Pressure-induced enhancement of non-polar to polar transition temperature in metallic LiOsO$_3$

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LiOsO$_3$ undergoes a continuous transition from a centrosymmetric $R3c$ structure to a polar $R3c$ structure at $T_s=140$ K. By combining transport measurements and first-principles calculations, we find that $T_s$ is enhanced by applied pressure, and it reaches a value of $\sim$250 K at $\sim$6.5 GPa. The enhancement is due to the fact that the polar $R3c$ structure of LiOsO$_3$ has a smaller volume than the centrosymmetric $R3c$ structure. Pressure generically favors the structure with the smallest volume, and therefore further stabilizes the polar $R3c$ structure over the $R3c$ structure, leading to the increase in $T_s$.

Ferroelectric materials are actively explored in both fundamental science and applied research for their potential industrial applications such as non-volatile memory devices, sensors and solar cells [1–9]. In ferroelectric materials, a continuous displacive phase transition from a centrosymmetric structure to a non-centrosymmetric structure occurs at Curie temperature $T_C$, below which a spontaneous polarization develops. Since itinerant electrons can effectively screen internal electric fields, it is a result of the electrons at the Fermi level that are responsible for the formation of a polar axis and the disappearance of the inversion center, analogous to that of displacive ferroelectrics, in a ferroelectric-like metal. Pugzdoni et al. [12] further deduced that such transition may be a result of the electrons at the Fermi level that are only weakly coupled to the soft phonon mode that drives the second-order phase transition into the polar structure. Recently, Shi et al. [10] showed clear evidence of a polar metallic state in LiOsO$_3$, which has stimulated many further experimental and theoretical works [12–21]. At a critical temperature $T_s = 140$ K, LiOsO$_3$ undergoes a structural transition from centrosymmetric $R3c$ (space group 167) at high temperature to a polar, non-centrosymmetric $R3c$ (space group 161) below $T_s$. This structural transition is analogous to that in LiNbO$_3$, which is a well-known ferroelectric compound ($T_C = 1483$ K [22]) and thus the insulating equivalent of LiOsO$_3$. The heat capacity data displays a broad peak at $T_s$ without any thermal hysteresis, which is characteristic of a second-order phase transition. The temperature dependence ($T$) of the electrical resistivity ($\rho$) exhibits a positive $\mathrm{d}\rho/\mathrm{d}T$ from 300 K to 2 K, indicating the metallic nature of the system over the entire temperature range studied.

The polar properties of both conventional (insulating) ferroelectrics and polar metals can be tuned by external factors such as atomic substitution, chemical ordering and pressure. In a classical paper, Samara et al. [23] showed that hydrostatic pressure decreases the transition temperature in conventional ferroelectrics and ultimately destabilizes the polarization. That is because pressure increases short-range interactions much more rapidly than long-range interactions and as a result, the harmonic soft-mode frequency becomes less negative with increasing pressure [24]. Such pressure-induced suppression of ferroelectricity is observed in BaTiO$_3$ [25–27] and BiFeO$_3$ [28]. On the other hand, negative pressure is found to increase ferroelectric Curie temperature and polarization in freestanding PbTiO$_3$ particles [29].

In this work, we combine transport measurements up to 6.5 GPa and first-principles calculations to show that hydrostatic (positive) pressure can enhance the transition temperature of LiOsO$_3$, in contrast to conventional ferroelectrics. Recently, a novel “cubic Dirac point” is predicted in the $R3c$ phase, which transforms into three mutually crossed nodal rings in the $R3c$ phase [21]. Thus, the prospect of stabilizing the nodal rings at elevated temperature is attractive. The pressure-induced enhancement of the transition temperature is due to the fact that the volume of the non-centrosymmetric structure ($R3c$) is smaller than that of the centrosymmetric structure ($R3c$). Pressure generically favors the structure with the smallest volume and therefore with pressure, the polar $R3c$ structure of LiOsO$_3$ becomes more stable over the $R3c$ structure and $T_s$ increases. The same analysis can be also applied to conventional ferroelectrics, which predicts an increase of $T_C$ and polarization in LiNbO$_3$ and ZnSnO$_3$ with pressure [30].

Single crystals of LiOsO$_3$ were synthesized by a high-pressure solid state reaction as described elsewhere [10].
Electrical resistance measurements were conducted using a standard four-probe technique. The electrodes were made with gold wires and silver paste (Dupont 6838) on the polished surface of the single crystals. High-pressure experiments were performed in a piston-cylinder clamp cell and a miniature moissanite anvil cell. The clamp cell provides a higher pressure-resolution than the anvil cell, which the data from both techniques are consistent with each other. At the high pressure region (>2 GPa), \( T_s(P) \) continues to increase. The overall \( T_s(P) \) is linear with a large slope of \( \sim 17.54 \) K/GPa. Therefore, our experimental results unambiguously demonstrate the enhanced stability of the polar phase.

DFT calculations were performed to understand the observed pressure effect on \( T_c \) of LiOsO\(_3\). Figure 2(b1) and (b2) show the fully relaxed centrosymmetric structure (R3c, non-polar) and the non-centrosymmetric structure (R3c, polar) of LiOsO\(_3\), respectively, obtained from DFT-PBEsol calculations at ambient conditions. In the R3c structure, the Os atom is located at the center of the oxygen octahedron, which is also the symmetric center of the two Li ions. In the R3c structure, the inversion symmetry is broken owing to the dominant contribu-
LiOsO₃ structures. The experimental [10] shown in brackets. The predicted Pbnm structure which is next to R3c LiOsO₃ in energy at 0 GPa is also shown as a comparison, more details on Pbnm phase can be found in the supplementary material. The volume is normalized to per formula unit of LiOsO₃, the bond angle corresponds to angle O1–Os–O4 in Fig. 2(b3), and the bond length corresponds to the average length of O–Os in Fig. 2(b3).

| structural parameter | space group |
|----------------------|-------------|
| R3c | R3c | Pbnm |
| volume (Å³) | 49.12 (48.90) | 48.71 (48.65) | 48.45 |
| bond angle (°) | 180 (180) | 178.03 (176.84) | 180 |
| bond length (Å) | 1.946 (1.944) | 1.947 (1.944) | 1.946 |

The left axis in Fig. 3 shows the pressure dependence of the lowest phonon frequency at Γ point of the non-polar R3c LiOsO₃ at zero temperature. The phonon frequency is found to be imaginary and its magnitude increases with pressure, indicating that the non-polar R3c structure is unstable and pressure enhances the instability of the zone-center phonon mode. On the other hand, the right axis in Fig. 3 shows the pressure dependence of the O1–Os–O4 bond angle of polar R3c LiOsO₃. As pressure increases, the bond angle decreases and deviates further from the ideal 180°. This shows that applying pressure can enhance the polar nature of R3c LiOsO₃. Therefore, both results show that external pressure not only destabilizes non-polar R3c LiOsO₃, but also renders R3c LiOsO₃ more polar.

To understand why pressure favors the polar structure R3c over the non-polar structure R3c, zero-temperature thermodynamic functions of LiOsO₃ were computed via DFT calculations. Figure 4(a) shows the zero-temperature enthalpy H of LiOsO₃ in three structures with the lowest enthalpy, R3c, R3c and Pbnm, based on

![Figure 2](image-url)

**FIG. 2.** (a) Pressure dependence of Tₘ. The blue dots (red squares) with blue (red) error bars represent the data obtained via the anvil (clamp) cell technique. The dashed straight line is obtained by a least-squares fitting to the anvil cell data. (b) Crystal structures of (b1) centrosymmetric (R3c) and (b2) non-centrosymmetric (R3c) LiOsO₃. The magenta horizontal lines representing the (111) planes across the high symmetry points (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) are shown to guide the eyes. Here, (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) are fractional coordinates that are parallel to the crystallographic axes. (b3) An OsO₆ oxygen octahedron.

![Figure 3](image-url)

**FIG. 3.** (Left vertical axis) Lowest zone-center phonon frequency of R3c LiOsO₃ as a function of pressure. (Right vertical axis) O1–Os–O4 bond angle of R3c LiOsO₃ as a function of pressure. The O1–Os–O4 bond angle is shown in Fig. 2(b3).
Under pressure, enthalpy replaces energy as the thermodynamic function. Therefore, the increasing enthalpy difference between $R3c$ and $R3c$ structures leads to the enhancement of $T_s$, which is consistent with our experiment. Furthermore, the enthalpy difference between $R3c$ and $R3c$ structures, and the Li displacement squared in $R3c$ LiOsO$_3$ (see the supplementary material) almost increase linearly with pressure, which is also consistent with the experimentally observed linear $T_s(P)$ displayed in Fig. 3(a).

Using the relation $H = E + PV$, the total energy $E$ and $PV$ for different structures of LiOsO$_3$, with respect to $R3c$, are illustrated in Figs. 3(b) and (c), respectively. As pressure increases, $\Delta E$ only changes slightly. Moreover, the pressure dependence of $\Delta E$ is opposite to that of $\Delta H$. This indicates that the pressure dependence of $\Delta H$ is dominated by $P \Delta V$. As the inset of Fig. 3(c) shows, the volume of the polar $R3c$ LiOsO$_3$ is always smaller than that of the non-polar $R3c$ LiOsO$_3$, and $\Delta V$ is almost a constant within the pressure range we study. As a result, $P \Delta V$ increases linearly with $P$ and so does $\Delta H$ because $\Delta E$ has weak dependence on $P$.

Figure 4 provides a simple criterion to predict the pressure effects on polar metals. If the volume of the polar structure is smaller than that of the non-polar structure at ambient pressure, pressure enhances the polar properties (increasing $T_s$ and polar distortions). Conversely, if the volume of polar structure is larger, pressure will suppress the polar properties (decreasing $T_s$). This simple criterion can also be applied to conventional insulating ferroelectrics (see supplementary material). For example, LiNbO$_3$ and ZnSnO$_3$ belong to the former class ($V$(pol) < $V$(non-pol)), which have been predicted to feature a pressure-enhanced ground state polarization and $T_c$ [30, 37]. On the other hand, BaTiO$_3$ and BiFeO$_3$ belong to the latter class ($V$(pol) > $V$(non-pol)), and it has been observed that pressure reduces the polarization and eventually destabilizes the ferroelectric ground state [25, 28].

Note that the enhancement of $T_s$ via pressure in LiOsO$_3$ will be thwarted by the stabilization of a different structure. As Fig. 4(a) shows, the non-polar $Pbnm$ structure becomes more stable than the non-polar $R3c$ structure above 8 GPa, and becomes more stable than the polar $R3c$ structure above 21 GPa. As a conservative estimation using the linear pressure dependence, $T_s$ in LiOsO$_3$ can be enhanced up to $\sim 274$ K at 8 GPa. The robustness of our conclusions is also tested by considering the effects of Hubbard $U$, spin-orbital coupling (SOC) and possible magnetic ordering. The results from DFT+$U$, DFT+SOC and DFT+$U$+SOC calculations all agree qualitatively with Fig. 4(a) (see the supplementary material for details).

In summary, the pressure dependence of structural transition temperature $T_s$ in polar metal LiOsO$_3$ was measured up to $\sim 6.5$ GPa. $T_s$ increases linearly under pressure, reaching 250 K at $\sim 6.5$ GPa. The experimental result is corroborated by first-principle
calculations which show that pressure further stabilizes the polar R3c phase over the centrosymmetric R3c phase and enhances the polar properties in the R3c structure. The enhancement of $T_c$ arises from the fact that the volume of the polar R3c structure is smaller than that of the non-polar R3c structure, and pressure generically favors the structure with the smallest volume. This criterion can also be applied to insulating ferroelectrics, which predicts pressure increases polarization and $T_c$ in ZnSnO$_3$ and LiNbO$_3$.

See supplementary material for the method for determining $T_c$ and further details on theoretical investigations including the structure search and the connection between the volume and oxygen octahedra rotations.

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