Possible evidence for high-pressure induced charge transfer in thallium rhenium oxide at room temperature

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The electronic structure of thallium rhenium oxide ($TlReO_4$) at room temperature is explored as a function of applied pressure using a diamond-anvil cell and high-resolution x-ray absorption spectroscopy. We show possible evidence of charge transfer from the thallium to the rhenium atom in the high-pressure phase of this compound, thus suggesting a previous proposition made several decades ago. This study provides further insight into the nature of high-pressure phase transitions in ABO_4 type compounds.

I. INTRODUCTION

There has been a wealth of studies on the technical relevant ABO_4 type compounds over recent decades. These ternary type oxides are used in a wide variety of applied areas such as in scintallor crystals (e.g., $CdWO_4$ and $PbWO_4$), phosphors (e.g., $ZrGeO_4$ and $HfGeO_4$), laser host materials (e.g., $BaWO_4$ and $GdTaO_4$), and batteries (e.g., $CaMoO_4$ and $SrWO_4$), and an excellent overview of these and related systems can be found in the review article by Errandonea and Manjón and references therein [1]. Many of these compounds display a wide variety of structural and electronic phase transitions as a function of applied pressure and temperature, and it is the investigation of these phenomena which allows for the greater understanding of the behavior of these technological important materials. In particular, pressure and temperature studies on the scheelite type oxide $TlReO_4$ have been performed, although not extensively, over a number of years which provide the focus of this paper.

$TlReO_4$ is an insulating material at ambient pressure and temperature, forming a pseudoscheelite type structure which consists of isolated ReO_4 tetrahedra linked to highly coordinated Tl polyhedra. Temperature-dependent Raman and x-ray powder diffraction measurements on $TlReO_4$ at ambient pressure found pseudoscheelite to scheelite phase transitions above 400 K and below 200 K [2,3]. As pressure is gradually applied to the system, there are several subtle structural changes, basically involving a rotation and/or distortion of the ReO_4 tetrahedra. Ambient temperature *in situ* x-ray diffraction studies revealed three phase transitions occurring at $\sim$1, $\sim$2, and $\sim$10 GPa [4]. The transitions at 2 and 10 GPa displayed significant volume reductions of 2 and 9%, respectively. At 10 GPa, it was suggested that the Re atoms had become truly octahedrally coordinated with respect to the surrounding oxygen cage. A high-pressure room-temperature Raman study found phase transitions at $\sim$0.5, $\sim$1.9, and $\sim$9.7 GPa, where at 9.7 GPa the sample became black [5]. Increasing further the pressure to $\sim$15 GPa, the sample became totally opaque with a corresponding optical shift of 2 eV indicating a significant change in the electronic structure of the material and a possible change in the valency of the Tl and Re atoms. An ambient-temperature x-ray spectroscopic x-ray near-edge structure measurement performed at the rhenium L_3 absorption edge discovered a broadening of the white-line feature around 11 GPa indicating a possible distortion of the ReO_4 tetrahedra but found no evidence for the proposed valence change [6].

As described above, $TlReO_4$ exhibits a substantial volume collapse at around 10 GPa and becomes significantly dark in color. It is postulated that an electronic phase transition also occurs at or above this pressure where charge is transferred from the thallium to the rhenium atom, i.e., : $Tl^{1+}(Re^{7+}O^{4-})^{-1} \rightarrow Tl^{3+}(Re^{5+}O^{4-})^{-3}$ [5]. The goal of this study is to investigate this proposed charge transfer using x-ray absorption near-edge spectroscopy (XANES). As XANES is very sensitive to the local structure and chemical environment surrounding the absorbing atom, it is an ideal probe for investigating any electronic structural changes that may occur as a function of pressure in this material. In the hard x-ray region, the L absorption edges of both the rhenium and thallium atoms are available for studying the electronic structure of this compound and both essentially provide the same information, both probing the $2p \rightarrow$ empty d states in the conduction band. The measurements were performed during two experimental runs where high-energy resolution fluorescence detected (HERFD) XANES measurements were conducted at the Tl L_3 edge during the first run and a subsequent measurement was performed in standard transmission mode at the Re L_3 edge.

II. EXPERIMENTAL PROCEDURE

HERFD XANES measurements, which provide much improved energy resolution over conventional x-ray absorption spectroscopy due to the removal of $2p$ core-hole lifetime broadening in this experiment, were performed at the GALAXIES inelastic-scattering undulator beamline at the SOLEIL synchrotron radiation facility [7]. Finely ground $TlReO_4$ was loaded into a stainless steel gasket (hole diameter

125 μm and depth 12 μm) along with a few micron-sized ruby chips in order to measure the pressure within the sample cell using the pressure dependent shifts of the ruby fluorescence lines [8]. The diamond anvil cell consisted of 1.2-mm-thick, 300-μm-wide diamond cutlets and pressure was varied by increasing the gas pressure on a membrane connected to one of the diamonds. No pressure transmitting medium was used for the experiment as powder itself is known to transmit pressure well. The synchrotron radiation was monochromatized using a Si(111) nitrogen-cooled fixed-exit double-crystal monochromotor ($dE/E \sim 1.4 \times 10^{-4}$), followed by a Pd-coated spherical collimating mirror. The x-rays were then focused to a spot size of 30 μm (vertical) times 90 μm (horizontal) full width at half maximum (FWHM) at the sample position by a 3:1 toroidal Pd-coated mirror. The overall energy resolution for the experiment was measured to be $\sim$2.5 eV FWHM with $\sim 1 \times 10^{13}$ photons per second on the sample. The incident x-ray energy was scanned across the Tl L_3 absorption edge ($\sim$12 658 eV) while monitoring the intensity of the the the Tl $L\alpha_1$ emission line ($\sim$10 269 eV) using two silicon (555) spherical bent crystal analyzers (Bragg angle $\sim$74.3°, 1-m radius of curvature) in the Rowland circle geometry which focused the emitted x rays onto a silicon avalanche photodiode detector. The experiment was performed in the transmission geometry and helium flight paths were used to eliminate the effects of air absorption. Sample pressures between 0 and 26 GPa, well above the high-pressure phase transition where the valence change is proposed to occur, were recorded. A second subsequent experiment was performed to assess the position of the Re L_3 edge as a function of pressure in order to quantify the effects of the proposed valence change $Re^{7+} \rightarrow Re^{5+}$ using standard x-ray absorption spectroscopy where a photodiode was used to measure the transmission of the sample as a function of incident x-ray energy.

III. RESULTS AND DISCUSSION

Figure 1 shows high-pressure HERFD XANES measurements between 0 and 17 GPa. There are noticeable changes in the spectra which are an indication of the various low-pressure structural changes in this compound as previously reported using both high-pressure Raman and x-ray diffraction techniques. A small pre-edge feature immediately develops as pressure is applied to the material and remains relatively constant in intensity up to 17 GPa. The position of the absorption edge does not exhibit any significant change.

However, in increasing the pressure further, dramatic changes in the XANES profile develop as shown in the upper panel of Fig. 2, where we present the 0 and 17 GPa data shown in Fig. 1 with spectra taken at 20 GPa. As can be clearly seen, the 20 GPa data exhibit significant spectral changes, especially in the intensity of the pre-edge feature, compared with those of the lower-pressure data, indicating a dramatic change in the electronic structure of this material. XANES profiles taken at 24 and 26 GPa revealed exactly the same profile as obtained at 20 GPa. According to the charge transfer hypothesis, where the thallium atom goes from $Tl^{1+} \rightarrow Tl^{3+}$ in the high-pressure phase, we propose that this is evidenced by both the appearance of the strong pre-edge peak and the shift in the position of the absorption edge. These features are
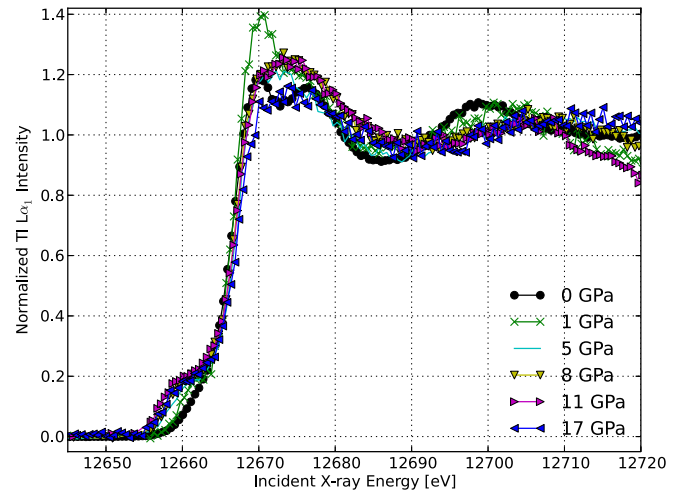

FIG. 1. (Color online) High-energy resolution fluorescence detected XANES of TlReO$_4$ as a function of applied pressure up to 17 GPa at the Tl L_3 absorption edge. On the onset of pressure, a small pre-edge feature is observed in the spectra. Other spectral changes signify changes in the local environment as a function of applied pressure. The incident x-ray energy was defined by using the calibrated position of the pre-edge feature found in Tl^{3+} based systems by Studer et $al.$ [10].

relatively straightforward to understand: the pre-edge peak is governed by $2p_{3/2} \rightarrow 6s$ transitions. These transitions in the XANES spectra have already been observed in lead oxide [9] and some thallium cuprates [10].

At ambient pressure, Tl is in the 1^+ state where its $6s$ electrons remain bound to the atom. As the pressure is increased, the $6s$ electrons become more delocalized and thus $2p_{3/2} \rightarrow 6s$ transitions become more favorable. This manifests itself as a relatively weak pre-edge feature in the low-pressure data (Fig. 1) but which becomes an intense peak in the 20 GPa data (Fig. 2 upper panel). As stated in Ref. [10], "The A-transition (pre-edge peak) requires empty or partially empty 6s orbitals so that it should be clearly visible in Tl(III) oxides." We therefore suggest that this intense pre-edge peak enhancement around 20 GPa data could be due to charge transfer between Tl and Re ($Tl^{1+} \rightarrow Tl^{3+}$, $Re^{7+} \rightarrow Re^{5+}$), where the rhenium atom accepts electrons into its empty $5d$ and $6s$ bands. This proposition is further substantiated by the position of the Tl L_3 absorption edge, governed by $2p_{3/2} \rightarrow 6d$ transitions, which shifts upwards in energy by $\sim$3.4eV from ambient pressure to 20 GPa, indicating an increase in valency as the core electrons become less screened from the atomic nucleus. Both the emergence of the strong pre-edge peak and the shift in the position of the absorption edge thus provide possible evidence of charge transfer between the Tl and Re atoms in this material at high pressure. Due to a lack of structural phase information for TlReO$_4$, we performed ab $initio$ density functional calculations using the known atomic coordinates and space groups of the low- and high-pressure phases of PbWO$_4$, substituting the Pb and W atoms with Tl and Re atoms, in order to provide a qualitative measure of the change of the near-edge structure as a function of pressure in TlReO$_4$. This should be a reasonable assumption given the
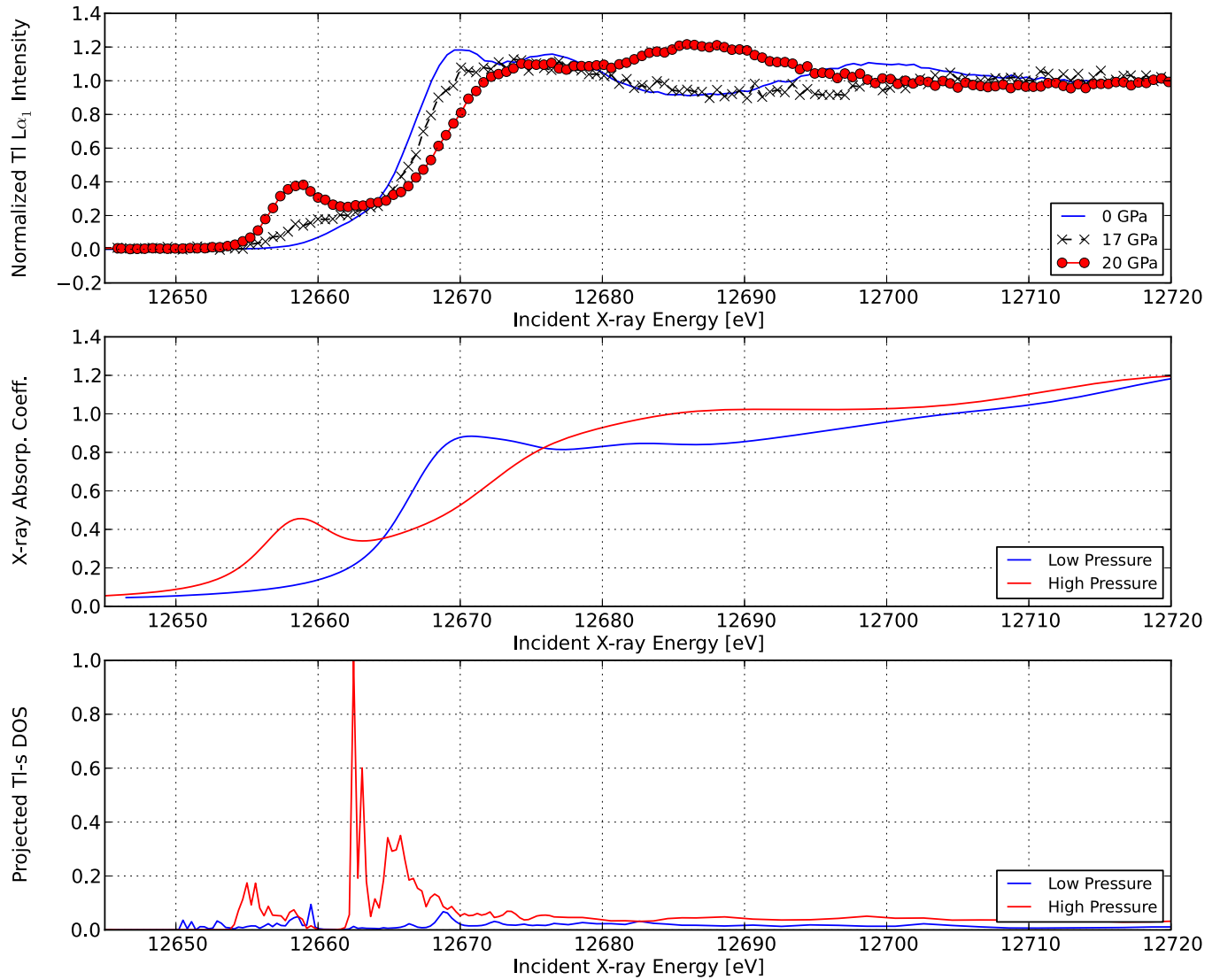
FIG. 2. (Color online) Experimental (upper panel) and calculations (center and lower panels) of the low- and high-pressure phases of TlReO$_4$ at the Tl L_3 absorption edge. Upper panel: Experimental normalized x-ray absorption coefficient, where the incident x-ray energy was defined by using the calibrated position of the pre-edge feature found in Tl^{3+} based systems by Studer *et al.* [10]. Center panel: FDMNES *ab initio* density functional code calculations of the x-ray absorption coefficient of TlReO$_4$ using the structural parameters of PbWO$_4$ in the low-pressure (0.7 GPa, $I4_1/n$) and in the high-pressure (12 GPa, $P2_1/n$) phases [11]. Lower panel: Projected available s states on the Tl atom as a function of pressure, which when convoluted with the experimental resolution ($\sim$2.5 eV) are the nature of the large pre-edge peak as shown in the experimental and theoretical spectra in the above panels.

similar structures and ionic radii of these two compounds, although we note that their ambient pressure bulk moduli are quite different: 26 GPa for TlReO$_4$ [4] and 66 GPa for PbWO$_4$ [11]. This difference in compressibility is known to be dependent upon the formal charge of the cation, i.e., Tl^{1+} in TlReO$_4$ and Pb^{2+} in PbWO$_4$, where the compounds become less compressible with an increase in cation valency. The low-pressure scheelite structural parameters (space group $I4_1/a$) and those of the high pressure (space group $P2_1/n$) of PbWO$_4$ were taken from the values given by Errandonea *et al.* [11]. These calculations were performed with the FDMNES code [12] using the Green multiple scattering formulism, a cluster radius of 9 Å ($\approx$250 atoms), and a Gaussian broadening of 2.5 eV in order to simulate the experimental resolution. The center and lower panels of Fig. 2 show the results of these

calculations. The normalized absorption coefficient (center panel of Fig. 2) exhibits broadly the same profile as the high- and low-pressure data shown in the upper panel of Fig. 2, thus suggesting the structural and electronic phase transitions exhibited in TlReO$_4$ are very similar to those found in PbWO$_4$. It should be noted that a shift of a few eV was introduced between the high-pressure and low-pressure calculations in order to be in close agreement with the experimental results. Also shown in Fig. 2 (lower panel) are the projected partial density of s states on the Tl atom as a function of pressure, as it is only these states which show any noticeable change between the low- and high-pressure phases. As can be clearly seen in the high-pressure phase, there is a substantial increase in the available s states in the high-pressure phase, which when convoluted with the experimental resolution ($\sim$2.5 eV) are the
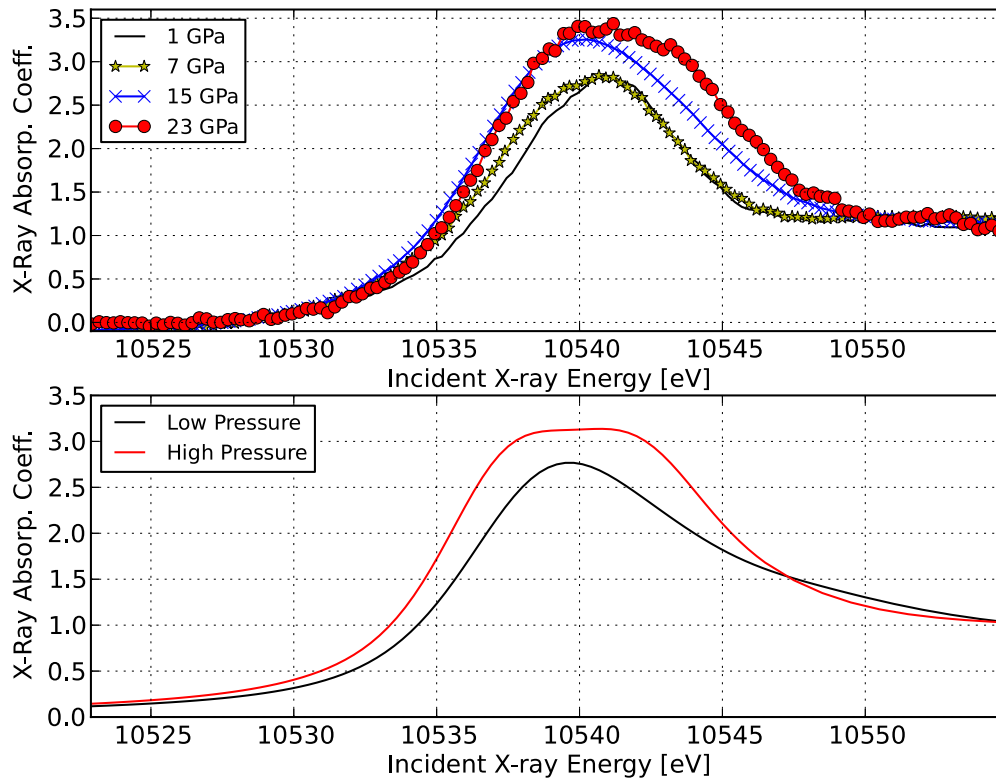
FIG. 3. (Color online) Experimental (upper panel) and calculations (lower panel) of the low- and high-pressure phases of TlReO$_4$ at the Re L_3 absorption edge. Upper panel: Normalized x-ray absorption coefficient of TlReO$_4$ taken in transmission mode at the Re L_3 absorption edge as a function of applied pressure up to 23 GPa where the incident x-ray energy was defined by using the known Re L_3 edge positions as a function of the Re valence state [6] and assuming that Re remains in the 7+ oxidation state at 1 GPa. At 15 and 23 GPa the spectral weight is shifted toward lower energies which is consistent with a decrease in the valency of the Re atom. The 15 GPa data exhibits considerable broadening when compared to the lower-pressure data, increasing dramatically further at 23 GPa. Lower panel: FDMNES *ab initio* density functional code calculated x-ray absorption coefficient at the Re L_3 absorption edge for the high-pressure and low-pressure phases of TlReO$_4$ using the structural parameters of PbWO$_4$ as described in the caption of Fig. 2.

nature of the large pre-edge peak in the high-pressure phase. This increased density of s states in the high-pressure phase could be an indication of charge transfer from the Tl atom. Following on from our main goal of investigating the nature of the electronic structure of TlReO$_4$ at the Tl L_3 edge, it was decided that a measurement of the absorption edge position at the Re L_3 edge would be advantageous: If the charge transfer hypothesis Tl^{1+}(Re^{7+}O^{4-})$^{-1}$ → Tl^{3+}(Re^{5+}O^{4-})$^{-3}$ is correct, we should expect a shift in the main Re L_3 edge position to lower energy. Previous studies on various rhenium compounds have shown that a valence change of −2 should equate to a small ≈0.8-eV shift in the Re L_3 absorption edge position toward lower energy [6]. Figure 3 (upper panel) shows the normalized x-ray absorption coefficient taken at the Re L_3 in TlReO$_4$ in standard transmission mode as a function of applied pressure. The absorption edge position as a function of pressure exhibits much smaller changes than those found at the Tl L_3 absorption edge and they are not entirely correlated: there is a shift to lower energies around 7 GPa followed by a further shift at higher pressures, although this shift is difficult to assess because there is also a corresponding increase in the width of the white-line feature. This broadening could be attributed to increased hybridization at the rhenium site and/or distortions in the ReO$_4$ tetrahedra. The very small shift back toward higher energies at 23 GPa could be due to

uncertainties in the background subtraction and normalization scheme employed in the data treatment. The data do however tend to show a small but clear shift in the main edge position toward lower energy, that could possibly signify a decrease in the rhenium oxidation state. The position of the maximum of the derivative (not shown), which gives an indication of the edge position, shows a shift of ≈ −0.8 eV between the 1- and 23 GPa data, which is in accord with a decrease in the oxidation state of 2 for the Re atom. The FDMNES calculations of the x-ray absorption coefficient at the Re L_3 absorption edge are shown in the lower panel of Fig. 3 and are in good agreement with the general shape of the experimental data. It should be noted that, as for the Tl L_3 edge data, a shift of a few eV between the high- and low-pressure phases is introduced in order to be in good agreement with the experimental results.

In conclusion, we have performed high-pressure HERFD XANES measurements at ambient temperature on TlReO$_4$. Dramatic changes in the XANES profile between 17 and 20 GPa at the Tl L_3 absorption edge indicate a significant change in the electronic structure in this material. A charge transfer between the thallium and rhenium atoms, as first proposed several decades ago, is possibly evidenced by the emergence of a strong pre-edge peak and a shift in the Tl L_3 absorption edge position toward higher energy. Density

functional calculations confirm an increase in the available *s* states on the Tl site in the high-pressure phase, thus suggesting a charge transfer from the thallium to the rhenium atom. The XANES data taken at the Re L_3 absorption edge are less clear due to the much smaller shift in the absorption edge position and an increase in the width of the white-line feature, although the shift in the absorption edge is toward lower energies and less than 1 eV as expected. It should be also mentioned that although we suggest that the proposed charge transfer is directly from the Tl to the Re atom it would be more precise to state it is from the Tl to the Re–O covalent bond in the ReO_4 tetrahedral unit. $TlReO_4$ is an intriguing material that exhibits a number of interesting phase transitions as a function of temperature and pressure. Metallic and even superconductivity behavior has been predicted for this material and these could be fruitful areas for future studies [5].

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