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Observation of pressure-induced electron transfer in SnC_2O_4

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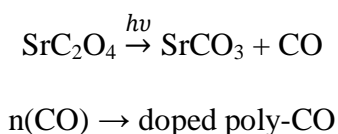
We examined the high pressure behavior of stannous oxalate via Raman and x-ray absorption spectroscopy (XAS) inside a diamond anvil cell. Phase transitions were observed to occur near 2.6 and 15 GPa which were reversible upon decompression to ambient conditions. When further pressurized above 15 GPa, the colorless material sustains irreversible chemical alterations and becomes bright red colored - darkening at higher pressures. Another irreversible phase transition occurred above 20 GPa. Concomitant with color change of the sample, we observed a softening of the $\nu(\text{C}-\text{C})$ modes of the $\text{C}_2\text{O}_4^{2-}$ anion via Raman spectroscopy. We performed a separate XAS experiment which indicates that the Sn^{2+} cation undergoes a partial reduction of the +2 oxidation state with pressure which persists when the sample was depressurized to ambient conditions. Thus, electron density within the C-C bond in the oxalate anion appears to migrate toward the tin cation with pressure. This observation suggests that pressure can offer a very controllable means to vary cation-anion and unit cell dimensions (and thus the electric interactions causing electron movement) and thus the pressure-induced synthesis of novel materials.

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Introduction:

We have recently performed a number of studies pertaining to oxalate salts¹⁻⁴ that, when irradiated with synchrotron hard x-rays (>7keV) produce novel compounds¹⁻³ and novel structures of known compounds⁴ under ambient and high pressure conditions depending on the cation⁶, x-ray energy³ and possibly pressure⁵. In the case of divalent Sr, we suspect the following chemical reactions²:



In the case of (Cs)₂C₂O₄, a novel structure of cesium superoxide was produced.⁴ Thus, there is a strong correlation with the choice of cation in the oxalate salt and the x-ray induced photochemical reactions that occur when the salt is irradiated. There is also a strong dependence on pressure on the rate of reaction and possibly on the products⁵⁻⁶. We have argued that x-rays of sufficient energy (just above the K-shell energies) ionize core K-shell electrons producing low energy photoelectrons which can damage neighboring anions³. On top of this, the transiently-supercharged cation encourages electrons to fill the K-shell vacancy which then creates vacancies in the cation's valence levels. This may encourage electron migration from the electron-abundant anion which then causes irreversible chemistry.

In an effort to better examine the role of cation-anion distance in the oxalate salts (mediated by high pressure) and how it may aid electron transfer from the anion to cation, we studied stannous oxalate. We have examined strontium oxalate in prior experiments but found no irreversible chemistry occurring at high pressure up to 25 GPa (with no x-ray irradiation). We were interested in Sn as a cation because of its curious position (just below semimetal Ge) in the periodic table with 5s²5p² available valence electrons. In the case of tin, a post-transition metal,

the metal exists in mostly two known oxidation states: II and IV. Thus, when examining the effects of cations and anions with pressure, one natural question would be the ability of the tin cation to change its oxidation state with pressure.

In this paper, we report our studies of SnC_2O_4 at high pressure using Raman, XAS, far- and mid-IR spectroscopic means. To the best of our knowledge, this is the first reported study of stannous oxalate at high pressure.

Experimental:

Raman

Our Raman experiments were performed in the Pravica Group laboratory using a Jobin-Yvon U1000® Raman spectrometer (resolution 0.4 cm^{-1}) and a LASOS ® diode-pumped laser producing 532 nm light (typically less 30mW or less at the sample). Acquisition times of Raman spectra were 30 sec each. Stannous oxalate (Sigma Aldrich 99%) was used as the sample material and diamond anvil cell (DAC) was employed for pressurization. A 250 μm thick stainless-steel (SS) gasket was preintended using $\sim 300 \mu\text{m}$ culet diameter ultralow fluorescence Type II diamonds. A $\sim 140 \mu\text{m}$ diameter hole was drilled via electric discharge machining into the center of the preindentation. After ultrasonically cleaning the drilled gasket and sandwiching it between the diamonds, white stannous oxalate powder was manually introduced into the hole along with a $\sim 10 \mu\text{m}$ ruby sphere for pressure measurement and the two halves of the DAC were translated together to seal and pressurize the sample. Pressure was also measured using our Raman spectrometer. No pressure-transmitting medium was used in any of our experiments and all measurements were conducted at room temperature.

XAS:

X-ray absorption spectra on Sn K-edge (29.2 keV) were collected at the BioXAS-Spectroscopy beamline (07ID-2) at the Canadian Light Source (CLS). The beamline was equipped with the cryogenic Si220 Double Crystal Monochromator; Rh-coated toroidal mirrors focused the beam into a 2x0.3mm (HxV) spot and provided higher harmonics rejection. Beam size was further reduced to 0.3x0.1mm by a set of slits, total flux on the sample was estimated at $\sim 10^{11}$ ph/s. The experiment was carried out in the Partial Fluorescence Yield mode, where the characteristic X-Ray fluorescence from Sn was collected by an energy dispersive 32-element HPGE detector (Canberra); N₂-filled ionization chambers were used to measure the intensity of the incident and transmitted beam. Due to the need to detect emitted x-rays perpendicular to the x-ray beam axis, we used an x-ray transmitting Be gasket that had to confine the SnC₂O₄ powder which was also loaded with a ruby for pressure measurement purposes so that the x-ray beam passed through the gasket, perpendicular to the diamond-diamond axis. Emitted X-rays were detected through wide open ports in a Paderborn-style DAC.

Tin K-edge (29200 eV) absorption on the tin reference foil was measured with every scan for energy calibration. The CLS storage ring was operated at 140–200 mA during the measurements.

All the collected spectra were processed and analyzed using the IFEFFIT software package including Athena and Artemis⁷. Data from multiple scans were processed using Athena by aligning and merging the spectra followed by background subtraction using the AUTOBK algorithm. Pressure was measured using a home built ruby-fluorimeter system constructed at the CLS.

Results:

Raman:

The results of our Raman experiment are displayed in Fig. 1 below. All Raman modes are present in the spectrum recorded near 1 GPa⁸. This includes the $\nu(\text{SnO}) + \delta_{\text{ring}}$ mode near 508 cm^{-1} , the $\nu(\text{C-C})$ modes near 847 and 908 cm^{-1} , $\nu(\text{C-O})$ modes near 1408, 1463, 1486 and 1617 cm^{-1} , and a possible $\nu(\text{C-C})$ overtone near 1702 cm^{-1} .⁸ When subjected to high pressure, most modes move toward high higher frequencies with the exception of the $\nu(\text{C-C})$ and its overtone which weaken with pressure and splits near 15 GPa. The $\nu(\text{SnO}) + \delta_{\text{ring}}$ mode splits below 5 GPa suggesting a phase transition only to remerge around 15 GPa. The $\nu(\text{C-O})$ strong mode near 1463 cm^{-1} splits into two modes near 2.6 GPa with the higher frequency mode increasing in amplitude and moving toward higher frequency with pressure at a faster rate than the lower frequency mode. Near 20 GPa, the higher frequency mode is dampened and is reduced in amplitude compared with the lower frequency mode near it.

Visually, the sample, which is originally white in color at low pressures until around 15 GPa, when the sample was observed to have an orange-reddish hue (see Fig. 2). At higher pressure, the sample darkened. When reducing the sample pressure to ambient, the sample did not return to its original white color. The behavior of selected modal frequencies with pressure are plotted in Fig. 3. An ambient pressure decompressed Raman spectrum is displayed in Fig. 4.

XAS:

We display the results of our experiments in Figs. 5 and 6. In Fig. 5, we took an absorption spectrum of ambient SnC_2O_4 powder (sealed by kapton tape) and compared this measured curve to a calculated spectrum using the FDMNES program⁹ using known unit cell parameters of stannous oxalate¹⁰. Fig. 6 presents data from the high pressure experiment. The sample was initially pressurized to 5.5 GPa and then further pressurized up to 20 GPa. In the 5.5 GPa

spectrum (labeled “up” in Fig. 6), two peaks are evident - one near the original ambient peak around 29205 eV and a second one near 29185 eV. When the sample was pressurized to 20 GPa, the XAS spectrum, the original ambient peak has largely vanished and the second peak near 29188 eV has increased in amplitude. When the sample was decompressed back to 5.5 GPa (labeled “down” in Fig 6) from 20 GPa, the spectrum is very similar to the pattern near 20 GPa but dramatically different from the spectrum taken at 5.5 GPa in compression suggesting an irreversible oxidation state change. An ambient Sn foil spectrum was also recorded for comparison and calibration purposes.

Discussion:

In the solid state, the Sn^{2+} is connected to two oxalate anions which link as infinite chains¹¹. The unit cells are displayed in various orientations in Fig. 7. From the Raman experiments, there is strong evidence of a phase transition in the 2-3 GPa range evidenced in part by the splitting of the mode near 508 cm^{-1} which is ascribed to the $\nu(\text{SnO})+\delta_{\text{ring}}$ vibrations and a splitting of the $\nu(\text{CO})$ mode commencing near 1470 cm^{-1} . Pressure would be expected to reduce the distance between these oxalate anions and the Sn^{2+} cations. As often happens at high pressure, crystalline symmetries are broken which will cause deviations in the ambient vibrational spectra. If the Sn cation moves relative to the two oxalate groups that it is close to, it will move closer to one and further from the other which would explain the splitting of this mode associated with an atomic shift of Sn^{2+} within the unit cell and thus a phase transition near 2.6 GPa.

There is also an indication of a phase transition near 15 GPa or, more likely, the beginning of a phase transition which begins at 15 GPa and then completes at 20 GPa leading to irreversible chemistry. Modes above 18 GPa dramatically reduce in intensity which we argue is due to loss of molecular order and possible polymerization/formation of an extended CO-based network. It

is also due in part to the increase in inhomogeneous stress which build in samples without a pressure-transmitting medium.

Examining the behavior of the frequency vs. pressure for the Raman $\nu(\text{C-C})$ mode commencing near 845 cm^{-1} , it appears that electron density is shifting from the C-C bond presumably toward the positively charged cation with pressure, causing a softening of the vibrational C-C stretching mode. We have observed this behavior previously with the high explosive, triamino trinitrobenzene (TATB)¹² which we had argued was due to increasing hydrogen bonding at high pressure between the amino and nitro groups with pressure. As the groups come closer to one another with pressure, the nitro group draws electron density from a nearby amino group on a neighboring molecule which weakened the N-H stretch as observed. No chemical reaction occurred in TATB at least up to 30 GPa¹² and all spectrally-observed changes were reversible with pressure.

In the present case, we strongly suspect that the weakening C-C vibration was due to the Sn^{2+} cation approaching the oxalate anion and drawing away electron density from the anion with pressure due to increasing electric fields from the tin cation. If that explanation is accurate, we reasoned that there should be a measurable oxidation state change in Sn with pressure as electron density migrates toward the Sn^{2+} cation. The concomitant XAS experiment indeed observed a significant oxidation state change of Sn toward a less positive state which was irreversible once the sample was pressurized to 20 GPa and apparently remained even when the sample was depressurized to 5.5 GPa. When compressing the sample at 5.5 GPa, a mixed phase and nonhydrostatic conditions indicated that the sample was in an intermediate state where some electrons had migrated toward Sn cations whereas others at lower pressure did not. When

pressurized to 20 GPa, electronic migration completes for all Sn and irreversible chemistry occurs coupled with irreversible change of Sn oxidation state as evidenced in Fig. 6.

Though pressure-induced oxidation state change of cations such as Mn has been observed at high pressure in prior studies¹³ leading to dramatic volume reduction of the unit cell, the present study is, as far as we are aware, the first reported observation of pressure-induced oxidation state change of a cation caused by electron transfer from an anion that leads to irreversible chemical reaction.

Color change of the initially translucent white powdered sample at pressures above 14 GPa may be indicative of mobile electrons moving from the anion toward the cation in the solid state, perhaps rehybridizing with tin valence electrons resulting in novel electronic energy levels that optically absorb. We also note another possibility that poly-CO is orange to red depending on pressure applied as is the stable doped poly-CO that we have synthesized via useful hard x-ray photochemistry¹⁴. It is possible that chemical reaction initiated in the oxalate anion at high pressure in the present study is similar to that initiated via x-rays leading to similar electronic states producing these colors. Possible evidence for this can be observed in the top trace of Fig. 4 which displays the spectrum of the recovered sample after depressurization. One new line near 1510 cm^{-1} may be related to a broad line (centered at 1600 cm^{-1} at high pressure) observed in poly-CO at high pressure which was ascribed to a graphitic C=C stretching mode¹⁵. New modes near 800 cm^{-1} may be related to tin oxide¹ or tin carbonate². Future study will be engaged in answering this question.

Conclusion:

We have examined stannous oxalate at high pressure for the first time using Raman, mid- far-IR, and XAS, to the best of our knowledge. The vibrationally-related spectroscopies largely

examined the behavior of the oxalate ion at high pressure within the matrix of Sn^{2+} cations. The XAS study was focused on examining the behavior of the Sn cation at various pressures. We have found evidence for a phase transition commencing near 2.6 GPa. A second phase transition just below 15 GPa entails a color change from translucent to yellow/orange which darkens at higher pressures. Above 20 GPa, the sample darkens further and irreversibly alters. The $\nu(\text{C-C})$ mode near 847 cm^{-1} softens with pressure which suggests that electron density migrates from the anion toward the Sn^{2+} cation. To confirm this, XAS was performed on the Sn K-edge and a dramatic change of the Sn XAS spectrum was observed portending oxidation state reduction (as observed from the shift of the XAS edge toward lower energy) of Sn due to electron transfer from the anion toward the cation. Thus, with increased pressure, the cation-anion distances decrease which increases the force attracting electrons from the oxalate anion toward the positively charge cation. As electrons begin migrating toward the tin cation, the C-C bond they came from weakens until a certain pressure that leads toward novel chemistry above 20 GPa, suggesting that the bond breaks completely enabling reaction chemistry to occur. Further studies will be performed to prove this.

We have observed widely varying behavior between different oxalate salts with x-ray irradiation (which also promotes electron transfer by ionizing and producing photo-, Auger- and other free energetic electrons⁴) suggesting the critical importance of the cation species (along with oxidation state) that have produced novel compounds and have produced novel structures of known compounds. What is important here is that we have observed that we can initiate electron transfer in an oxalate without the need for x-rays which will give us deeper insights into the nature of this pressure-induced electron transfer.

This experiment presents a unique demonstration of the tunability of pressure as a means to very controllably alter intermolecular and interatomic potentials leading to electron transfer as a means of highly controllable chemistry on a much slower time scale than common chemical reaction times. It will also offer insight into the kinds of forces required to initiate and ultimately complete this electron transfer. Further work will endeavor to model this electron transfer and examine the chemical products synthesized here.

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References:

1. M. Pravica, D. Sneed, Q. Smith, B. Billingham, T. May, M. White and K. Dziubek, 2016, *Cogent Phys.*, **3**, 1-8.
2. M. Pravica, E. Evlyukhin, P. Cifligu, B. Harris, N. Chen, Y. Wang, *Chem. Phys. Lett.* 2017, **686**, 183-188.
3. D. Goldberger, E. Evlyukhin, P. Cifligu, Y. Wang, and M. Pravica, *J. Phys. Chem. A*, 2017, **121**, 7108–7113.

4. E. Evlyukhin, E. Kim, D. Goldberger, P. Cifligu, S. Schyck, P. Weck and M. Pravica *Phys. Chem. Chem. Phys.*, 2018, **20**, 18949-18956.
5. E. Evlyukhin, E. Kim, P. Cifligu, D. Goldberger, S. Schyck, B. Harris, S. Torres, G. R. Rossman, and Michael Pravica *J. Mater. Chem. C* 2018, **6**, 12473-12478.
6. D. Goldberger, C. Park, E. Evlyukhin, P. Cifligu, and M. Pravica, *J. Phys. Chem. A*, 2018, **22 (44)**, 8722–8728.
7. B. Ravel and M. Newville, *J. Synchrotron Rad.*, 2005, **12**, 537-541.
8. A. Wladimirsky, D. Palacios, M. C. D'Antonio, A. C. González-Baró, and E J. Baran, *Spectrochim. Act. A*, 2010, **77**, 334–335.
9. <http://fdmnes.neel.cnrs.fr/>
10. A. Gleizes and J. Galy, *J. Sol. St. Chem.* **30**, 1979, 23-33.
11. A.D. Christie, R.A. Howie and W. Moser, *Inorg. Chim. Act.*, 1979, **36**, L447-L448.
12. M. Pravica, B. Yulga, S. Tkachev and Z. Liu, *J. Phys. Chem. A*, 2009, **113 (32)**, 9133-9137.
13. Y. Wang, L. Bai, T. Wen, L. Yang, H. Gou, Y. Xiao, P. Chow, M. Pravica, W. Yang, and Y. Zhao, *Angew. Chem. Int. Ed.*, 2016, **55**, 10350–10353 ().
14. M. Pravica, M. Rabasovic, A. Krmpot, P. Cifligu, B. Harris, E. Evlyukhin, and M. Nikolic, *Mater. Lett.*, 2019, **256**, 126629 1-4.
15. W. Evans, M. Lipp, C.-S. Yoo, J. Cynn, J. Herberg and J. R. Maxwell, *Chem. Mater.*, 2006, **18**, 2520–2531.

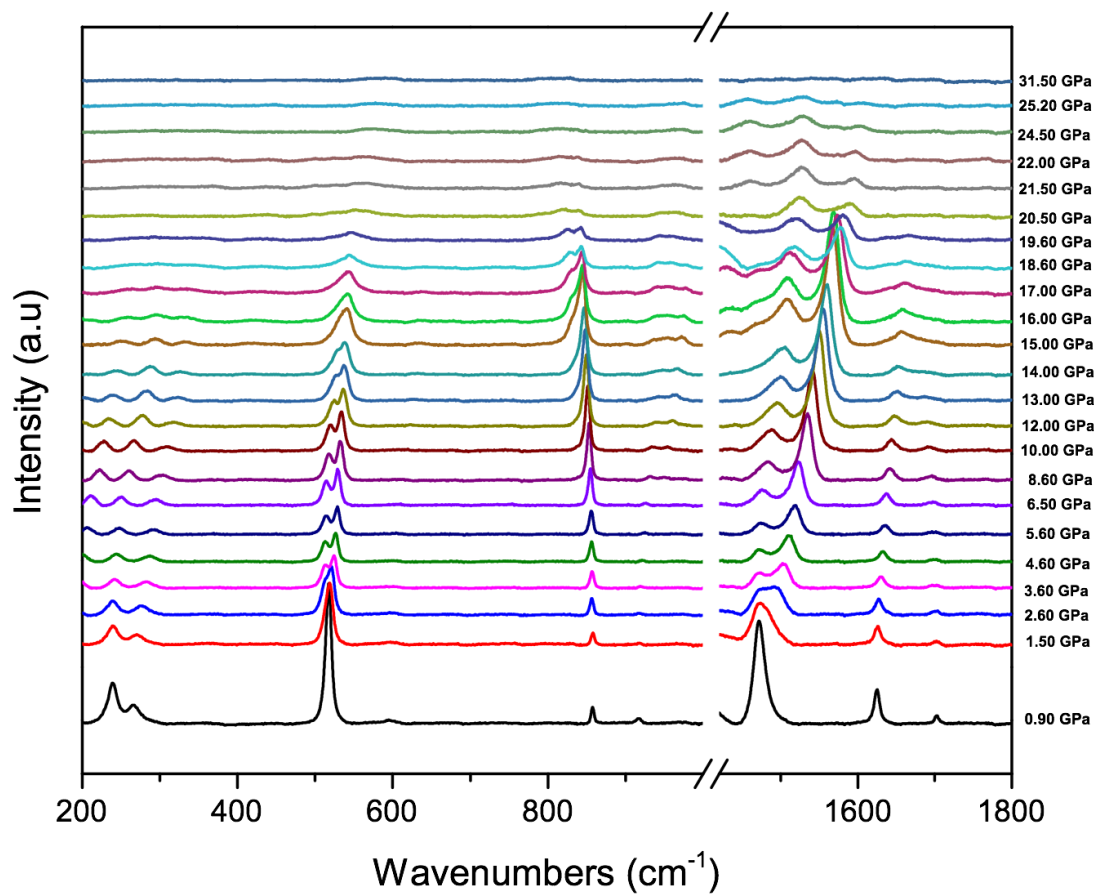


Fig 1: Raman spectra of tin (II) oxalate as a function of pressure. The disconnected region between 1000 – 1300 cm^{-1} has been excised due to the presence of the strong diamond anvil Raman signal.

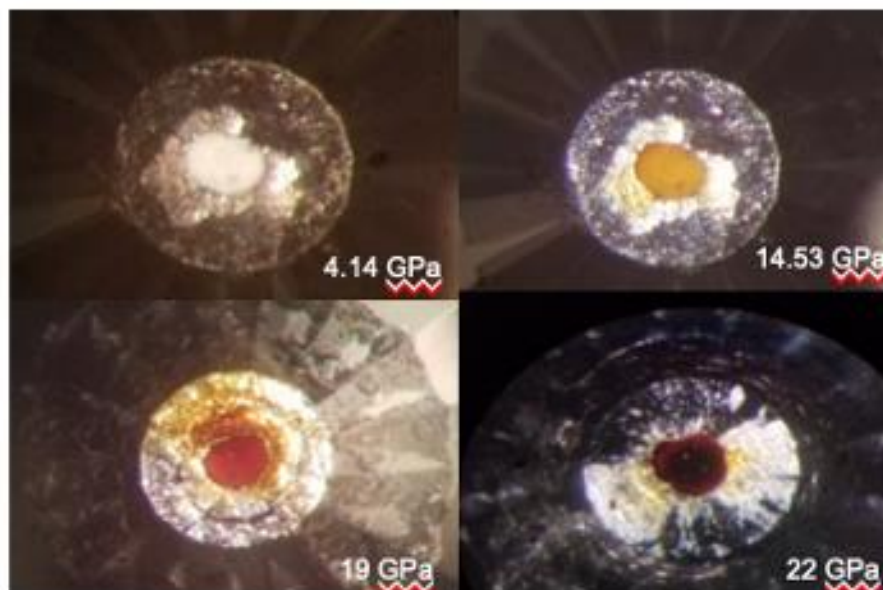


Fig 2: Photos of stannous oxalate pressurized (starting from top left photo going clockwise) at 4.1 GPa, 14.5 GPa, 19 GPa and 22 GPa. decompressed from 20 GPa to ambient pressure which differs markedly from the initially translucent sample before it was pressurized. In all photos, the same sample is viewed through one of the diamonds. A small sphere visible inside the sample chamber [see the 5 O’Clock position in the top two photos] is a ruby sphere for pressure measurement purposes. Color change begins appearing just below 15 GPa.

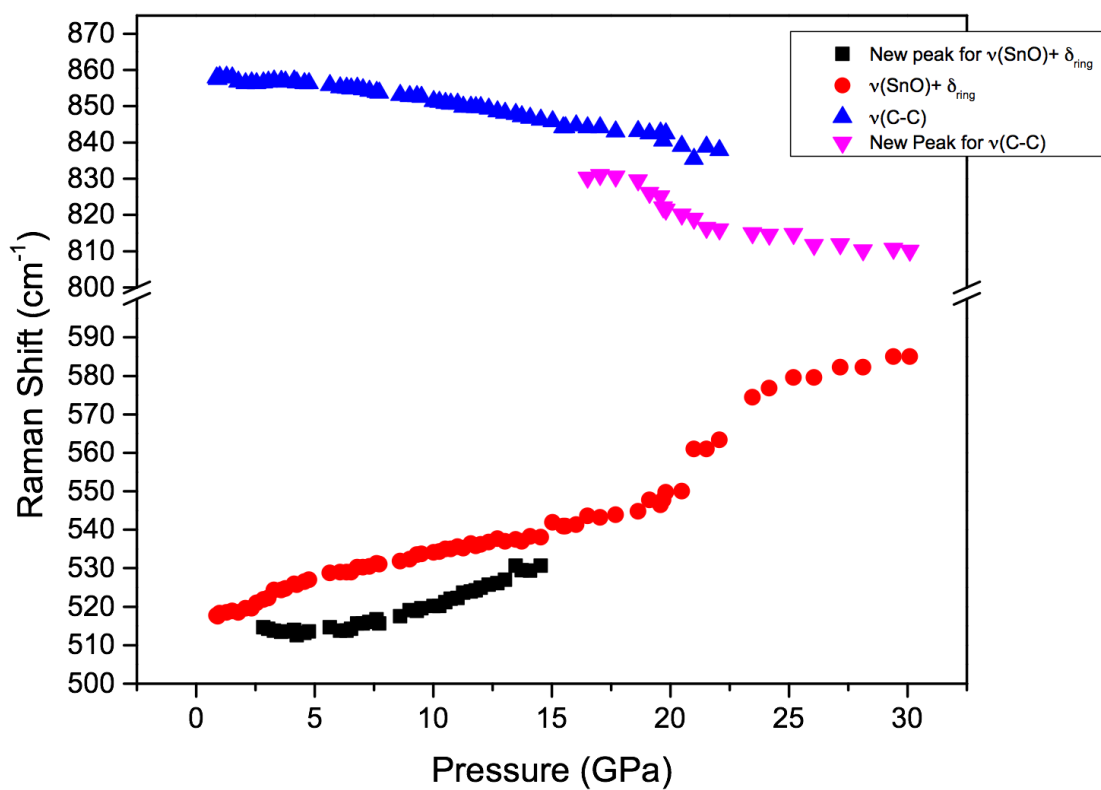


Fig 3. Plots of selected Raman modes of SnC₂O₄ as a function of pressure.

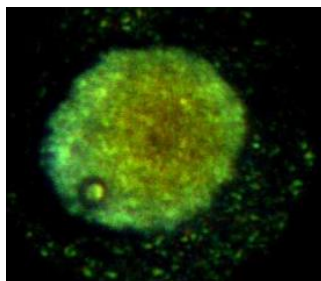
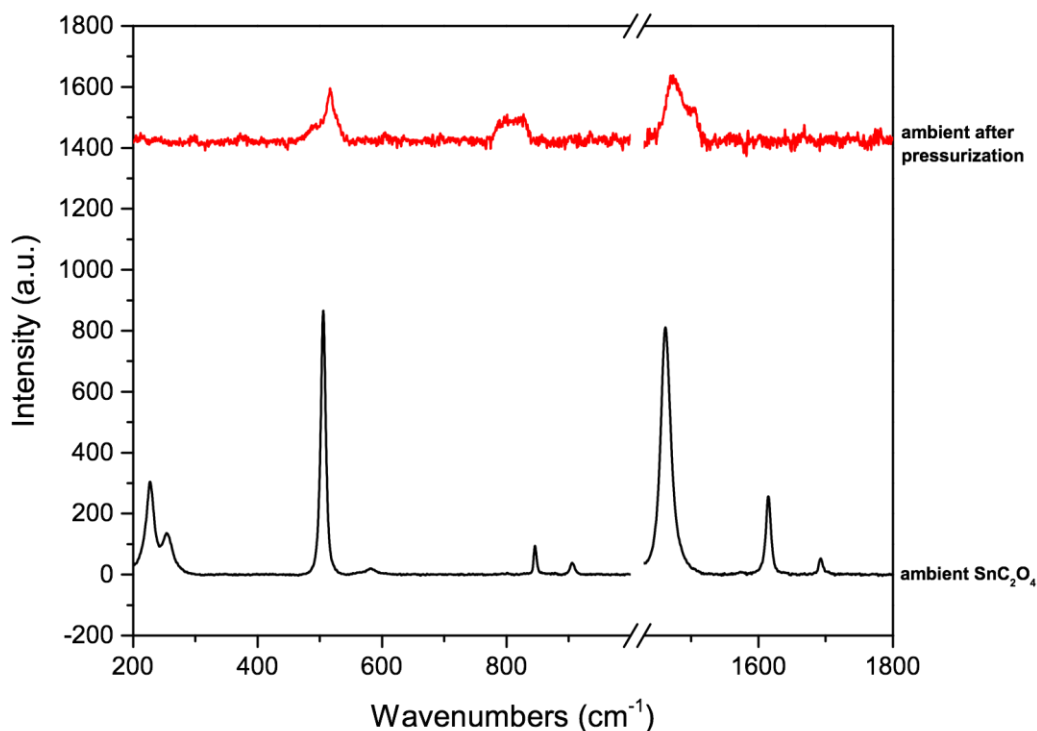


Fig. 4: Raman spectra at ambient conditions before being pressurized (bottom trace) and after pressure cycling to ambient demonstrating that pressurization caused irreversible changes. The photo below displays the irreversible nature of the chemical transitions from an earlier experiment where the sample was pressurized to 25 GPa and then recovered to ambient conditions. A small spherical ruby for pressure measurement is visible in the 7 O’Clock position near the edge of the gasket hole.

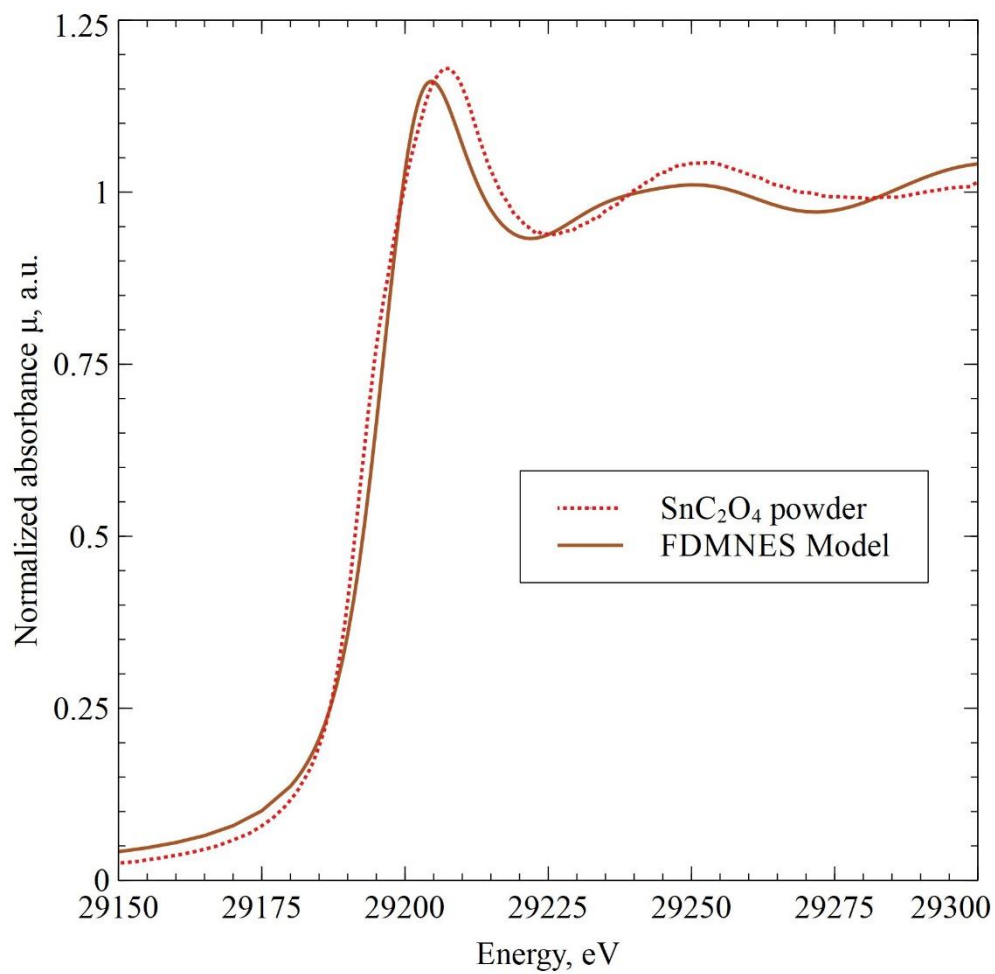


Fig 5: XAS spectrum of SnC₂O₄ powder and a calculated spectrum using the FDMNES model.

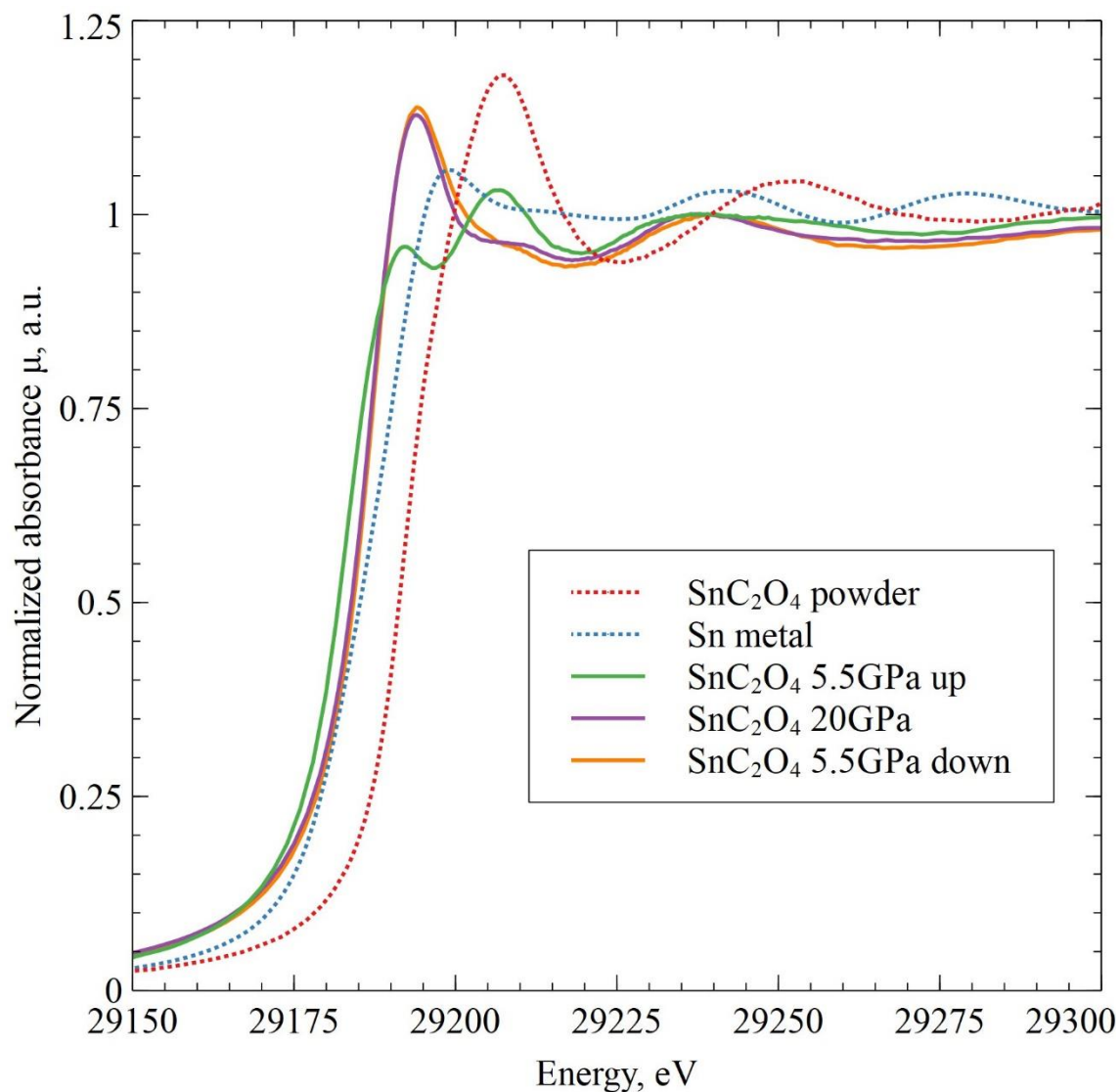


Fig. 6: XAS spectrum of stannous oxalate powder as a function of pressure including depressurization demonstrating the irreversible chemical reaction which occurred near 20 GPa involves an oxidation state change of the Sn²⁺ cation.

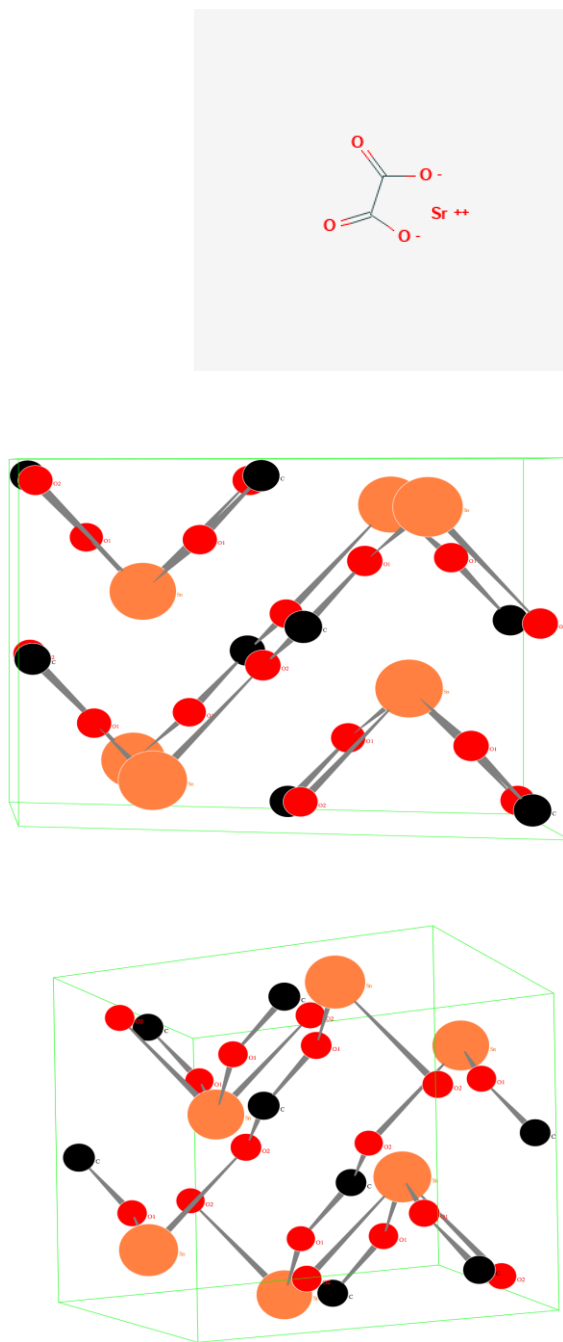


Fig. 7: Strontium oxalate unit cells in different orientations. The black atoms are carbon, oxygen is represented by the red atoms, and Sn atoms are the orange colored spheres.