

Investigating the Varying Behaviors of Tin Oxalate (SnC_2O_4) and Barium Oxalate (BaC_2O_4)
Under Extreme Conditions

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Abstract

Recent developments in the field of *useful hard x-ray induced chemistry* synthesized a novel strontium-based CO derived material under extreme conditions. In hopes of synthesizing this material in larger quantities and in less expensive costs, we report a high-pressure experiment on Tin Oxalate (SnC_2O_4) and Barium Oxalate (BaC_2O_4) subjected to extreme conditions without the use of hard x-rays. In the first experiment, Raman spectra of SnC_2O_4 were acquired up to 32 GPa. In the second experiment, Raman spectra of BaC_2O_4 were acquired up to 50 GPa. Our results demonstrated that both materials formed crystallized films after pressurization, which could indicate polymerization of a new material.

1. Introduction

X-ray damaged materials are a nuisance to many scientific fields. For example, through x-ray-related studies (e.g of viruses, DNA, proteins) are impaired by X-ray damage, which causes difficulty when analyzing data. For this reason, many scientific fields stay away from the damage and have tried to inhibit it all together. However, Dr. Pravica and his team are one of the few groups in the world that is currently studying x-ray damage as a means to drive novel chemistry. In our technique we use highly penetrating, highly ionizing, and highly energetic properties of hard x-rays (>7 Kev) to irradiate substances to initiate unusual yet controlled chemistry in isolated and or pressurized environments [1].

Through X-ray induced damage of materials under high pressure, simple diatomic molecules have been formed such as O_2 , Cl_2 , N_2 , F_2 [2-5]. Also, novel materials, including CsO_2 , OF_2 , possibly CsF_2 and CF_3 and most recently stable doped solid carbon monoxide (P-CO) [3, 6-8]. The oxalate anion ($\text{C}_2\text{O}_4^{2-}$) has the potential of synthesizing a carbon source substance. Since

previously studied strontium oxalate (SrC_2O_4) synthesized P-CO via hard x-ray induced chemistry, we suspected that similar results can occur within the oxalate salt family. Specifically, tin oxalate, barium oxalate, and lead oxalate.

Since we do not have access to an x-ray beam at UNLV, this investigation sought a more efficient way of synthesizing novel materials (e.g. P-CO) without the hard x-rays. By doing so, we could further develop methods of producing large quantities of these novel materials. In this article, we report on two high pressure studies of tin oxalate (SnC_2O_4) and barium oxalate (BaC_2O_4) using a Diamond Anvil Cell to generate high pressures.

2. Methods

Diamond Anvil Cell

A diamond anvil cell (DAC) is one of the most utilized instruments for conducting experiments for very high pressures. To operate it, we place a small amount of material on top of a flat face of a diamond. This diamond is held together in a cell. Then we obtain another diamond, of the same size, and push them together with the sample in between. Due to the fact that pressure is defined as force divided by area, $P=F/A$ mathematically, very large pressures can be generated between very small faces with relatively modest forces [9]. For the pressure studies, tin oxalate and barium oxalate were placed in a DAC to analyze the material's behavior at different pressures.

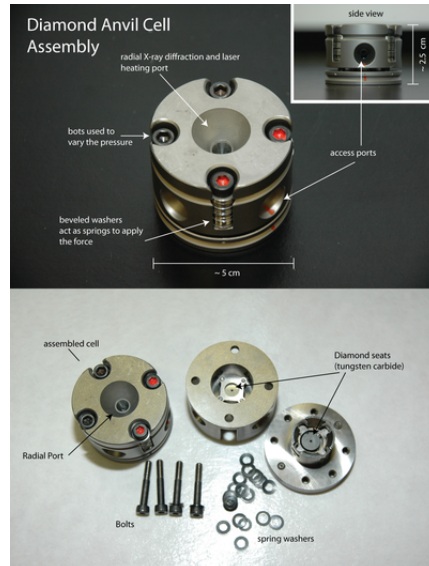


Fig 1 Symmetric Style DAC and its components

Raman Spectroscopy

Raman spectroscopy is one of the vibrational spectroscopic techniques that utilizes a laser to analyze the properties of the material. Properties such as stretching, bending, wagging, rocking, torsional, and rotational aspects of molecules in material can be investigated under this system.

The theory behind a Raman graph is based on the scattering of electrons within a system. There are three important types of scattering in the context of the Raman system. Elastic scattering occurs when an electron, after being excited by light, returns to its initial ground state. That is, it emits an electron equal in energy to that of the absorbed electron. This is called Rayleigh scattering. If the atom returns to an energy vibrational state higher than the ground state it is called Stokes scattering. If the atoms return to an energy vibrational state lower than the ground state it is called anti-Stokes scattering [10]. This behavior that occurs helps us understand various properties of the material being studied.

A Raman system uses a laser to focus on the sample. Then, filters in the system remove the elastic scattered light. Depending on the Stokes and anti-Stokes scattered light, we can determine the difference in energy levels between the final state of the atom to the initial. This difference is considered the Raman shift. With this difference we can determine the energy of phonons (very small particles) in a system, and this will give us the ability to understand the nature of the chemical bonds within the material we are studying. Therefore, we will be able to analyze how the bonds in SnC_2O_4 and BaC_2O_4 change under various extreme conditions via Raman Spectroscopy.

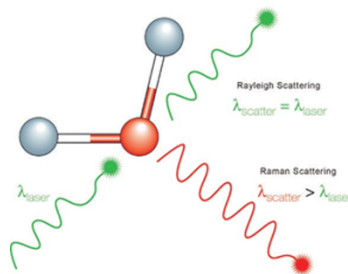


Fig 2 Rayleigh and Raman scattered light

Ruby Fluorescence

Ruby fluorescence is used for high pressure measurements. Measuring the position of the fluorescence lines of ruby allows us to determine the pressure of the sample. The fluorescence spectrum is composed by the R1 and R2 lines occurring respectively at about 694.25 nm and 692.7 nm at room pressure [9]. Photoexcitation of the R-lines luminescence is provided by a laser, in our case a Raman laser. A small ruby chip is placed in a diamond anvil cell along with the material being studied. As we increase the pressure the ruby fluorescence lines shift towards longer wavelengths. Pressure measurement is performed through different calibrations of the R1 line shift.

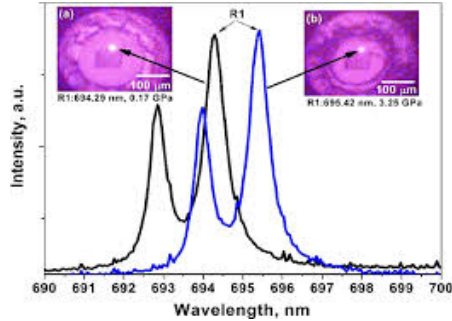


Fig 3 Intensity of ruby fluorescence vs. wavelength at two different pressures within a DAC

3. Experimental Technique

In the pressure and irradiation study a symmetric style Diamond anvil cell was utilized to pressurize the samples. Stainless steel gaskets were preindented to $\sim 50 \mu\text{m}$ initial thickness using $478 \mu\text{m}$ culet diameter, low fluorescence Raman-quality diamonds. Roughly $90 \mu\text{m}$ diameter holes were drilled into the gaskets via electric discharge machining to contain the samples. No pressure transmitting medium was used in these experiment

A Lasos® type solid state laser tuned to 532 nm and set at 100mW (15 mW at the samples) served as the excitation source. Rayleigh scattered light was removed using a Kaiser optics 532 nm holographic notch filter. Raman light was directed into a Horiba U1000® spectrometer, dispersing the scattered light, which was then detected via an ISA Instruments Spectrum One® detector. The Raman spectrometer instrumental resolution was $\sim 1 \text{cm}^{-1}$. Acquisitions typically required 30s to complete.

4. Results (High Pressure SnC_2O_4 study)

Fig 4 represents the Raman spectra of SnC_2O_4 compressed up to 31 GPa. At around 3.5 GPa, the peak corresponding at 508cm^{-1} splits from one peak to two. There is also a jump in the intensity of the 908cm^{-1} vibrational mode and continues until 20 GPa. As the pressure was

increased from 15 – 31 GPa the vibrational modes broadened significantly and lowered in intensity. The decompression spectra's of SnC_2O_4 vibrational modes (not shown here) were non-reversible. Thus, provides evidence that the material itself did not return to its original structure after pressurization.

As we increased the pressure the material changed from a white color, to light orange, to dark red. After and during depressurization the material did not return back to its original pure white color. However, it did stay at a dark golden color. The recovered material was highly fluorescent. Fig 5 shows the color changes of SnC_2O_4 .

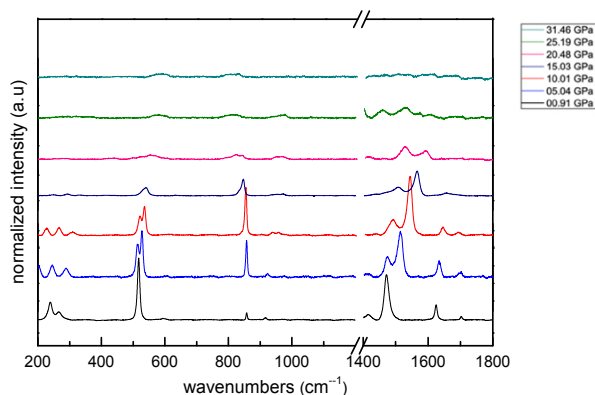


Fig 4. Raman spectra of SnC_2O_4 as a function of pressure in the wavenumber region of 200-2000 cm^{-1} . The results are similar to a previous study [11]. A new peak emerges on the left-hand shoulder of the 908 cm^{-1} stretching mode around 3.50 GPa (spectra not shown here). The peaks corresponding the SnO and C-C stretching mode, located at 570 cm^{-1} and 908 cm^{-1} respectively, suggest possible electron transfer with increase in pressure.

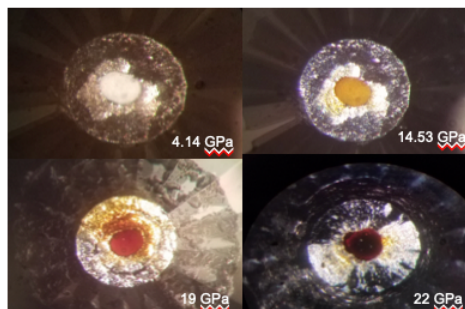


Fig 5. Pictorial representation of the color induced pressure effects of SnC_2O_4 .

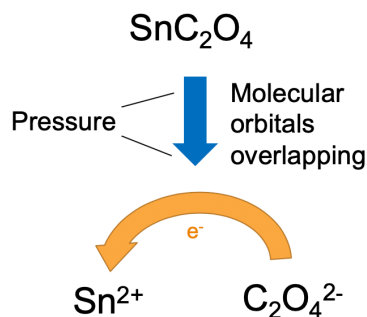


Fig 6. Schematic diagram of what we suspect is occurring with Tin Oxalate at higher pressures. That is, electrons being transferred between the molecular orbitals of the tin cation and the oxalate anion.

Raman	Assignment
1702 vw	<i>overtone of $\nu(C - C)$</i>
1617 m	$\nu(CO)$
1486 vw, 1463 vs	$\nu(CO)$
1408 w	$\nu(CO)$
908 vw, 847 vw	$\nu(C - C)$
570 vw	δ_{ring}
508 vs	$\nu(SnO) + \delta_{ring}$

Assignment of the Raman bands (in cm^{-1}) of SnC_2O_4

Fig 7 Assignments of Raman bands (in cm^{-1}) of SnC_2O_4 [12]

5. Results (High pressure BaC_2O_4 study)

Fig 8 shows the Raman spectra of Barium Oxalate at various pressure. At around 3.00 GPa, there is a new formation of peak at roughly 980 cm^{-1} . The peaks roughly at 470 cm^{-1} , 900 cm^{-1} , 1450 cm^{-1} , and including the newly formed peak each merge into a single peak at higher pressures. Lastly, the vibrational modes broaden significantly between 20 – 50 GPa. The decompression spectra's of BaC_2O_4 vibrational modes (not shown here) were non-reversible. This shows evidence that the material did not return back to its original configuration.

In this experimental study the material did not change color. However, the material became translucent around 10 GPa. Fig 9 shows this pressure induced effect. At the end of the experiment the material recovered was highly fluorescent.

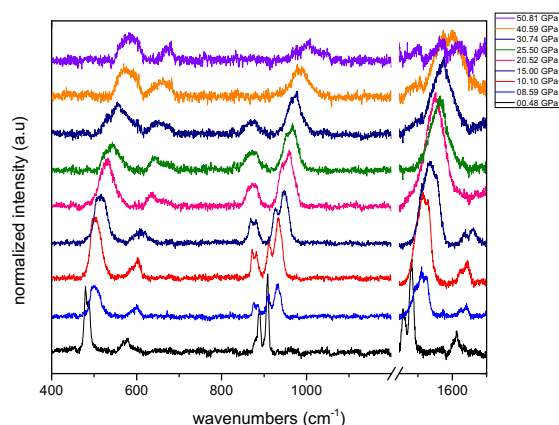


Fig 8. Raman spectra of BaC_2O_4 as a function of pressure in the wavenumber range of 400 cm^{-1} - 1600 cm^{-1} . New peak emerges around 3.00 GPa (spectra not shown here) indicating a possible phase transition similar to previously studied strontium oxalate. Above 20 GPa all Raman spectral modes broaden extensively.

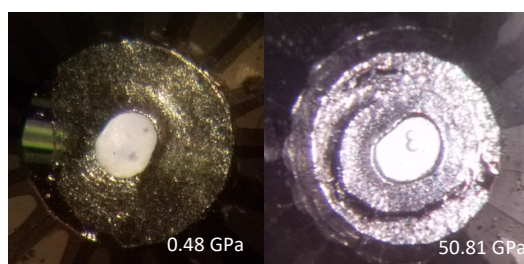


Fig 9. Pictorial representation of the translucent pressure induced effects of BaC_2O_4

6. Discussion

We suspect that between $5 - 20\text{ GPa}$, tin oxalate undergoes an electron transfer process during pressurization. This is likely the reason it changes color (a white to red color) under pressure. If this electron transfer is true, then molecular orbitals of the tin cation and oxalate anion are overlapping. The peaks corresponding the SnO and C-C stretching mode, located at 570 cm^{-1} and 908 cm^{-1} respectively, suggest the possible electron transfer with increase in pressure. As we increase the pressure notice that the SnO mode shifts to the right, while the C-C mode shifts toward the left. During this change we believe the d -shells are being accessed. Aside

from electron transfer the C-C bond, due to weakening, can possibly be forming a double bond. The sample was highly fluorescence after the pressure study indicating possible polymerization.

In the barium oxalate pressure study, the material did not change color. This may be due to the difference in the molecular orbitals (or lack thereof) of the material. Barium is much heavier than tin, making it more difficult to access the empty orbitals for electron transfer. F-shells of Barium, which are empty, can possibly be accessed at higher pressures (>50 GPa), and we suspect color changes could occur.

Barium might also be undergoing a phase transition similar to strontium oxalate. Fig 3 shows the Raman spectra of previously studied strontium oxalate (SrC_2O_4) as a function of pressure. Two structures (original-monoclinic and new-triclinic) of SrC_2O_4 coexist during pressurization at 3.5 GPa [7]. Peaks located at $\sim 880 \text{ cm}^{-1}$ shows this transition from 0-5 GPa. In the barium spectra's new peaks emerge from 0-5 GPa indicating a possible phase transition similar to strontium oxalate.

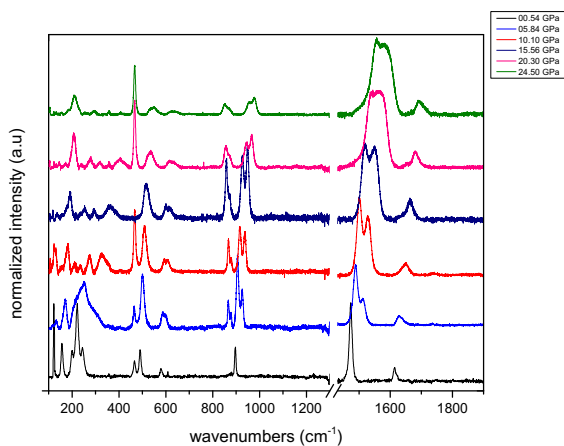


Fig 10 Raman spectra of previously studied strontium oxalate (SrC_2O_4) as a function of pressure. Two structures (original-monoclinic and new-triclinic) of SrC_2O_4 coexist during pressurization at 3.5 GPa [7]. Peaks located at $\sim 880 \text{ cm}^{-1}$ shows this transition from 0-5 GPa.

7. Conclusion

Two successful high pressure studies of SnC_2O_4 and BaC_2O_4 were accomplished. The SnC_2O_4 pressure study was conducted up to 31 GPa. From 5 to 20 GPa, we suspect that an electron transfer process is occurring. The material was non-reversible and did not return to its original color. The BaC_2O_4 pressure study was conducted up to 50 GPa and showed indication of a phase transition between 0-5 GPa. At the end of each experiment, both materials synthesized crystal like films. However, further studies, such as band gap measurements, will need to be conducted to understand what was synthesized.

Future investigation will also include studying lead oxalate at extreme conditions. Aside from the high-pressure experiments, we will continue working with oxalates in several other extreme conditions. Environments such as, low pressure-high temperature via large volume press or oven, irradiation studies via YAG laser, low temperature-high pressure study via cooling with liquid nitrogen, and future x-ray diffraction studies.

This field shows promise in creating new radiation hardened materials that have application and optical devices that can benefit humanity in many diverse ways. Although electron transfer has been studied extensively in the field of solid state, we are studying electron transfer with a purpose to synthesize novel and industrially-useful materials. P-CO is an energetic material indicating a possible source for military usages such as a stable rocket propellant, and has the capability of helping us understand how complex molecules have been formed across the universe. These two successful pressure studies have taken us a step closer in understanding the complexity behind possible synthesis, and with future investigations we will hopefully be able to harness these photochemical and pressure induced processes.

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