Characterization of spinel oxides using lasers and X-rays

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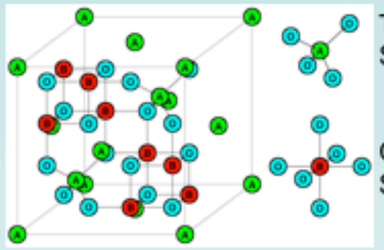
Motivation

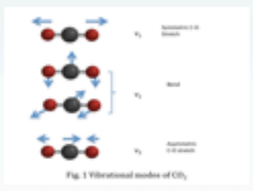
The spinel structure is a cubic metal oxide of the form AB_2O_4 with eight tetrahedral sites and sixteen octahedral sites occupied by the cations. Spinel is versatile and can incorporate many different cation species in its structure. There are over one hundred known spinel compounds. A common example is magnetite (Fe_3O_4). However, much is still unclear about the assignment of the vibrational spectra of many spinel compounds. More experimental data is needed to understand the vibrational modes and atomic spacing in many spinel oxides. The goal eventually is to acquire experimental data on families of spinels in hope of stimulating theoretical interest. These compounds can vary continuously in composition, potentially enabling the development of custom materials.

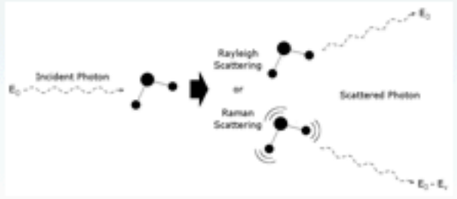
Spinel Structure Diagram



Raman Spectroscopy

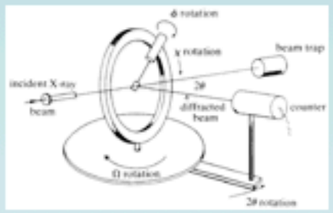
Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules. When a laser beam strikes a molecule, part of the light is scattered. Most of the scattered light has same wavelength as the laser beam. However, a small percentage of the light is inelastically scattered by the molecule. Study of the inelastically scattered light, can reveal a lot about the vibrational modes of the molecule. Typical application of Raman Spectroscopy is in structure determination, and qualitative analysis.



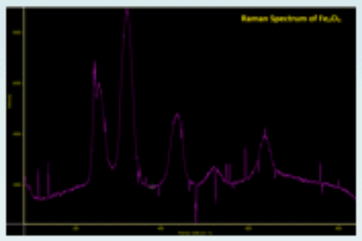


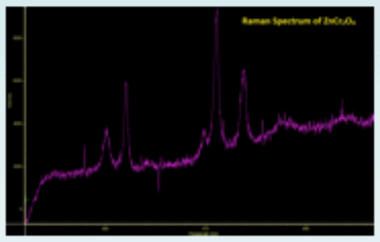
X-Ray Diffraction

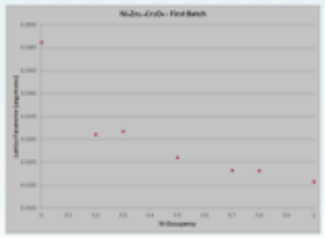
The technique of X-ray diffraction is the scattering of x-rays on contact with matter, resulting in change in radiation intensity, which is used for studying atomic structure. Two-dimension diffraction patterns shows rings of scattering peaks, which correspond to various spacing's in the crystal lattice. The position of these peaks can then be used to determine information about the atomic structure of the sample. X-ray scattering techniques and computed tomography offer a versatile, non-destructive method to reveal detailed information about the chemical composition, crystallographic and microstructure of all types of natural and manufactured materials.

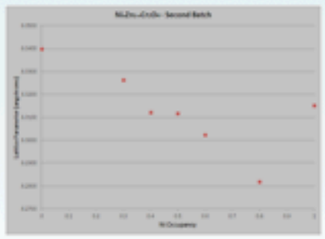


Results









The first batch was prepared with the minimum amount of water needed to dissolve the ingredients. The second batch had approximately 50% more water than the first batch, resulting in a longer cooking time. This may account for the noticeable difference in the lattice parameter as zinc is replaced with nickel.

Experiment

Solid solution spinel oxides of the form $Ni_xZn_{1-x}Cr_2O_4$ were synthesized via combustion reaction in intervals of 0.1 from x = 0 to x = 1. Eleven samples were synthesized using nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$, zinc nitrate $Zn(NO_3)_2{\cdot}6H_2O$, and chromium nitrate $Cr(NO_3)_3{\cdot}9H_2O$ and urea $CO(NH_2)_2$ as fuel. The ingredients were combined in stoichiometric mixture, combined with a small amount of water and placed in a box furnace, at approximately 375 C for 30-40 minutes depending on how much water was added.

For the first time, micro-Raman spectral studies were performed on this series to observe its vibrational spectrum. The micro-Raman microscope system consisted of a Lexel RamanIon krypton ion laser tuned to 647.1 nm as the excitation source. The laser light is sent to the entrance port of a Nikon MM-40 Measuring Microscope. The laser light is redirected by a beam splitter through the microscope and focused onto the sample. A 10X objective was used for all data acquisition. The light is then directed to a Horiba Jobin Yvon TRIAX 550 monochromator, and a Princeton instruments liquid nitrogen cooled Spec 10 CCD detector, which was used for photon counting and sending the information to the computer software.

Also for the first time, X-ray diffraction was performed on this series to observe changes in the atomic spacing, using powder XRD. A small amount of silicon, used as an internal standard, was mixed into the sample. Silicon gives very strong peaks in an XRD acquisition, making it easier to fit the peaks from the data. A Bruker D8 Advance XRD machine was used.

Conclusion

Our data from the XRD shows that the two different cooking methods noticeably affected the lattice parameter of the samples. When cooked with a minimal amount of water, the lattice parameter ranged from 8.3462 Å (pure zinc chromate) to 8.3158 Å (pure nickel chromate). When cooked with excess water the lattice parameter ranged from 8.3399 Å (pure zinc chromate) to 8.3152 Å (pure nickel chromate). These all disagree with literature values of the lattice parameter[2]. Neither batch yielded detectable raman spectra for $Ni_xZn_{1-x}Cr_2O_4$. We will continue the efforts along these lines.

Acknowledgements

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References

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