Investigating the Varying Behaviors of Magnesium, Tin, and Lead Oxalate Under High-Pressure

Kevin Ayala Pineda, Michael Pravica Phd, Petrika Cifligu

Department of Physics and Astronomy, University of Nevada Las Vegas (UNLV).

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 three high-pressure Diamond Anvil Cell investigations on Tin Oxalate (SnC2O4), Magnesium Oxalate (MgC2O4), and Lead Oxalate (PbC2O4) subjected to extreme conditions without the use of hard x-rays. MgC2O4 were acquired up to 25 GPa, with a possible phase transition at 2.4 Gpa. SnC2O4 was pressurized up to 31 GPa inducing irreversible changes in both the Raman spectra and its qualitative properties. Three phase transitions were observed at 2.6 GPa, 15 GPa, and 20 GPa. PbC2O4 was compressed up to 64 GPa, showing very similar behavior as in SnC2O4. Our results demonstrated that each material formed crystallized films after pressurization, which could indicate polymerization of new material(s).

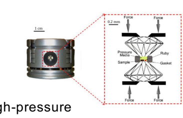
Introduction

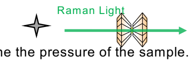
- X-ray damaged materials are a nuisance to many scientific fields. However, Dr. Pravica and his team welcome the x-ray damage.
- In the field of *useful hard x-ray induced chemistry,* we use the properties of hard x-rays (>7 Kev) to expose substances to irradiation so that unique and controlled chemistry takes place in isolated and or pressurized environments.
- Through x-ray induced damage of materials under high pressure, many materials have been synthesized such as Poly-CO
- Applications include: Solid fuel rocket propellent, electrical such as wide-bandgap semiconductors, optical second harmonic generator properties (can create powerful lasers), and this chemical process can help us better understanding on how complex molecules have been formed across our universe.

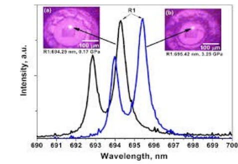
Methodology

- The goal is to investigate if new chemical routes can be harnessed without x-rays
- These high-pressure studies utilized Symmetric Diamond Anvil Cells
- Raman spectroscopy was utilized to analyze the properties of the material under high-pressure
- Ruby fluorescence was used for high-pressure measurements.
- Measuring the position of the fluorescence lines of ruby allows us to determine the pressure of the sample.

Diamond anvil cell



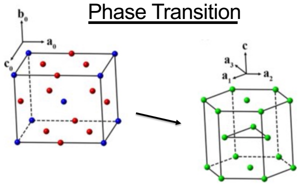




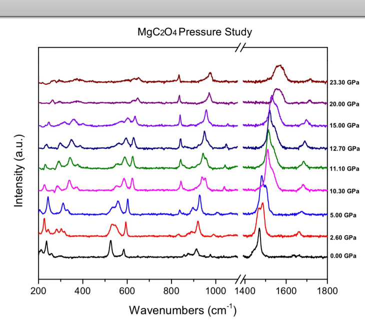
Intensity of ruby fluorescence vs. wavelength at two difference pressures within a DAC.

High pressure study of MgC_2O_4 by means of Raman spectroscopies

Phase Transition

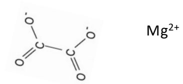


- Unit Cell is the Smallest portion of the Crystal Structure
- Adding Pressure Changes the unit cell structure



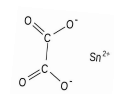
Raman spectra of MgC_2O_4 at selected pressures upon compression

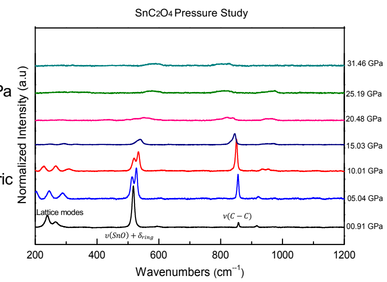
- Summary:
  - Compressed up to 23 Gpa
  - Potential Phase Transition 2.4 GPa: Monoclinic to Triclinic phases
  - New Peak near 550 cm^{-1} after 2.4 GPa
  - No Phase transition is apparent after 2.4 GPa: Peaks Broaden



High pressure study of SnC_2O_4 by means of Raman spectroscopies

- Summary:
  - Compressed up to 31 Gpa:
  - Phase transition from 2- 3 GPa and 15 – 20 GPa leads to irreversible chemistry
  - Pressure breaks the symmetric nature of the material

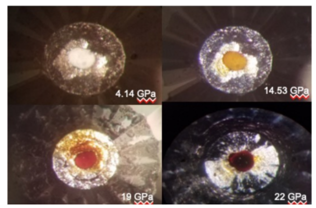




Raman spectra of SnC_2O_4 at selected pressures upon compression

Color Induced Pressure Effects

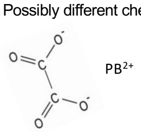
- SnC2O4 under various pressures changed various colors. Started at 10 GPa

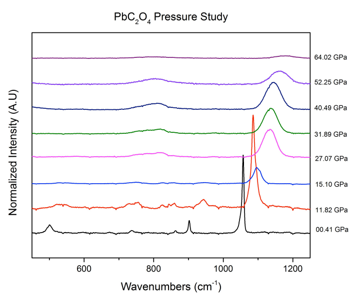


Pressure color induced effects of SnC_2O_4

High Pressure Study of PbC_2O_4 by means of Raman spectroscopies

- Summary:
  - Compressed up to 64 Gpa: Non-reversible
  - Electronic configuration is different compared to Tin
  - Possibly different chemistry

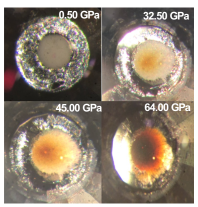




Raman spectra of PbC_2O_4 at selected pressures upon compression

Color Induced Pressure Effects

- PbC2O4 under various pressures changed various colors. Started at 32 GPa

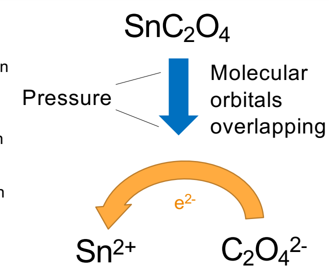


Pressure color induced effects of PbC_2O_4

Electron Transfer

Electron Transfer

- Tin Oxalate is undergoing an electron transfer during pressurization.
- Oxidation State changes when the electron density of the Oxalate anion overlaps with Tin cation
- Group Performed XAS studies on Sn k-edge to confirm this
- Showed oxidation state reduction



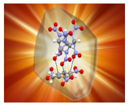
Schematic diagram of what we suspect is occurring with Tin Oxalate at higher pressures

Implications

- Applying pressure to watch chemistry take place in slow motion
- Initiating electron transfer without the use of Hard X-rays
- Accessing new routes of chemistry and therefore synthesis
- Controlled irreversible electron transfer at the quantum level.

Conclusions and Future Directions

- Three successful high-pressure studies of MgC2O4, SnC2O4, and PbC2O4 were accomplished to various pressures
- Each Material gave us deeper insights into the molecular behavior of the material at high pressure: Mg and Sn studies were published
- Future investigations will include low pressure-high temperature via large volume press, irradiation studies, and 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.



References

1. Evlyukhin, E., Kim, E., Goldberger, D., Cifligu, P., Schyck, S., Weck P., and Pravica, M. (2018). High-pressure-assisted X-ray-induced damage as a new route for chemical and structural synthesis, Physical Chemistry Chemical Physics, 20, 18949-18956.
2. Pravica, M., Sneed, D., White, M., & Wang, Y. (2014). Communication: A novel method for generating molecular mixtures at extreme conditions: The case of hydrogen and oxygen. *The Journal of Chemical Physics, 141*, 091101.
3. Pravica, M., White, M., & Wang, Y. (2015). A novel method for generating molecular mixtures at extreme conditions: The case of fluorine and oxygen. *APS SCCM Conference Proceedings.*
4. W Bassett, Diamond anvil cell, 50th birthday, High pressure Research, 2009, 29:2, 163-186
5. Wladimirsky, A., Palacios, D., D'Antonio, M., González-Baró, A., and E. Baran. (2010). Vibrational spectra of tin(II) oxalate, Spectrochima Acta 77, 334-335
6. Apollo, Manuel. (2015) X-ray Raman scattering on a carbonatitic glass. Master's thesis.

ACKNOWLEDGEMENT

I am thankful for the Pravica Lab for letting me work alongside them to help me with this project. I would like to thank Petrika Cifligu for patiently working alongside me in the lab setting and challenging me to think more like a scientist. And I would like to give special acknowledgement to Dr. Michael Pravica for his wisdom and guidance throughout the entire project thus far. I would also like to thank NASA, the NSF, and UNLV's Office of Undergraduate Research for allowing me to pursue this amazing opportunity.

This material is based upon work supported by NVSGC under Grant No. 80NSSC20M0043. This material is also supported by the National Science Foundation under Grant No. IIA-1301726.