Aug 9th, 10:15 AM - 12:00 PM

Investigation of Raman active modes of MgxZn1-xCr2O4

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Investigation of Raman-Active Modes of $Mg_xZn_{1-x}Cr_2O_4$

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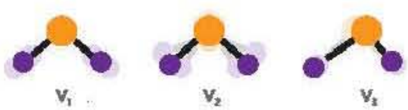
RAMAN SPECTROSCOPY

Raman spectroscopy is a spectroscopic technique for studying the vibrational modes of molecules. Typically, the object of study is illuminated with a laser beam. Light scattered by the sample is collected and examined. The vast majority of photons are scattered elastically, and have the same energy as the incident laser photons. However, a small fraction of the photons can give up some of their energy to cause vibrational excitation of the molecule. This results in a scattered photon with less energy than the incident photons. By comparing the energies of the incident and scattered photons, we can determine the vibrational behavior of molecules and crystals.

Elastic Scattering

Inelastic Scattering

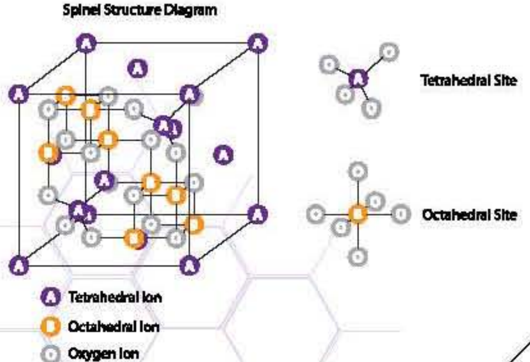
Vibrational Modes of Water



SPINEL STRUCTURE

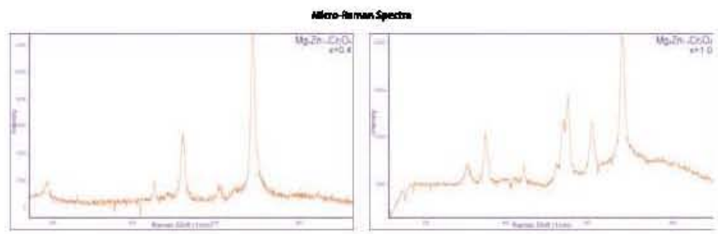
The spinel structure is a cubic close-packed mixed metal oxide of the form AB_2O_4 with eight tetrahedral sites and sixteen octahedral sites occupied by the cations. Spinel is versatile in that it can incorporate many different cation species in its structure. There are over one hundred known spinel compounds. A common example is magnetite (Fe_3O_4). Many spinels have industrial applications, such as lithium manganese oxide ($LiMn_2O_4$) for use as a cathode material in lithium ion batteries.

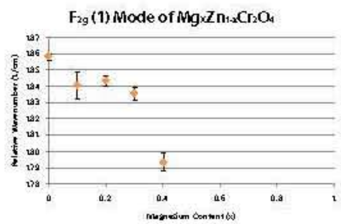
Spinel Structure Diagram

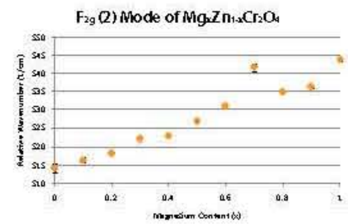


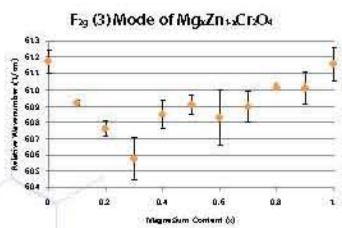
RESULTS

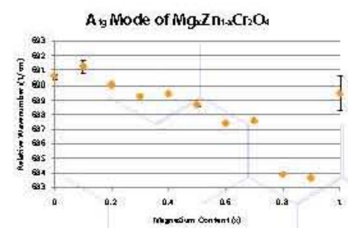
Micro-Raman Spectra











CONCLUSIONS

Our data shows that some of the observed Raman-active modes depend upon the magnesium content. Our $F_{2g}(1)$ mode disagrees with literature[2] in that we observed this mode at lower energies than reported in every data acquisition. Additionally, our $F_{2g}(1)$ mode was no longer visible at x>0.4. The $F_{2g}(2)$ mode showed a linear dependence upon magnesium content with the largest percent change of any other observed mode at 5.56%. The $F_{2g}(3)$ mode exhibited the most peculiar behavior in that the two end points were equivalent, though the solid solutions showed a variation in the mode's energy. This behavior requires more investigation. Lastly, the A_{1g} mode showed the most independent behavior with respect to magnesium content. However, the mode's energy decreased slightly through the series. This may be due to a small increase in the lattice parameter between zinc chromite (8.327Å)[3] and magnesium chromite(8.3344Å)[4].

MOTIVATION

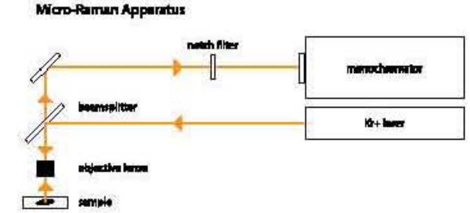
With the vibrational understanding relatively unknown for many spinel oxides, experimental data are needed to test theory and to gain a better understanding of the dependence of these modes on the tetrahedral and octahedral cations. This experimental data allows theorists to validate theory with experiment, which leads to a better understanding of this structure. Additionally, unpredicted material properties could be found that have use in industrial applications.

EXPERIMENT

Solid solution spinel oxides of the form $Mg_xZn_{1-x}Cr_2O_4$ were synthesized via combustion reaction in x=0.1 intervals from 0 to 1. Eleven samples were generated using magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$, zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$, and chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ with urea $CO(NH_2)_2$ as fuel. The stoichiometric composition of each sample was found based on the total oxidizing and reducing valencies of the oxidizer and fuel[1]. Resulting in a combined molar proportion of x:1-x:2:6.67 of magnesium nitrate, zinc nitrate, chromium nitrate and urea respectively. The reactions were performed in a box furnace, at approximately 350°C for 20-25 minutes.

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 was passed through a spatial filter containing a 10 μm pinhole, and then 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 50X 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. This setup can be seen below. Multiple data acquisitions were taken for all eleven samples in the series, in which we tracked the gradual shifts in the Raman peaks as the sample transitioned from zinc chromite (x=0), to magnesium chromite (x=1). This allowed us to gain information about the dependence of the lattice vibrations on the tetrahedral and octahedral cations. In all, four modes were tracked through the transition.

Micro-Raman Apparatus



ACKNOWLEDGEMENTS

Support from the REU program of the National Science Foundation under grant DMR-1005247 is gratefully acknowledged.

We would also like to acknowledge Daniel Sneed for his work in the laboratory.

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