

Crystal Structures and Lattice Constants of Alkali Halide Compounds
Experiment #1
Characterization of Materials (96.445/545)

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Objective

The purpose of this lab is to determine the crystal structure, components elements, and lattice constant(s) of alkali halide samples. Greater understanding and systematic trends of the lattice properties may be found from the measurement of the crystal structure and lattice constants(s) of alkali halides.

Experimental Equipment and Procedure

The experimental equipment used for this lab included:

- Powdered alkali halide sample
- The inXitu BTX system of hardware and software
- The X Powder software on the laboratory computer

Samples

The samples were already prepared by the instructor, and labeled with a number so that their chemical composition was indeterminate from visual assessment. To be compatible with the BTX, the sample has to be dry, small enough to pass through a 150 micrometer sieve, and large enough to not stick together and to convect inside the sample holder. At least 15 micrograms are needed in the sample holder.

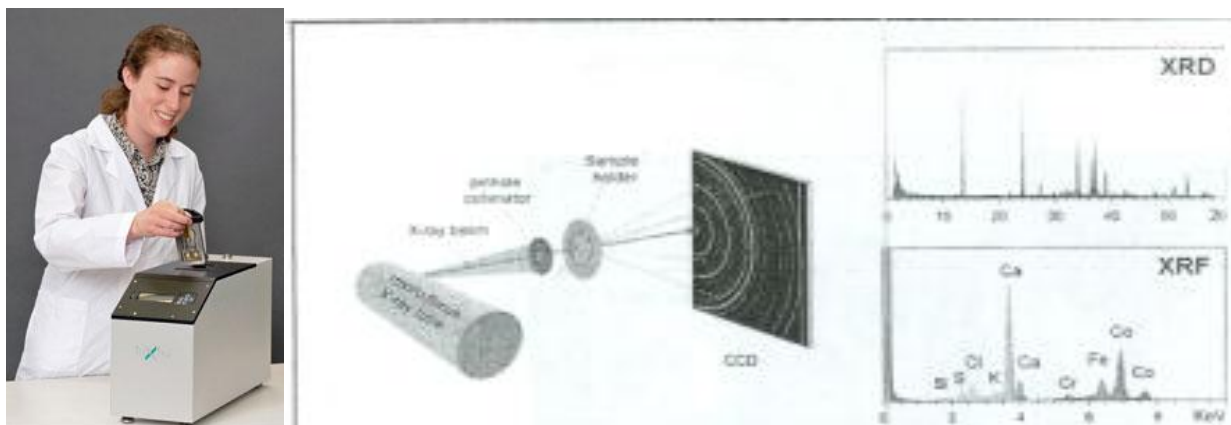
The samples measured in this laboratory report were #1 and #2. Samples were handled while wearing rubber gloves, and a spatula inserted into the vile was used to transfer powder from the vile to the BTX specimen holder. The following 12 are possible chemical compounds of the mystery powder:

NaCl	NaBr	NaI
KCl	KBr	KI
RbCl	RbBr	RbI
CsCl	CsBr	CsI

inXitu BTX System

The BTX is a benchtop X-Ray diffraction and X-Ray fluorescence instrument with the intended uses of identification of minerals and phases of materials and processing of captured data to generate output compatible with post-processing pattern matching of diffraction data and quantitative analysis of fluorescence data [1].

The basic procedure for operating the BTX is: 1) Power up the machine and computer. 2) Load the sample. 3) Start the data acquisition. 4) Monitor the data acquisition through enough exposures to ensure good signal-to-noise (150 exposures for this report). 4) Save the data files to disk. 5) Power down the machine.



Left: Photo from <http://www.inxitu.com/html/BTX.html> showing the BTX being loaded with sample holder. Right: BTX uses a 30Kv X-ray tube to generate X-rays necessary for XRF and XRD analysis.

The power up phase may take several minutes since the system has to cool to -45 C. When the detector temperature stabilizes, the data acquisition menu is displayed on the front panel:

```
> Start acquisition
  Shake
  Do USB transfer
  Shut Down
```

To load the sample, lift the sample chamber cell release handle and pull up on the sample chamber cell. The sample is loaded into the sample cell by pouring the powder down the sample cell guide. The BXT has an external shaker for the sample cell. Place the sample cell in the shaker so that the contacts meet. Select Shake from the main front control panel on the BTX. The ultrasonic shake results in a better loading of the powder. Look at the sample, and tap the sample holder to the powder into the cell. By hand shake out larger chunks that are stuck in the sample cell guide. Ensure that the sample cell is at least half-full.

Next, start the BTX software on the computer, and set the values for data acquisition. The default values were used for this laboratory report. Select Start Acquisition from the main front control panel of the BTX. Data will be displayed in the windows on the computer. To monitor both the X-Ray fluorescence data (XRF) and the X-Ray diffraction data (XRD), right click the links on the tabs of the main window of the BTX software, and open in a new window. Drag to different monitors.

Acquire data until a good signal to noise is visually obvious, and the software has identified components of the material. For lines that are close, the software might mis-identify a chemical. Double check the peak energies against known X-Ray spectral data. Save the data from the software tools. The outputs are automatically indexed with incrementing value for each new acquisition. Filenames for output text files is:

<acquisition index>-xrf.txt and <acquisition index>-xrd.txt

for X-Ray fluorescence and X-Ray diffraction respectively. Image files can also be generated. Finally, shut down the BTX.

XPowder

The XPowder software was used to determine the crystal structure by automated processing of the diffraction data. XPowder is described at <http://www.xpowder.com> [2]. XPowder provides qualitative, quantitative, and microtextural powder X-Ray diffraction analysis. XPowder has five main functions: 1) Identification of crystalline compounds, 2) Quantification of compounds, 3) Determining crystal size, strain, and thermal expansion tensor, 4) Other related tools for noise reduction and modification of peak intensity search criteria or shifting the theta values of a diffraction pattern, 5) Graphical output. The identification of crystalline compounds through search match against either is necessary to have a database, such as *PDF2.DAT* of the International Center for Diffraction Data (ICDD) and, or, *Difdata.txt*, the American Mineralogist Crystal Structure Database (AMSCD). Only the AMSCD database was used for this analysis.

The International Centre for Diffraction Data® (ICDD®), a non-profit scientific organization, has a mission to collect, edit, publish, and distribute powder diffraction data for the identification of crystalline materials [3]. There are 628,155 unique material data sets in release 2009 of the Powder Diffraction File. A data set is comprised of diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions, and select physical properties in a common standardized format. This database was not available to use for the experiment.

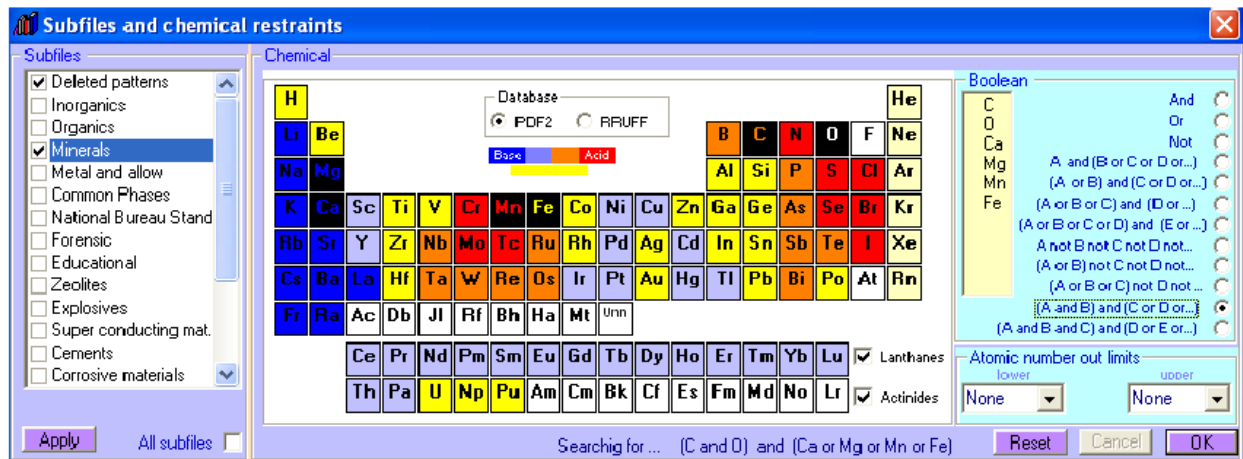
The AMSCD databases is described at the RRUFF™ Project website containing an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals [4]. The RRUFF™ Project is creating a complete set of high quality spectral data from well characterized minerals and is developing the technology to share this information with the world. Our collected data provides a standard for mineralogists, geoscientists, gemologists and the general public for the identification of minerals both on earth and for planetary exploration. The database can be downloaded from <ftp://geo.arizona.edu/pub/xtal/>.

The procedure for using XPowder software is:

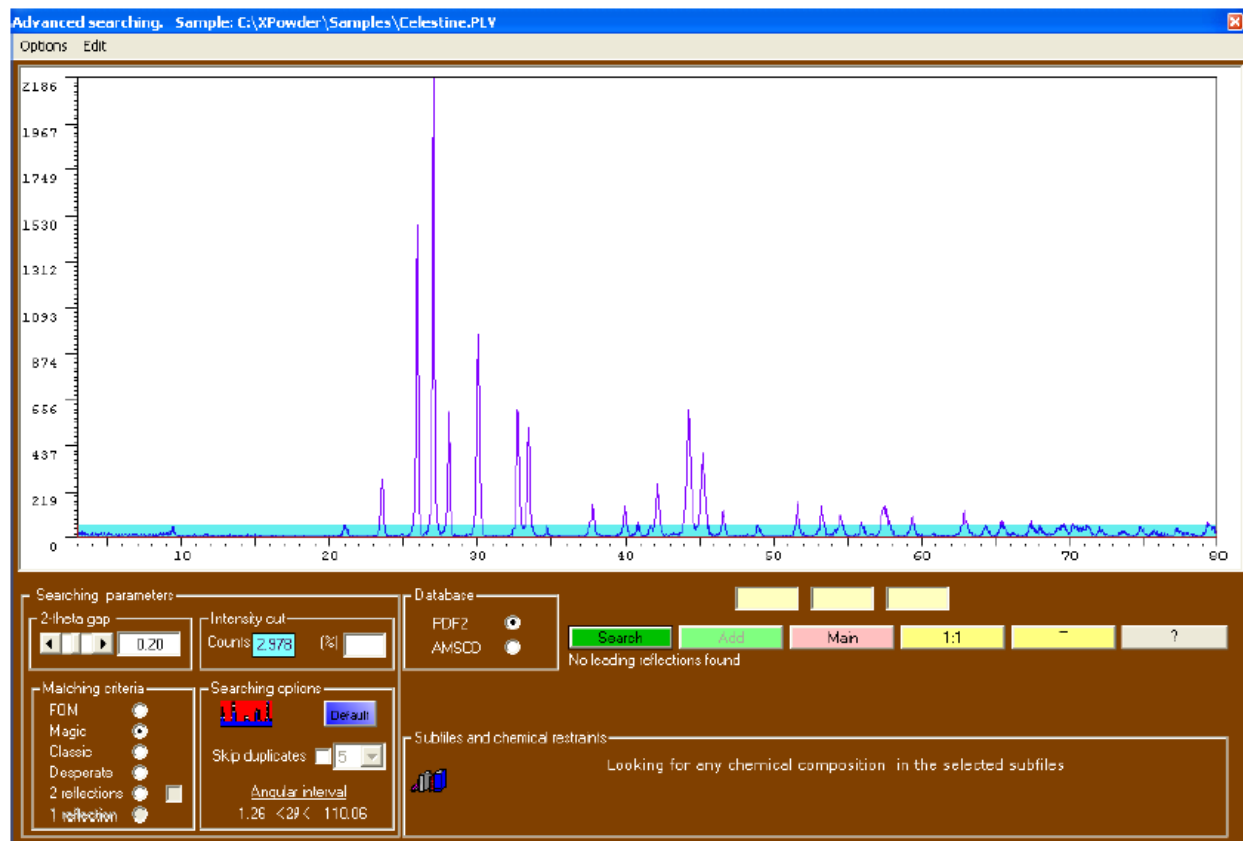
1. Read the XRD file created by the BTX system.
2. Perform an unsupervised search of the crystal database (One-click searching) for minerals have the peak intensities at the positions and relative values of the XRD file.
3. Set search constraints on chemical composition (based on BTX chemical identification) if the unsupervised search has ambiguous or too many hits.
4. Perform a supervised search of the crystal database with those constraints. (Advanced Searching)

To open the file, select File | Open from the main screen. Select 'txt' file format in the fileopen dialog box. Navigate to the directory with the output XRD file and select it to load. perform an unsupervised automated search of the crystal database for minerals have the peak intensities at the positions and relative values of the XRD file.

When the chemical and subfiles search conditions icon is selected the following dialog screen is used to set the chemicals:

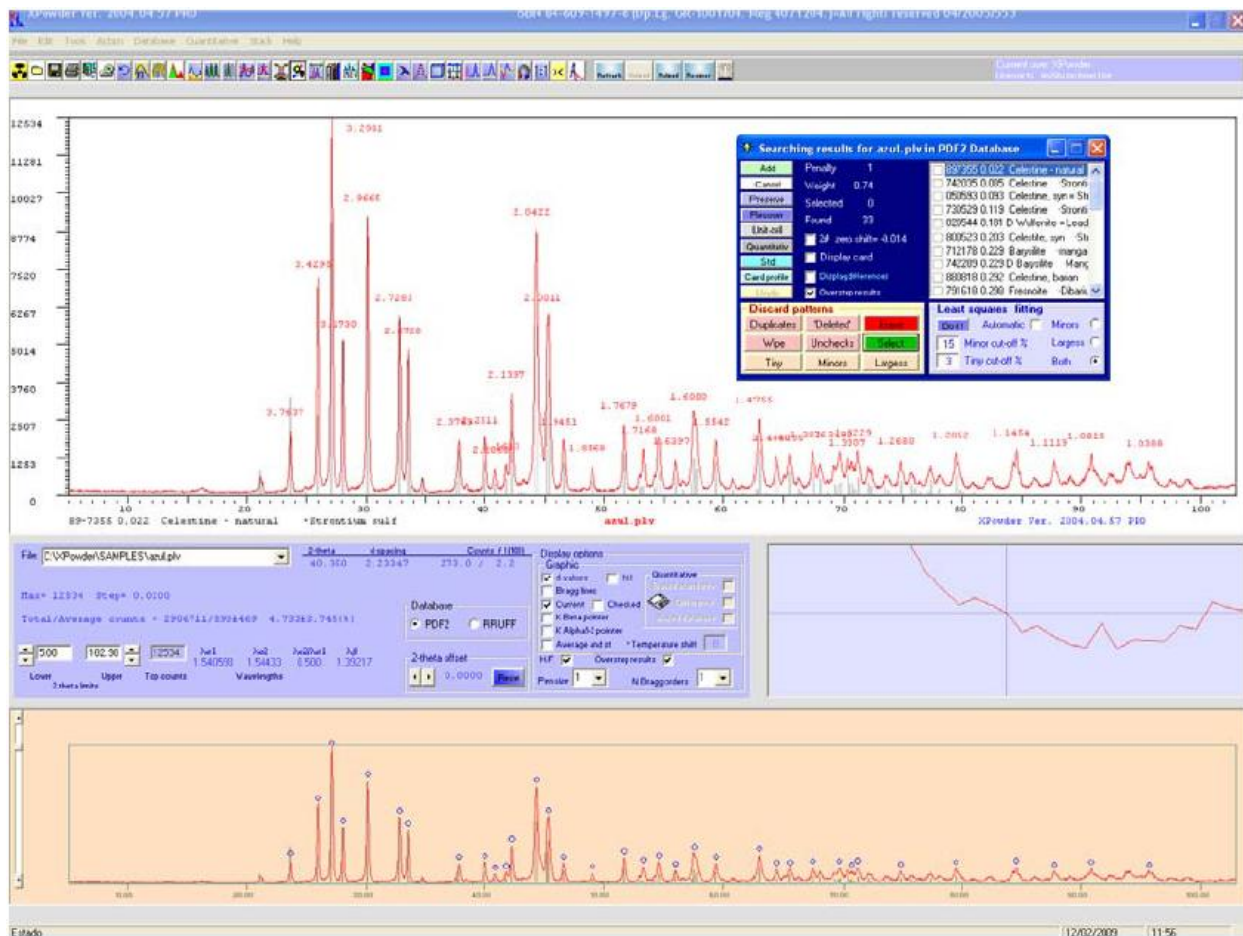


When the advanced search icon is selected, this dialog screen is used to set additional search parameters:



The Magic match criteria, which does not depend on error of the zero of the diffractometer angular position, was used for the analysis in this lab report.

When either the one-click search or the advanced search Search Button is selected, the results of the search are displayed in the main screen with a dialog box for interactive analysis:



From this screen and dialog box, the user interactively selects one or more crystalline structures that were identified, and can perform qualitative analysis. Pressing the Unit Cell icon yields the lattice constants of the crystal. Here the user can also refine the unit cell of the crystalline phase corresponding to the actual record in automated or controlled ways. Pressing the Quantitative icon results in a non linear least squares quantitative analysis for of the phases identified including statistical and global amorphous stuff, overall from the database records. The program takes chemical composition and density from the database in order to calculate the linear mass absorption coefficients, or for compounds not in the database, the program assigns approximate coefficients. The overall mass absorption coefficient of the sample is calculated during the process. The relative amounts of crystals in a mixture can be determined, and sometimes powders are mixed with reference standards such as Al_2O_3 to get a better Reference Intensity Ratio.

Procedure for this laboratory experiment

1. Identify the elements which can be identified by X-Ray fluorescence.
2. Identify the crystal structure and the compound by X-Ray diffraction:
The procedures for using the laboratory equipment was discussed in the sections above. This procedure was used for the laboratory for each of the two unknown samples:
 - Turn on the BTX.
 - Load the sample holder (previously cleaned) using the external shaker, and return the sample holder to the BTX.
 - Start data acquisition.
 - Monitor acquisition progress on the computer screens. Do enough exposures (150 for this report) to get decent signal-to-noise and chemical identification.
 - Note the chemical species identified in the sample from the X-Ray fluorescence data.
 - Double check peak intensities to determine if the BTX software had possible mis-identifications of chemical components.
 - Load the X-Ray diffraction data into the X Powder software to do crystal analysis.
3. Determine the lattice constant a and compare it with the standard value.
 - Load the X-Ray diffraction data into the X Powder software to do crystal analysis.
 - Do an internet search to find standard values.
 - Look for trends.
4. Determine the peak intensities and compare them with the standard values. (I/I_{std}).
5. Determine the crystallite size from the FWHM of the peaks.

Results and Discussion

Elements that can be identified with X-Ray fluorescence

From the tables X-Ray spectra [5], the following lines are associated with each possible chemical:

Average Energy in keV of X-Ray Lines of Alkali-Halide compounds.

	K α	K β	L α	L β
Na	None, sodium can't be identified with X-Ray fluorescence,			
K	3.32	3.598	-	-
Rb	13.395	15.106	-	-
Cs	-	-	4.289	4.646
Cl	None, chlorine can't be identified with X-Ray fluorescence,			
Br	11.927	13.41	-	-
I	28.527	-	3.941	4.249

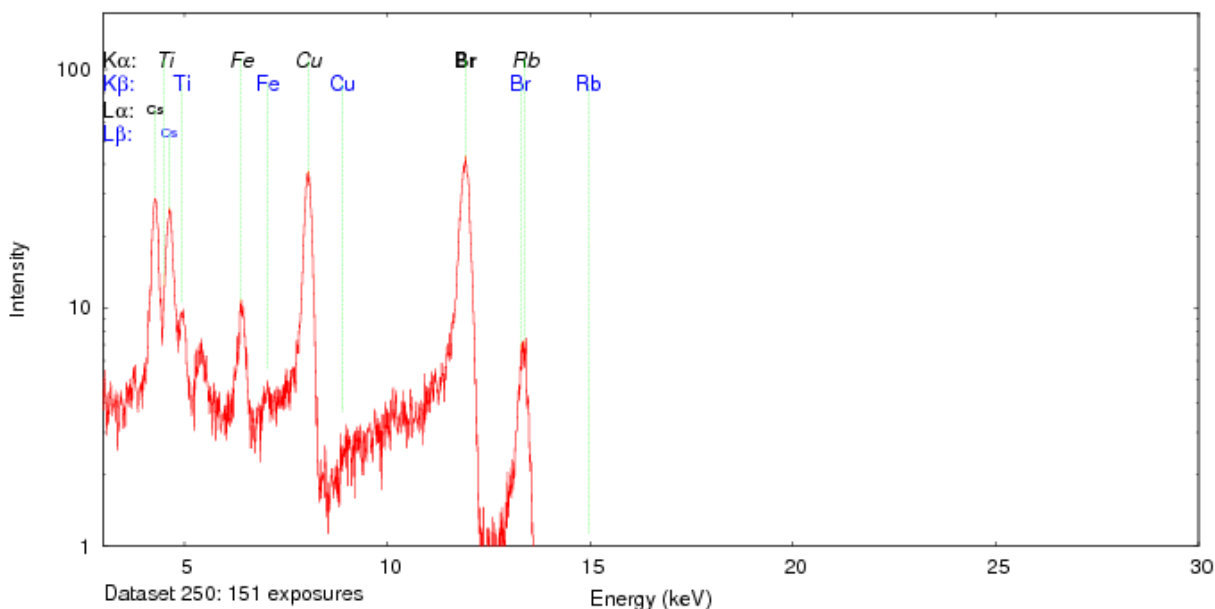
This data is also used to determine the validity of the lines automatically identified by the BTX software.

Analysis of Unknown #1

The fluorescence data identified Cesium and Bromine with energy values in agreement within two percent of the textbook values for the $L\alpha$ and $L\beta$ lines. The table below shows the chemicals identified during the acquisition and the plot below shows the spectrum with the lines identified by the BTX software. The Fe, and Cu are part of the instrument's signature and not part of our sample. The Ti and the Rb lines are most likely mis-identifications.

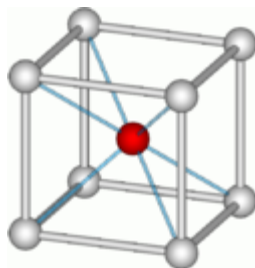
X-Ray Fluorescence Identifies Cs and Br

Element	Series	Measured Energy (keV)	Textbook Energy (keV)	Measured Intensities
Cs	$L\alpha$	4.31241	4.289	26.8874
Cs	$L\beta$	4.62553	4.646	26.2914
Fe	$K\alpha$	6.40458	6.411	10.7947
Fe	$K\beta$	7.05927	7.074	4.96689
Cu	$K\alpha$	8.05553	8.056	37.4834
Cu	$K\beta$	8.99487	8.961	3.24503
Br	$K\alpha$	11.941	11.927	43.3775
Br	$K\beta$	13.4211	13.41	7.48344
Rb	$K\alpha$	13.4069	13.395	7.21854
Rb	$K\beta$	15.0436	15.106	0.52981
Ti	$K\alpha$		4.517	
Ti	$K\beta$		4.942	



The diffraction data was analyzed in the X Powder software, searching for compounds that have Cs, Rb and Br. One possible match was a cubic $Pm\bar{3}m$ crystal matching the relative peak

intensities of CsBr. The RbBr crystal structure was not identified as a possible match. The lattice constant was very close to the value in the AMSCD database. It is concluded that the unknown sample is CsBr.



Cesium Chloride unit cell (Wiki)

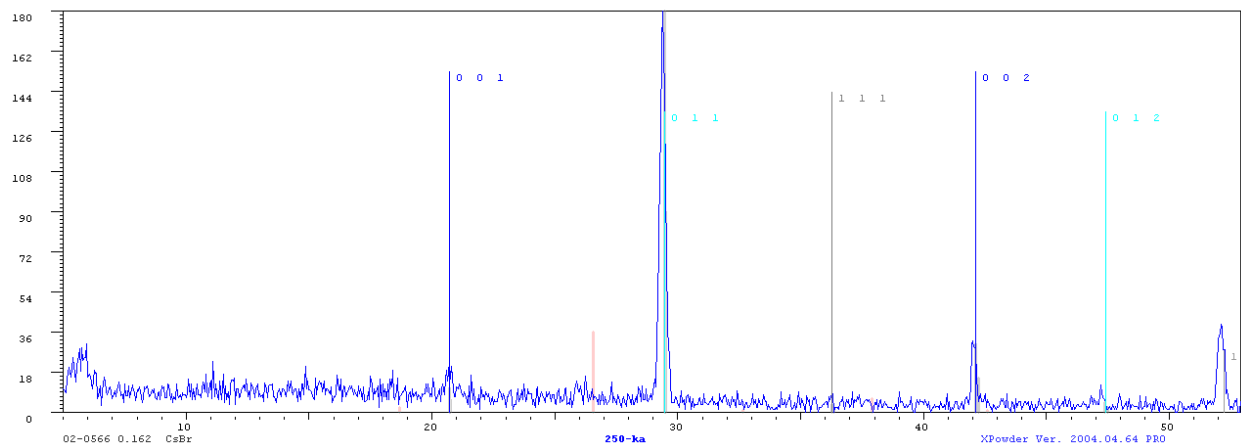
Lattice Constant a for Pm3m structure.

Observed	4.2972 Å
AMSCD standard for CsBr	4.2860 Å

The table below provides the peak position and intensities determined from our measurements, and compares them to the AMSCD database. After smoothing with a 2-point interpolation, the intensities were re-computed and two of the lines were no longer identified.

Peak intensities found in the diffractogram.

h	k	l	2θ	d observed [Å]	d standard [Å]	Intensity observed	Intensity observed smoothed	Intensity standard	I/Istd
0	0	1	24.11°	4.2875	4.2860	12.3	12.3	6.07	2.03
0	0	2	49.38°	2.1470	2.1430	16.2	16.7	17.06	0.95
0	1	1	34.36°	3.0356	3.0307	100.0	99.9	100.0	1.00
0	1	2	55.68°	1.9241	1.9168	6.7	22.0	2.40	2.80
1	1	1	42.41°	2.4827	2.4745	3.9	-	1.85	2.11
1	1	2	Not reported	1.7540	1.7498	22.0	-	Not reported	-



Plot produced by X Powder showing the Peaks. (unsmoothed)

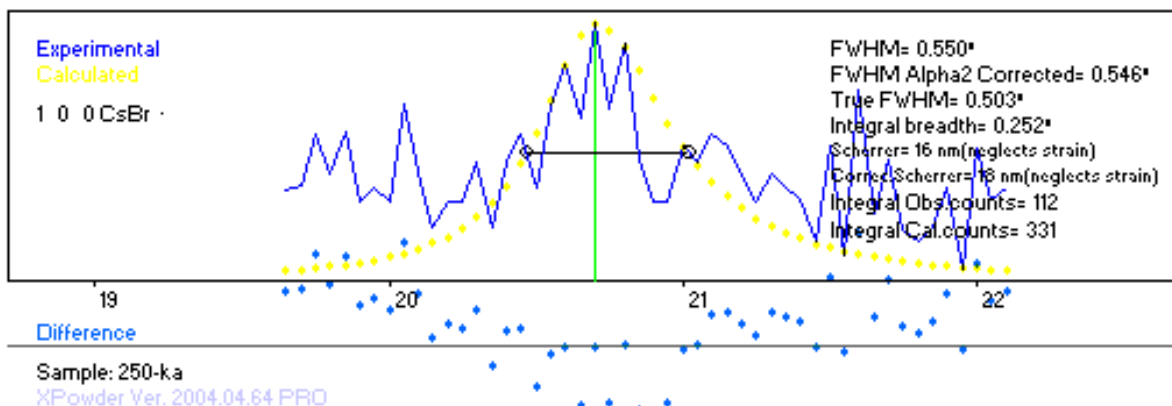
The Scherrer equation can be used to determine the crystallite size. It uses a shape factor in x-ray diffraction and crystallography to correlate the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. In the X Powder software, this equation is [2,6,7,8]:

$$\text{Size}(\mu\text{m}) = K \cdot \lambda(\text{\AA}) / (10 \cdot \beta \cos\theta)$$

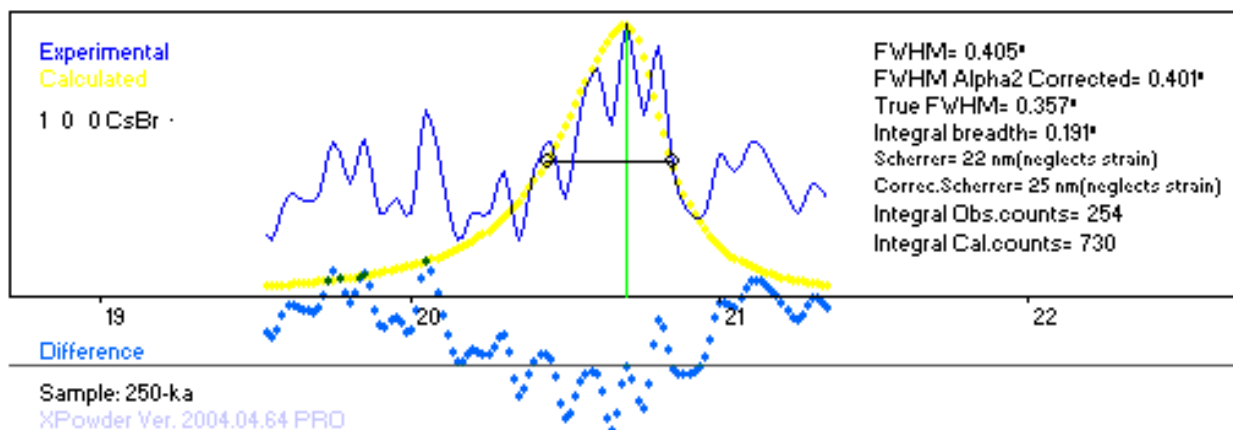
where K is the shape factor, λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. Values for the shape factor, K ($0.8 < K < 1.1$) are experimental constants, which is different when FWHM or β are used. The result is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. Since the Scherrer equation is limited to nanoparticles, and not applicable to grain sizes greater than 0.1 μm , it has questionable value for our powder. The table below provides the values found for both the raw and smoothed XRD data.

FWHM Analysis to find Scherrer Crystallite Size

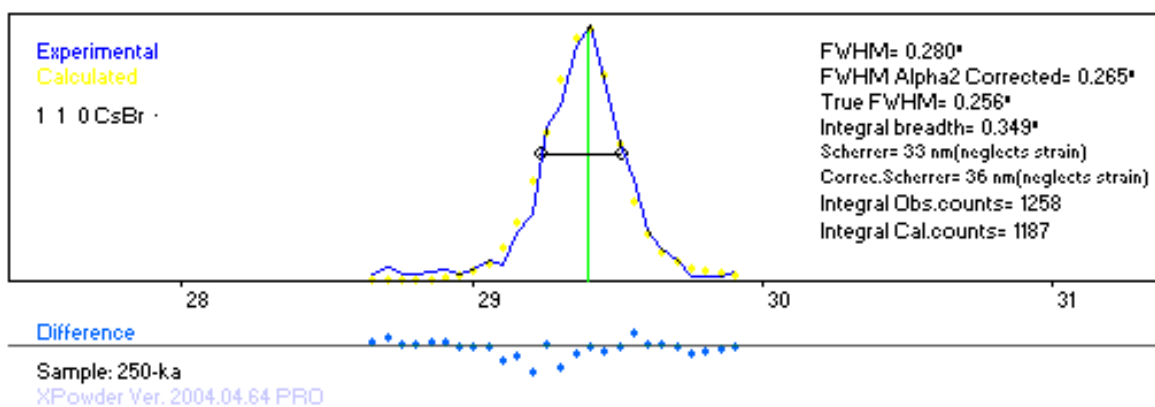
h	k	l	FWHM (unsmoothed)	FWHM (smoothed)	Scherrer crystallite size (unsmoothed)	Scherrer crystallite size (smoothed)
2	0	0	0.137°	0.133	40 nm	41.0
2	0	0	0.256°	0.256	33 nm	33.0
2	2	0	0.503°	0.405	16 nm	22.0



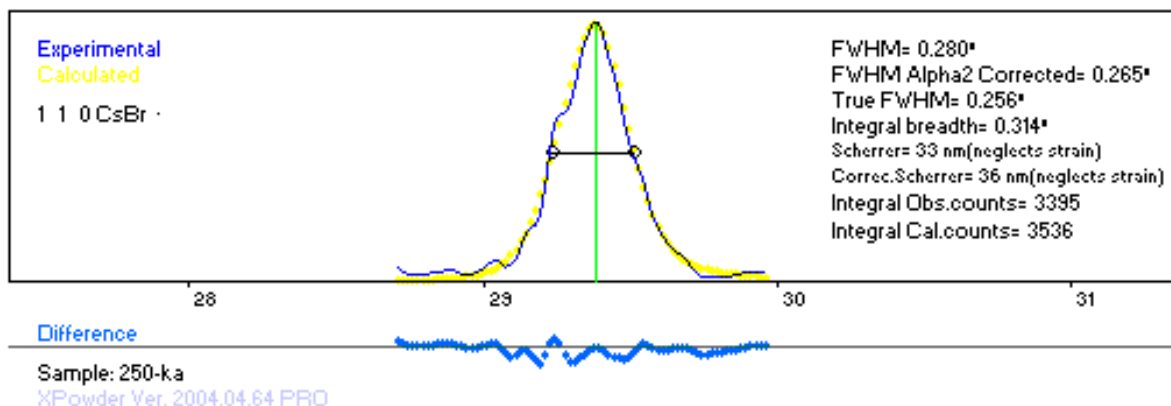
100 Unsmoothed FWHM and Scherrer Size



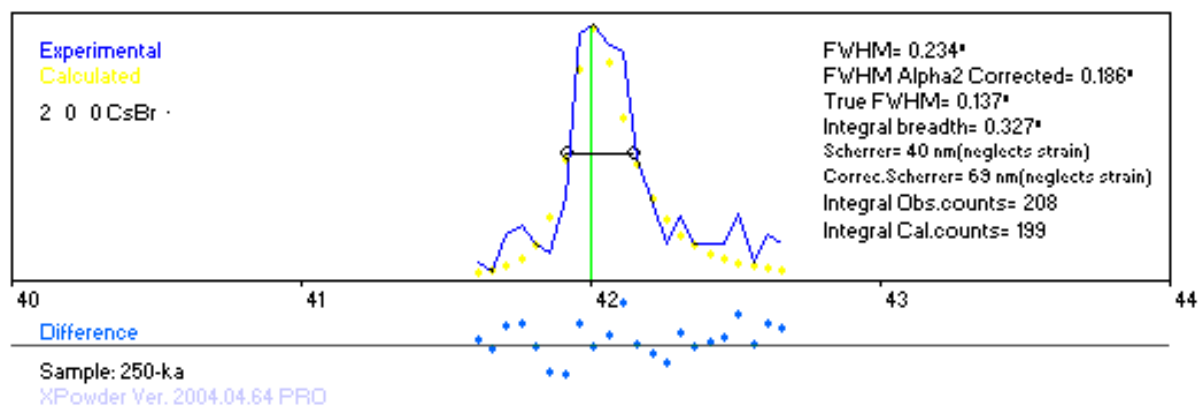
100 Smoothed FWHM and Scherrer Size



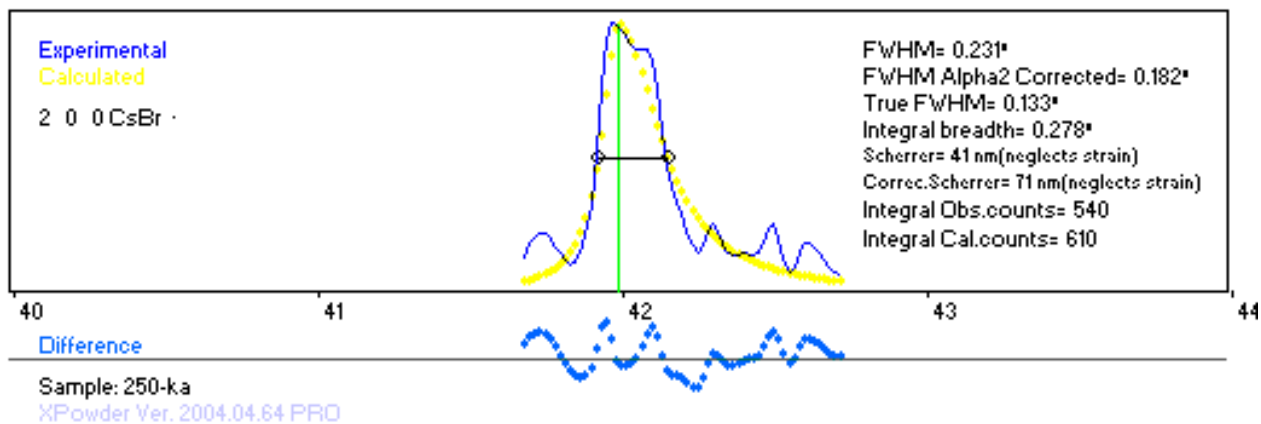
110 Unsmoothed FWHM and Scherrer Size



110 Smoothed FWHM and Scherrer Size



200 Unsmoothed FWHM and Scherrer Size



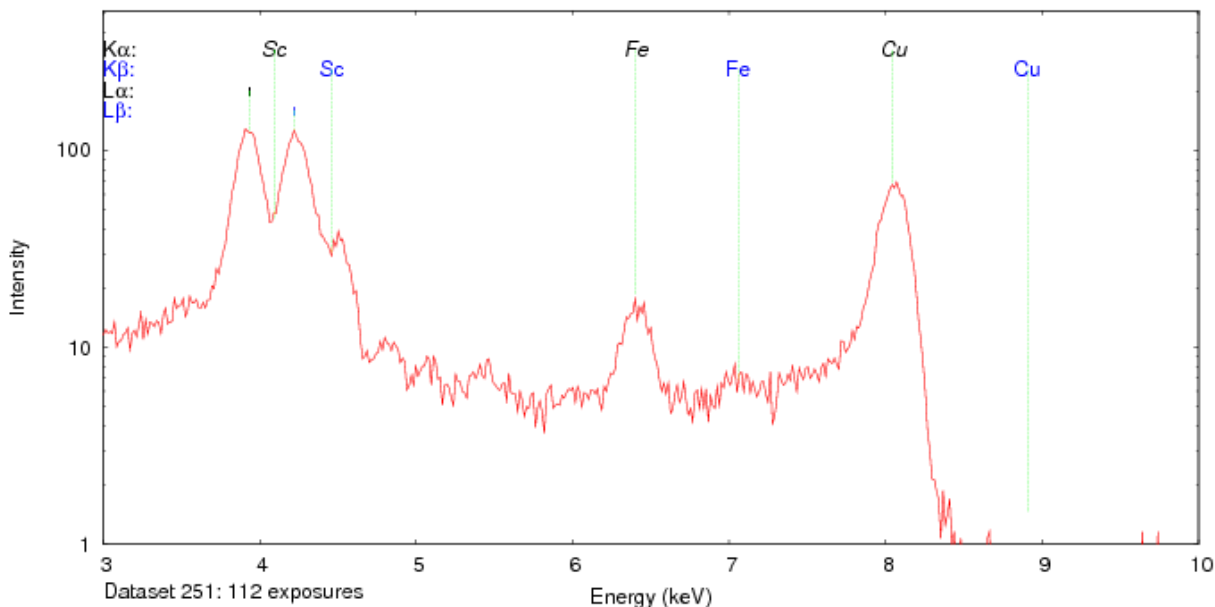
200 Smoothed FWHM and Scherrer Size

Analysis of Unknown #2

The fluorescence data identified Iodine with energy values in agreement within two percent of the textbook values for the $L\alpha$ and $L\beta$ lines. The table below shows the chemicals identified during the acquisition and the plot below shows the spectrum with the lines identified by the BTX software. Again,, the Fe, and Cu are part of the instrument's signature and not part of our sample. The Scandium is a bit of a mystery, but given that the $K\alpha$ and $K\beta$ lines identified, as Scandium are close to, and bracket, the $L\beta$ line of Iodine, and given the proximity to the $L\alpha$ line of Iodine, it is most likely a mis-identification in the BTX software.

X-Ray Fluorescence Identifies Iodine

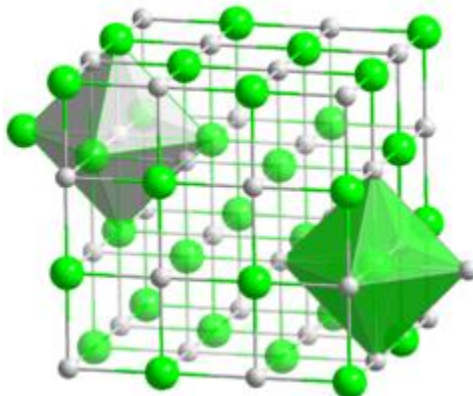
Element	Series	Measured Energy (keV)	Textbook Energy (keV)	Measured Intensities
I	$L\alpha$	3.90739	3.941	129.107
I	$L\beta$	4.21885	4.249	126.875
Sc	$K\alpha$	4.06312	4.097	43.3036
Sc	$K\beta$	4.45952	4.470	29.1964
Fe	$K\alpha$	6.45569	6.411	16.875
Fe	$K\beta$	7.03614	7.074	8.21429
Cu	$K\alpha$	8.06961	8.056	69.2857
Cu	$K\beta$	8.89073	8.961	0.892857



Plot created by the BTX software with identified elements.

The diffraction data was analyzed in the X Powder software, searching for compounds that have Iodine. One possible match was a cubic $Fm\bar{3}m$ crystal matching the relative peak intensities of NaI. Based on this, and the fact that K, Rb, and Cs were not identified by the fluorescence, we

concluded that the unknown is NaI. The lattice constant was very close to the value in the AMSCD database.



Sodium Chloride (Fm3m) structure from Wiki

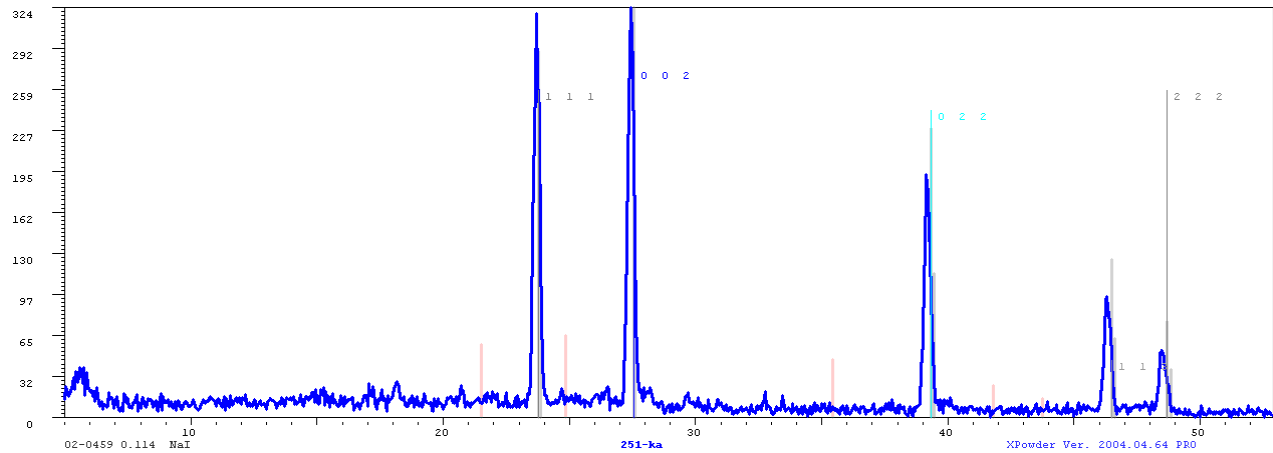
Lattice Constant a for Fm3m structure.

Observed	6.4908 Å
AMSCD standard for NaI	6.4728 Å

The table below provides the peak position and intensities determined from our measurements, and compares them to the AMSCD database.

Peak intensities found in the diffractogram.

h	k	l	2θ	d observed [Å]	d standard [Å]	Intensity observed	Intensity standard	I/Istd
1	1	1	27.72°	3.7434	3.7371	81.6	89.20	0.91
2	0	0	32.11°	3.2466	3.2364	100.0	100.0	1.00
2	2	0	46.05°	2.2879	2.2885	28.4	70.30	0.40
3	1	1	54.60°	1.9594	1.9516	29.5	38.42	0.77
2	2	2	57.25°	1.8755	1.8685	16.3	23.39	0.70

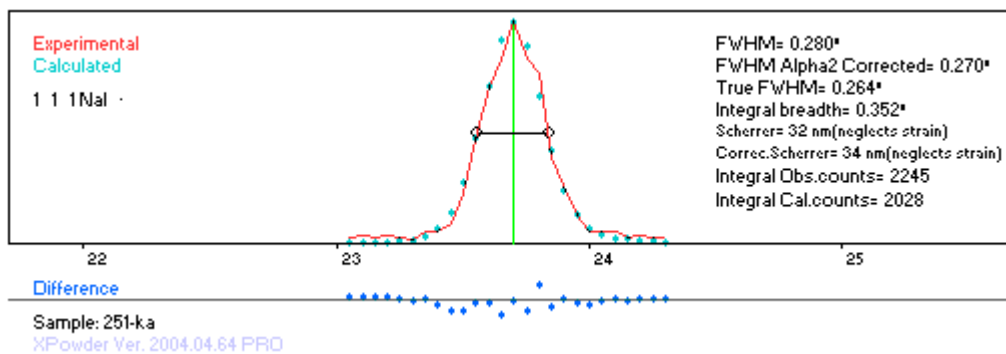


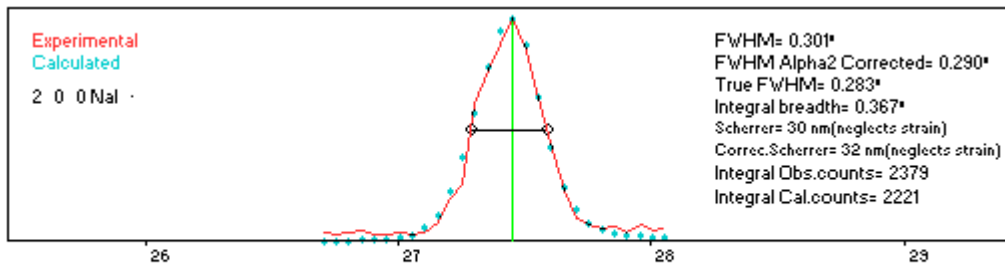
Plot produced by X Powder showing the Peaks. The vertical bars show the expected intensities L-alpha lines. The pink vertical bars are for the L-beta lines.

Finally, the FWHM was determined and Scherrer crystallite size computed. The table below gives the values and the plots follow.

FWHM Analysis to find Scherrer Crystallite Size

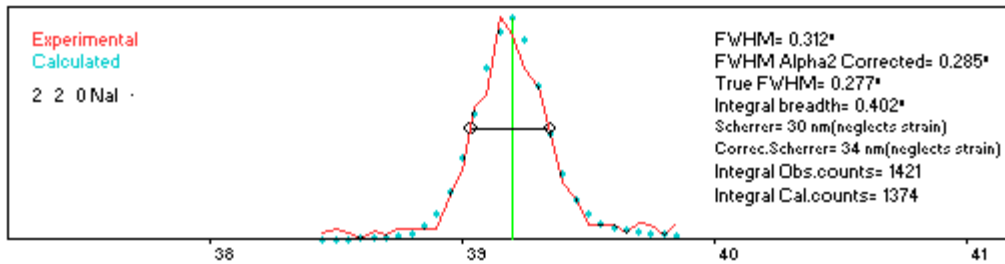
h	k	l	FWHM	Scherrer crystallite size
1	1	1	0.264°	32 nm
2	0	0	0.283°	30 nm
2	2	0	0.277°	30 nm
3	1	1	0.268°	30 nm
2	2	2	0.303°	26 nm





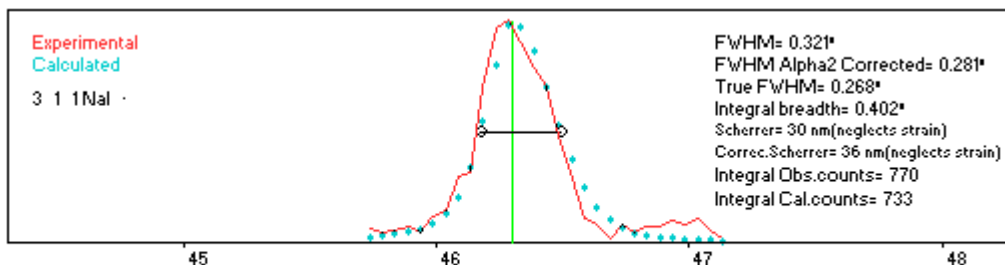
Difference

Sample: 251-ka
XPowder Ver. 2004.04.64 PRO



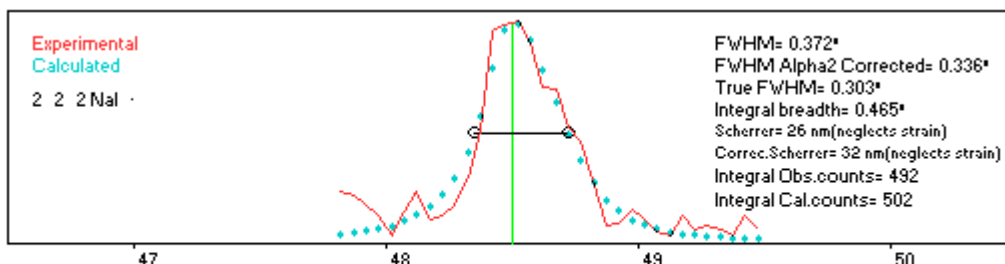
Difference

Sample: 251-ka
XPowder Ver. 2004.04.64 PRO



Difference

Sample: 251-ka
XPowder Ver. 2004.04.64 PRO



Difference

Sample: 251-ka
XPowder Ver. 2004.04.64 PRO

Halide-Alkali Crystal Analysis

In this section, the data from all experiments is put together and analysed. The tables below give the measured lattice constants and the crystal structures identified. From this the interatomic

spacing was calculated by multiplying the lattice constant by a factor of $\sqrt{3}/2$ for the Pm3m structures and by $1/2$ for the Fm3m structures.

Lattice Constant a (Å)

	Cl	Br	I
Na	5.6402		6.4728
K	6.292188[9]	6.5992	7.0932
Rb		6.9266	7.3345
Cs	4.123	4.286	

Structure of the Crystal

	Cl	Br	I
Na	Fm3m	Fm3m	Fm3m
K	Fm3m	Fm3m	Fm3m
Rb	Fm3m	Fm3m	Fm3m
Cs	Pm3m	Pm3m	Pm3m

Interatomic Distance (Å)

	Cl	Br	I
Na	2.82	-	3.24
K	3.15	3.30	3.55
Rb	-	3.46	3.67
Cs	3.57	3.70	-

Comparison to Literature Values (Å) [10]

	F	Cl	Br	I
Li	1.996	2.539	2.731	2.951
Na	2.295	2.789	2.954	3.194
K	2.648	3.116	3.262	3.489
Rb	2.789	3.259	3.41	3.628

Conclusions

The BXF system was able to identify the crystal structure and elements of several alkali halide compounds. The fluorescence data The peak intensities and positions compared well with standard values. The lattice constants and interatomic distances of the structures compared well with the literature values. As a further analysis the crystalline sizes were determined using the Scherrer equation. But the values were shared, so no trend information can be found from our two samples.

Since the chemical explanation of the alkali halide compounds is that an electron is moved from the highest shell of the Li, Na, K, Rb, Cs atom to fill the highest shell of the F, Cl, Br, I atom, the systems can be regarded as two ions with equal and opposite net charge. The expected interatomic distance would be the same since classical electrostatics predicts the same minimum energy distance. Comparing the $1/r$, where r is the interatomic spacing, for our measured

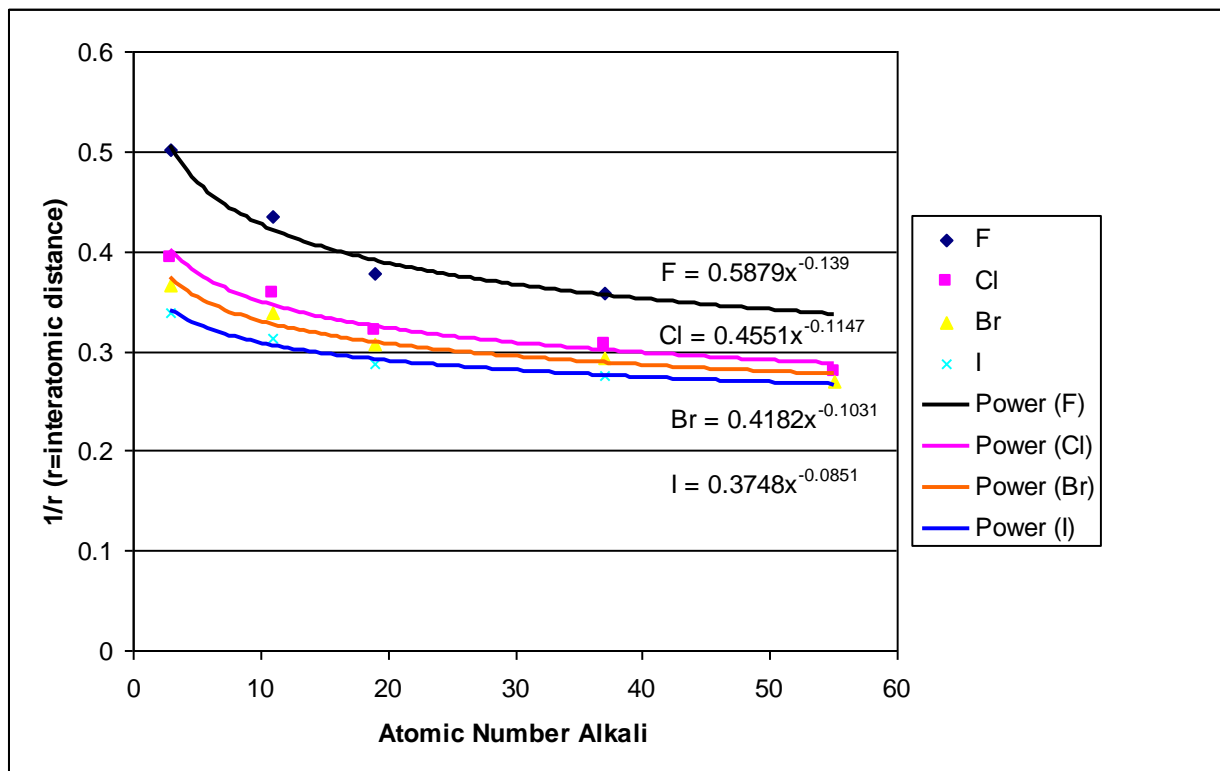
systems and ones in the literature there are some trends in the coulomb potential between ions even though all systems have the same charges on the ions. As the alkali ions increase in atomic number for any given halide ion, the coulomb $1/r$ interaction energy decreases. Likewise as the halide ions increase in atomic number for any given alkali ion, the $1/r$ interaction energy decreases. This suggests that the greater number of electrons in the electron cloud shields the nucleus. The plots show that the inverse of the interatomic distance (proportional to interaction energy of ions) can be fit to a power function of atomic number.

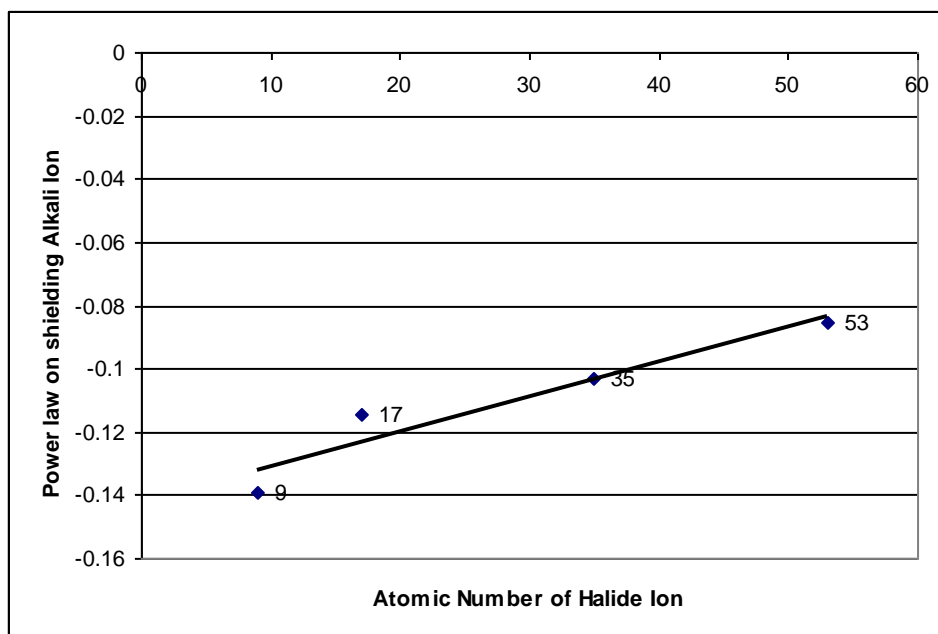
$1/r$ where r is interatomic distance [Å] from measured values

	Cl	Br	I
Na	0.35		0.31
K	0.32	0.30	0.28
Rb		0.29	0.27
Cs	0.28	0.27	

$1/r$ where r is the interatomic spacing of the literature values [10]

	F	Cl	Br	I
Li	0.50	0.39	0.37	0.34
Na	0.44	0.36	0.34	0.31
K	0.38	0.32	0.31	0.29
Rb	0.36	0.31	0.29	0.28





References

- [1] User Guide BTX User Guide V1.3
- [2] Martin, J.D. (2008) X Powder, A Software Package for Powder X-Ray Diffraction Analysis, User Guide, Version 2004.04.50 <http://www.xpowder.com/download/xpowder.pdf>
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- [4] Downs R T (2006) The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan. O03-13
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