Linear and nonlinear optical probe of the ferroelectric-like phase transition in a polar metal, LiOsO₃

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LiOsO₃ is one of the first materials identified in recent literature as a 'polar metal', a class of materials that are simultaneously noncentrosymmetric and metallic. In this work, the linear and nonlinear optical susceptibility of LiOsO₃ is studied by means of ellipsometry and optical second harmonic generation (SHG). Strong optical birefringence is observed using spectroscopic ellipsometry. The nonlinear optical susceptibility extracted from SHG polarimetry reveals that the tensor components are of the same magnitude as in isostructural insulators LiNbO₃, except the component along the polar axis d₃₃, which is suppressed by an order of magnitude. Temperature-dependent SHG measurements in combination with Raman spectroscopy indicate a continuous order-disorder type phase transition at 140 K. Linear and nonlinear optical microscopy reveal 109°/71° ferroelastic domain walls, like in other trigonal ferroelectrics. No 180° polar domain walls are observed to emerge across the phase transition.

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Polar metals are a relatively rare class of materials that exhibit ferroelectric-like long-range polar order in a metallic state. These materials are of much interest because of the seeming incompatibility of polar order and metallicity, since free electrons in a metal are typically expected to screen the long-range electrostatic forces that stabilize polar ordering. The recent identification of a ferroelectric-like phase transition in metallic lithium osmate (LiOsO₃) has led to a flurry of activity to understand the origin of polar metallicity in these materials. From the point of view of applications, a ferroelectric-like structure in a metallic state leads to another intriguing question - how do functional properties typical of insulating ferroelectrics manifest themselves in a metal?

Optical properties are one such example, with the strong optical birefringence and nonlinear susceptibility of classical ferroelectrics such as LiNbO₃ and BaTiO₃ finding extensive application in optical materials and in optoelectronic devices. Nonlinear optical processes are also the foundation behind several important condensed matter phenomena such as higher harmonic generation, the optical Kerr effect, and photo-induced shift current. In this context, it is of interest to study and understand the optical properties of this unique class of polar materials. A recent study has reported that polar metals in the family of TaAs exhibit a giant nonlinear optical coefficient, with an enhanced response along the polar direction, providing further motivation for the present study. In this work, we consider one of the first identified polar metals, LiOsO₃. It is notable that this material has a lattice structure and polar phase transition that are isostructural to the ubiquitous insulating optical nonlinear materials LiNbO₃ and LiTaO₃. A study of the optical properties of LiOsO₃ would hence be of interest not only from the point of view of potential applications, but also as a model system to understand the role of metallicity in the emergence of these properties.

Furthermore, the nonlinear optical response can be used as a sensitive probe of important physical quanti-ties such as spontaneous polarization, phase transitions, ferroic domain formation, and coupling between different order parameters, all of which are critical to understanding the physics underlying this unique class of materials. Characterization methods based on nonlinear optics assume further importance given that the presence of free carriers makes it difficult to study these materials using traditional techniques like piezo-force microscopy and P-E loop measurements.

In this work, the linear and nonlinear optical properties of single crystal LiOsO₃ were measured using spectroscopic ellipsometry and optical second harmonic generation (SHG) at a fundamental wavelength of 800 nm. Strong optical birefringence was observed in the complex linear refractive index. The optical SHG tensor coefficients extracted from SHG polarimetry revealed that the susceptibility along the polar direction is suppressed by an order of magnitude, compared to isostructural in-

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ultralizing ferroelectrics LiNbO$_3$ and LiTaO$_3$, as a consequence of the weak coupling mechanism that stabilizes the polar metal phase in LiOsO$_3$. We then use SHG in combination with Raman spectroscopy as a probe of the unique ferroelectric-like phase transition in LiOsO$_3$. These measurements showed that the polar phase transition in LiOsO$_3$ is continuous, exhibiting signatures of an order-disorder nature, with long-range order setting in at around 80 K. Linear and nonlinear optical microscopy and electron backscattering diffraction are used to identify 109°/71° ferroelastic domain walls. No 180° polar domain walls were observed across the phase transition.

Optical second harmonic generation (SHG) is a second order nonlinear optical response to incident electromagnetic radiation. In this process, light incident on a material at frequency $\omega$ is converted into light at frequency $2\omega$, through the creation of a nonlinear polarization in the material, $P_{2\omega} = \epsilon_0 \chi^{(2)}_{ijk} E_i E_j E_k$, where $P_{2\omega}$ is the second harmonic polarization, $E^{\omega}$ is the electric field of the incident light, and $\chi^{(2)}$ is the optical SHG susceptibility tensor. With $\chi^{(2)}$ being an odd ranked tensor, a non-zero SHG response is only allowed in noncentrosymmetric materials. SHG is thus a sensitive probe of inversion symmetry breaking, whether it is at interfaces such as surfaces, or in the bulk, through electric dipoles and multipoles. The bulk contribution is expected to dominate over the surface contribution. It is noteworthy that results of common theoretical models used to describe SHG, based on the anharmonic Lorentz oscillator, such as Miller’s rule and Kleinman symmetry, would in principle be invalid in polar metals, due to the finite intraband absorption associated with the bandgap.

LiOsO$_3$ single crystals were grown using solid state reaction under high pressure, as in the previous work by Shi et al. First, spectroscopic ellipsometry was used to obtain the linear optical constants at 300 K, between 200 nm and 1000 nm. The ellipsometry data was fitted using Lorentz oscillators (see Fig. S2), and the complex dielectric function $\tilde{\epsilon}$ and refractive index $\tilde{n}$ were extracted. The complex dielectric function plotted in Fig. 1a shows a strong absorption at around 350 nm, which likely corresponds to Os-5d interband transitions from occupied $t_{2g}$ states to $e_g$ states above the Fermi energy. Notably, significant anisotropy is observed between the hexagonal [100] and [001] directions, contrary to previously reported data. This anisotropy is likely primarily due to the Os-5d interband absorption, which was not accounted for in the reported work. The complex refractive indices in Fig. 1a are used in the subsequent analysis of the measured nonlinear optical constants.

The SHG tensor coefficients of LiOsO$_3$ were probed using SHG polarimetry as follows. The measurements were done in a far-field reflection geometry at normal incidence. The fundamental was a pulsed laser beam from a Ti:sapphire femtosecond laser with a wavelength of 800 nm (pulse width 80 fs, repetition rate 80 MHz). A beam with a power of 20 mW was focused on the (120) surface of a LiOsO$_3$ single crystal using a 50x objective, onto a spot size of ~0.5 µm. SHG polarimetry was done following the schematic in Fig. 1b. The crystal was aligned so that the [120] axis was coincident with the fundamental, while the [100] and [001] were along mutually perpendicular directions in the plane of the probed surface. It was confirmed using electron back-scattering diffraction that the probed region was a single domain. The fundamental was linearly polarized, with the polarization within the (120) plane, making an angle $\phi$ with [100]. The reflected second harmonic light was collected using a photomultiplier tube, after passing through an analyzer. Note that all Miller indices are in the hexagonal setting.

Since LiOsO$_3$ is centrosymmetric (space group $R\bar{3}c$) at room temperature, the SHG at room temperature is likely primarily from inversion symmetry breaking at the surface and multipole contribution of bulk charges. The detector was calibrated so as to set this as the zero level. Measurements were then carried out at 20 K, which is below the reported non-polar ($R\bar{3}c$) to polar ($R\bar{3}c$) phase transition temperature of 140 K. A pair of complementary polar plots were obtained by measuring the SHG signal as a function of the polarization of the fundamental.
tal, \( \phi \), with the analyzer oriented along the [100] direction (\( P_{100}^2(\phi) \)), and [001] direction (\( P_{001}^2(\phi) \)), shown in Fig. 1c. To obtain the SHG tensor coefficients, these experimental polar plots were fitted to a theoretical model based on the 3m point group symmetry of LiOsO\(_3\). The third rank tensor \( \chi_{ijk} \) is usually written using the Voigt notation \( a_{ij} \), in a pseudomatrix form. For 3m symmetry, the non-zero coefficients of \( a_{ij} \) are \( a_{15} = a_{21} \), \( -a_{22} = a_{16} = a_{21} \), \( a_{31} = a_{32} \), and \( a_{33} \). Note that since LiOsO\(_3\) is a metal with finite dispersion in the spectral range of interest, Kleinman symmetry, which allows for the permutation of certain tensor indices for materials that are dispersionless, is violated. The associated additional condition \( a_{15} = a_{31} \) that is valid for isovector insulators LiNbO\(_3\) and LiTaO\(_3\) is thus invalid for LiOsO\(_3\).

Since the fundamental was linearly polarized in the (120) plane, \( E_1 = E_0\cos(\phi) \), \( E_2 = 0 \), and \( E_3 = E_0\sin(\phi) \). With the analyzer oriented along the [100] and [001] directions, the theoretical expressions for the two polar plots respectively simplify to

\[
P_{100}^2(\phi) = |E_{100}^2(\phi)|^2 \propto |a_{15}E_0^2\sin^2(2\phi)|^2
\]

\[
P_{001}^2(\phi) = |E_{001}^2(\phi)|^2 \propto |a_{31}E_0^2\cos^2(\phi) + a_{33}E_0^2\sin^2(\phi)|^2.
\]

As Eq. 1 shows, \( a_{22} \) is not accessible using the (120) surface at normal incidence. This was instead obtained through an additional measurement at an angle of incidence of 45° (see Fig. S3). The experimental polar plots were fitted to these equations to obtain the ratios of the \( a_{ij} \) coefficients. The SHG signal was calibrated with respect to congruently grown (001) LiTaO\(_3\) to estimate the absolute magnitude of the coefficients. The expression derived by Bloembergen and Pershan\(^{10} \) was used to account for changes in reflectance due to differences in the linear refractive indices of LiTaO\(_3\)\(^{27} \) and LiOsO\(_3\). The results are tabulated in Table 1, and the values of the SHG tensor coefficients of LiNbO\(_3\) and LiTaO\(_3\) are also given for comparison.

Although \( a_{15} \), \( a_{22} \), and \( a_{31} \) are of the same order of magnitude across all three materials, \( a_{33} \) is lower by an order of magnitude in LiOsO\(_3\) as compared to those in LiNbO\(_3\) and LiTaO\(_3\), Table S2. Qualitatively, the ratio of these bond lengths projected onto the [100] and [100] directions can be related to the degree of anharmonicity along these two directions, and hence to the SHG coefficients associated with them.\(^{15,20} \) That is, M-O(l)/M-O(s) projected along [001] will affect \( a_{33} \), whereas M-O(l)/M-O(s) projected along [100] will affect \( a_{22} \) and \( a_{31} \).

![Fig. 2](image)

**Fig. 2.** The variation in \( a_{33} \) as a function of MO\(_6\) acentric displacements along [001], as quantified by the ratio of the [001] projections of long (l) and short (s) M-O bonds in LiMO\(_3\) with M = (Nb, Ta, Os). Bond lengths are taken from references 22, 23, and 11 respectively, and \( a_{33} \) values from 21.

**TABLE I.** SHG tensor coefficients of LiOsO\(_3\) in pm/V, obtained from polar plots at 20 K, with those of LiNbO\(_3\) and LiTaO\(_3\) for comparison. Error bars are shown in parentheses.

|                | LiOsO\(_3\) | LiNbO\(_3\) | LiTaO\(_3\) |
|----------------|-------------|-------------|-------------|
| \( a_{15} \)    | ±2.8 (0.4)  | -5.2 (0.8)  | -1.1 (0.2)  |
| \( a_{31} \)    | ±1.9 (0.2)  | -5.2 (0.8)  | -1.1 (0.2)  |
| \( a_{22} \)    | ±2.3 (0.3)  | 2.8 (0.2)   | 1.9 (0.2)   |
| \( a_{33} \)    | ±0.93 (0.1) | -36.3 (8.9) | -17.5 (2.2) |

\(^{a}\) Values at 800 nm, 20 K from present work.

\(^{b}\) Values at 1060 nm, 300 K from reference 21.
of temperature, can be used to identify order-disorder in the system, and hence when studied as a function of temperature, with $\chi_{ijk}(T < T_0) = \chi_{ijk}(Q^3)$. The SHG susceptibility $\chi_{ijk}$ is thus linearly proportional to the polar order parameter $Q$, and the measured SHG response $\chi$ is proportional to $Q^2$. The temperature dependence of the SHG response in the present study is thus an indirect probe of the polar order parameter across the phase transition in LiOsO$_3$.

The SHG response and the associated polar order parameter gradually increase as the sample is cooled below 140 K, before increasing rapidly and saturating at around 80 K, as seen in Fig. 3a. It is pertinent to ask whether this behavior is due to the occurrence of an order-disorder phase transition as opposed to a displacive phase transition, as this is a point of contention in the literature. To shed more light on this, Raman spectroscopy measurements were carried out to study the behavior of phonon modes across the phase transition. Temperature increase due to laser heating was taken into account using the Stokes-anti-Stokes relation. To begin with, no Raman active soft modes that might result in a displacive phase transition were observed in the Raman spectra, consistent with previous studies. Raman linewidths are directly related to disorder in the system, and hence when studied as a function of temperature, can be used to identify order-disorder phase transitions, as done in previous work on complex oxides. Previous studies showed a large decrease in Raman peak linewidths below 140 K, and attributed that to the order-disorder nature of the phase transition. In the present work, we repeat these measurements and expand on the analysis, paying particular attention to the Raman modes corresponding to displacements of Li atoms. The proposed order-disorder transition consists of ordering of off-centered Li atoms, so it is reasonable to expect that if the phase transition is indeed order-disorder in nature, the Raman phonon modes consisting of Li displacements would exhibit the largest change in linewidth. The linewidths of the three dominant $E$ modes (see Fig. S5 for peak labels) are plotted in Fig. 3b, of which only one, $E$, involves the displacement of Li atoms. Clearly this mode, consisting of antiparallel Li translation perpendicular to the polar direction, shows the largest increase in linewidth, with a clear discontinuity in the slope near the critical temperature. This linewidth increase is more than twice that of the $E$ and $E$ modes, which consist of OsO$_6$ octahedra bending and rotation respectively. Additionally, the present measurements were limited to around 98 K, but the Raman peak linewidths in the work by Jin et al. with data collected down to 10 K, appear to saturate at the same temperature as the SHG response in the present work, at around 80 K, providing further evidence that these two results may be complementary signatures of the onset of long-range polar order through an order-disorder transition.

Finally, linear and nonlinear optical microscopy was used to study the influence of the ferroelectric-like phase transition on the mesoscale structure of LiOsO$_3$. The linear optical micrograph in Fig. 4a shows a striped domain structure observed in the nonpolar phase. These stripes were oriented using electron back-scattering diffraction (EBSD) (see Fig. S6) and identified as ferroelastic domains, with the [100] crystallographic axes in adjacent domains forming an angle of 90° relative to each other, as shown in Fig. 4b. This geometry is consistent with $\bar{1}3c$, with data collected down to 10 K, appear to saturate at the same temperature as the SHG response in the present work, at around 80 K, providing further evidence that these two results may be complementary signatures of the onset of long-range polar order through an order-disorder transition. A schematic of the domains is shown on the right, with the arrows denoting the direction of the [100] crystallographic axis, obtained from electron back-scattering diffraction (see Fig. S5). The scale bar in (a) is 10 µm.
The SHG map confirms that these domains are polar below the phase transition, and the contrast between stripes is consistent with the EBSD orientation information. Such measurements can also be used to identify any additional 180° ferroelectric domains that nucleate across the nonpolar-to-polar phase transition in the form of suppressed SHG intensity at domain walls. However, there were no such domains observed, despite the presence of ferroelastic domain walls, which are generally expected to be preferential nucleation sites for such features. This observation, while surprising for a polar material, is consistent with the metallic nature of Li Os O₃. In insulating ferroelectrics, the depolarizing field created by ordered electric dipoles destabilizes a single domain configuration and drives the formation of 180° polar domain walls. Such a depolarizing field would be expected to be screened by free electrons in a metal such as Li Os O₃, allowing the single domain configuration to be stable.

To summarize, the linear and nonlinear optical properties of Li Os O₃ were measured, and used to probe its unique phase transition. The optical SHG susceptibility was found to be suppressed along [001] owing to a reduction in the Os-O bond anisotropy along the polar axis. Temperature-dependent SHG and Raman measurements were consistent with the occurrence of a continuous order-disorder phase transition at 140 K. Polar ferroelastic domains were observed using SHG microscopy, however no 180° domain walls were observed.

SUPPLEMENTARY MATERIAL

The supplementary material contains detailed information on the crystal orientation using electron back-scattering diffraction, spectroscopic ellipsometry, SHG polarimetry, supporting information for the bond anisotropy, and complete Raman spectra over the measured temperature range.

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