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HIGH-PRESSURE X-RAY NEAR-EDGE ABSORPTION STUDY OF THALLIUM RHENIUM OXIDE UP TO 10.86 GPa

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High-pressure X-ray near-edge absorption measurements have been performed on thallium rhenium oxide (TlReO₄) up to 10.86 GPa at room temperature and in a diamond-anvil cell. At ~10 GPa, TlReO₄ undergoes a large volume collapse and a striking optical transition, changing from transparent to opaque. A model has been proposed by Jayaraman *et al.* that the high-pressure phase transition is associated with a charge transfer from the thallium to rhenium atom; $\text{Ti}^{1+}(\text{Re}^{7+}\text{O}_4)^{-1} \rightarrow \text{Ti}^{3+}(\text{Re}^{5+}\text{O}_4)^{-3}$ and an accompanying truly octahedral coordination of the rhenium atom with respect to the surrounding oxygen cage. In this article, we find a significant broadening of ~1.5 eV of the white-line feature at the rhenium L₃(2p_{3/2} → 5d) absorption-edge above this transition, and no evidence for the proposed valence change.

Keywords: X-ray absorption; Thallium rhenium oxide

INTRODUCTION

There are many interesting compounds that have the ternary oxide formula ABO₄ (A and B are metals, and O represents oxygen), and most undergo high-pressure phase transitions. Some of these compounds are of great interest because of their importance as scintillator crystals [1–4]. To explain these high-pressure changes, theoretical considerations have focused on the ionic size and valence of the A and B cations from which ABO₄ crystal-structures are postulated [5, 6], which generally consist of linked polyhedra in orthorhombic or tetragonal arrangements. Thus, by varying the atomic species and the pressure applied, these related families of materials provide an opportunity to study the stability of these structures and pressure-induced phase transitions in general.

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A number of ABO_4 -type compounds crystallize in the scheelite (body-centered tetragonal, space group $I4_1/a$) or pseudoscheelite (orthorhombic, space group P_{nma}) under ambient conditions. The pseudoscheelite crystal structure [1] of TlReO_4 at ambient conditions is shown in Figure 1 (left). The structure is highly ionic with Ti^{+1} cations and $(\text{ReO}_4)^{-1}$ anions running along the c -axis, and the dashed box indicates a potential site where the oxygen atoms could edge-share. Edge-sharing has been suggested to occur for scheelite-type structures when pressure is applied to the system. When edge-sharing occurs, a wolframite structure would be formed as shown in Figure 1 (right) [1, 7, 8].

Structural stability and pressure-induced phase transitions of ABO_4 -type compounds have been studied using high-pressure Raman spectroscopy for more than two decades. Among these compounds, it has been suggested that the AReO_4 perrhenates transform from the scheelite-type to the wolframite-type structures with compression, and finally to a lower symmetry matrix [7, 9, 10]. In particular, thallium rhenium oxide has been studied at high pressure using Raman spectroscopy [11] and X-ray diffraction [12, 13]. From these data, it was discovered that there were three distinct pressure-induced structural phase transitions: TlReO_4 crystallizes in the pseudoscheelite structure under ambient conditions (phase I). As pressure is applied to this compound, three phase transitions are encountered at 1 GPa (phase II), ~ 2 GPa (phase III) and ~ 10 GPa (phase IV). All transitions are first order, and found to be reversible with some hysteresis. In the Raman spectra, there are only subtle changes between phases I and II, with perhaps only a rotation or tilting of the ReO_4 tetrahedra [7, 11]. The interpretation of X-ray diffraction data implied that the phase III transition takes place within a broad pressure range (2 GPa \rightarrow 5 GPa) into the assumed wolframite structure. The crystal volume change between the wolframite and scheelite structures is of the order of 2% [12]. The high-pressure phase transition that occurs at around 10 GPa has been interpreted to being that of the high-temperature phase of BaWO_4 (type 2) [14, 15] due to similarities between the derived lattice parameters [12]. Moreover, TlReO_4 transforms optically from transparent to opaque at the third phase transition (phase IV) [11], with

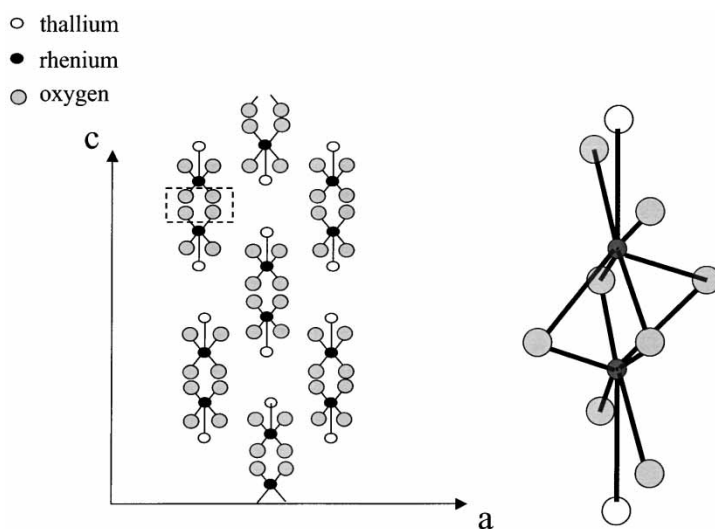


FIGURE 1 Left—Crystal structure of TlReO_4 under ambient conditions. The dashed box indicates a potential site for edge-sharing between the oxygen atoms. Right—The assumed change in TlReO_4 structure with applied pressure (pseudoscheelite to wolframite) when edge-sharing occurs.

a volume-collapse of $\sim 10\%$ [12]. It is this striking optical change and volume-collapse that is of interest because it provides evidence of a modification of both the electronic and crystal structure. It was proposed that this dramatic color change is due to a change in the valence state of the two cations: $\text{Re}^{+7} \rightarrow \text{Re}^{+5}$ and $\text{Ti}^{+1} \rightarrow \text{Ti}^{+3}$ [7, 11] and an accompanying truly octahedral coordination of the rhenium atom with respect to the surrounding oxygen cage. Due to the change in optical absorption, a change in the band-gap is implicated and hence an X-ray absorption measurement around the rhenium L_3 absorption-edge could provide some indication as to the nature of this transition.

EXPERIMENTAL PROCEDURES

High-pressure X-ray near-edge absorption spectra of TiReO_4 were obtained at the National Synchrotron Light Source (NSLS) X13B undulator beamline [16–20]. The beamline consisted of a water-cooled double-crystal $\text{Si}(111)$ monochromator and a Kirkpatrick–Baez pair of elliptically shaped mirrors to focus the incoming X-rays onto the sample [21]. High pressure was generated using a diamond-anvil cell (DAC) of the Mao–Bell type with beryllium-gasket [22]. Finely ground TiReO_4 powder was loaded into the DAC sample chamber with an ethanol–methanol mixture that acted as a pressure-transmitting medium. In addition, a few ruby chips were also incorporated into the sample cell to allow for accurate pressure calibration [23]. X-ray absorption near-edge spectra were collected with the DAC arranged such that the incident X-rays propagated through both diamond-anvils (with the sample sandwiched in between) and the transmitted X-rays were detected using a silicon photodiode. Energy calibration was ensured throughout the experiment by performing periodic absorption scans through a rhenium metal foil, and the high-pressure phase transition was verified by viewing the sample through an optical microscope.

RESULTS AND DISCUSSION

To assess the validity of the proposition that TiReO_4 undergoes a change in the valence state between the two cations ($\text{Re}^{+7} \rightarrow \text{Re}^{+5}$ and $\text{Ti}^{+1} \rightarrow \text{Ti}^{+3}$) at the high-pressure phase transition, absorption-edge spectra of various rhenium compounds were obtained at the NSLS. Figure 2 shows the spectra of Re_2O_7 , NH_4ReO_4 , ReO_3 , ReO_2 and Re , and Figure 3 is a plot of the edge-shift against formal valence of the rhenium atom. From this data, a shift of 0.8 eV towards lower energy of the $\text{Re } L_3$ edge is expected if the charge-transfer proposal suggested by Jayaraman *et al.* is correct [7, 11].

The high-pressure rhenium L_3 X-ray absorption edge results are shown in Figure 4. The spectra have been normalized to unit edge-jump to compensate for variations in sample thickness as pressure is applied to the system. We find no evidence pointing to an absorption-edge shift in the high-pressure spectra compared to ambient pressure data. Instead, we discover that at a pressure of 10.86 GPa, beyond the phase transition where the sample is opaque, there is a very large broadening of the white-line feature of more than 1.5 eV and a decrease in the peak intensity. A possible explanation of this broadening could be that the high-pressure phase is a distorted one, most likely due to pressure-induced distortions within the ReO_4 tetrahedra. An example of the effect that distortions play in the white-line profile is well demonstrated in the X-ray absorption spectral differences between crystalline and amorphous silicon [24]. In lead tungstate (PbWO_4), band-structure calculations indicate that the valence band is dominated by O 2p–W 5d contributions and the lower part of the

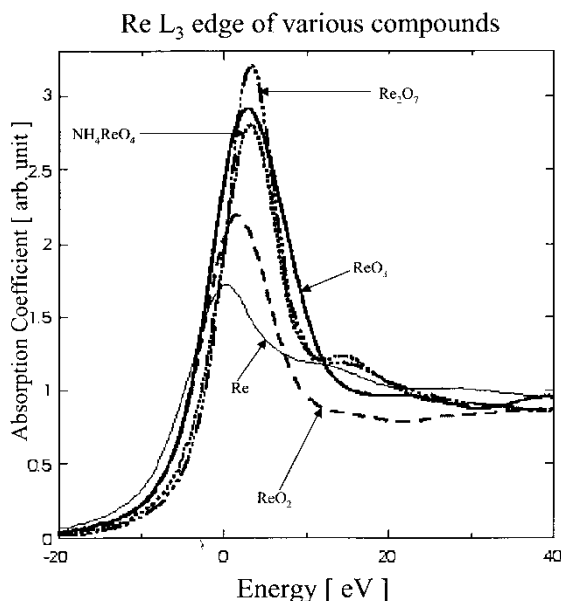


FIGURE 2 Re L_3 XANES spectra from a number of rhenium compounds.

empty conduction band is mostly of W 5d character [3]. TiReO_4 could be expected to have a similar make-up, with the electronic structure being heavily influenced by effects within the ReO_4 tetrahedra. It is therefore possible that any distortion of the oxygen cage surrounding the rhenium atom could produce significant changes to the electronic structure and trigger structural instabilities.

Finally, optical investigation of the high-pressure phase transition indicates that TiReO_4 remains an insulator due to continued transmission in the deep red part of the optical spectrum [11]. It has been proposed that subjecting this compound to pressures in excess of 20 GPa could make it metallic [11], which is an intriguing area for further study.

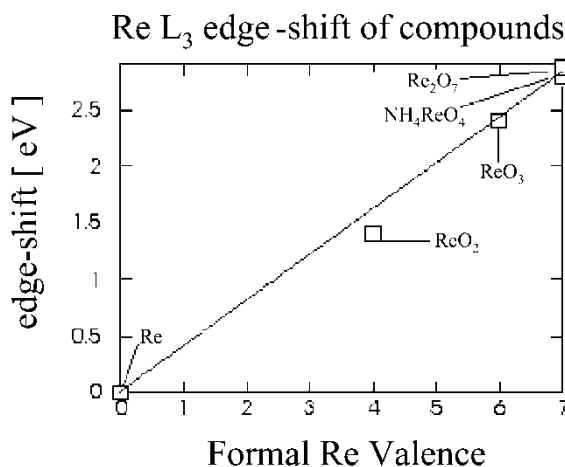


FIGURE 3 Plots of the rhenium L_3 absorption-edge shift for the various oxidation states of the rhenium atom of the compounds used in Figure 2.

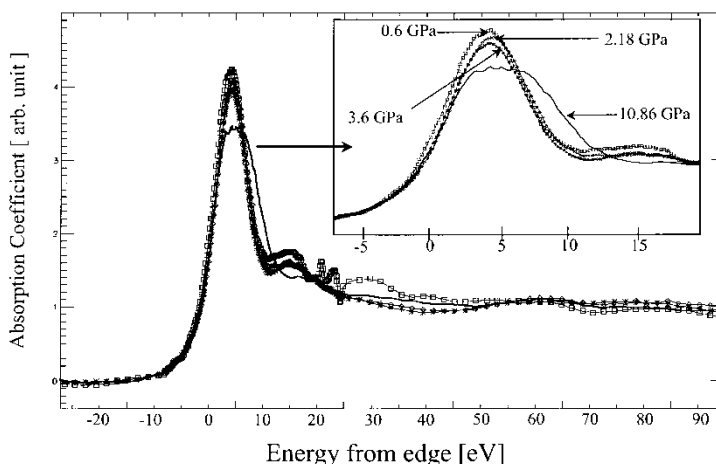


FIGURE 4 Pressure-dependent X-ray near-edge structure at the rhenium L_3 absorption-edge in TiReO_4 . Pressure was applied using a diamond-anvil cell and the data were collected in the transmission geometry.

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