high-energy molecular vibrations) and varying symmetries of these modes suggest their absence can be mode-specific. One possible factor leading to the absence of a mode is a small magnitude of the relevant component in the Raman tensor. The magnitude of the Raman tensor originates from $d\alpha/dq$, the change of polarizability in response to the vibration pattern. Modes with certain vibration patterns can have $d\alpha/dq$ that is too small to be detected. The computation suggests the absence of #71/ $cc(A_g)$, #8(B_{1g}), #74/ $aa(A_g)$, #81(B_{1g}) is likely due to the small tensor component. The calculated tensor components (Table 5-4) for #71/ $cc(A_g)$, #8(B_{1g}) are less than 0.01, two orders of magnitudes smaller than the tensor component for #92/ $cc(A_g)$, #91(B_{1g}). Tensor component for mode #74/ $aa(A_g)$, #81(B_{1g}) are 0.018, 0.014, respectively, only slightly larger than #71/ $cc(A_g)$, #8(B_{1g}). Note that Raman intensity is proportional to the square of the tensor component.

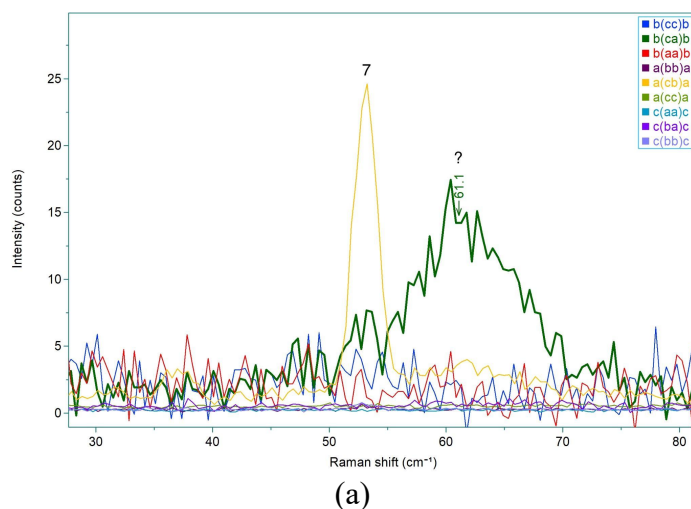
Table 5-5. The absent Raman-active vibration modes grouped by their symmetries

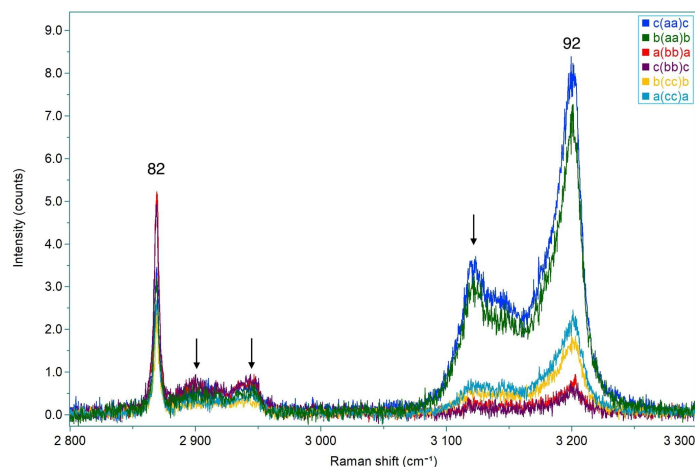
A_g	
#41/aa,bb	N-C-C-N stretching along b; adjacent N-C in phase; adjacent molecules in phase
#57/cc	N-C-C-N stretching along b; adjacent N-C out of phase; adjacent molecules in phase
#71/cc	very small Raman tensor
#74/aa	small Raman tensor
B_{1g}/B_{2g}/B_{3g}	
#8(B _{1g})	very small Raman tensor
#15(B _{2g})	C-C motion along <i>c</i> -axis; adjacent molecules out of phase
#16(B _{3g})	C-C motion along <i>c</i> -axis; adjacent molecules in phase
#22(B _{3g})	N-C-C-N bending along c; adjacent molecules in phase
#23(B _{2g})	N-C-C-N bending along c; adjacent molecules out of phase
#38(B _{1g})	
#49(B _{2g})	
#81(B _{1g})	small Raman tensor

The computed Raman tensor does not explain the absence of #41/aa,bb(A_g) and #57/cc(A_g).

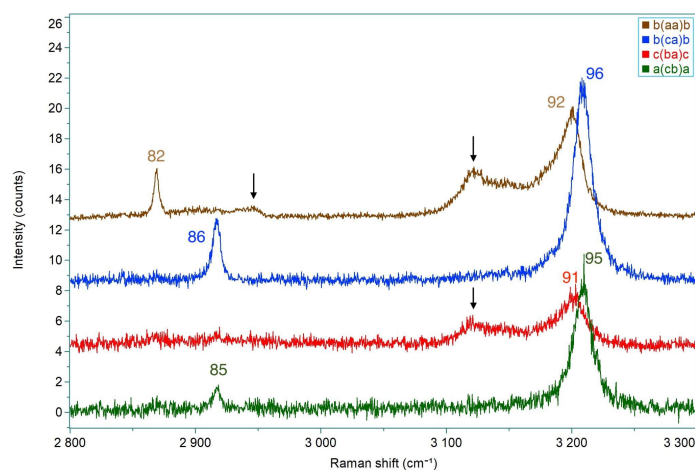
However, we notice that both #41(A_g) and #57(A_g) has the molecular vibration pattern: N-C-C-N stretching along the *b*-axis. As has been discussed in the paragraph before Figure 5-4, the interpretation that #15(B_{2g})/#16(B_{3g}) and #22(B_{3g})/#23(B_{2g}) are absent can be ambiguous because of their frequencies are close to the strong signal of #14 and tellurium contamination. Note those modes share the molecular vibration pattern: N-C-C-N bending along the *c*-axis. It remains unclear the origin of the absence of #38(B_{1g}) and #49(B_{2g}).

The polarized Raman spectra exhibit two additional features. Figure 5-6(a) shows the unexpected Raman mode at 61 cm^{-1} under the $b(ca)\bar{b}$ configuration. Its absence in the other polarizations suggests that it resembles a TO mode having B_{2g} symmetry. Figure 5-6(b,c) shows the additional modes in the $\nu(\text{CH}_2)$ (near #82) and $\nu(\text{NH}_2)$ (near #92) frequencies. The signal near #82 is $\sim 60\text{ cm}^{-1}$ in width, with two recognizable peaks centered at 2898 cm^{-1} , 2943 cm^{-1} . The signals show up in the six parallel configurations but are absent in the cross configurations. The other signal in the $\nu(\text{NH}_2)$ region, with one peak centered at 3121 cm^{-1} , is visible not only in the six parallel configurations, but also in the cross configuration $c(ba)\bar{c}$. The origin of those signals remains unclear.





(b)



(c)

Figure 5-6. Additional features in the polarized Raman spectra: unexpected Raman mode at 61 cm^{-1} under the $b(ca)\bar{b}$ configuration (a); Satellite peaks in the $\nu(\text{CH}_2)$ (near #82) and $\nu(\text{NH}_2)$ (near #92) frequencies under the six parallel configurations (b) and cross configurations (c). The parallel configuration $b(aa)\bar{b}$ is plotted in (c) to show the $\nu(\text{CH}_2)$ satellite peaks (near #82) are visible in the parallel configurations but are absent in the cross configurations.

Last, A_g modes with very strong intensities are found leaking to the cross configurations. For example: #14, #20 in $b(ac)\bar{b}$; #14, #51 in $a(bc)\bar{a}$; #20 in $c(ba)\bar{c}$. Note that those are the

strongest A_g modes within each propagating direction, suggesting a non-ideal polarization setup may cause them to leak into the cross configurations. The phenomena also occurs under the B_{2g} and B_{3g} symmetry, where #7(B_{3g}), #67(B_{3g}) leak from $a(bc)\bar{a}$ to $c(bb)\bar{c}$, and mode #4(B_{2g}) leaks from $b(ac)\bar{b}$ to $b(aa)\bar{b}$, $a(bc)\bar{a}$, and $c(ba)\bar{c}$.

5.4. Estimate β -ZnTe(en)_{0.5}'s Raman tensors using the on-axis polarization and angle-resolved method

5.4.1. Estimate Raman tensors from on-axis polarization spectra

Because β -ZnTe(en)_{0.5}'s 3x3 Raman tensors are symmetric across their diagonal lines, for each tensor, there are six independent components. The value of the six components can be estimated from the spectra of the twelve polarization configurations using the selection rule (Table 5-3). For example, the first diagonal component – a, its squared value a^2 can be read from either $c(aa)\bar{c}$ or $b(aa)\bar{b}$; the off-diagonal component d of the B_{1g} tensors, its squared value d^2 can be read from $c(ab)\bar{c}$ or $c(ba)\bar{c}$. Using this method to estimate Raman tensor must consider the deviation of system response under (1) different polarization configurations and (2) different propagating directions.

In this study, Raman tensors of A_g modes are estimated using the six parallel configurations. For $B_{1g}/B_{2g}/B_{3g}$ tensors, their components are estimated from the spectra under the $c(ab)\bar{c}$, $b(ac)\bar{b}$, $a(bc)\bar{a}$ configurations. The deviation arising from polarization configurations can be compensated by careful measurement of the system response in the incident path and scattering path [87,88].

5.4.2. Estimate Raman tensors using the angle-resolved method

The angle-resolved method is another approach to estimate Raman tensors. Because varying polarization is achieved by rotating the crystal, from the perspective of the measurement system, the polarization setup remains unchanged. Therefore, in principle, the deviation of system response that arises from the different polarization setups is eliminated.

The angle-resolved method uses the parallel polarization setup in which the incident light and scattered light have the same polarization. In the following discussion, we assume backscattering geometry having on-axis propagating direction. When measuring A_g modes, each propagating direction measures two components. Therefore, only two of the three on-axis propagating directions need to be measured in order to estimate the three diagonal components in A_g tensors. When measuring $B_{1g}/B_{2g}/B_{3g}$ modes, each plane contains exactly one off-diagonal component. Therefore, all three propagating directions need to be studied.

In this study, we first performed an angle-resolved study on ac plane (the stacking faces) and ab plane (one of the two perpendicular cleavage). Then, for each mode, we plot the measured intensity versus the angle (θ), defined as the angle between the light polarization and the a -axis. Referring to Equation 5-6 and setting offset ϕ to zero, the Raman intensity of A_g modes as a function of θ has the following relationship.

$$RC_{A_g}(\theta|ac) = (a \cos^2(\theta) + c \sin^2(\theta))^2 \quad (5-7a)$$

$$RC_{A_g}(\theta|ab) = (a \cos^2(\theta) + b \sin^2(\theta))^2 \quad (5-7b)$$

To find the Raman intensity for the B_{1g} modes, we replace the tensor $R(A_g)$ with $R(B_{1g})$ in Equation 5-6:

$$RC_{B1g}(\theta|ab) = d^2 \sin^2(2\theta) \quad (5-7c)$$

In Equation 5-7a, 5-7b, $RC_{Ag}(\theta|ac)$ and $RC_{Ag}(\theta|ab)$ describe the Raman intensity of A_g modes measured from the ac plane, ab plane, respectively. In Equation 5-7c, $RC_{B1g}(\theta|ab)$ describes the Raman intensity of B_{1g} modes measured from the ab plane. Figure 5-7 shows simulated angular dependences of $RC_{Ag}(\theta)$ and $RC_{B1g}(\theta)$ in linear and polar plots. The distinct periods of $RC_{Ag}(\theta)$ and $RC_{B1g}(\theta)$ enable the differentiation of mode symmetry.

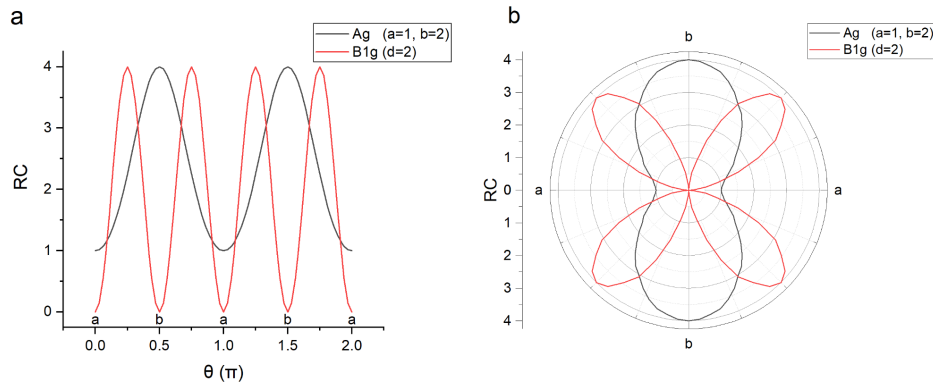


Figure 5-7. The angular dependence of $RC_{Ag}(\theta)$ (in black) and $RC_{B1g}(\theta)$ (in red) in linear plot (a) and polar plot (b), assuming tensor components a and b are in phase. $RC_{Ag}(\theta)$ reaches its local maxima/minima at $n\pi/2$ ($n=0,1,2,3,4$), having a period of π , while RC_{B1g} reaches local maxima at $n\pi/4$ ($n=1,3,5,7$), having a period of $\pi/2$.

From Equation 5-7a, we can estimate Raman component a and c :

$$\hat{a}_{ac}^2 = RC(\theta=0|ac); \quad \hat{c}_{ac}^2 = RC(\theta=\pi/2|ac) \quad (5-8a)$$

From Equation 5-7b, we can estimate Raman component a and b

$$\hat{a}_{ab}^2 = RC(\theta=0|ab); \quad \hat{b}_{ab}^2 = RC(\theta=\pi/2|ab) \quad (5-8b)$$

From Equation 5-7c, we can estimate Raman component d

$$\hat{d}^2 = RC(\theta = n\pi/4|ab), n=1,3,5,7 \quad (5-8c)$$

For example, Figure 5-8 shows the linear plot and polar plot of the measured $RC_{14}(\theta|ac)$ and $RC_{14}(\theta|ab)$ for mode #14. First, by noticing $RC_{14}(\theta|ac)$ and $RC_{14}(\theta|ab)$ have a period of π , it can be confirmed that #14 is an A_g mode. Second, from $RC_{14}(\theta|ac)$, we estimate $\hat{a}_{ac}^2 = 7.49$, $\hat{c}_{ac}^2 = 12.00$ (Equation 5-8a), and from $RC(\theta|ab)$, we estimate $\hat{a}_{ab}^2 = 5.00$, $\hat{b}_{ab}^2 = 14.93$ (Equation 5-8b).

Compared to the simulated plot in Figure 5-7, at $\theta = n\pi/4$ ($n=1,3,5,7$), both $RC_{14}(\theta|ac)$ and $RC_{14}(\theta|ab)$ reach a local minimum at $n\pi/4$ ($n=1,3,5,7$). To account for this new feature, a phase difference φ ¹² between the two measured components is introduced when fitting the measured $RC(\theta)$ [89]. Specifically, the Raman tensor A_g in Equation 5-5 becomes [89]

$$A_g = \begin{pmatrix} a e^{i\varphi_a} & 0 & 0 \\ 0 & b e^{i\varphi_b} & 0 \\ 0 & 0 & c e^{i\varphi_c} \end{pmatrix} \quad (5-9)$$

In Equation 5-9, a , b , c are positive real numbers representing magnitudes of the tensor components, φ_a , φ_b , and φ_c represent the phases of the three tensor components, respectively.

With Equation 5-9, the corresponding Raman component $RC_{A_g}(\theta|ac)$ and $RC_{A_g}(\theta|ab)$ in Equation 5-7 becomes

$$RC_{A_g}(\theta|ac) = a^2 \cos^4(\theta) + c^2 \sin^4(\theta) + \frac{1}{2} a c \sin^2(2\theta) \cos(\varphi_{ac}) \quad (5-10a)$$

$$RC_{A_g}(\theta|ab) = a^2 \cos^4(\theta) + b^2 \sin^4(\theta) + \frac{1}{2} a b \sin^2(2\theta) \cos(\varphi_{ab}) \quad (5-10b)$$

¹² This phase difference should not be confused from that introduced earlier. Here it is due to absorption, and previously, it was due to an off-set angle that would not change the shape.

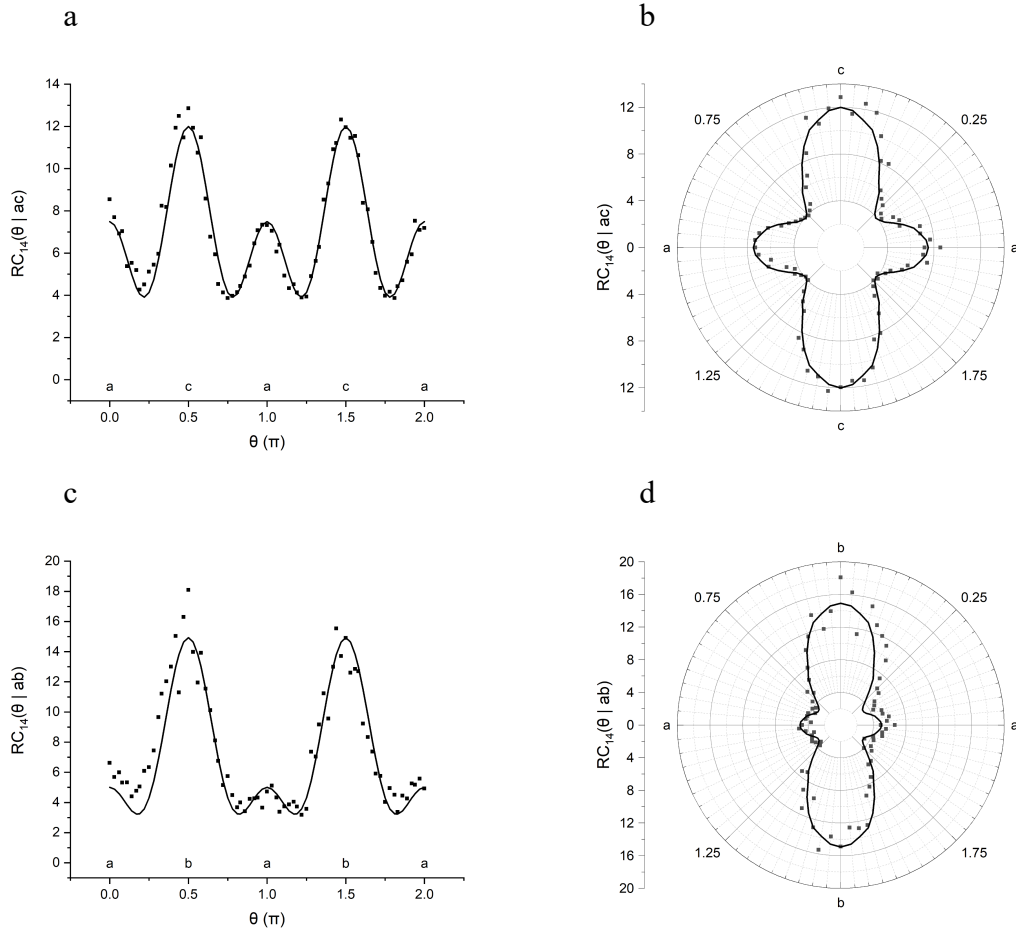


Figure 5-8. Measured $RC_{14}(\theta|ac)$ and $RC_{14}(\theta|ab)$ in the linear plot (a) and polar plot (b).

The measured data points are overlapped with a fitted curve using Equation 5-7. A relative phase difference $\varphi=0.55\pi$ between tensor components a, b, and a, c, is introduced to get the fitted lines.

The phase controls the value of RC_{Ag} when $\theta=n\pi/4$ ($n=1,3,5,7$). For the measured $RC_{14}(\theta|ac)$ and $RC_{14}(\theta|ab)$, a phase difference $\varphi_{ac} = \varphi_{ab} = 0.55\pi$ is obtained by fitting the data.

Note that different response from plane ab and plane ac may arise from the different reflection and light extraction due to the anisotropic refractive index. To investigate Raman tensor

components in improved resolutions, a careful correction is needed. $RC_{A_g}(\theta|ac)$ and $RC_{A_g}(\theta|ab)$ of other A_g modes are provided in Appendix E.

Figure 5-9 shows the linear plot and polar plot of the measured $RC_{11}(\theta|ab)$. First, it can be confirmed that #11 is a B_{1g} mode since it has a period $\pi/2$. Second, we estimate $\hat{d}^2 = 0.84$ from the maxima values. $RC(\theta|ab)$ of other B_{1g} modes, and $RC(\theta|ac)$ of other B_{2g} modes can be found in Appendix E.

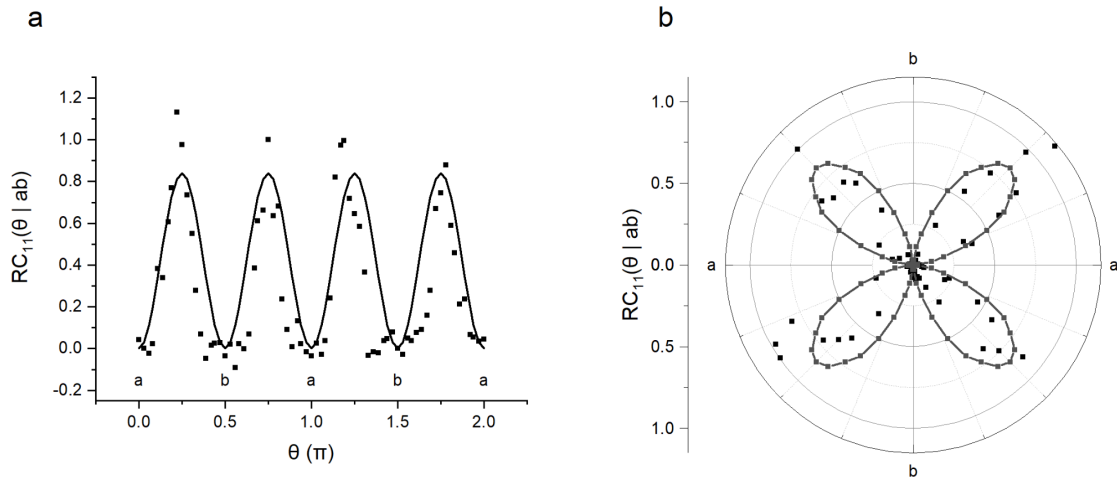


Figure 5-9. Measured $RC_{11}(\theta|ab)$ in the linear plot (a) and polar plot (b).

5.4.3. Discussion

Now we have estimated β -ZnTe(en)_{0.5}'s Raman tensors using two independent measurements – the on-axis polarization and the angle-resolved polarization. In Figure 5-10 we compare the A_g tensors estimated from the two different measurements. Note that the relative intensities of the three components (a^2 , b^2 , c^2) of each A_g mode are consistent between the two measurements. For example, the estimated tensor of #14(A_g) in both on-axis polarization (Figure 5-10a) and angle-

resolved polarization (Figure 5-10b) show $b^2 > c^2 > a^2$, and the intensity of b^2 is four times as much as a^2 or c^2 .

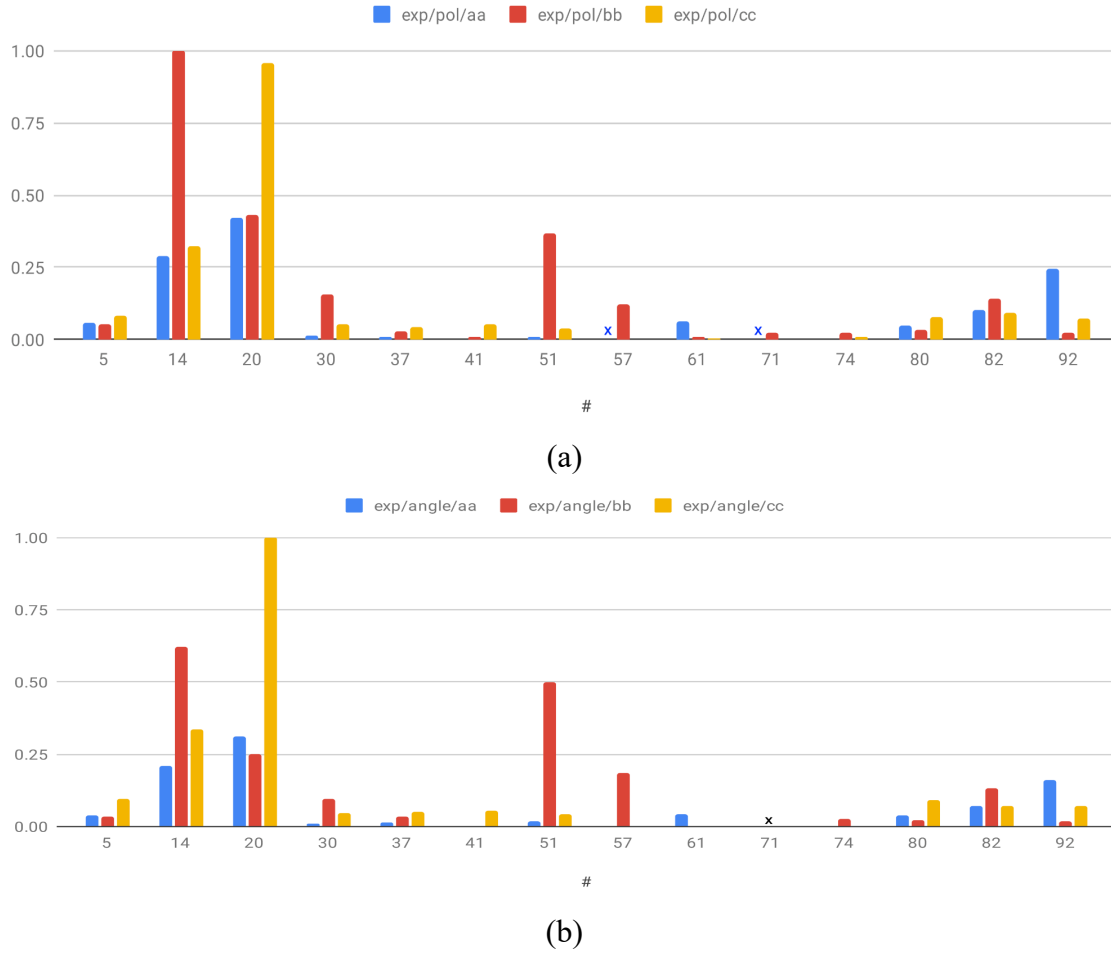


Figure 5-10. Estimated A_g tensors using the on-axis polarization (a) and angle-resolved polarization (b). In the on-axis polarization, #57/aa, #71/aa are not available (denoted ‘X’) due to the abnormalities described in the previous section. In the angle-resolved method, #71 is not available because it is masked by the stronger #72(B_{1g}). Within each of the two measurements, a single scaling factor is applied across all tensor components so that the 1.00 level corresponds to the component with the highest intensity. Within each A_g mode, $\hat{a}_{ab} = \hat{a}_{ac}$ is imposed to normalize its three tensor components, although this

might not be valid because it assumes the crystal momentum $\mathbf{q} = 0$ while in the Raman measurement $\mathbf{q}$ is only close to 0 and some modes can be sensitive to $\mathbf{q}$.

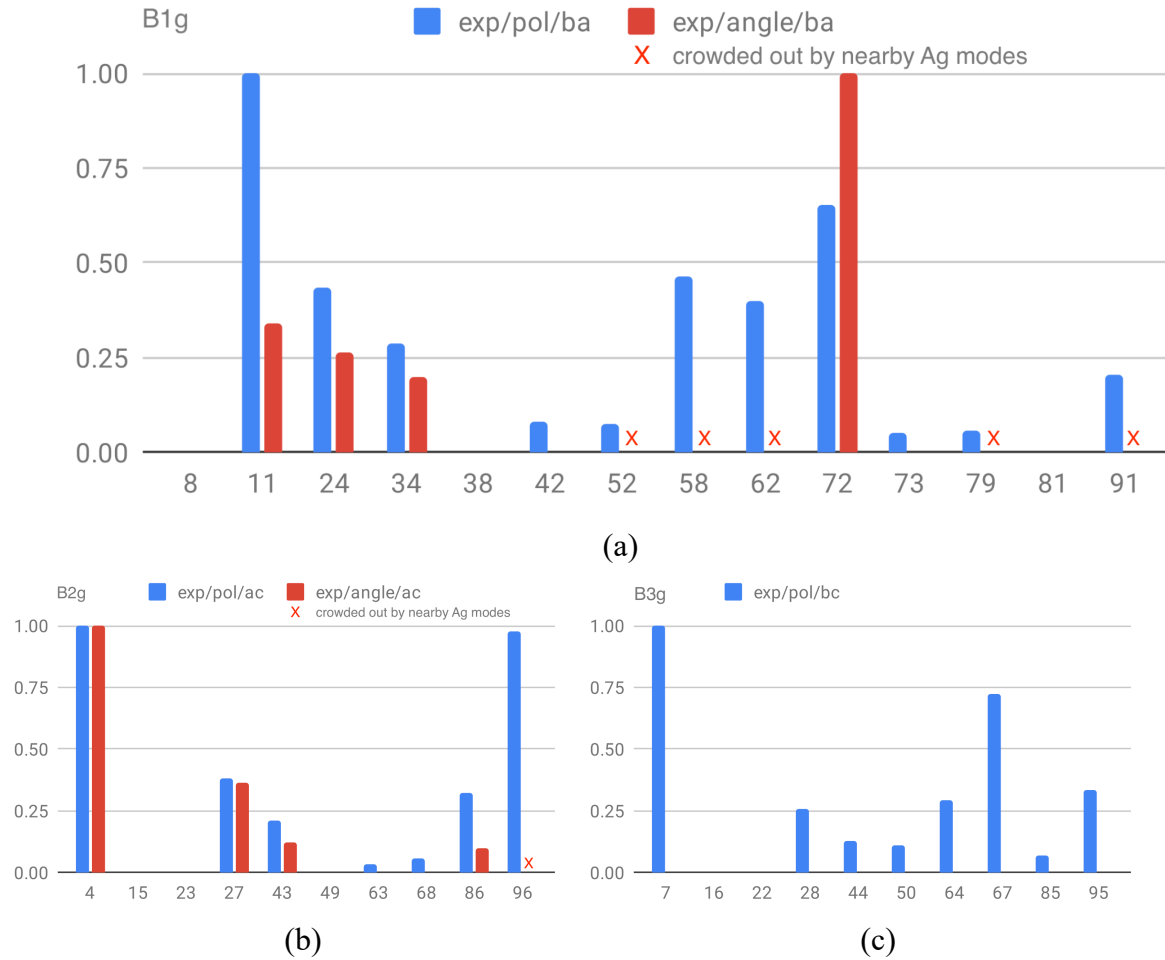
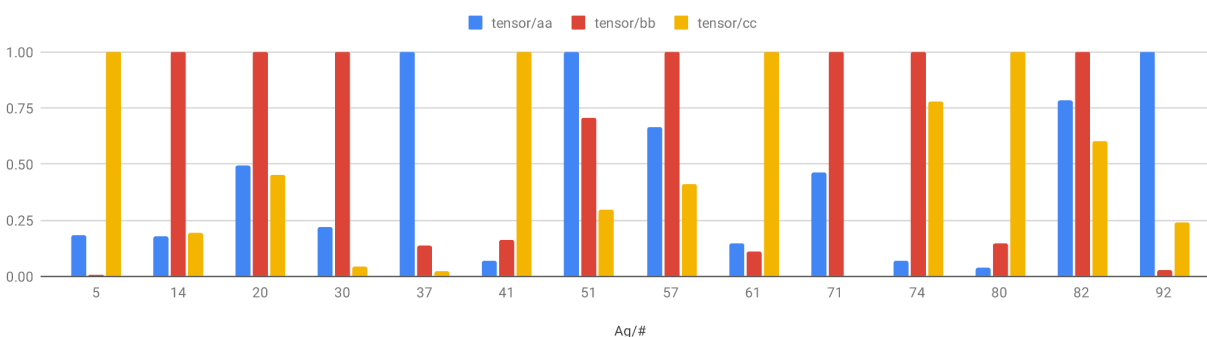


Figure 5-11. Estimated B_{1g} (a) B_{2g} (b) B_{3g} (c) tensors using the on-axis polarization and angle-resolved polarization. For B_{3g} modes, angle-resolved estimated components are not shown due to the unavailable *bc* cleavage in the angle-resolved study. Tensor components are scaled to the maxima within each symmetry. In the angle-resolved method, #52(B_{1g}), #58(B_{1g}), #62(B_{1g}), #79(B_{1g}), #91(B_{1g}), #96(B_{2g}) are not available because they are crowded out by #51(A_g), #57(A_g), #61(A_g), #80(A_g), #92(A_g), #92(A_g),

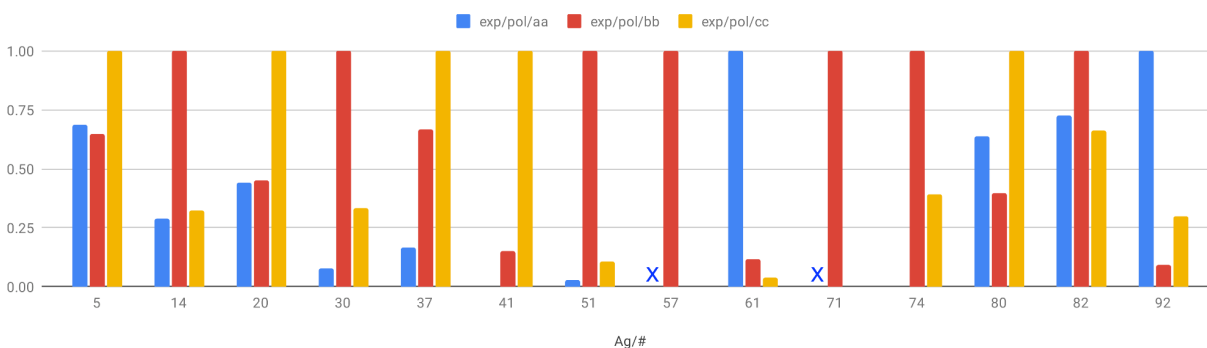
respectively. These A_g modes have higher intensities, and they are located within 3 cm^{-1} from the peak center of the corresponding B_{1g}/B_{2g} modes.

Figure 5-11 compares the $B_{1g}/B_{2g}/B_{3g}$ tensors estimated from the on-axis polarization and angle-resolved polarization. The two approaches yield a consistent estimation of d^2 with a few exceptions. For example, examining the ratio $\eta = d^2(\text{on-axis})/d^2(\text{angle-resolved})$, $\eta(\#72, B_{1g})$ is higher than η of the other B_{1g} modes, $\eta(\#86, B_{2g})$ is higher than the other B_{2g} modes.

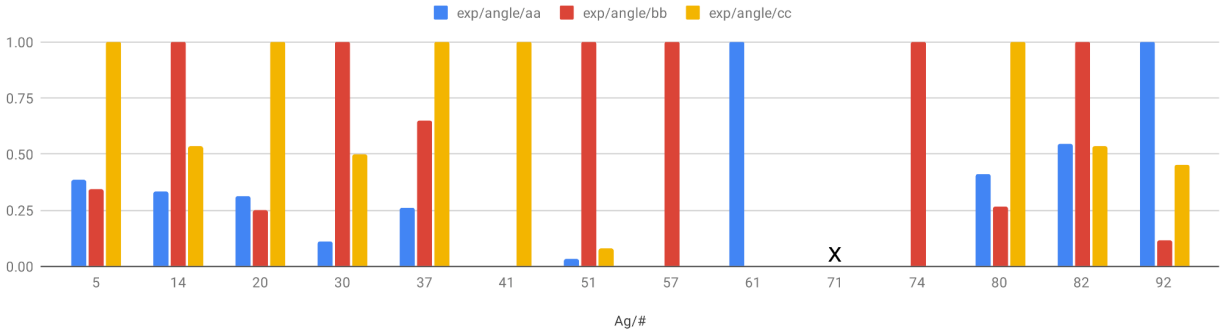
Figure 5-12 compares the computed A_g tensor components with the estimation from the on-axis polarization and angle-resolved polarization. Because the focus will be on the relative intensities of a^2 , b^2 , c^2 of each mode, the three components within each mode are scaled to their maxima.



(a)



(b)



(c)

Figure 5-12. Compare the computed A_g tensor components (a) with the estimated A_g tensors (b–c). (b) estimation from the on-axis polarization measurement; (c) estimation from the angle-resolved polarization measurement

Table 5-6 summarizes the discrepancies between the calculation and the measurements. To consider the error caused by the experiment, the consistency between the two independent measurements and signal-to-noise ratio (SNR) is examined for each mode. We have used ‘√’ to stand for a good match or large SNR, ‘Δ’ to stand for minute discrepancy or fair SNR, ‘X’ to stand for significant discrepancy or weak SNR. Note that despite large SNR and good consistencies between the two independent measurements, significant discrepancies remain in #20, #30, #37, #80. The discrepancies suggest a first-principle calculation does not fully capture β -ZnTe(en)_{0.5}’s vibrational properties. Note that the calculated Raman tensors only consider the mechanism of deformation potential, whereas Frohlich interaction is not considered [90–92]. These two mechanisms may interfere with each other, which might explain why some strong Raman modes predicted by the calculation turned out to be weak or even missing.

Table 5-6. The discrepancy between the predicted A_g tensor components and the measured A_g components from the on-axis polarization and angle-resolved polarization

Mode#	s/n	Between the two measurements	Compare with calculation
5	✓	✓	Δ (large b)
14	✓	✓	✓
20	✓	✓	X bc
30	✓	✓	X ac
37	✓	✓	X ac
41	Δ	Δ miss a	✓
51	✓	✓	X small a
57	X	✓	X miss a and c
61	Δ	✓	X ac
71	X	X unavailable (angle-resolved)	X miss a
74	X	X miss c (angle-resolved)	Δ miss c (angle-resolved)
80	✓	✓	X ab
82	✓	✓	✓
92	✓	✓	✓

5.5. Summary

Thanks to its highly-ordered structure, β -ZnTe(en)_{0.5}'s Raman spectra present Raman-active vibration modes that arise from its pristine structure with few complications. In the chapter, two polarized Raman techniques are applied to study β -ZnTe(en)_{0.5}'s vibration modes: the on-axis polarization and the angle-resolved polarization.

The on-axis polarization was used to decouple the vibration modes according to their symmetries. A mode-by-mode analysis allows unambiguous assignment for the Raman-active

modes. A few exceptions and additional features are discussed. With the assignment, we demonstrated that the Raman tensor can be estimated from both the on-axis technique and the angle-resolved technique. The two independent measurements yield consistent estimations. In addition, it has been shown that a combination of the two techniques enables unambiguous determination of the crystal orientations.

Chapter 6: Conclusion and future works

6.1. Conclusion

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By providing a comprehensive characterization of one prototype system, β -ZnTe(en)_{0.5}, with some samples being monitored over 16 years, this work illustrates the interplay of intrinsic and extrinsic degradation mechanisms in determining the long-term stability of an organic-inorganic hybrid material. Benefiting from its relatively large intrinsic formation energy as well as a large kinetic barrier and stable surface, even without encapsulation, β -ZnTe(en)_{0.5} has been shown to exhibit over 15-year shelf life, whereas its intrinsic lifetime could be as long as 1.9×10^8 years.

The observed deterioration of structural integrity is actually caused primarily by extrinsic effects, such as surface imperfection, exposed edge, and structural defects. This study indicates that formation energy can serve as an effective screening parameter for the long-term stability prospective of a new hybrid material. However, when the formation energy is adequately high, extrinsic degradation paths could be practically more significant for the long-term stability of the hybrid.

The study on β -ZnTe(en)_{0.5} demonstrated that despite the complex structure, a hybrid can have an exceptionally high degree of both macroscopic and microscopic scale structural perfectness, manifesting as small XRD and Raman linewidths comparable to the high-quality ZnTe and near

100 % internal PL quantum efficiency superior to most known high bandgap inorganic semiconductors such as ZnO and GaN. This attribute can offer much-needed quantum coherence for electronic processes in next-generation (opto)electronic technologies.

This and other related II-VI based hybrids demonstrate a totally different approach for forming a perfectly abrupt heterostructure, that is, combining two structures with drastically different materials, instead of two structurally similar ones, to eliminate the intermixing that occurs in most conventional heterostructures. An inorganic analog is the abrupt interface between rock-salt PbTe and zinc-blende CdTe along their [111] direction [93].

This study provides practical guidance for selecting different organic-inorganic hybrid materials to suit different application needs and reveals the potential of the II-VI based hybrids for a wide range of scientific explorations and applications with excellent long-term stability.

Using the polarized Raman techniques, this work demonstrated a systematic analysis of β -ZnTe(en)_{0.5}'s Raman-active modes. Thanks to its highly-ordered structure, an unambiguous assignment was achieved, with few exceptions and additional features. It has been shown that a combination of the polarized Raman techniques enables unambiguous determination of the crystal orientations.

6.2. Future works

This work demonstrated β -ZnTe(en)_{0.5}'s high-degree crystallinity and superior long-term stability to other crystalline hybrids such as hybrid perovskites. In this section we discuss a spectrum of directions to improve the work.

β -ZnTe(en)_{0.5}'s lifetime under different moisture levels

Because moisture can affect device lifetime, common testing protocols on device stability specify relative humidity in addition to temperature. While estimating $\beta\text{-ZnTe(en)}_{0.5}$'s lifetime in ambient air, we did not explicitly discuss the lifetime's dependence on moisture. A preliminary observation is that after being treated in water with ultrasonication, tellurium islands can be found on the hybrid's surface, suggesting that like other oxidation agents in ambient air, H_2O molecules can trigger an oxidation process on the sample surface. A quantitative study on hybrid lifetime's dependence on relative humidity can provide important practical value.

Search alternative structure for higher oxidation barrier

$\beta\text{-ZnTe(en)}_{0.5}$'s lifetime in ambient air is significantly reduced (~ 10 years) compared with the lifetime in N_2 protected environment ($\sim 10^8$ years), due to the lower kinetic barrier of oxidation. It invites us to think if one can achieve a longer ambient air lifetime by picking alternative structures with higher oxidation barriers. One thought is to replace the ethylenediamine, the organic part of $\beta\text{-ZnTe(en)}_{0.5}$, with 1,2-ethanediyldiphosphine. The idea is that since phosphorus has a lower electronegativity compared with nitrogen, it takes more energy for the molecules to pull electrons from the ZnTe slabs. Because the 1 atm boiling point of 1,2-ethanediyldiphosphine ($109\text{-}110^\circ\text{C}$) is close to ethylenediamine (118°C), a starting point of the synthesis strategy is to modify the procedure of $\beta\text{-ZnTe(en)}_{0.5}$ by using 1,2-ethanediyldiphosphine as the new organic solvent.

Build a prototype device

Moving forward, the goal is to build a prototype device, such as a UV emitter. In preparation, two immediate steps can be taken: (1) introduce dopants into the hybrid and demonstrate their electrical conductivity, and (2) study $\beta\text{-ZnTe(en)}_{0.5}$'s carrier diffusion length.

When choosing the dopants for $\beta\text{-ZnTe(en)}_{0.5}$, there are several considerations. (1) One should try p-type dopants first, considering that ZnTe is unique among the II-VI compound in that it can be doped p-type rather easily [94], (2) One should consider cation dopants. Because $\text{Zn(NO}_3)_2$ or ZnCl_2 is among the precursors in the hybrid synthesis, the cation dopants can be easily introduced in the en solutions in the synthesis stage. (3) One should consider cation sizes similar to Zn, e.g., Ag^+ , Cu^+ , etc. Demonstrating $\beta\text{-ZnTe(en)}_{0.5}$'s electrical conductivity is not only a necessary preparation for a prototype device but itself can be an interesting topic. Because $\beta\text{-ZnTe(en)}_{0.5}$ has sharp structural differences along the in-plane and stacking directions, one should expect anisotropic electrical conductivity.

Carrier diffusion length affects device-level performance. With $\sim 100\%$ IQE, it would be interesting to study $\beta\text{-ZnTe(en)}_{0.5}$'s carrier diffusion length and gain a complete picture of carrier transport in $\beta\text{-ZnTe(en)}_{0.5}$. A straightforward approach to investigating the diffusion of photo-generated carriers is using a tightly focused laser beam to generate carriers locally, then imaging the spatial distribution of the PL signal in the vicinity of the illumination site [16].

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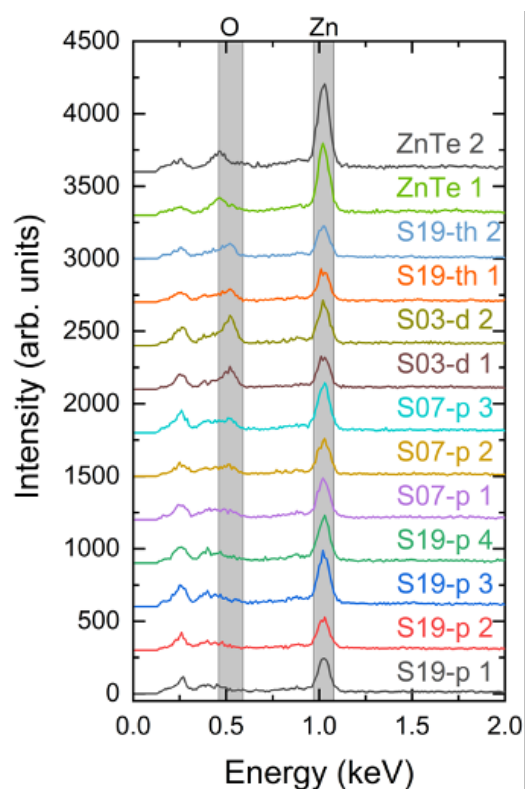
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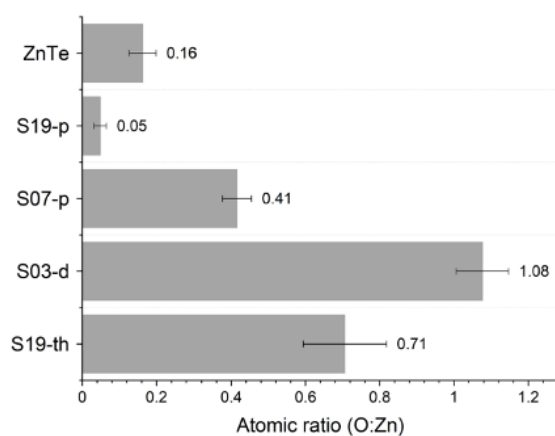
Appendix A: EDX spectra and atomic ratios of O:Zn

EDX spectra of different samples:



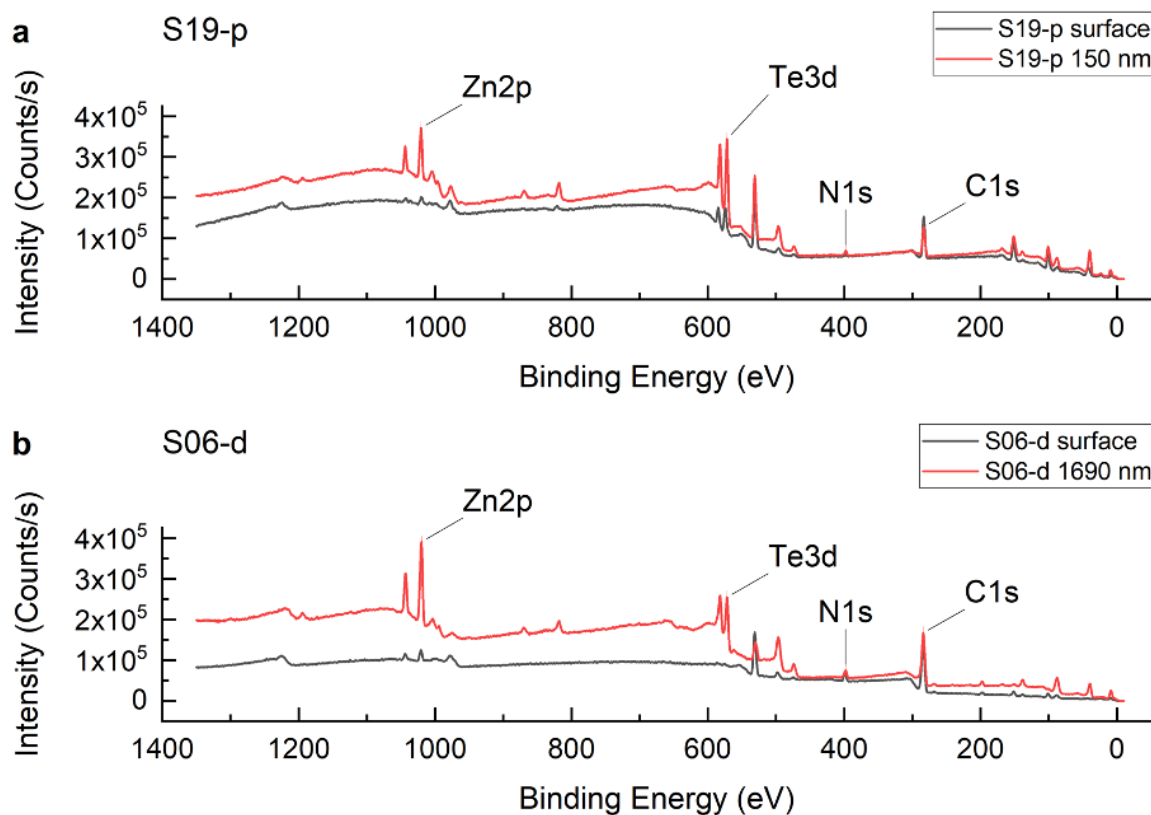
Atomic ratios of O:Zn obtained from integrated peak intensities of EDX spectra:

	Mean	Std error
ZnTe	0.16	0.04
S19-p	0.05	0.02
S07-p	0.41	0.04
S03-d	1.08	0.07
S19-th	0.71	0.11

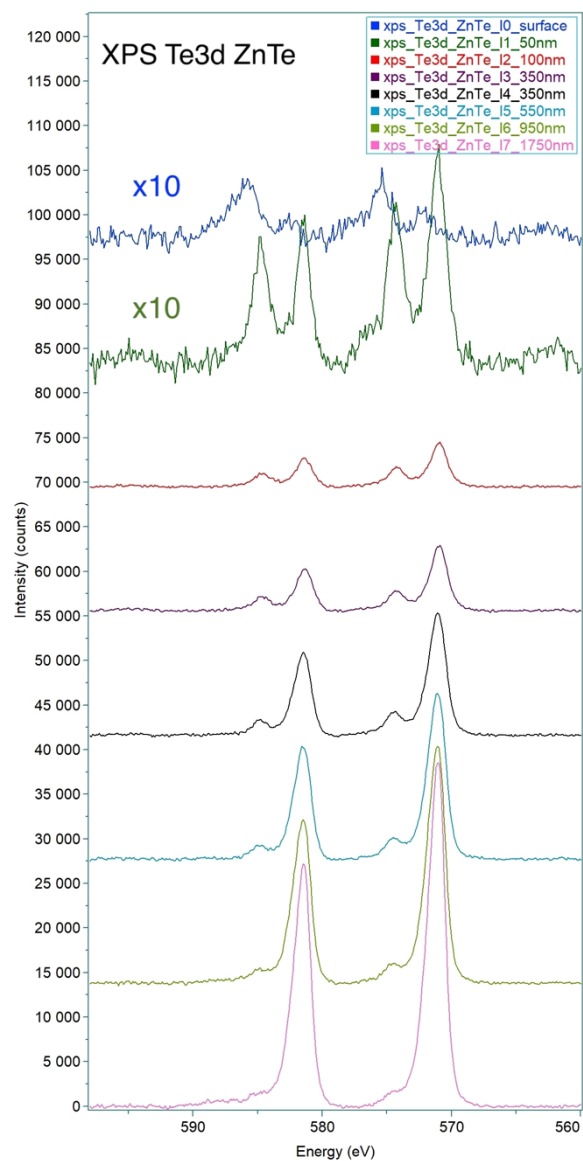
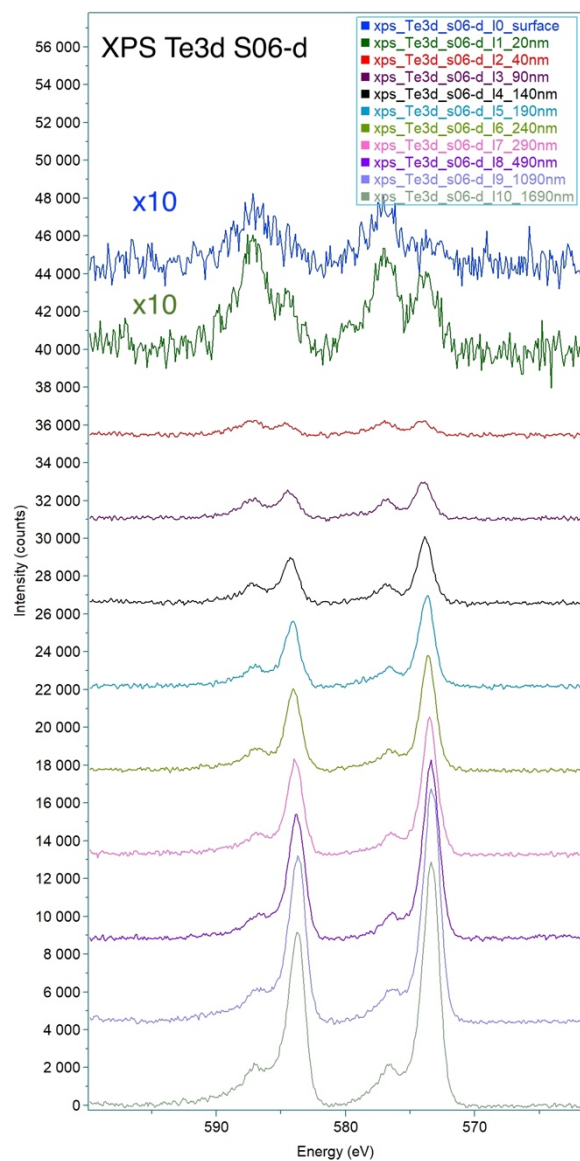


Appendix B: XPS scans of a broader energy range

XPS spectra at different etching times or depths in an extended spectral range. a) a pristine sample S19-p, b) an optically degraded sample S06-d.

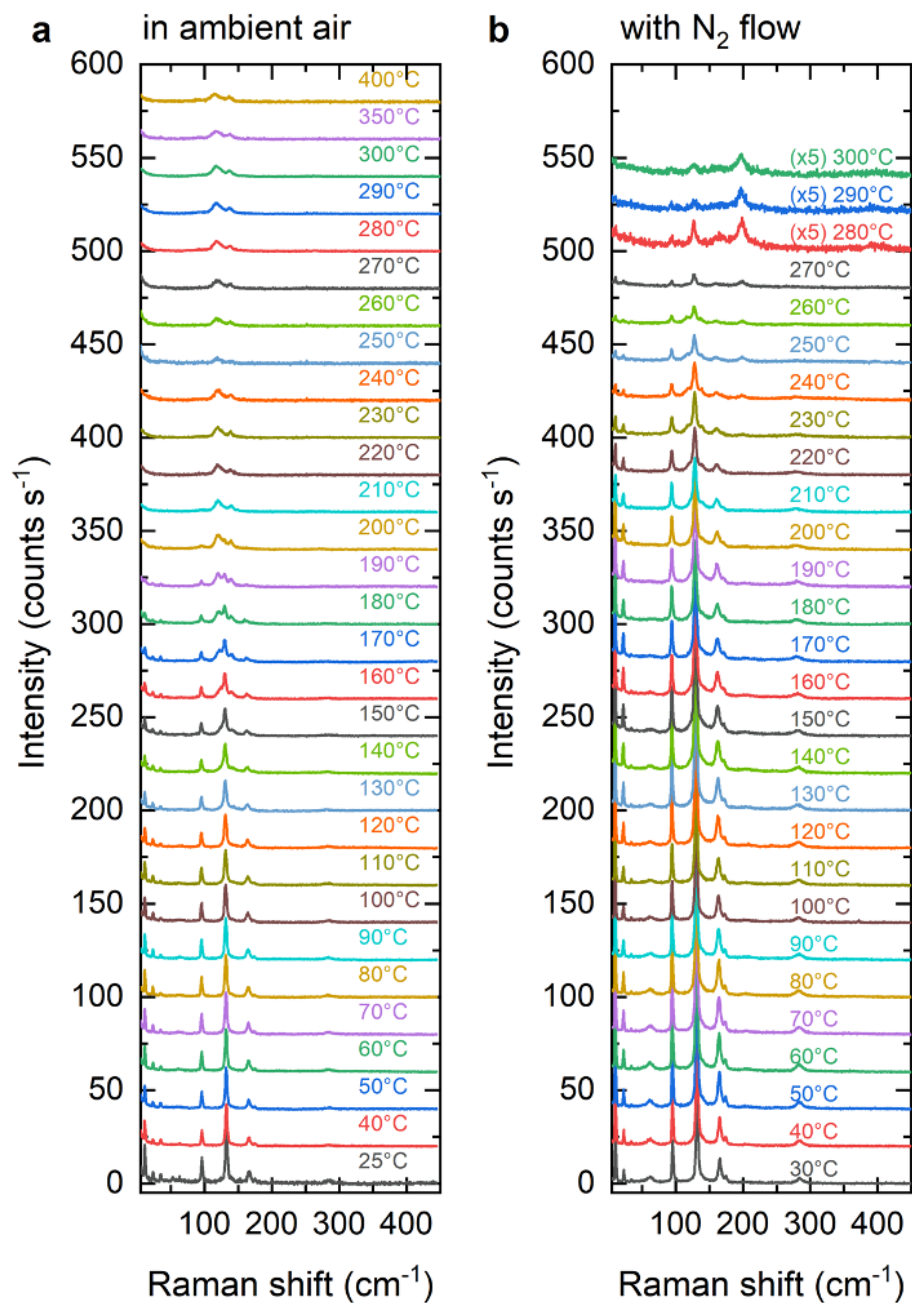


XPS spectra at finer etching times or depths of S06-d and ZnTe:



Appendix C: In-situ Raman spectroscopy at more temperature points

In-situ heating studies using Raman spectroscopy for a freshly made sample S19-p in air (a) and N₂ (b).



Appendix D: Correspondance between en modes and β -ZnTe(en)_{0.5}

modes

The map between a subset of en modes and β -ZnTe(en)_{0.5} modes. The en modes are reproduced from *M.G. Giorgini, M.R. Pelletti, G. Paliani, R.S. Cataliotti, J Raman Spectrosc 14 (1983) 16–21*.

en mode	en mode frequency/cm ⁻¹	β -ZnTe(en) _{0.5} mode# (frequency)
w(CH ₂), A _g	1368	65 (1286.4) 66 (1287.1) 71 (1340.4) 72 (1340.6)
w(CH ₂), A _u	1379	
δ (CH ₂), A _g	1439	73 (1432.7) 74 (1433.1)
δ (CH ₂), B _u	1457	75 (1443.7) 76 (1443.8)
δ (NH ₂), A _g	1623	77 (1577.4) 78 (1577.6)
δ (NH ₂), B _u	1606	79 (1578.6) 80 (1579.4)
ν (CH ₂), A _g	2858	81 (2928.4) 82 (2928.9)
ν (CH ₂), B _u	2860	83 (2941.2) 84 (2942.1)

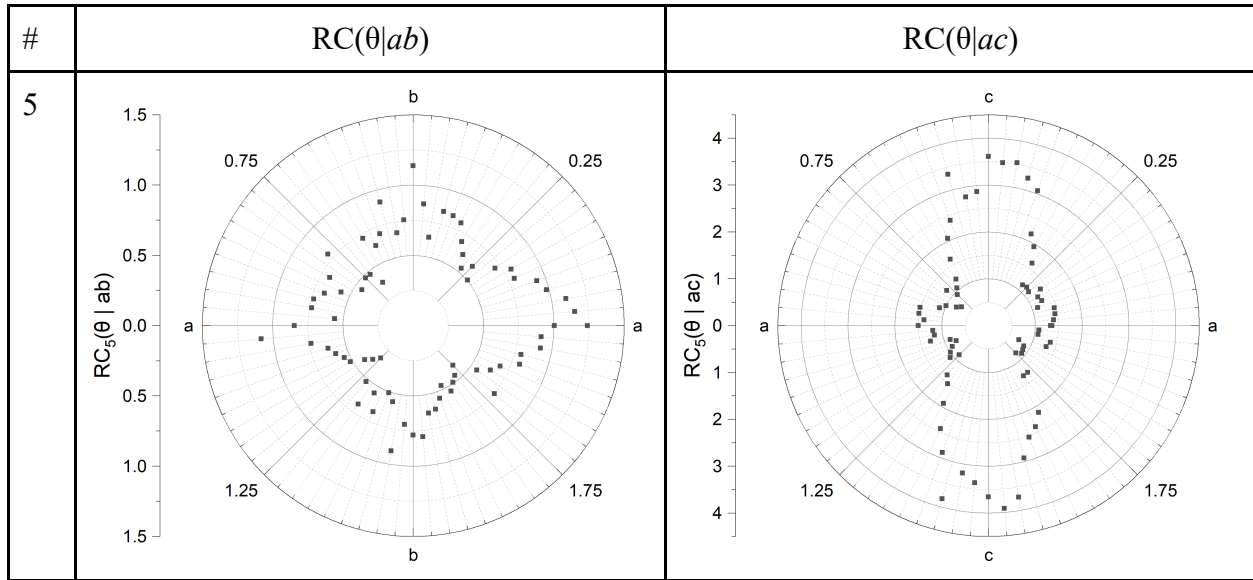
$\nu(\text{CH}_2)$, B_g	2910	85 (2965.6) 86 (2965.6)
$\nu(\text{CH}_2)$, A_u	2914	87 (2990.5) 88 (2990.5)
$\nu(\text{NH}_2)$, A_g	3170	89 (3175.6) 90 (3178.2)
$\nu(\text{NH}_2)$, B_u	3170	91 (3178.7) 92 (3179.3)
$\nu(\text{NH}_2)$, B_g	3335	93 (3207.9) 94 (3207.9)
$\nu(\text{NH}_2)$, A_u	3332	95 (3208.2) 96 (3208.3)

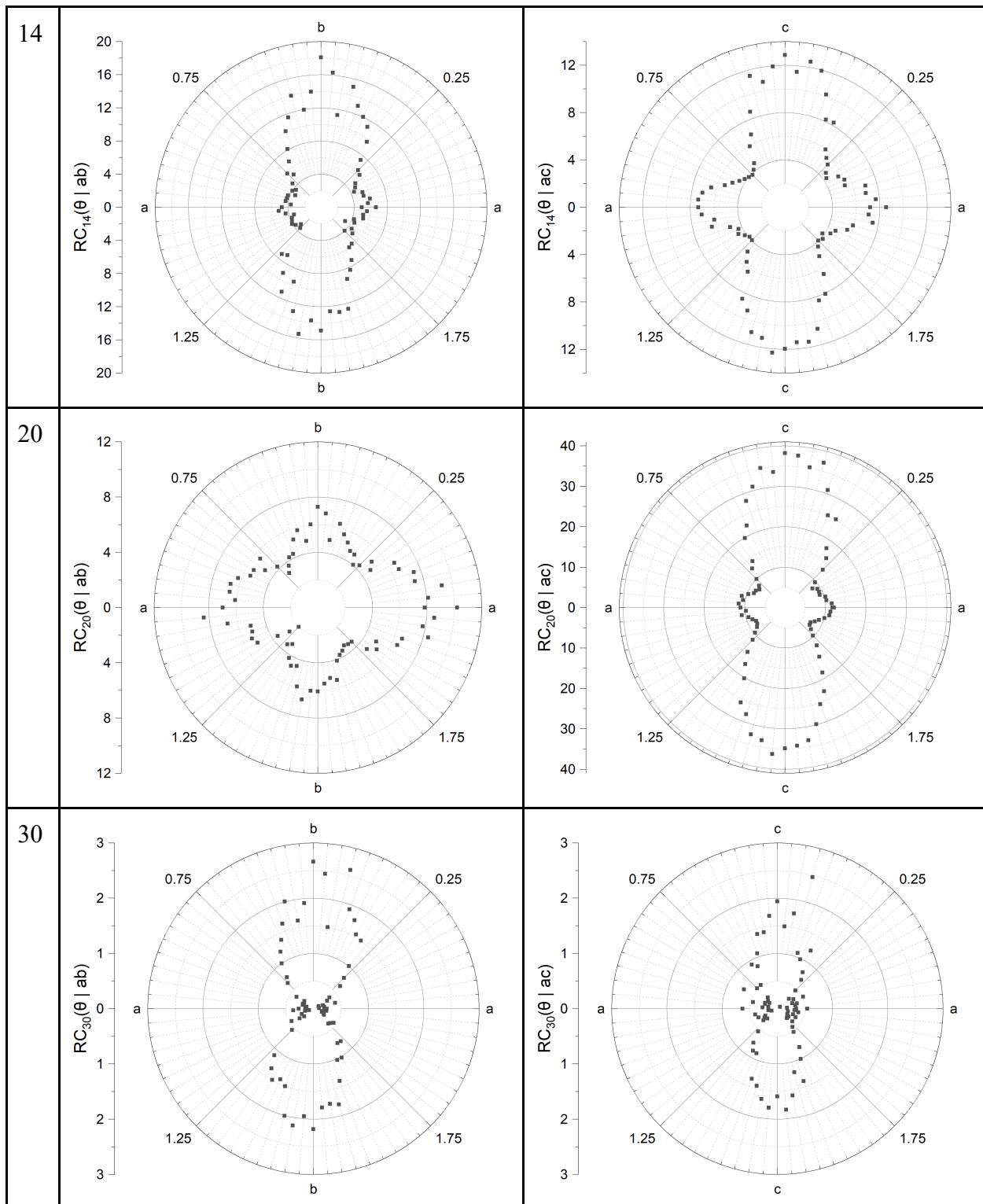
Abbreviation used: ν —stretch; δ —deformation; w—wag.

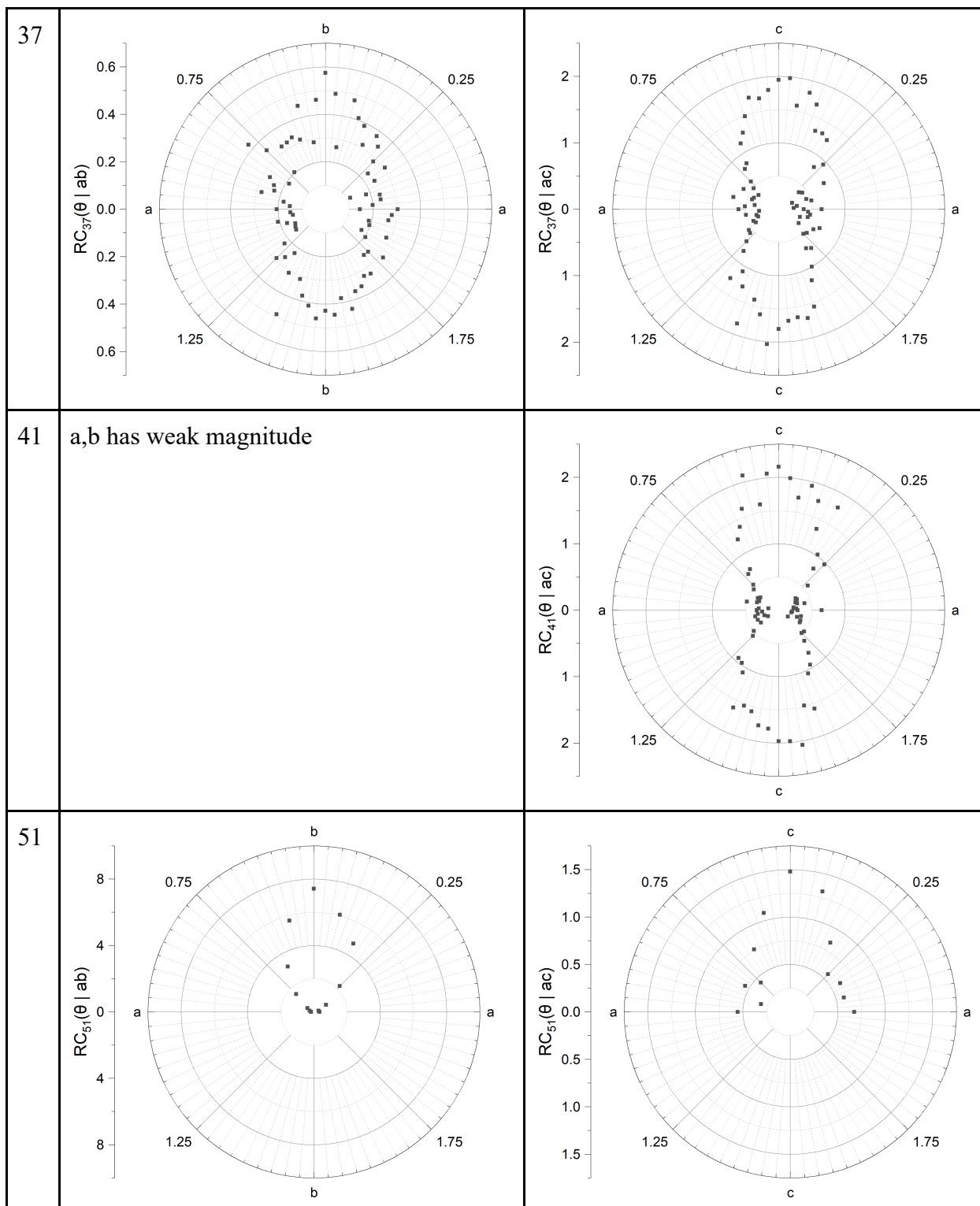
Appendix E: RC(θ) of other A_g , B_{ig} modes

Here we organized RC(θ) plot from the angle-resolved Raman measurement for β -ZnTe(en)_{0.5}'s vibrational modes. β -ZnTe(en)_{0.5} has 14 A_g modes, 14 B_{1g} modes, 10 B_{2g} modes, and 10 B_{3g} modes. The measurement was performed using a parallel configuration, and backscattering geometry having the incident and scattered light propagating along c -axis (ab-plane) and b -axis (ac-plane). Measurement for B_{3g} modes are not shown due to the unavailable bc cleavage at the moment of the experiment. For a few modes, RC(θ) are not available either because the Raman intensity is too weak to be resolved as a function of θ , or the mode under consideration is crowded out by a nearby mode with higher intensity, in such case, the mode number and symmetry of the stronger mode will be indicated.

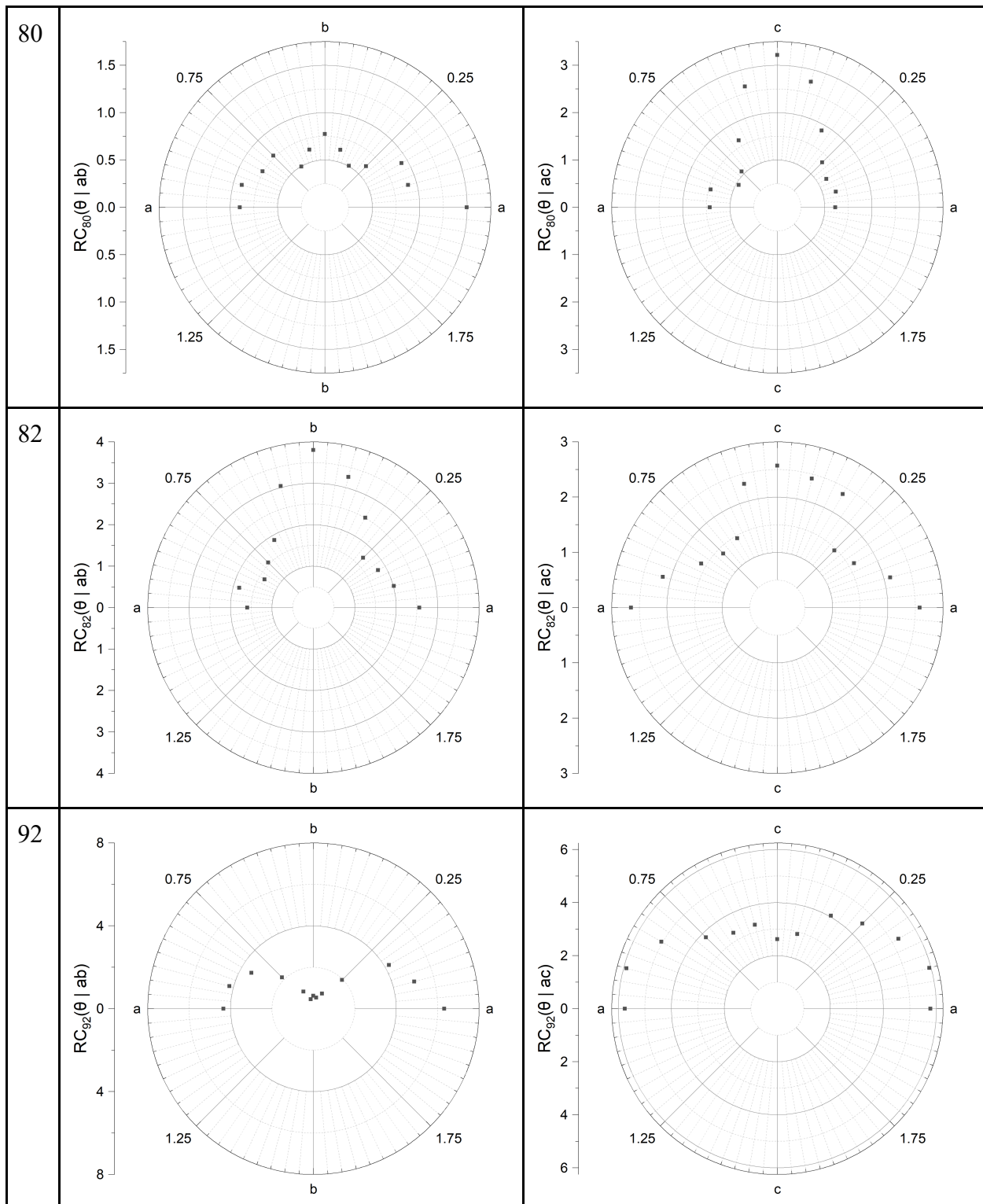
14 A_g modes







57	$RC_{57}(\theta ab)$	a,c has weak magnitude
61	$RC_{61}(\theta ab)$	$RC_{61}(\theta ac)$
71	crowded out by #72(B_{1g})	crowded out by #72(B_{1g})
74	$RC_{74}(\theta ab)$	a,c has weak magnitude



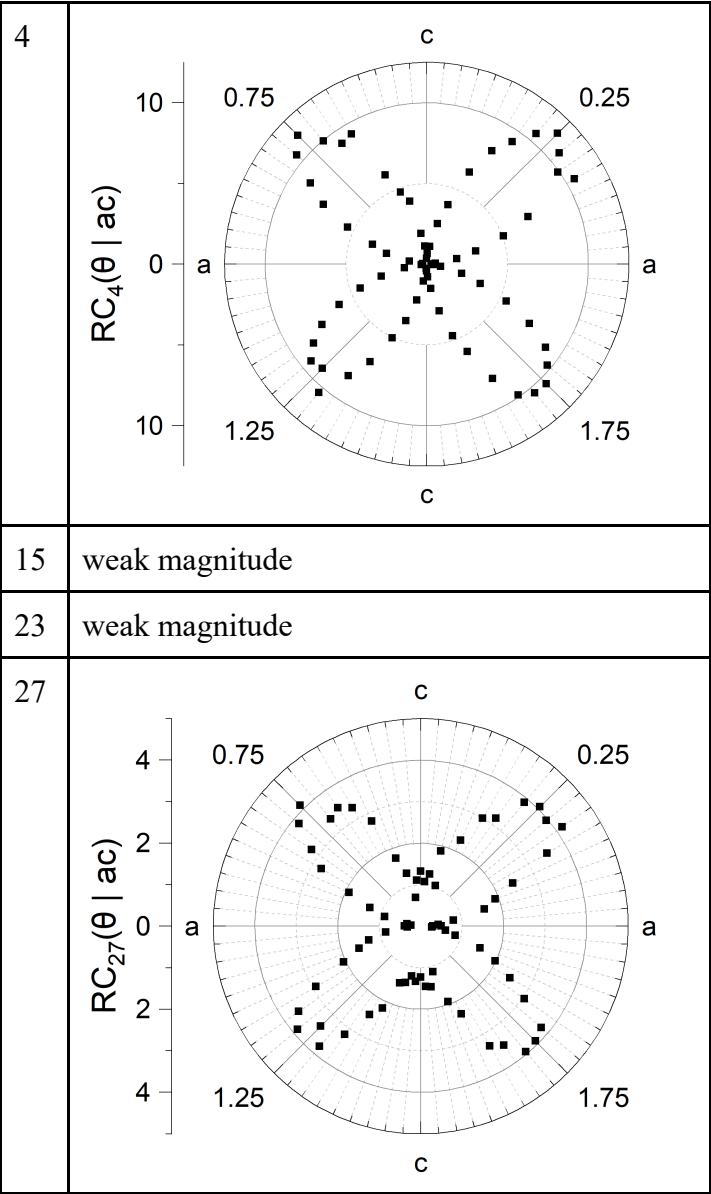
14 B_{1g} modes

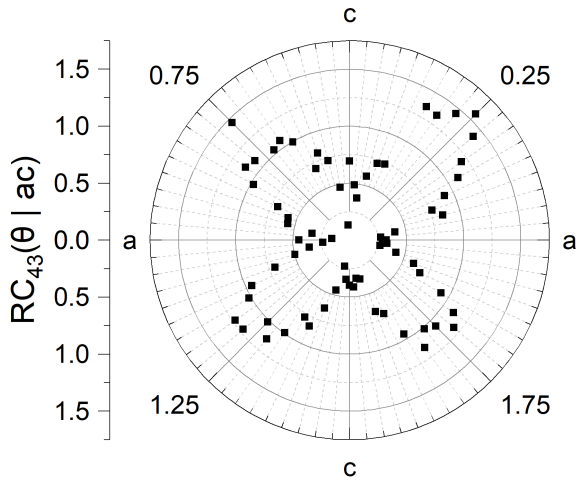
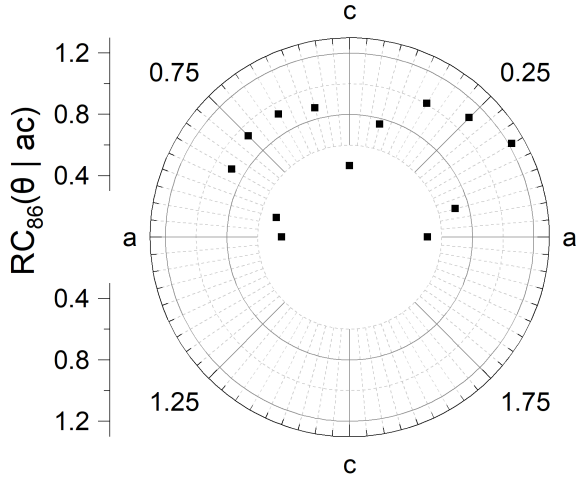
#	$RC(\theta ab)$
8	weak magnitude
11	
24	
34	

38	weak magnitude
42	weak magnitude
52	crowded out by #51(A_g)
58	crowded out by #57(A_g)
62	crowded out by #61(A_g)
72	
73	weak magnitude
79	crowded out by #80(A_g)
81	weak magnitude
91	crowded out by #92(A_g)

10 B_{2g} modes

#	$RC(\theta ac)$
---	-----------------



43	
49	weak magnitude
63	weak magnitude
68	weak magnitude
86	
96	crowded out by #92(A _g)