In situ micro-Raman studies of laser-induced bismuth oxidation reveals metastability of beta-Bi2O3 microislands

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In situ micro-Raman studies of laser-induced bismuth oxidation reveals metastability of $\beta$-Bi$_2$O$_3$ microislands

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Abstract: We report the laser irradiation-induced oxidation of bismuth metal investigated in situ by micro-Raman spectroscopy as a function of irradiation power and time. The purely optical synthesis and characterization of $\beta$-Bi$_2$O$_3$ oxide microislands on metallic Bi surfaces is shown to be stable over time, even at room-temperature. By closely examining possible reactions on simple Bi morphologies it is revealed for the first time that the ensuing oxide phase is critically dependent on the final oxide volume and follows a fixed kinetic transformation sequence: $\frac{1}{2}$O$_2$(g) + 2Bi(l) $\rightarrow$ $\beta$-Bi$_2$O$_3$(s) $\rightarrow$ $\alpha$-Bi$_2$O$_3$(s). These findings are unusual within the framework of traditional Bi$_2$O$_3$ thermal transformation relations. An electrostatic mechanism involving a changing Bi$_2$O$_3$ surface-to-volume ratio is proposed to explain the room-temperature metastability of small $\beta$-Bi$_2$O$_3$ volumes and the subsequent transformation sequence, as well as unifying the results of previous studies.

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1. Introduction

Bismuth trioxide (Bi₂O₃; also known as bismuth oxide and bismuthsesquioxide) polymorphs are fascinating optical materials with wide bandgap, high refractive index, large dielectric permittivity, remarkable photoconductivity, and ionic conductivity. The versatility of Bi₂O₃ nanomaterials has fostered considerable attention for scientific and technological advances over the past decade, with applications spanning electrical ceramics, solid-state electrolytes, gas sensors, medical disinfection/sterilization, and energy generation [1–4]. Within the context of current research on Bi₂O₃, surprisingly little is known about its phase properties at the nano- and micron-scale.

Of the four main Bi₂O₃ polymorphs [5–8] by far the most interesting are the high temperature metastable β and δ modifications, because of their extremely high oxygen ion conductivity (δ-Bi₂O₃ possessing the highest among all binary metal sesquioxides) and their strong visible-light-driven photocatalytic activity (β-Bi₂O₃ being the most active). While thermal oxidation of bismuth is inexpensive and easily controlled [9–11], synthesis of the desirable β-Bi₂O₃ and its stabilization at room temperature is not straightforward [12–16]. Attempts to better understand phase transformation relations among Bi₂O₃ polymorphs are currently underway [17], however a comprehensive model of the transient stages of oxidation is yet to fully explain the varied and seemingly anomalous oxidation phase results reported in the literature [11, 18–29]. From the nucleation of Bi₂O₃ molecules on the bismuth surface to the coalescence of a thermodynamically stable oxide represents a scientifically challenging and technologically important terra incognita. In most studies of bismuth oxidation to date, the only real-time in situ diagnostics have been through thermogravimetric analysis or X-ray diffraction (XRD) measurements. Usually, neither of these techniques is versatile enough to provide information suitable for process control or for elucidating transformation dynamics [30–33].

In this paper, we shed light on the bismuth oxidation process through novel laser irradiation-induced oxidation experiments, monitored in situ by micro-Raman scattering. Our findings reveal that the resultant Bi₂O₃ phase is critically dependent on oxide volume (at the micron-scale) and follows a fixed transformation sequence. An electrostatic mechanism — based on a changing Bi₂O₃ surface-to-volume ratio — is invoked to explain how small volumes of undoped β-Bi₂O₃ acquire room-temperature metastability, as well as permitting the interpretation of previous studies.

2. Experiment

2.1. Sample details

Bismuth samples were prepared using a high purity (99.99% pure) bismuth ingot. Flakes scraped off by scalpel allowed measurements on larger (bulk) samples, while the production
of smaller bismuth particles (0.3 - 3 μm) was achieved using a mortar and pestle, followed by selection under microscope. No further sample preparation was required.

2.2. Raman scattering experiments

Room-temperature micro-Raman spectra were acquired in a quasi-backscattering configuration using a Jobin-Yvon HR800 integrated micro-Raman system with confocal microscope, 20 mW HeNe 632.8 nm laser, and air-cooled CCD detector. Laser spot diameters of 1.7 μm and 4.2 μm were defined by use of either an Olympus ×100 or ×50 objective, respectively. Spot size was determined using a combination of highly-attenuated optical images and charting across a cleaved Si crystal edge. Laser power densities were controlled by a neutral variable density filter incorporated before the microscope optics. Dispersion was achieved through a 1800 g/mm diffraction grating (spectral resolution 0.2 cm⁻¹) and instrument calibration was verified through checking the position of the Si band at ±520.7 cm⁻¹. Implementing an appropriate notch filter to limit Rayleigh backscatter detection meant low-frequency portions of the Raman spectra (below 58 cm⁻¹) are partially truncated. All spectra are presented as raw data (no background subtracting or smoothing has been performed) and are recorded using the Raman laser power densities indicated in corresponding figure captions.

![Optical micrographs of representative Bi surfaces examined in this study.](image)

Fig. 1. Optical micrographs of representative Bi surfaces examined in this study. (a) Smooth, (b) rough, and (c) small particulates on a glass slide. (d) The micro-Raman spectra measured at very low laser power density (5 × 10² W·cm⁻²) from a smooth Bi surface with the inset expanded over the second-order bismuth harmonics.
3. Results and discussion

The melting point of bismuth is much lower than that of Bi₂O₃ (see Fig. 3), so atomic rearrangement immediately after oxide formation is inhibited. The tendency for Bi₂O₃ to be glass-forming on metallic Bi surfaces [34] means it is useful to investigate small-scale surface reactions. Figure 1 shows optical microscope images of the three kinds of bismuth surfaces examined in this study, along with a typical bismuth Raman spectrum exhibiting two modes at 71 cm⁻¹ and 98 cm⁻¹, which are consistent with the two first-order optical bands of rhombohedral bismuth corresponding to doubly degenerate $E_g$ and non-degenerate $A_{1g}$ phonon modes, respectively [35]. Enlarged in the inset are the weak second-order bands at $\sim 188$ cm⁻¹ consisting of three overtones of similar frequencies [36].

The development of laser-induced oxidation on a smooth Bi surface is plotted in Fig. 2(a) for increasing laser power densities from $0.6 \times 10^4$ to $12.5 \times 10^4$ W·cm⁻², where additional modes at 128, 315, and 461 cm⁻¹ contribute to the Raman lineshape for irradiances in excess of $2.7 \times 10^4$ W·cm⁻². These three bands correspond to unique Bi-O stretches and are attributed to the $\beta$-phase Bi₂O₃ [37]. Their appearance confirms laser irradiation-induced oxidation of the bismuth surface (using ambient oxygen) and indicates that, for sufficiently large...
power densities, there are two induced effects: an oxidation reaction followed by the arranging into $\beta$-Bi$_2$O$_3$. The second-order scattering mode (with heavy $A_{1g}$ phonon composition [36]) also intensifies and appears connected to the surface oxidation; however, it is not. As the laser power increases the probed area rises in temperature and causes first-order bands to grow. Consequently, this also increases the intensity of the second-order harmonics. Figure 2(b) presents similar data for a decreasing probe irradiance. Here the $\beta$-Bi$_2$O$_3$ signatures represent a prominent and unchanging contribution to the overall Raman lineshape. At the relatively low power density of $0.5 \times 10^4$ W·cm$^{-2}$, where temperature estimates based on non-degenerate $A_{1g}$ redshifts place the bismuth crystal close to room-temperature [38, 39], no changes are observed.

Given 632.8 nm HeNe laser light is used for excitation, the photolytically activated influences are small compared to the isothermally driven process [40]. Many metal oxidation reactions promoted by laser irradiation are largely thermally driven, and isolating non-thermal radiation effects is difficult. For the specific case of a specular bismuth surface [41] irradiated by low intensity 632.8 nm laser light, Raman measurements demonstrated no evidence of oxidation following long exposures; only once temperatures in the laser heated volume surpass the bismuth melting point will an oxidation reaction occur. This is verified by the insets of Figs. 2(a) and 2(b), where phonon mode redshifting is attributed to large changes in local temperature [38, 39]. Decreasing laser powers reveal these phonon bands returning to their original energies. This is important, as it removes factors such as laser-induced defects, resulting in quantum confinement, from influencing the observed redshift; the shifting is driven by non-destructive and purely thermal mechanisms.

The stability of the transformed $\beta$-Bi$_2$O$_3$ material was investigated over time. Raman spectra were recorded before and after exposure to high irradiance and in both cases an extremely low power density of $I_R < 5 \times 10^3$ W·cm$^{-2}$ was used. The absence of Bi-O stretches before irradiation and their presence two weeks after irradiation (spectra not shown) reveal a stable synthesis of $\beta$-Bi$_2$O$_3$. Furthermore, no decrease in the relative Raman scattering intensities of these peaks was observed. Thus laser-induced $\beta$-Bi$_2$O$_3$ oxidation is not only demonstrated, but shown to be stable at room temperature.
Figure 3 displays the traditional existence domains and transformation relations (broken light arrows) for the four main Bi$_2$O$_3$ polymorphs [5–8], represented as $\alpha$- (monoclinic), $\beta$- (tetragonal), $\gamma$- (bcc), and $\delta$-phase (fcc), along with the oxidation sequence observed in this study (solid heavy arrows). The existence of at least three other modifications have been realized ($\omega$, $\varepsilon$ and $\eta$), although these are synthesized under atypical conditions [42–44] and are omitted for clarity. A striking feature of Fig. 3 is a tendency for all polymorphs to transform into the $\delta$-phase at sufficiently high temperatures, and ultimately to transform into the $\alpha$-phase when cooled to room temperature. Of the phases, $\alpha$-Bi$_2$O$_3$ is thermodynamically stable from room temperature up to 1003 K, where it transforms into $\delta$-Bi$_2$O$_3$ phase, which is stable until melting at 1097 K. When cooling from $\delta$-Bi$_2$O$_3$, large thermal hysteresis effects regulate the transformation into one of two high-temperature metastable phases, $\beta$-Bi$_2$O$_3$ or $\gamma$-Bi$_2$O$_3$. Below approximately 641-923 K the metastable phase transforms into $\alpha$-Bi$_2$O$_3$, unless chemically stabilized [12]. Within this framework, our findings are unusual for two reasons. Firstly, the laser-induced oxidation results reveal a purely $\beta$-Bi$_2$O$_3$ oxide layer. This is directly verified through no observation of $\alpha$-Bi$_2$O$_3$ vibrations (see Fig. 4(a)) in the Raman spectra. Secondly, the laser-induced $\beta$-Bi$_2$O$_3$ violates the traditional temperature domains for Bi$_2$O$_3$ by exhibiting phase stability at room temperature.

To understand these results, we next investigate the laser-induced changes which are possible with the more textured Bi surfaces of Figs. 1(a) – 1(c). Laser-induced oxidations were carried out using a maximum irradiance of $12.5 \times 10^4$ W·cm$^{-2}$ and $3.2 \times 10^4$ W·cm$^{-2}$ for 1.7 $\mu$m and 4.2 $\mu$m laser spots, respectively, and spectra recorded at fixed time intervals. Final resultant phases were determined in situ only after temporal changes in the Raman spectra ceased. Due to the micro-beam profile, laser spot sizes are not equal to the size of the oxide formed, but represent the size of the probed area. Depending on incident power densities and surface morphology, the laser-induced oxides can be much smaller.

Plotted in Fig. 4(a) are representative Raman spectra of bismuth [35] and the two single $\beta$- [45] and $\alpha$-phase [46] oxides achievable with our experimental setup. The arrows between
Table 1 summarizes the laser-induced oxidation results for all bismuth surface types examined. Here ‘smooth’ corresponds to a highly specular surface (Fig. 1(a)) and ‘rough’ represents a granulated surface on the scale of 0.2 - 4 µm (Fig. 1(b)). Smaller particles ranging from roughly 0.3 to 3 µm were also examined (Fig. 1(c)). Differences in the relative texture of the particulates were insignificant (when compared to size) in determining oxide phase and are not considered further. The oxidation results in Table 1 suggest an inability for Bi$_2$O$_3$ to retain β-phase structure above the critical dimension (~1.5 µm). This is highlighted by a complete absence of α-Bi$_2$O$_3$ when irradiating with a 1.7 µm laser spot. This is a consequence of the small (< 1.7 µm) and limited volume of oxides formed when employing this beam spot size. Raman spectra revealing a combination of β and α were most favored, with the notable exception of using a 4.2 µm beam on smaller particles. To this point, measurements made with the larger spot size proved to be a better gauge for assessing size dependencies; a distinct shift in subsequent phase was observed for particles transitioning across ~1.5 µm range. Furthermore, rough surfaces with elevated structure were more likely to produce α-Bi$_2$O$_3$.

Given the 632.8 nm laser-induced oxidation process is thermally driven, the observation of a new governing oxidation/transformation sequence

\[ \frac{3}{2} \text{O}_2(g) + 2\text{Bi}(l) \rightarrow \beta-\text{Bi}_2\text{O}_3(s) \rightarrow \alpha-\text{Bi}_2\text{O}_3(s), \]  

(1)

traces here indicate observed sequential intermediates. Optical imaging of pure α-phase oxidation (not shown) exhibited the characteristic light yellow color associated with α-Bi$_2$O$_3$. While a laser-induced δ-phase transformation was recently realized [30] in Bi$_2$O$_3$, the characteristic 625 cm$^{-1}$ Raman signature was never observed in our data. A stunning aspect of these results is that we observe an initial β-phase (or β) in all transformations; laser-induced oxidation of α-Bi$_2$O$_3$ is never achieved without first passing through an intermediate β-phase. This is highlighted by the temporal data shown in Fig. 4(b), where for longer exposure times the β Raman spectra is shown to evolve into single-phase α (these spectra have been normalized to the bottom β trace by the factors given). The phase transition is matched by broadband temporal growth of the Raman signal, increasing by a factor of approximately 15. The increase in Raman signal here is evenly weighted for both existing β-Bi$_2$O$_3$ modes and transitioning α-Bi$_2$O$_3$ modes (for example, the peak just above 300 cm$^{-1}$ undergoes a continuous intensification during the transformation), indicating a dramatic change in the scattering volume and the formation of new oxide material, rather than a pronounced shift in scattering cross-section. The tipping point between phases appears to be connected to the size of Bi$_2$O$_3$ produced and is schematically represented in Fig. 4(c); after some well-defined critical volume, the Bi$_2$O$_3$ transforms its structure from β-phase to α-phase. 

Table 1. Laser-induced bismuth oxide phase results for varying bismuth surfaces (corresponding to those shown in Figs. 1(a)–1(c)) irradiated by a large (4.2 µm) and small (1.7 µm) focused 632.8 nm laser beam. Representative Raman spectra of resulting phase(s) match with those given in Fig. 4(a).
extends the traditional phase relations of Fig. 3 and should hold true for all thermal oxidations of bismuth. It is emphasized that a laser-induced $\beta$-Bi$_2$O$_3 \rightarrow \alpha$-Bi$_2$O$_3$ transition occurs in direct opposition to conventional isothermal existence domains, since longer laser exposures generally increase local temperatures rather than decrease them.

Examining the varied Bi oxidation studies in the literature we make the observation that the sequence described by Eq. 1 is both accurate for high temperature annealing methods [18–23] and laser-induced techniques [11, 24–26]. For the specific cases of thermally-treated nanoparticles [18, 21] and nanotextured films [22, 23], lower oxidation temperatures produced single-phase $\beta$-Bi$_2$O$_3$, while higher temperatures resulted in single-phase $\alpha$-Bi$_2$O$_3$. More importantly, scanning electron microscope (SEM) images revealed an increased tendency for bismuth oxide microislands to coalesce and form larger aggregated oxide volumes (see Fig. 4(c)) with increasing temperature, depicting a critical oxide size comparable to ours, for which the $\beta$-Bi$_2$O$_3 \rightarrow \alpha$-Bi$_2$O$_3$ transition is observed. It was even demonstrated by XRD measurements that for temperatures between the synthesis of pure $\beta$-phase or $\alpha$-phase oxides, a transitional mixed phase is observed — reminiscent of Fig. 4(b) — which bridged the two single-phases [22]. Huang et al. [23] also inadvertently reported similar results, however, accounting for their findings using a model based on the differing crystallographic orientations of electrodeposited Bi films. In the pursuit of laser-induced oxidation of Bi nanowires [26] and nanotextured films [11, 24], several authors have pointed to the role laser power plays in determining the resulting oxide phase(s).

In brief, all studies demonstrated an initial $\beta$-phase and oxidations under higher irradiance favored $\alpha$-Bi$_2$O$_3$ formation. Similar to elevated temperatures in thermal annealing processes, the increased $\alpha$-Bi$_2$O$_3$ formation demonstrated an enhanced capacity for the laser-heated area to produce larger oxides [11, 24]. The consistency of results across the very different oxidation schemes means oxide/metal interface effects (i.e. mismatch or strain relief/dislocations) can be neglected. In light of these findings, the one feature which unifies the synthesis of room-temperature metastable $\beta$-Bi$_2$O$_3$ becomes clear: size.

The fundamental relationships between bismuth oxidation and ensuing phases are still unresolved. For example, why is an initial $\beta$-phase favorable over an $\alpha$-phase and how does undoped $\beta$-Bi$_2$O$_3$ oxide remain stable at room temperature? From the viewpoint of joining small $\beta$-Bi$_2$O$_3$ volumes to form an aggregated $\alpha$-phase, a likely explanation lies in their respective molecular structures; the $\beta$-phase Bi$_2$O$_3$ polyhedra are proposed to be BiO$_6$ octahedra with all Bi-O bonds equivalent at 2.4 Å and very similar to that of $\alpha$-Bi$_2$O$_3$. However, given the volumic nature of results, a detailed answer presumably resides in how the electrostatics of the ionic Bi$_2$O$_3$ crystal change with an evolving surface-to-volume ratio [47].

The electrostatic energy of a unit cell deep within the interior of a Bi$_2$O$_3$ crystal is composed of two parts. One part is morphology-independent, and the other is morphology-dependent and varies with the structure/phase concerned and the distribution of ions within a unit cell. Morphology dependencies are conditional to crystal shape and are equal to zero if the dipole moment of the unit cell zero. In Tasker’s model of ionic crystal surfaces [48], the surface of Bi$_2$O$_3$ has a dipole moment perpendicular to the surface which is exposed favorably in a practical environment. Moreover the surface is electrostatically unstable. The electrostatic energy of the whole Bi$_2$O$_3$ volume therefore is the electrostatic energy of a unit cell multiplied by the number of unit cells plus the corrections proportional to the surface area of the crystal [49].

Thus, the bulk energy of diminutive Bi$_2$O$_3$ is heavily dependent on surface-to-volume ratio. Harwig and Weenk [50] have already pointed out that there is only a very small difference in the electrostatic energy of $\alpha$-phase and $\beta$-phase Bi$_2$O$_3$, with a Madelung constant marginally lower in the former. The surface stability has also been shown to relate to the stability of different crystal planes and, if polar or nonpolar terminations are present, due to alternate stacking of Bi layers and O layers. However, since $\alpha$-Bi$_2$O$_3$ is never seen in the initial oxidation of
bismuth, it is not likely that crystal-plane effects are significant.

The temporal data shown in Fig. 4(b) permits the evaluation of real-time phase and structure, as well as allowing the general assessment of mode shifting magnitude and direction. Through a purely empirical interpretation of phonon frequencies, the Bi-O stretching frequency is inversely related to the bond lengths [37]. While \( \alpha \)-phase nucleation points take hold in the \( \beta \)-\( \text{Bi}_2\text{O}_3 \) volume, new interactions are established between Bi and O atoms in the transitioning oxide. Early in the transformation, new bonds formed within the oxide experience very little of the pressures exerted by a surrounding external network. New vibrational frequencies are set up and appear at lower frequencies due to this lack of internal pressure and longer bond lengths. With the notable exception of the Bi-Bi vibration just below 70 cm\(^{-1}\), all modes appear to strongly harden to higher frequencies for longer laser exposure times. This is paralleled by the entire spectra intensifying over the course of the transformation, until a pure \( \alpha \)-phase is reached. It is reasonable to assume, therefore, a correlation between an increasing oxide volume and the direction of the transformation. Rising pressure introduced by a growing crystal network reduces bond lengths and results in phonon mode hardening. As the budding \( \alpha \)-\( \text{Bi}_2\text{O}_3 \) condenses, the electrostatic potential of unit cells is further reduced and the dipole moment is lowered toward a final equilibrium.

For reasons that are at present unclear, the synthesis and stabilization of \( \beta \)-\( \text{Bi}_2\text{O}_3 \) is much easier than that of \( \gamma \)-\( \text{Bi}_2\text{O}_3 \). This suggests \( \beta \)-\( \text{Bi}_2\text{O}_3 \) has a strong tendency to remain stable when its electrostatic energy occupies a local minimum. As far as we know, there is little information about the relative stability, geometries, and electronic structures of \( \text{Bi}_2\text{O}_3 \) polymorph surfaces, which hinders the understanding of their properties and reactivity at small scales. While a comprehensive physical model to aid explanation is lacking, our results and conclusions present merely a plausibility argument; one that points toward oxide volume at the micron-scale as playing a central role in defining \( \text{Bi}_2\text{O}_3 \) phase. This aspect of bismuth oxidation has thus far been overlooked and is particularly significant. In terms of engineering practical \( \text{Bi}_2\text{O}_3 \) elements, fine control over the transformation process is favorable to the exacting preparation of functional materials with specific crystal structure.

4. Conclusion

In conclusion, we have elucidated the dynamics of Bi oxidation through micro-Raman scattering experiments. Our optical results reveal the unexpected and seemingly fixed bismuth oxidation/transformation sequence: \( \frac{1}{2}\text{O}_2(\text{g}) + 2\text{Bi}(\text{l}) \rightarrow \beta\text{-Bi}_2\text{O}_3 \rightarrow \alpha\text{-Bi}_2\text{O}_3 \). The phenomenon of room-temperature metastable \( \beta\text{-Bi}_2\text{O}_3 \) is examined within this sequence and the tipping point is attributed to \( \text{Bi}_2\text{O}_3 \) volume dependencies. We invoke an electrostatic model based on the changing \( \text{Bi}_2\text{O}_3 \) surface-to-volume ratio to account for our findings and also to unlock the interpretation to previous studies. Considering the wide variety of applications for bismuth oxide nanomaterials, these findings represent a timely stimulus to further theoretical and experimental investigation of bismuth oxidation, as well as possible methods of material synthesis/fabrication.

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