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Materials Characterization Using X-Ray Spectroscopy Technique

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Abstract

Scientists have been using X-ray spectroscopy to learn about atomic structures since around 1910, shortly after the discovery of X-rays. The purpose of this research is to investigate the workings of a new X-ray apparatus to perform X-ray spectroscopy experiments and teach other students how to use the equipment properly. In this research, X-rays are generated using molybdenum, and detected using different means such as a fluorescent screen, plate capacitor, and Geiger-Müller Detector. The X-rays are then used to determine the lattice plane spacing in NaCl, LiF, and Si crystals using Bragg diffraction. Further ongoing research involves determining the identity of unknown crystalline substances by determining the atomic structure of the crystals using the X-ray apparatus and Bragg diffraction.

Background

Wilhelm Conrad Röntgen discovered a new form of radiation when he was working on cathode ray tubes and he noticed a barium screen sitting nearby began to fluoresce even though there were other objects between the screen and the tube. He

immediately recognized that it was an unknown form of radiation that was able to pass through the objects[3,5]. X-rays are now used in many applications such as medicine, crystallography, microscope analysis, and fluorescence[3].

X-rays are a form of electromagnetic radiation with wavelengths around 10^{-10} meters, or between 10 and 0.01 nm, which is comparable to the spacing between atomic planes in crystals. They fall between gamma rays and ultraviolet rays on the electromagnetic spectrum[1,2,3,5]. X-rays are produced by accelerating electrons through a potential difference in order to collide with a metallic source. The collision can knock out an electron from the inner shell of an atom in the source, and when a higher energy electron fills the space, an X-ray photon is produced.[2]

A useful application of X-rays is X-ray crystallography. Since X-rays have wavelengths comparable to lattice spacing of atoms, they can be used to determine the spacing between planes of atoms in regular crystals using a method called Bragg Diffraction. Bragg diffraction was first proposed in 1913 by William Lawrence Bragg and William Henry Bragg when they discovered that crystalline solids produced reflection patterns of X-rays with peaks at certain angles of incidence.[3,5] Solids with very regular atomic structures will cause interference patterns when electromagnetic waves are reflected off of their lattice planes. Since X-rays have wavelengths comparable to the spacing of the planes, constructive interference of the reflected waves will occur if the extra distance one wave has to cover to reflect off of a lower plane equals an integer multiple of the wavelength of the wave. When this occurs the emerging waves are in phase and constructive interference causes a peak in the intensity of the wave. This follows the equation known as Bragg's Law:

$$n\lambda = 2d\sin\theta \ldots(1)$$

Where n is the integer multiple of the wavelength of the incident rays, λ is the wavelength of incident rays, d is the distance between atomic planes, and θ is angle of incidence and reflection as shown in Fig. 1.

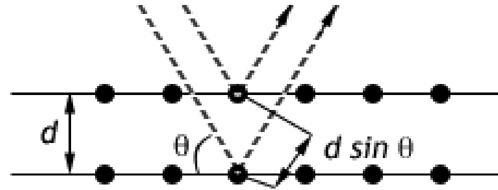

Figure 1. Diagram of Bragg Diffraction. If the extra distance the wave reflecting off of the lower plane equals an integer multiple of wavelengths, the emerging reflected waves will be in phase. This causes constructive interference and a very sharp peak in the intensity of the X-rays.[1,3]

Equation (1) can be used along with another equation involving the Miller indices of the reflected plane to find the lattice constant, a, of the material. The lattice constant for a cubic structure is the length of the sides of one unit cell. The formula for this second equation depends on the structure of the crystal. Cubic structured crystals are the only type investigated throughout this experiment and the relation for cubic structures is as follows:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \ldots(2)$$

Where *a* is the lattice constant, *d* is the distance between the planes, and *h, k* & *l* are the Miller indices of the reflection plane. A couple of examples of planes associated with different Miller indices (hkl) can be seen below along with the method used to determine the indices.[1,2]

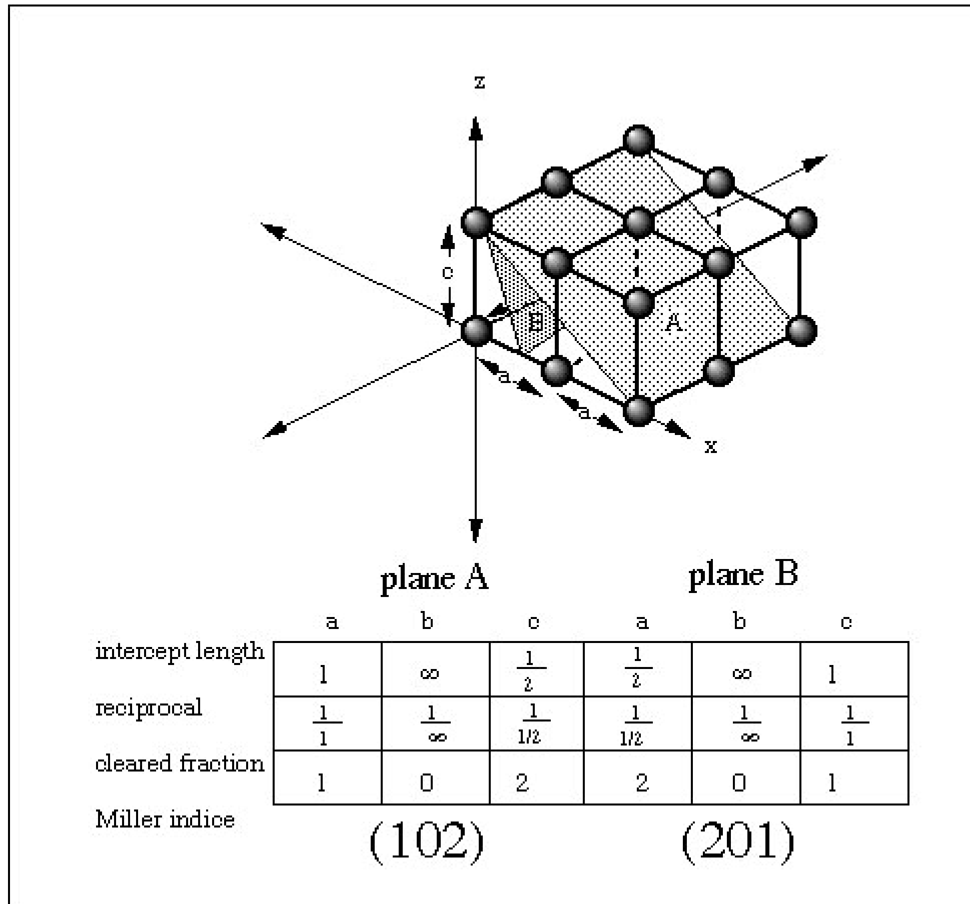

Figure 2: Example of planes associated with Miller indices (102) and (201). The indices are determined by finding the intercepts of the plane with each of the axis, taking the reciprocal of these intercepts, and reducing them to the lowest ratio.[7]

Different types of crystal structures only allow reflections off of certain planes. A table of the selection rules for the Miller indices of these planes can be seen in Table 1 below.

Table 1: Allowed and forbidden Miller indices for Bragg diffraction of different structures.[2]

Structure	Example Compounds	Allowed Reflections	Forbidden Reflections
Simple Cubic	Simple Cubic	Any h,k,l	None
Body-Centered Cubic	Body-Centered Cubic	h+k+l even	h+k+l odd
Face-Centered Cubic	NaCl, KCl, Zinc Blende	h,k,l all odd or all even	h,k,l mixed odd or even
Hexagonal	Hexagonal close packed	l even, $h+2k \neq 3n$	$h + 2k = 3n$ for odd l

When the locations of the peaks for a given crystal have been determined, the above equations and selection rules are used to determine the lattice constant.

Experiment

The X-ray spectrometer creates X-rays by accelerating electrons into a molybdenum source. The rays produced have a wavelength of $\lambda_\alpha = 71.08$ pm, $\lambda_\beta=63.09$ pm.[6] The two different wavelengths are caused by the different energy levels of the electrons removed from the inner shells of the molybdenum source. The intensity of the X-rays produced can be controlled by changing the voltage (0-35 kV) and current (0-1mA) applied. It has lead glass doors and windows for easy and safe viewing, with safety locks which will turn off the high voltage when the door is opened. The machine is fully computer interfaced. The voltage and current can be controlled from a PC as well as

the movement of the goniometer, while keeping track of the intensity reading from a Geiger-Müller detector.[6] Picture of X-ray spectrometer used can be seen below in Fig. 3.

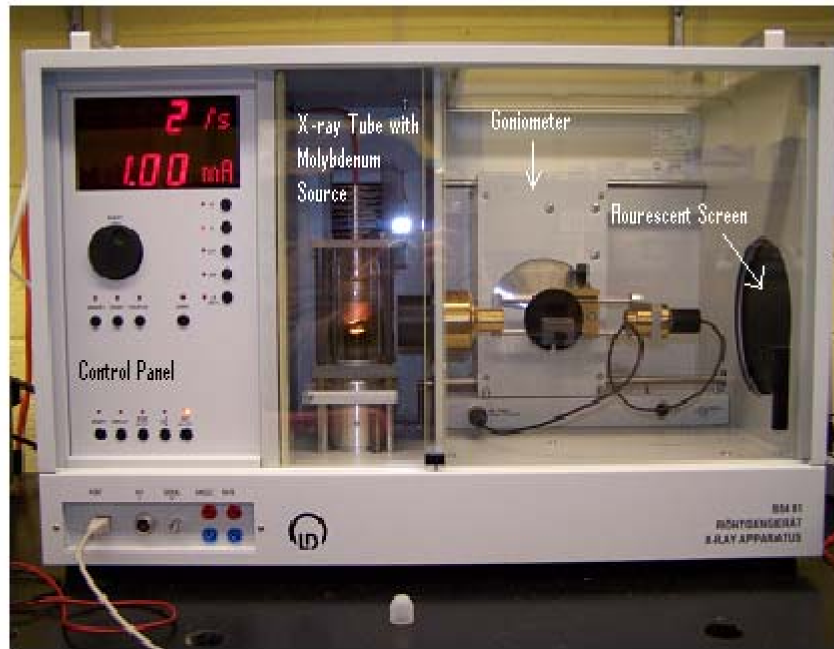

Figure 3: Picture of X-ray spectrometer used to perform diffraction studies of various crystals.

Simple experiments were performed first to detect X-rays and ensure the proper function of the apparatus. The first experiment involved using a fluorescent screen to detect X-rays and observe the change in the intensity of the rays as the source voltage and current varied. A television remote control was placed close to the fluorescent screen between the source and the screen. Pictures were taken of the fluorescent screen with the spectrometer voltage set at 15, 20, 25, 30, & 35 kV, and with the current set at 1mA. Pictures were also taken every 0.2 mA, with the voltage set at 35 kV. Examples of these pictures taken can be seen in Fig. 4.

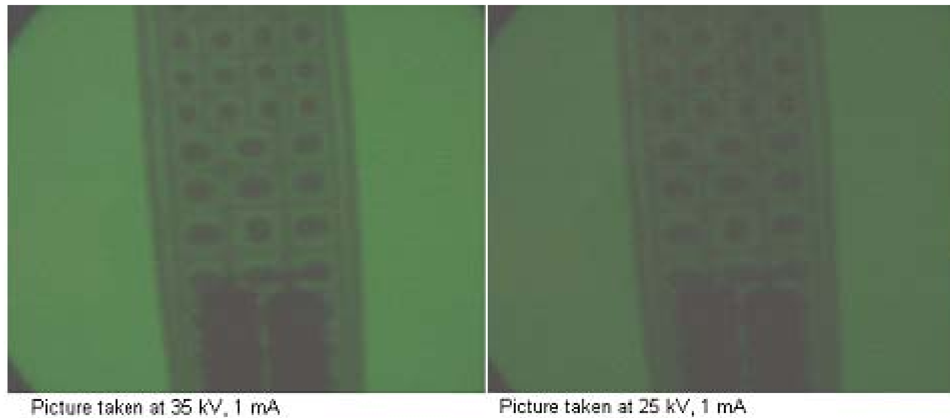

Figure 4: Pictures of fluorescent screen showing the variation in the intensity of the X-rays as the source voltage is changed. These were taken with the source voltage set at 35 kV and 25 kV with the current set at 1mA.

The next experiment performed involved detecting X-rays using a plate capacitor. Ions (atoms or molecules having a net positive or negative charge) are produced when X-rays strike gas molecules. These charged ions are then accelerated by the electric field created between the plates of the capacitor. This flow of charges produces a current that is detected by the plate capacitor and circuit.[6] For this experiment we used a digital multimeter to read the changes in the intensity of voltage produced by the ions as we changed the potential difference and current associated with the production of the X-rays. A picture of the setup can be seen below in Figure 5.

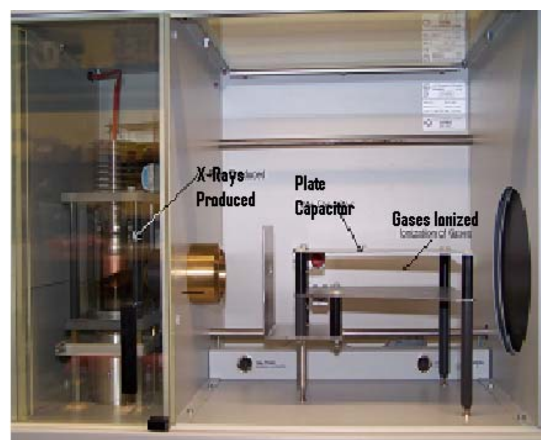

Figure 5: Picture of setup of plate capacitor experiment to detect X-rays by ionization of gases.

Once it was determined the apparatus was in proper function, crystallography experiments were performed to determine the lattice spacing of several crystals. Bragg diffraction experiments were performed on four samples: NaCl, LiF, Si, and one unknown sample. All of the samples were solid crystals. A Geiger-Müller detector was used to detect the intensity of the X-rays. Detectors of this type consist of a gas filled metal cylinder with a thin wire along its axis. When the detector is in the presence of radiation the gas molecules become ionized and the circuit between the metal cylinder and thin wire becomes complete allowing current to flow. This flow of current allows detector to count the number of ionized particles which is directly proportional to intensity of the X-rays.[6] This gives a reading of counts/second when used to detect the intensity of the X-rays. The computer interfaced goniometer was used to move the detector and target (crystal) coupled in a ratio of 2:1, but it can be used to move each separately. The X-ray apparatus software was used to record counts per sec every 0.1°. The software also controlled the change in angle per time step for the goniometer, and also kept the voltage of the X-ray source set at 35kV and 1mA. Data was taken using the same procedure for each of the crystals. The lattice constant for each of these materials with the exception of the unknown crystal was determined using equations (1) & (2), and the Miller indices selection rules.

Results

The NaCl crystal, which has a cubic structure, showed an atomic spacing of d= 0.2851 nm, which for cubic crystals corresponds to ½ the lattice constant, a, for a cubic crystal structure. The determined value for a=0.5702 nm, while the actual value for a=0.5640 nm[6]; Error: 1.10%. The LiF crystal has a cubic structure and showed an atomic lattice spacing of a= 0.4022 nm, which is very close to the known value, a= 0.4027nm[6] with an error of 0.124%. The results for the Si crystal, which is a known cubic crystal showed an atomic lattice spacing a=0.6212 nm. This gives an error of 9.7% when compared to the actual value of 0.566 nm.[4] The results for the atomic spacing of the unknown crystal will be determined in future research involving the use of Debye-Sherrer powder diffraction methods. The graphs of the intensity peaks can be seen below for each of the crystals in Figures 6-9. Each large peak has a smaller peak associated with it because of the two different wavelengths produced by the source. The α rays are the most common and are associated with the highest peak of each pair. The numbers above the peaks are the Miller indices of the planes reflected. For NaCl, LiF, and Si crystals, only the (200) planes were showing reflection peaks, with the different peaks associated with different integer multiples (n) of the wavelengths.

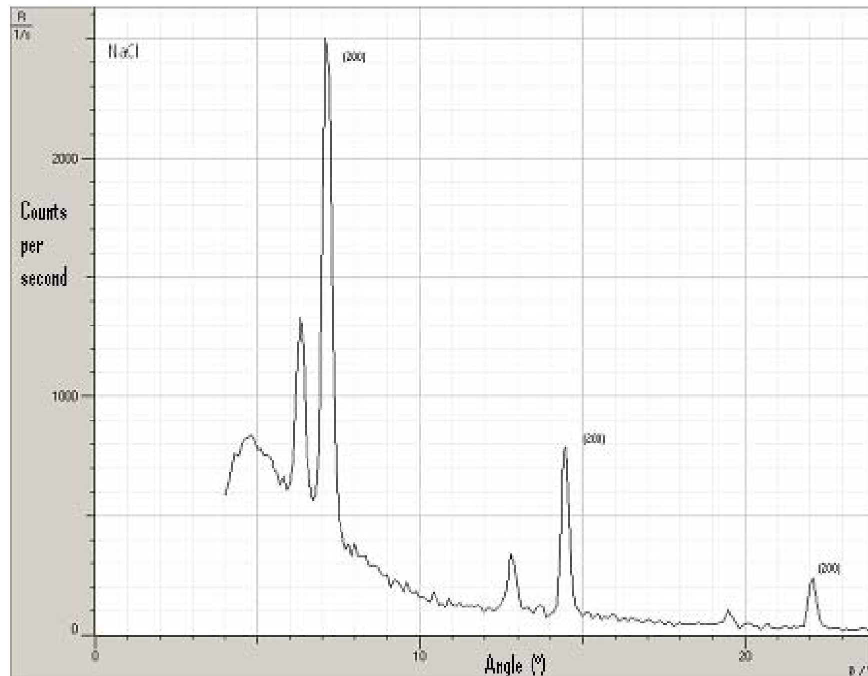

Figure 6: Diffraction spectrum of X-rays in Bragg reflection of a NaCl crystal. The graph shows up to the third order of diffraction (n=3).

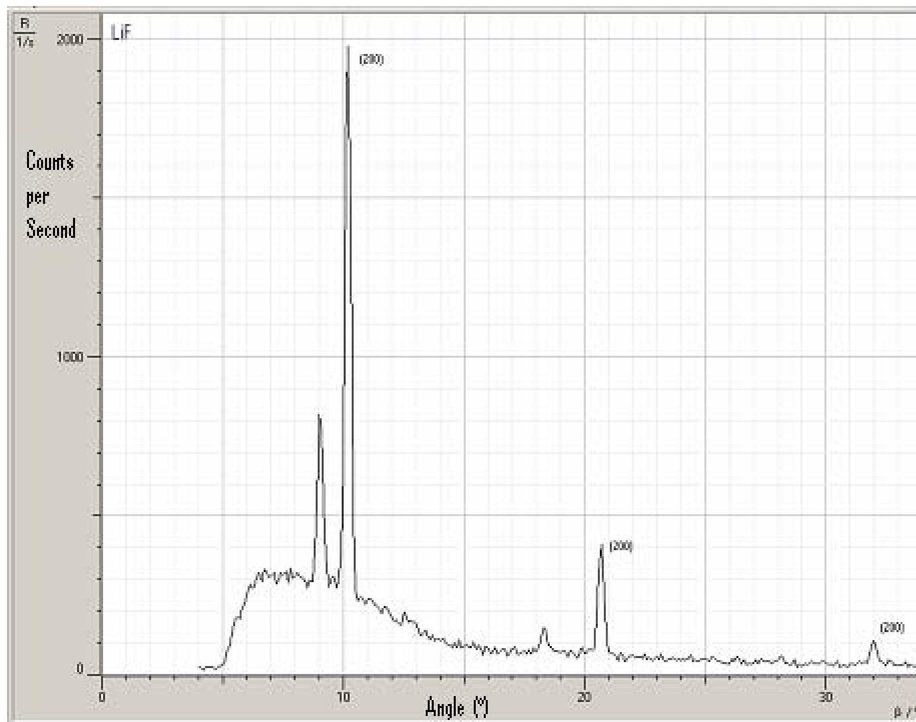

Figure 7: Diffraction spectrum of X-rays in Bragg reflection of a LiF crystal. The graph shows up to the third order of diffraction (n=3).

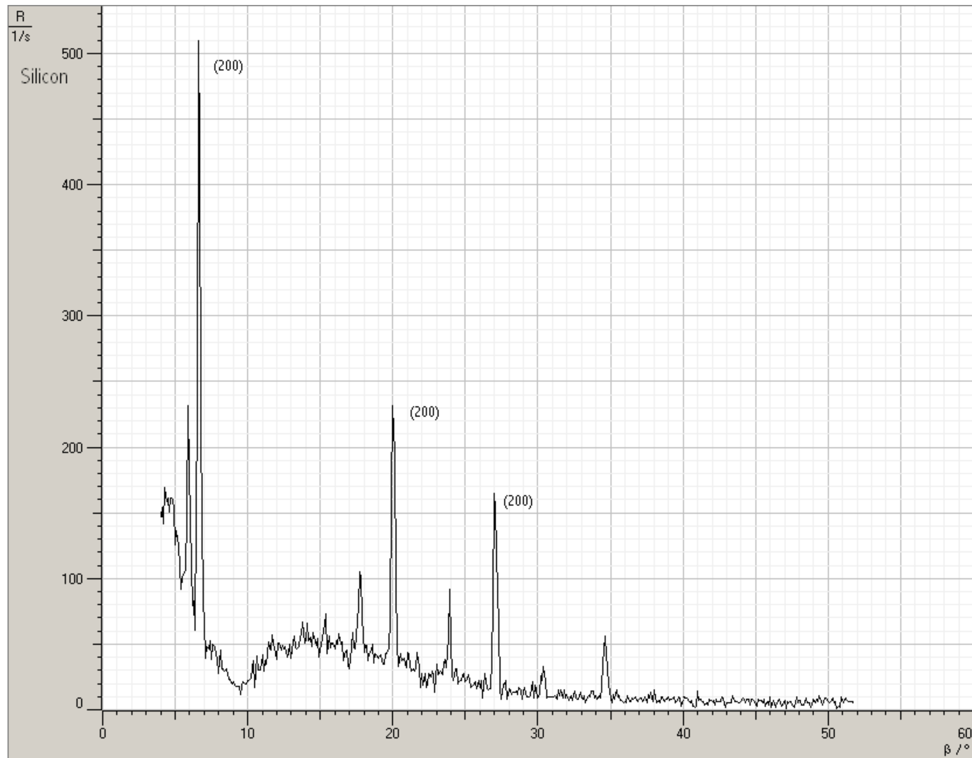

Figure 8: Diffraction spectrum of X-rays in Bragg reflection of a Si crystal. The graph shows up to the fourth order of diffraction (n=4).

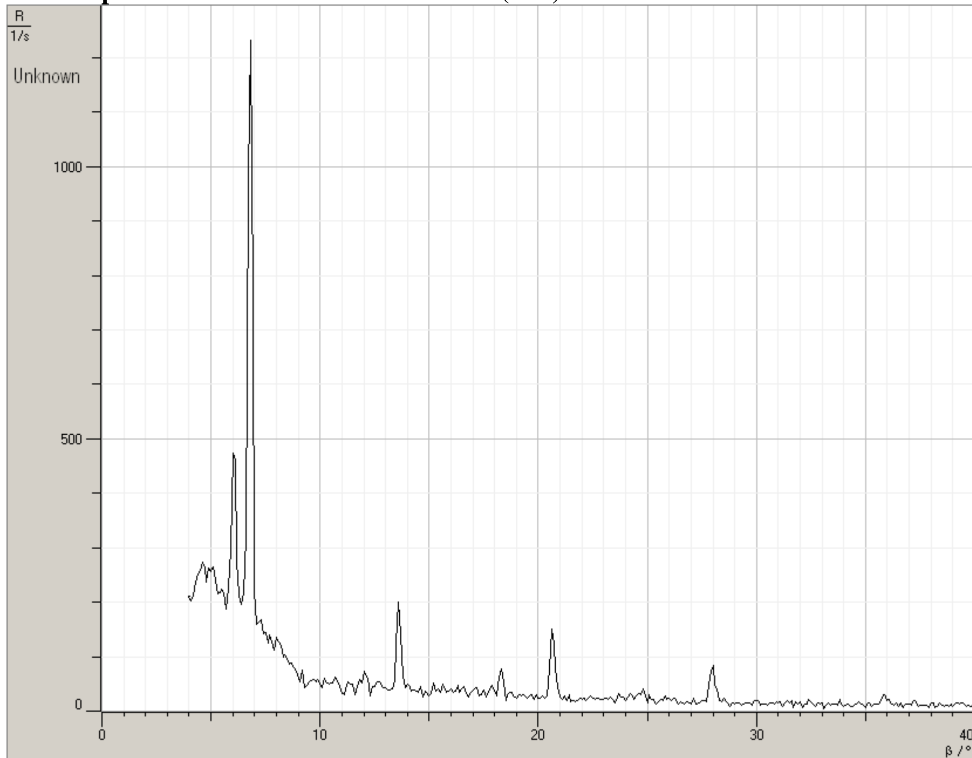

Figure 9: Diffraction spectrum of X-rays in Bragg reflection of unknown crystal. The structure of the crystal is unknown so further analysis of the diffraction spectrum can not be performed.

The results of the X-ray diffraction analysis of NaCl and LiF were consistent with the known values for the atomic lattice spacing. NaCl error was 1.10% and LiF error was 0.124%. The silicon crystal showed an error of 9.7%. This error could result from impurities in the crystal which would alter the location and intensity of the peaks. Also, if we could have seen peaks from planes other than just the (200) plane our results would have been better. The reason for this lack of ability of the apparatus to see other planes could be because the X-rays emitted are less intense than those of X-ray spectrometers that are typically used in diffraction studies, and also the Molybdenum source used has a more limited range of plane reflection peaks than that of a copper because the wavelength of the X-rays produced is smaller, but the benefit of a shorter wavelength X-ray is that it has better resolution.[2] If more peaks from other planes could have been detected, the silicon results may have improved. The unknown crystal showed distinct peaks as well, but the spacing of the crystal is yet to be determined because further analysis, such as Debye-Scherrer photography, must be done to determine the structure of the crystal.

Conclusions

The computer-interfaced X-ray apparatus was investigated for the purpose of being used in X-ray crystallography experiments. In order to become familiar with the device, simple X-ray detection experiments were performed using a fluorescent screen and plate capacitor. Using this spectrometer, X-ray diffraction studies were performed on NaCl, LiF, & Si crystals. The results for these crystals showed an error 1.10% for NaCl, 0.12% for LiF, and 9.7% for Si. An analysis was also performed on an unknown crystal. Further research involves determining the identity of this crystal along with other unknown crystals using X-ray diffraction.

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