Preliminary Work in
Detection of Defects in Minerals
Using X-Ray Diffraction

Kristen Woffinden
Brigham Young University- Idaho
April 2005

Advisors:
Dan Moore
David Oliphant
Jack Weyland

Physics Department Chair:
Brian Tonks
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Abstract

The scope of this project was to identify minerals and detect line and plane defects in the crystalline structure of minerals using X-ray diffraction techniques. Because of problems that had to be resolved for preliminary work to be completed, the task of identifying defects by peak broadening will be saved for future research. However, we were able to resolve some problems with the computer program, instrumentation, calibration and electronics of the system. We also annealed two samples, quartz and fluorite, and compared their spectra to the pre-annealed sample spectra.
I. Background

X-ray diffraction is used in a variety of applications in Physics and Geology. X-rays are especially useful when analyzing the crystal structure of minerals. They can be used to analyze the crystal structure of minerals because a mineral’s d-spacing is of the same magnitude as an X-ray (both are on the order of angstroms).

i. Bragg’s Law

W.L. Bragg, a pioneer in the field of diffraction studies, found that diffraction with X-rays in a crystal acts much like a reflection off of the atomic planes. His equation, known as Bragg’s Law, relates the incident X-ray’s wavelength with the d-spacing of a mineral’s atomic structure and the angle of diffraction. The equation is:

\[ N\lambda = 2 d \sin \theta \]

where \( \lambda \) is the incident X-ray’s wavelength, \( d \) is the atomic spacing between the crystal planes (known as the d-spacing), and \( \theta \) is the angle of the diffracted beam. \( N \) is an integer used to account for constructive interference between rays diffracted by different planes.

In our case, we used \( N = 1 \) as a standard practice.

For XRD studies, we rotate the angles of incidence so that we can see the diffraction for many different d-values. After the X-ray is diffracted, it travels with an
angle of $2\theta$ from the incident x-ray beam. “Because a crystal contains many differently spaced planes with atoms on them, diffraction occurs at many $2\theta$ angles. We must remember to divide $2\theta$ values by 2 before we use them with the Bragg Law to calculate d-values (Perkins, p.257-259).” Figure 1 shows how X-rays travel by diffraction.

**ii. About the X-Ray Diffractometer**

An x-ray diffractometer has three main parts that contribute to producing a spectrum of intensities of X-rays diffracted from a given sample at specific angles. These three parts are: an x-ray tube, a goniometer (which holds the sample and rotates the sample and detector), and a detector.

The Rigaku Miniflex X-Ray Diffractometer (XRD) we used for this project contained an evacuated x-ray tube with a monochromated wavelength of 1.5417 Å from a Cu target source.
The goniometer has a flat, circular plate that shows the angles of diffraction between the sample and X-ray beams. It rotates along with the detector so that the diffracted X-rays can be counted by the detector. Figure 1 shows the placement of parts and rotation within the XRD.

The detector used in our diffractometer is a gas ionization Geiger counter. Some of the gas in the tube is ionized by the diffracted X-rays and is attracted by a capacitor which measures the intensity (number of x-rays diffracted at that angle) as a current spike.

Figure 3: an x-ray tube

Figure 4: a gas ionization Geiger counter
iii.  Computer Program

During the summer of 2004, David Oliphant developed a computer program to integrate the goniometer and detector to run with a computer. This system was made in order to improve methods using the XRD. Using only the paper print-out and instruments provided with the XRD, it was difficult to analyze and compare spectra. Using the integrated computer program, specific values for intensity and angle are generated, there is less paper work to handle, it is no longer necessary for a person to wait and watch as the XRD takes data, and the process has been made easier all around. However, there are still a few difficulties that need to be handled in order for the program to be used in analyzing crystal structure. The issues encountered using this program and also some problems found with the XRD instrumentation are discussed later in more detail.
II. Work Performed

Because problems arose throughout the project that altered the scope of research at times, it is important to relate a sequence of events in order for the reader to understand certain aspects of this paper.

Initially, the scope of the project was to identify mineral samples and detect defects in mineral crystal structure by peak broadening analysis techniques. A sample was to be identified by its d-spacing according to Bragg’s Law. The sample could then be annealed and the peaks of the pre-annealed sample and the annealed sample could be compared to locate line or plane defects in the crystal structure. Line and plane defects can be detected using this procedure because they only affect the d-spacing of the crystal (Moore, 2005). One procedure to analyze peak broadening from crystal defects is called “crystallite size distribution”. This procedure is important in the field of Geology because “mineral particle size distributions may yield geological information about a mineral’s provenance, degree of metamorphism, degree of weathering, etc. (Snyder).” In brief, the procedure is to measure any degree of broadening in a peak that might have been caused by a crystal defect.

i. Preliminary Efforts

Preliminary work to the peak-broadening procedure showed discrepancies between the instrument reading and computer program that needed to be resolved so that the research would not be based on bad data. The preliminary work was to run a “known” sample on the XRD and identify it by its spectra. From the spectra of a sample, the angle of the most intense peaks can be found and substituted into Bragg’s law to obtain the mineral d-spacing. We used a database that showed d-spacings from the three most
prominent peaks of a spectra and the mineral name (webmineral.com). The database contained thousands of different minerals all listed in this way.

The first problem I encountered was calibrating the computer program to match with positions in the XRD. The previous procedure for calibrating the computer program was to run a known sample and calibrate the spectra by specifying the position of a prominent peak. The system had to be calibrated each time the computer was turned off and each time the goniometer position was changed by hand. Another problem with using the initial calibration technique was that the instrument had to run for a long time so that it had time to take high enough intensities for calibration. I followed this procedure until it became too time-consuming and we decided that it would be more efficient to add an internal standard to all of the unknown samples and calibrate spectra by a peak of the internal standard. The internal standard (I used fluorite) was added at about 5-10% by volume to the powdered sample.

After building confidence in my ability to identify known mineral samples by their spectra, I tried to identify some unknown samples. This produced another problem. If my data was as little as one one-thousandth different from the true value for that mineral, I could not identify the mineral. If there were any flaws in calibration, they produced a drastic affect on all of the other parameters in Bragg’s Law, including the d-spacing by which the mineral is identified. I found that I could not confidently identify any of the unknown samples because of this problem.

ii. Gear Accuracy

While running samples and analyzing the spectra, we noticed that the goniometer was not moving consistently (with the computer program). At some intervals it would slow down
and when the sample had finished running, the computer system disagreed with the goniometer position. So, some of the readings and printouts were not physically true. It was also difficult to obtain spectra with reasonably high intensities using the goniometer settings we had set (2°/min gear). We noticed that when a sample was running on this gear, the computer program did not read the correct positions (compared to the actual goniometer position). Some electrical problem caused the goniometer to slow down at certain intervals and not reach the desired end position as entered in the computer program. We also noticed that running the goniometer backward (i.e. from 80° to 10°) caused part of the problem. We thought that perhaps the gears moving the goniometer needed cleaning or that some of the teeth in the gear had run down, but the instrument parts had recently been cleaned and there was no sign of dramatic wear on the gears. We found that moving the goniometer by hand makes the process easier and decreases the chances of receiving bad data. Another thing that helped was using a different gear. We switched the ½ °/minute gear (which is a smaller gear and moves more slowly). We found that, using this gear, the goniometer ended very near the value that the computer system was showing. With the ½ angles, the computer program ended only about 1° to 3° off compared with 10° to 40° off with the N°/min. gear we had used initially.

We found that some samples (fluorite specifically), showed discrepancies in relative intensities between the two most intense peaks. Our biggest concern was whether the problem was physical or electrical. We ran samples and took spectra with both the computer program and the paper print-out contained within the XRD instrument. We deduced that it was not a physical problem after we ran the spectra with the paper print-out and compared it to the spectra on the computer program. When we compared the
two, the known values in the spectra matched well with the paper print-out. This helped us to understand that the problem was electrical and not physical. However, it raised concerns about the geometry of the system. We do not know why the other gears showed bad data, only that results were much improved by using the ½°/min. gear.

**iii. Geometry**

At some angles \(2\theta\), the area being struck by incident X-rays is large enough that the incident x-rays are spread thin over a large area and some of the diffracted X-rays are missed by the detector because its slit is too small to see them. When we noticed that the intensity of the K-\(\alpha\) peak was only about 1/3 the value it should be, we thought this might be the problem. However, this could not be because the position of the K-\(\alpha\) peak is more straight-on than the K-\(\beta\) peak, which measures a relatively high intensity.

As mentioned earlier, the fluorite spectra magnified a problem with the computer system. We noticed that the peaks in fluorite were always in the right position but that the second (K-\(\alpha\)) peak (at 47.06°) which was supposed to have a relative intensity of 100 counts compared to 94 counts at the K-\(\beta\) peak (28.30°) was reading only as about 1/3 of its size on the computer system, whereas the paper print-out showed the correct relative intensity between the K-\(\alpha\) and K-\(\beta\) peaks.
We thought that it might be a problem with geometry but deduced that it was not because if that was the case, the problem would be manifest in smaller angles, instead of the high angles at which relative intensities were low. We also ran a paper print-out comparison and found that the problem is not physical because intensities and positions are correct with the XRD print-out.

We tested to see if there was a difference between running a spectrum before allowing the X-rays to warm up versus running the X-rays all day and then obtaining a spectrum. After multiple trials we found that this is not a factor.

iv. Binary Code

We found unusual peaks in some sample spectra. It looked like the general shape of the peak was correct but in some areas the intensity dropped below the general trend in a way that suggested another non-physical problem. We suspected there might be a problem in the code. Brother Oliphant graphed the data points from the unusual peaks on Excel and looked at their shape. He entered the binary code associated with each data point on the graph and showed that with points that didn’t follow the “true” peak shape, the binary code was just incorrect. For those data points that seemed to distort the peak shape, he changed the binary code and found a graph of the true peak.
An electrical part of the detector that measures the intensity of diffracted X-rays at each angle has internal circuits that measures counts as “on” or “off”. If the voltage registered from an X-ray is 2 V or less, then no count is registered. When there is a potential difference of 3 V or more, then one count is measured. However, taking the measurement itself draws a current in the system which can drop the voltage reading, thus causing the measurement to read out as “no count” instead of registering a count. This is an electrical problem that can be resolved by purchasing higher quality electronics that can handle the current draw without changing the voltage.
III. Results

i. Annealing Samples

As a preliminary test to see if changes could be detected by annealing, we used an oven to anneal two samples. Samples of quartz (SiO2) and Fluorite (CaF2) were annealed at 300° Celsius (572° Fahrenheit) for 24 hours. The oven was monitored between the hours of 4:30 pm to 10:00 pm (start time was about 4:30 pm when oven started heating from room temperature). During the hours of 10:00 pm (4/5/05) and 8:00 am (4/6/05), the oven may have had various temperatures as it went unmonitored. When the oven was checked at 8:00am, its temperature read 400° C and was decreased and monitored from that time on. Overall, with temperature decreasing to 200° C after 8:00 am to cool the oven, the temperature varied from 200° C (for a short amount of time) to 400° C. We were concerned that some physical change might occur in the fluorite sample because of the high temperature but found that, when removed from the oven, the samples looked the same as before the anneal.

From here, we re-plated the samples and ran them on the XRD. Then we plotted the unannealed sample spectra against the annealed sample spectra for both samples in Excel. The graph shows that annealing the...
fluorite sample had little affect on the position of the peaks. The peaks in the fluorite sample were shifted a little bit to the left in the annealed sample (as shown in the graph) compared to the original. This shift may be because of calibration and not from a physical change. In order to find differences in defects, it will be important in future research to compare the peak shape in the spectra.

We graphed the annealed and pre-annealed samples of quartz and noticed a totally different spectra. We suspected that this was due to a phase changed and found that a phase change occurs in quartz around 580°C. From this we concluded that quartz will not be a good sample to use for measuring peak broadening defects. Following is a chart of the phase changes of quartz with temperature and pressure.
IV. Conclusion

i. Discussion of Results

Time spent resolving calibration problems prevented further work on detecting defects. However, some work was started for analyzing comparing peaks before and after an annealing process. Now that many issues have been identified and resolved, the XRD and integrated computer program are now better prepared for further use.

ii. Suggestions for Further Work:

1. Fit fluorite spectra to a curve and find out why the K-alpha peak has 1/3 intensity it should have.
2. Use geometry to find out how much the small slit size of the detector eliminates some of the diffracted x-rays so that intensity measurements might be off.
3. Another thing that will help is for the wiring for the computer system to be soldered so that no movement will affect it.
4. Another solution to the system will be to replace the current calibration system with an optical calibration system that will measure exactly where the goniometer is and that output will be shown in the computer system.
5. In further research it will be interesting to measure the degree of change that occurred in the defects of the crystal structure being taken away by the annealing process. This can be done by fitting the curves to a Lorenzian and comparing the full width at half max of the two curves. One equation that can be used to do this is:

   \[ y(E) = A(0) \cdot \frac{(\Gamma/2)(\pi)}{(E-E(0))^2 + (\Gamma/2)^2} \]

   where \( \Gamma \) is equal to the full width of the peak at half of its maximum intensity.
Appendix

Safety Measures

1. Don’t exceed 100° (2θ) because wiring may break.
2. Open cooling radiator to avoid overheating.
3. Keep cabinet door (where cooler is located) open to avoid overheating.
4. Unplug pump and power supply when not in use.
5. Check alarm lights whenever you turn on the XRD.
6. Any operator should also read and understand the “instruction Manual for X-Ray Diffractometer ‘Miniflex’ Cat. No 2005 Manual No ME200CY” and read through the X-Ray Safety manual and complete the test in it before using the XRD.

i. Procedure for Sample Preparation

Materials: sample plate and glass backing plate, pliers, tape, mineral, mortar and pestle, acetone, small spatula and pitre dish.

1. Prepare a sample plate by taping a glass plate to the back of it.
2. Break smaller pieces off of the mineral into the mortar. If pieces are too large, they will be difficult to crush.
3. Add enough acetone to cover the mineral in the mortar.
   a. The acetone is used to keep pieces from flying out of the mortar during the crushing process and to adhere the powder to the sample plate. Methyl Alcohol or some other highly volatile liquid may be used in place of acetone, but acetone works best. However, if using acetone, be careful not
to spill liquid much on sample plate because acetone will eat through the

tape you used to keep the glass plate and sample plate together.

4. Crush the mineral to a fine powder.

5. Add at least 5% by volume of a standard (I used fluorite) to the mixture.

6. Allow the powdered mineral to dry to a paste. You may place it under a fume

   hood to dry more quickly.

7. Use a spatula to scoop the paste onto a sample plate.

8. Put any excess material in a labeled pitre dish or small glass bottle.

**ii. Operating Procedure for XRD**

1. Load the program on your computer:
   
   a. My Computer → Local Drive (C) → Program Files→ XRD → XRD.exe

2. Choose a known sample to calibrate the sample peaks.

3. Turn switchbox to XRD mode.

4. Turn on the main power to the water pump and leave the cabinet door open so it

   doesn’t get too hot.

5. Turn on power to XRD (on front panel)

6. Make sure alarm lights are off

7. Make sure HV power supply is on

8. Turn ratemeter switch to “count” and rotate the knob to “100”

9. Insert the sample face-forward.

10. Close lid and turn the latch to close.

11. Turn on x-rays.
12. Enter current position (2*theta) on computer program and click “set”.
13. Choose a start 2*theta.
14. Choose an end 2*theta.
15. Choose a delta theta.
16. Choose time at each theta.
17. Check run time to make sure it is reasonable (this time can be increased or decreased by adjusting the delta theta and time at each theta).
18. Press “Go” to start running the program.
19. Calibrate the instrument
   a. Choose a start and end theta that will include known peaks
   b. Run the sample (click “Go”).
   c. Check to make sure that the knobs and tables in the XRD are moving.
   d. Move the cursor to the most prominent peak and enter the correct value for the known peak. (The box says: “set cursor value”). Click”set”.
   e. The system is now calibrated and an unknown sample can be run.
20. Turn off x-rays.
21. Open the lid, remove the calibration sample and replace it with your unknown sample.
22. Repeat process for the unknown sample.
23. Enter any notes needed to describe the sample.
References

1. Snyder, et. Al. “Crystallite size, size distribution and
   March, 2005.


   Ray.shtml.