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# Characterization Milestone Report on Test Plan TP 10-01, "Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility"

## Revision 0

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DEFINITION OF ABBREVIATIONS, ACRONYMS AND INITIALISMS

| Abbreviation or Acronym | Definition |
|---|---|
| DI | de-ionized |
| EDS | Energy dispersive system |
| ES&H | Environmental Safety and Health |
| Fe(II) | ferrous iron |
| IC | Ion Chromatography |
| ICP-AES | Inductively Coupled Plasma Atomic Emission Spectroscopy |
| m | molal (mol/kg $H_2O$) |
| M | molar (mol/L) |
| NA | Not Applicable |
| $Ox^{2-}$ | oxalate anion, $C_2O_4^{2-}$, conjugate base of oxalic acid |
| QA | quality assurance |
| SEM | Scanning electron microscope |
| SNL | Sandia National Laboratories |
| SNL/CPG | Sandia National Laboratories Carlsbad Programs Group |
| TP | Test Plan |
| WIPP | Waste Isolation Pilot Plant |
| XRD | X-Ray Diffractometer, X-Ray Diffraction |

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## 1 INTRODUCTION

The purpose of this report is to summarize the solids characterization of the experimental set-ups under Test Plan TP 10-01, "Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility" (Xiong, Y. 2010). The data that is presented in this milestone report is the cumulative analyses of all the solids characterization that has occurred to date for this Test Plan. Test Plan TP 10-01 supports the Waste Isolation Pilot Plant's (WIPP's) geochemical model used to predict the solubilities of actinide species present in the repository. This report documents the experimental set-up and X-Ray Diffraction (XRD) solid characterization of the solids collected from the TP 10-01 experiments. Solution chemistry data for this Test Plan, was presented in the Fifth Milestone Report for TP 08-02 "Fifth Milestone Report on Test Plan TP 10-01, Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility" (Xiong,Y and Kirkes.L. 2017). This milestone report is a companion report to the listed reference. Throughout this report, descriptions are offered of the experimental set-ups and XRD data gathered and to support determinations of thermodynamic constants and parameters. The sections into which this information is organized are identified by the Test Plan 10-01 task titles, which make direct reference to determinations of these constants and parameters. This approach to organizing the information may invite the reader to wonder where the determinations are to be found in the various section of this report. It is not the purpose of this report, however, to document the determinations, but simply to report the thermodynamic data that can be used to support such determinations. Therefore, the determinations themselves are not presented here.

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Table 1-1 Descriptions and Ion-pairs identified for investigation in Test Plan TP 10-01[a].

| ***Task Number*** | ***Description/Ion Pair*** |
|---|---|
| 1 | Boracite and Hydroboracite |
| 2 | $FeB(OH)_4^+$ |
| 3 | PbB4O7 |
| 4.1 | $PbB(OH)_4^+$-$Cl^-$ |
| 4.2 | $PbB(OH)_4^+$-$SO_4^{2-}$ |
| 4.3 | $Na^+$-$Pb[B(OH)_4]_3^-$ |
| 4.4 | $Mg^{2+}$-$Pb[B(OH)_4]_3^-$ |
| 4.5 | $MgB(OH)_4^+$-$SO_4^{2-}$ |
| 4.6 | $CaB(OH)_4^+$-$SO_4^{2-}$ |
| 4.7 | $Na^+$-$NaB(OH)_4$(aq) |
| 4.8 | $Mg^{2+}$-$NaB(OH)_4$(aq) |
| 4.9 | $NaB(OH)_4$(aq) with NaCl +$MgCl_2$ |
| 4.10 | $Na^+$-$PbB_4O_7$(aq) |
| 4.11 | $Mg^{2+}$-$PbB_4O_7$(aq) |
| 4.12 | $PbB_4O_7$(aq) with NaCl + $MgCl_2$ |

[a] Based on Table 2 of AP 155 (Xiong, 2014)

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## 2 MATERIALS AND METHODS

For all experimental materials and methods refer to TP 10-01 (Xiong, 2010) and the Fifth Milestone Report on Test Plan TP 10-01, Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility. (Xiong, Y.L. et al. 2017). This is a supplemental report supporting TP 10-01.

### 2.1 Solid Materials

Solid materials were collected from the experiments prepared for TP 10-01 at varying time intervals. The solid was allowed to dry in a desiccator, ground into a fine powder and analyzed by XRD. Most of the solid materials reported in this report were collected at the termination of the experiments.

It should be emphasized that the solid phases present in this report may not represent those present in the experiments at the last solution chemistry analysis contained in the Fifth Milestone Report for TP 08-02 "Fifth Milestone Report on Test Plan TP 10-01, Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility" (Xiong,Y and Kirkes.L. 2017). The reasons for this are detailed below.

XRD analyses were completed by collecting small amounts of solids together with the supporting electrolytes from the experiments; then, the solids were dried without any washing to remove the supporting electrolytes. Therefore, it is possible that some artificial phase(s) could be formed in this process. By artificial phase(s) it is meant that the phase may not be present in the experiment; they are formed only when the residual supporting solution becomes highly concentrated during the drying process, especially in a desiccator. In addition, the "termination" of the experiments, when the solids were collected for XRD analysis was much later than the last sampling for solution chemistry analysis (see Xiong, Y. and Kirkes, L. 2017). During the time periods between the last sampling for solution chemistry and the current sampling for XRD, the solution chemistry may have been changed, which could result in the formation of a different solid phase. In addition, accidental contamination could have occurred, also resulting in the formation of a different solid phase. Essentially, the following solids characterizations presented

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herein are believed to be the solid phases present in the experiments at the collection of the solids for the XRD analysis but may not represent solids present in the experiments at the last solution chemistry analysis. In order to ensure whether solution chemistry has been changed, resulting in a different solid, it would be preferred that new solution chemistry analysis be performed. New solution chemistry analysis will not be performed on these experiments. However, because some of the experimental results generated under this Test Plan have been challenged new experiments are needed to corroborate the findings in this report and will be set up and designed in a new Test Plan.

## 2.2 Instrumentation

A Bruker D8 Advance XRD (Serial Number 2037) was utilized for solid characterization. All procedures are documented in the Activity Specific Procedure SP 12-8: Use and Maintenance of Bruker Analytical X-Ray Systems D8 Advance X-Ray Diffractometer. The commercially available software from the International Centre for Diffraction Database (ICDD) PDF4+ 2019 was utilized for the analysis of the XRD scans in this document. Appendix A contains a list of the PDF4+2019 patterns listed in this report and their associated quality marks.

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# 3 RESULTS

The following sections describe the preparation of the experimental setups and solids characterization results for the selected tasks. This report is a supplemental data report to the fifth milestone report on TP 10-01 (Xiong and Kirkes, 2017). When solids were collected for characterization from the following experiments, it was determined that the solution concentrations reached equilibrium long before the solid sample collection time. Stability of solution concentrations was used to indicate equilibrium of the system as a whole. Therefore, because the attainment of equilibrium occurred before the collection time for solid samples used for characterization, the number of elapsed days is not significant.

## 3.1 Task 1: Experimental determination of solubility constants of boracite and hydroboracite

Table 3-1 shows the set-up of the boracite and hydroboracite experiments. Figures 1-4 document the XRD analysis of solids for the hydroboracite and boracite experiments. Since the experiments were not all set up at the same time, the days of collection were different for each sample. Sample SYN-Hydroboracite was collected at 2124 days, SYN-Hydroboracite-2 was collected at 2120 days, considered at the termination of the experiments. SYN-Boracite was collected by Y.-L. Xiong at 1642 days and SYN-Boracite-2 was collected by Y.-L. Xiong at 1629 days, corresponding to the solution samples of 8F reported in the fifth milestone report on TP 10-01 (Xiong and Kirkes, 2017). It should be mentioned that the solid phases for SYN-Boracite and SYN-Boracite-2 collected by L. Kirkes at the termination of the experiments are different from those collected when the experiments were sampled for solution chemistry. Further research into this system may be necessary in a follow-on experiment.

Sample SYN-Hydroboracite matches with good agreement to pdf patterns for halite (NaCl) PDF 04-002-178 and inyoite ($CaB_3O_3(OH)_5 \cdot 4H_2O$) PDF pattern 00-006-0361. SYN-Hydroboracite-2 shows a mixed system containing the solids ulexite ($NaCaB_5O_9 \cdot 8H_2O$) PDF pattern 00-012-0419, borax ($Na_2B_4O_5(OH)_4 \cdot 8(H_2O)$) PDF pattern 04-012-8356 and boracite ($Mg_3B_7O_{13}Cl$) PDF pattern 00-005-0710. SYN-Boracite and SYN-Boracite-2 show a mixed system with borax ($Na_2B_4O_5(OH)_4 \cdot 8(H_2O)$) PDF pattern 04-012-8356 and boracite

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($Mg_3B_7O_{13}Cl$) PDF pattern 04-007-8460. Aksaite ($MgB_6O_{10}\cdot 5H_2O$) PDF pattern 00-015-0564 was also identified along with bischofite ($MgCl_2\bullet\cdot 6H_2O$) PDF pattern 00-025-0515 and another form of hydrated $MgCl_2$ ($MgCl_2\cdot 2H_2O$) PDF pattern 00-053-0259 and kurnakovite ($Mg_2B_6O_{11}\cdot 15H_2O$) PDF pattern 00-024-0700. The Figures below show the XRD data.

Table 3-1 Preparation of experimental set-ups for investigation of solubility constants of boracite and hydroboracite.

| Set-up ID | NaCl (M) | $MgCl_2$ (M) | $CaCl_2$ (g) | $H_3BO_3$ (g) | NaOH (M) | Scientific Notebook Reference |
|---|---|---|---|---|---|---|
| SYN-Hydroboracite | 0.1 | 1.0 | 0.3675 | 0.7699 | 2.0114 | WIPP-Borate-3 Pg. 82,86 |
| SYN-Hydroboracite-2 | 0.1 | 1.0 | 0.3675 | 0.7699 | 2.0114 | WIPP-Borate-3 Pg. 86,89 |

| Set-up ID | $MgCl_2$ (M) | $H_3BO_3$ (g) | NaOH (M) | Scientific Notebook Reference |
|---|---|---|---|---|
| SYN-Boracite | 1.0 | 8.5023 | 2.0114 | WIPP-Borate-3 Pg. 81-82 |
| SYN-Boracite-2 | 1.0 | 8.5023 | NA | WIPP-Borate-3 Pg. 94 |

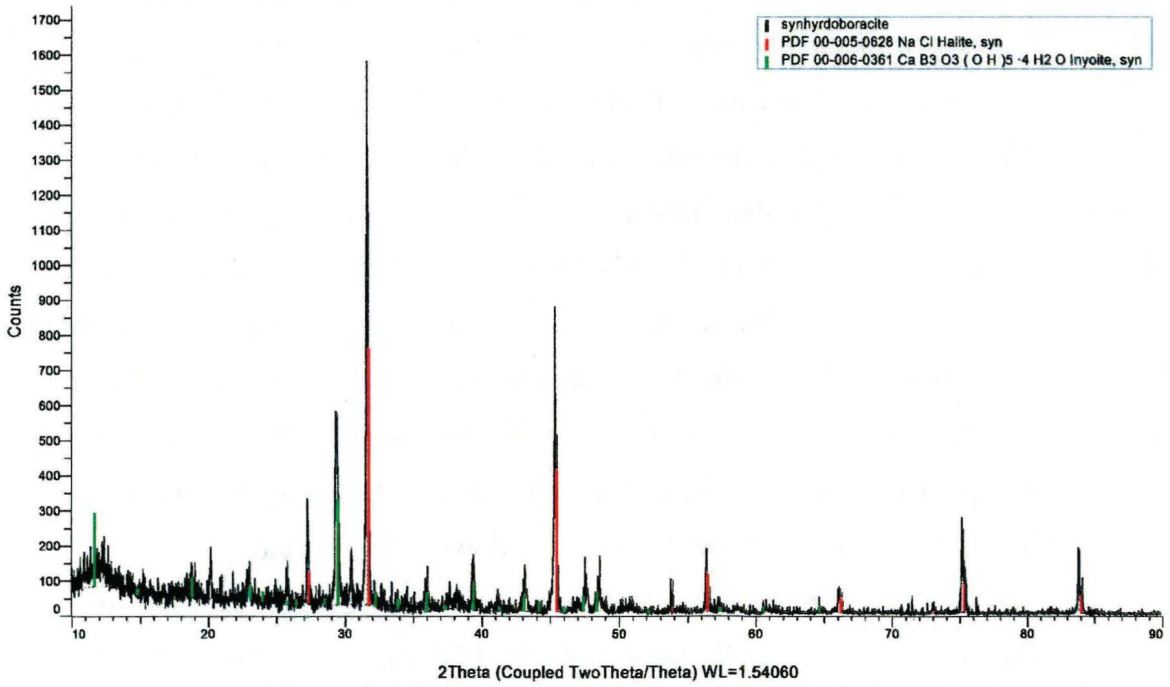



Figure 1 XRD analysis of sample SYN-Hydroboracite-1
Source of Figure 1: Scientific Notebook WIPP-Borate-10 Pg. 93

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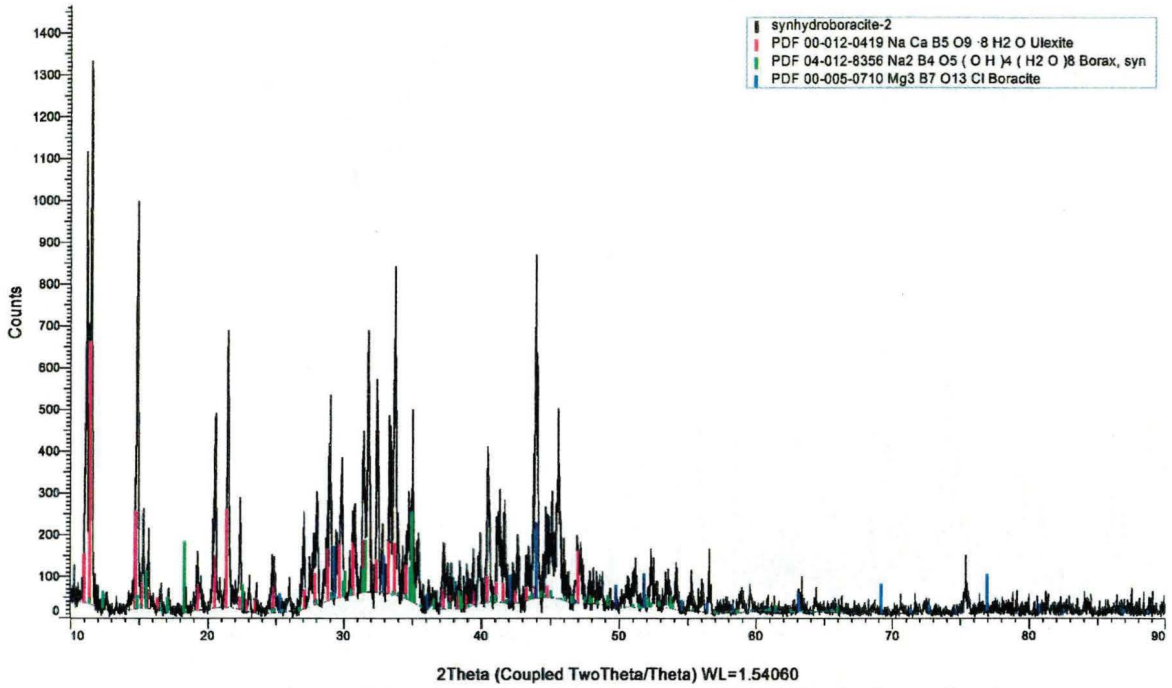



Figure 2 XRD analysis of sample SYN-Hydroboracite-2
Source of Figure 2: Scientific Notebook WIPP-Borate-10 Pg. 93

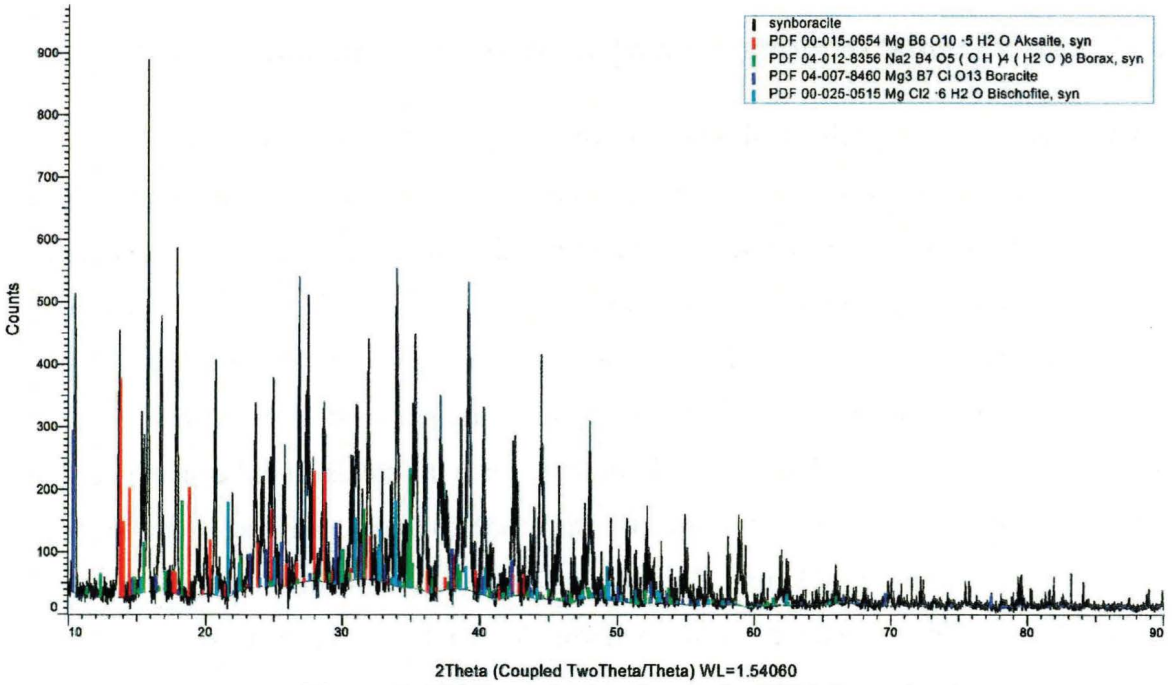



Figure 3 XRD analysis of sample SYN-Boracite-1
Source of Figure 3: Scientific Notebook WIPP-Borate-10 Pg. 93

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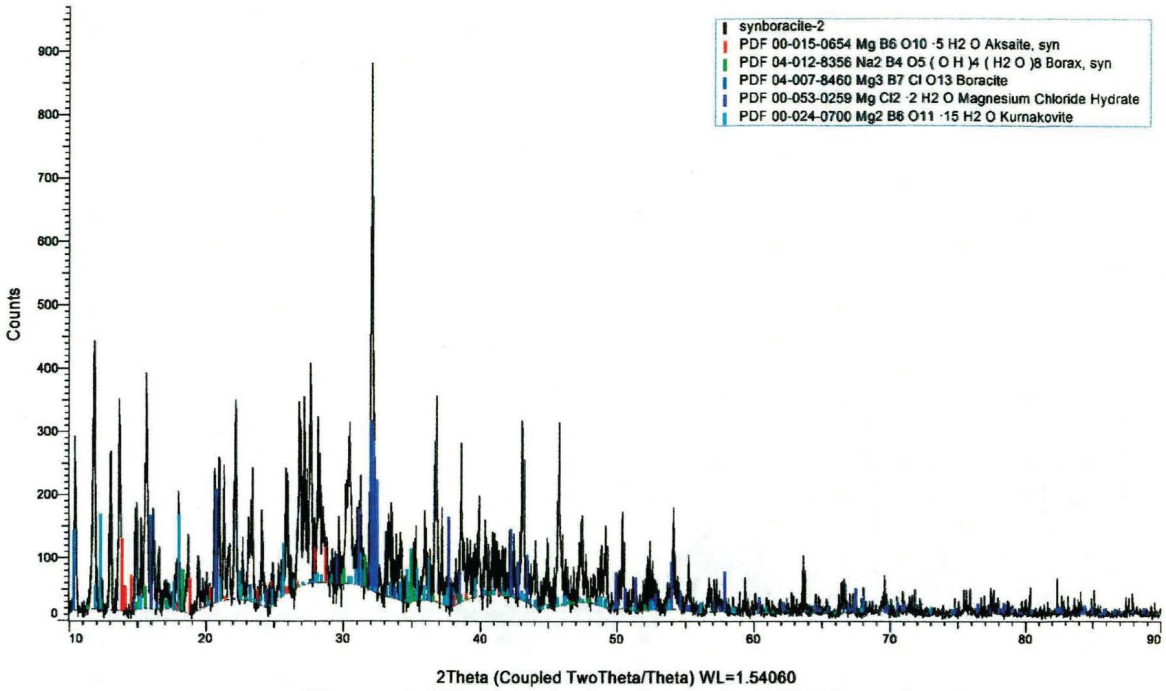



Figure 4 XRD analysis of sample SYN-Boracite-2
Source of Figure 4: Scientific Notebook WIPP-Borate-10 Pg. 93

### 3.2 Task 2: Experimental Determination of the formation constant of $FeB(OH)_4^+$

Table 3-3 shows the experimental set-ups of the $FeB(OH)_4^+$ experiments. Two sets of experiments were designed. The first set of experiments were set up with the solid $Fe_2Cl(OH)_3$ as the starting material and the second set of experiments designated "R" were set up with the solid $Fe(OH)_2$ as the starting material. Figures below document the XRD analysis results for the experiments containing $FeB(OH)_4^+$. Solid was collected from each of the experiments, allowed to dry inside a glovebox under anoxic conditions, ground to a fine powder, and then an XRD slide was made using an anoxic XRD holder. In order to keep the solids from being exposed to oxygen unnecessarily, the solids were collected two at a time and then analyzed after allowing them to dry in the glovebox for ~2 hours. Since the solids were not all collected at the same time, the days of collection were different for each sample. Table 3-2 summarizes the days at which the solid was analyzed for each sample. All of the samples in these two sets of experiments match with good agreement to iron hydroxide ($Fe(OH)_2$) PDF pattern 00-013-0089. In our solubility experimental design, we used $Fe_2Cl(OH)_3$ as the starting material (See Figure 5). The XRD analyses for the starting material was completed on 6/29/2011. When $Fe_2(OH)_3Cl$ is added to a solution with zero background $Cl^-$ concentration, the solid phase $Fe(OH)_2$ forms, as

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indicated by the following figures. This design, using the phase transformation, approaches the equilibrium from the direction of supersaturation. The Figures below show the XRD data.

Table 3-2 Days of solid collection for FeB(OH)4 experiments.

| Set-up ID | Experiment Start Date | Solid Collection Date | XRD Aging Days |
|---|---|---|---|
| FeB(OH)4-0.01B-1 | 1/25/2011 | 10/30/2017 | 2470 |
| FeB(OH)4-0.01B-2 | 1/25/2011 | 1/24/2018 | 2556 |
| FeB(OH)4-0.02B-1 | 1/25/2011 | 10/30/2017 | 2470 |
| FeB(OH)4-0.02B-2 | 1/25/2011 | 1/24/2018 | 2556 |
| FeB(OH)4-0.03B-1 | 1/25/2011 | 10/31/2017 | 2471 |
| FeB(OH)4-0.03B-2 | 1/25/2011 | 1/25/2018 | 2557 |
| **Set-up ID** | | | |
| FeB(OH)4 R-0.01B-1 | 1/19/2012 | 10/31/2017 | 2112 |
| FeB(OH)4 R-0.01B-2 | 1/19/2012 | 2/1/2018 | 2205 |
| FeB(OH)4 R-0.02B-1 | 1/19/2012 | 11/1/2017 | 2113 |
| FeB(OH)4 R-0.02B-2 | 1/19/2012 | 1/24/2018 | 2197 |
| FeB(OH)4 R-0.03B-1 | 1/19/2012 | 11/1/2017 | 2113 |
| FeB(OH)4 R-0.03B-2 | 1/19/2012 | 2/1/2018 | 2205 |

Table 3-3 Preparation of experimental set-ups for investigation of formation constant of $FeB(OH)_4^+$

| Set-up ID | $Fe_2Cl(OH)_3$ (g) | $H_3BO_3$ (m) | De-gassed DI water (g) | Scientific Notebook Reference |
|---|---|---|---|---|
| FeB(OH)4-0.01B-1 | 1.52 | 0.01 | 100.03 | WIPP-Borate-1 Pg. 53 |
| FeB(OH)4-0.01B-2 | 1.52 | 0.01 | 100.00 | WIPP-Borate-1 Pg. 53 |
| FeB(OH)4-0.02B-1 | 1.50 | 0.02 | 100.02 | WIPP-Borate-1 Pg. 53 |
| FeB(OH)4-0.02B-2 | 1.51 | 0.02 | 109.44 | WIPP-Borate-1 Pg. 53 |
| FeB(OH)4-0.03B-1 | 1.53 | 0.03 | 100.03 | WIPP-Borate-1 Pg. 53 |
| FeB(OH)4-0.03B-2 | 1.52 | 0.03 | 100.00 | WIPP-Borate-1 Pg. 53 |

| Set-up ID | $Fe(OH)_2$ (g) | $H_3BO_3$ (m) | De-gassed DI water (g) | Scientific Notebook Reference |
|---|---|---|---|---|
| FeB(OH)4 R-0.01B-1 | 1.25 | 0.01 | 100.02 | WIPP-Borate-5 Pg. 6 |
| FeB(OH)4 R-0.01B-2 | 1.29 | 0.01 | 100.02 | WIPP-Borate-5 Pg. 6 |
| FeB(OH)4 R-0.02B-1 | 1.27 | 0.02 | 100.15 | WIPP-Borate-5 Pg. 6 |

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| Set-up ID | $Fe(OH)_2$ (g) | $H_3BO_3$ (m) | De-gassed DI water (g) | Scientific Notebook Reference |
|---|---|---|---|---|
| FeB(OH)4 R-0.02B-2 | 1.27 | 0.02 | 100.03 | WIPP-Borate-5 Pg. 6 |
| FeB(OH)4 R-0.03B-1 | 1.22 | 0.03 | 100.05 | WIPP-Borate-5 Pg. 6 |
| FeB(OH)4 R-0.03B-2 | 1.29 | 0.03 | 100.03 | WIPP-Borate-5 Pg. 6 |

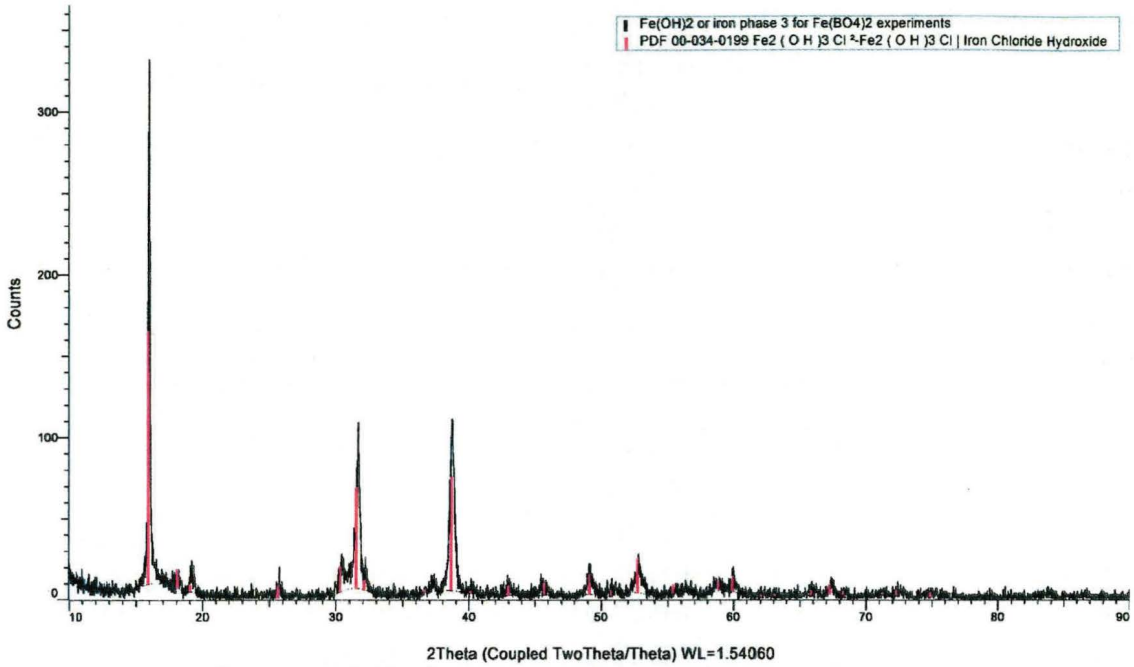



Figure 5 XRD of starting material for FeB(OH)4…B experiments.
Source of Figure 5: Scientific Notebook WIPP-Borate-1 Pg. 53

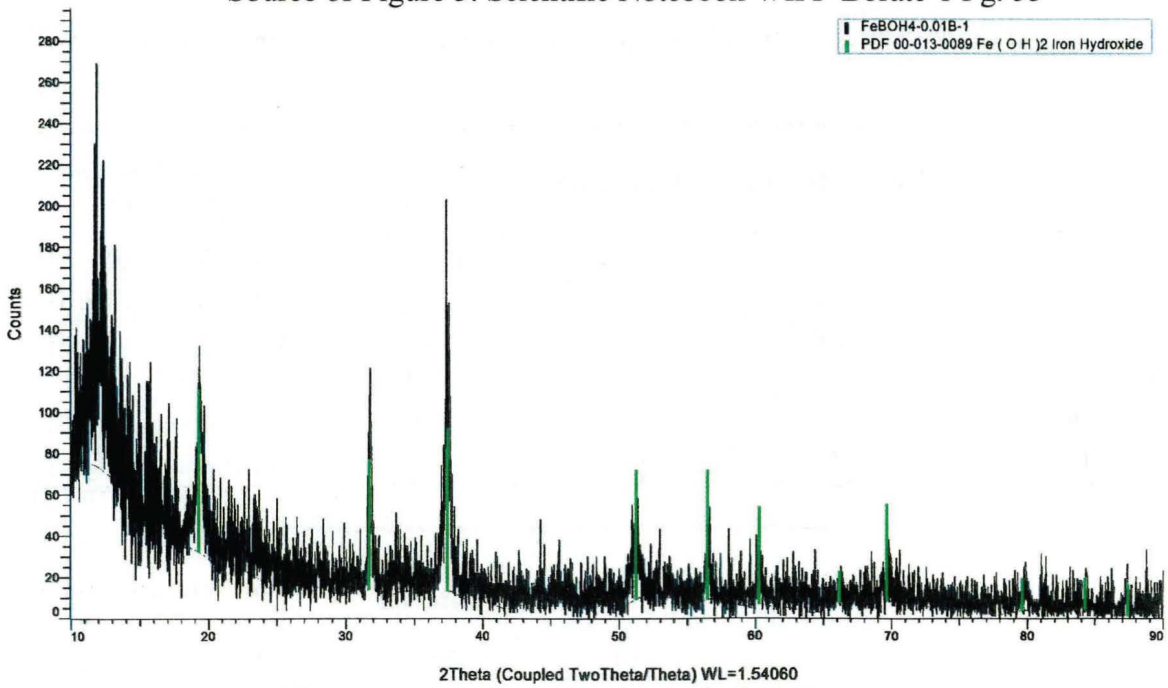



Figure 6 XRD analysis of sample FeB(OH)4-0.01B-1
Source of Figure 6: Scientific Notebook WIPP-Borate-10 Pg. 51

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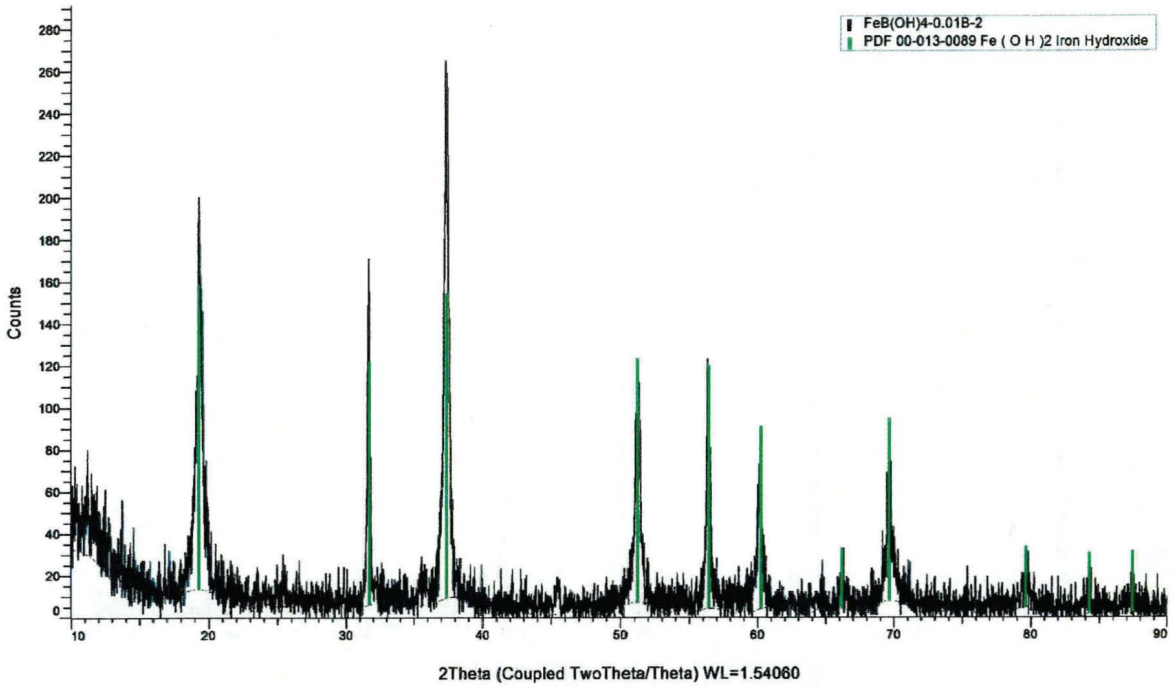



Figure 7 XRD analysis of sample FeB(OH)4-0.01B-2
Source of Figure 7: Scientific Notebook WIPP-Borate-10 Pg. 91

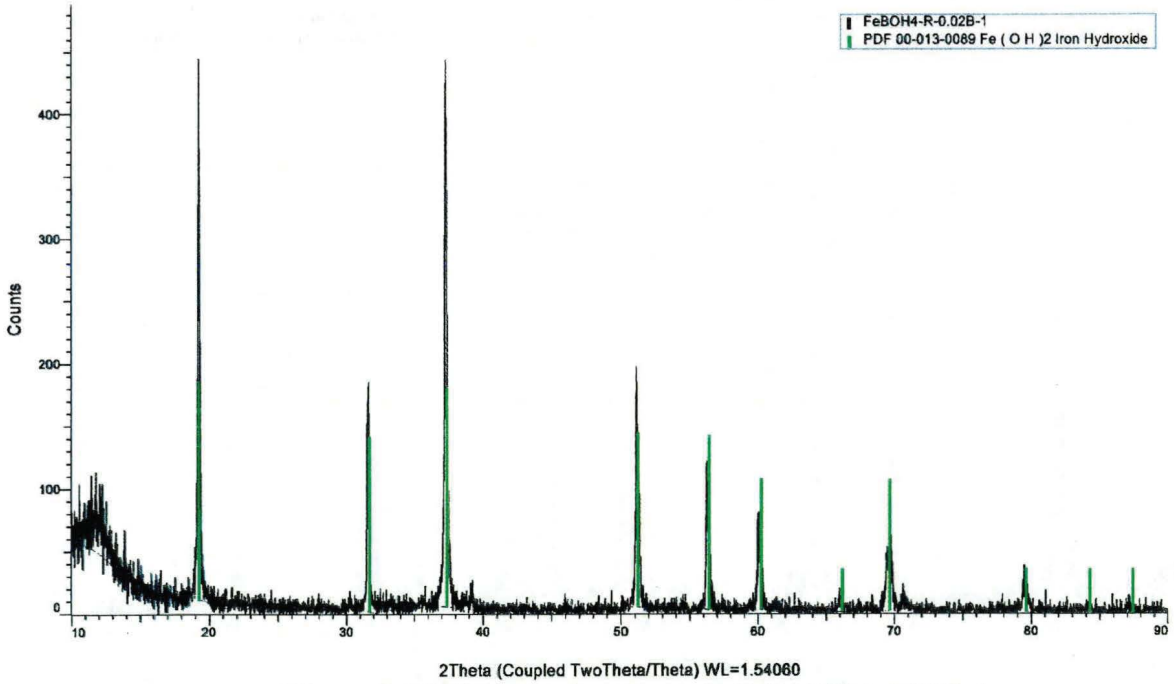



Figure 8 XRD analysis of sample FeB(OH)4-0.02B-1
Source of Figure 8: Scientific Notebook WIPP-Borate-10 Pg. 51

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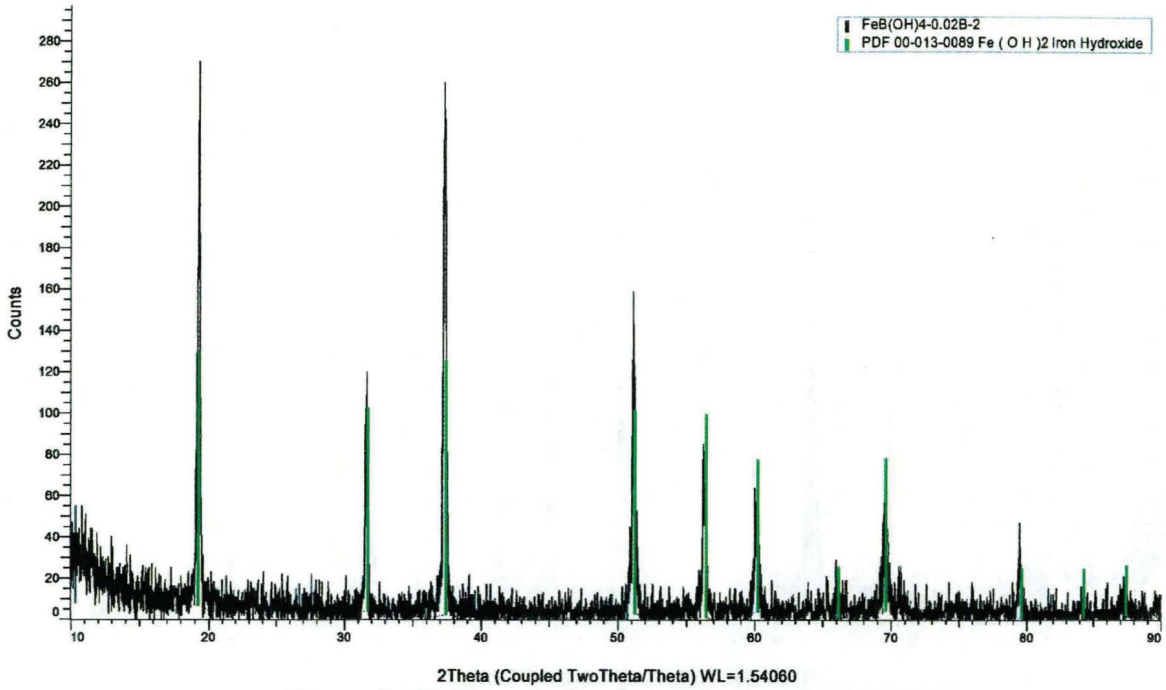



Figure 9 XRD analysis of sample FeB(OH)4-0.02B-2
Source of Figure 9: Scientific Notebook WIPP-Borate-10 Pg. 91

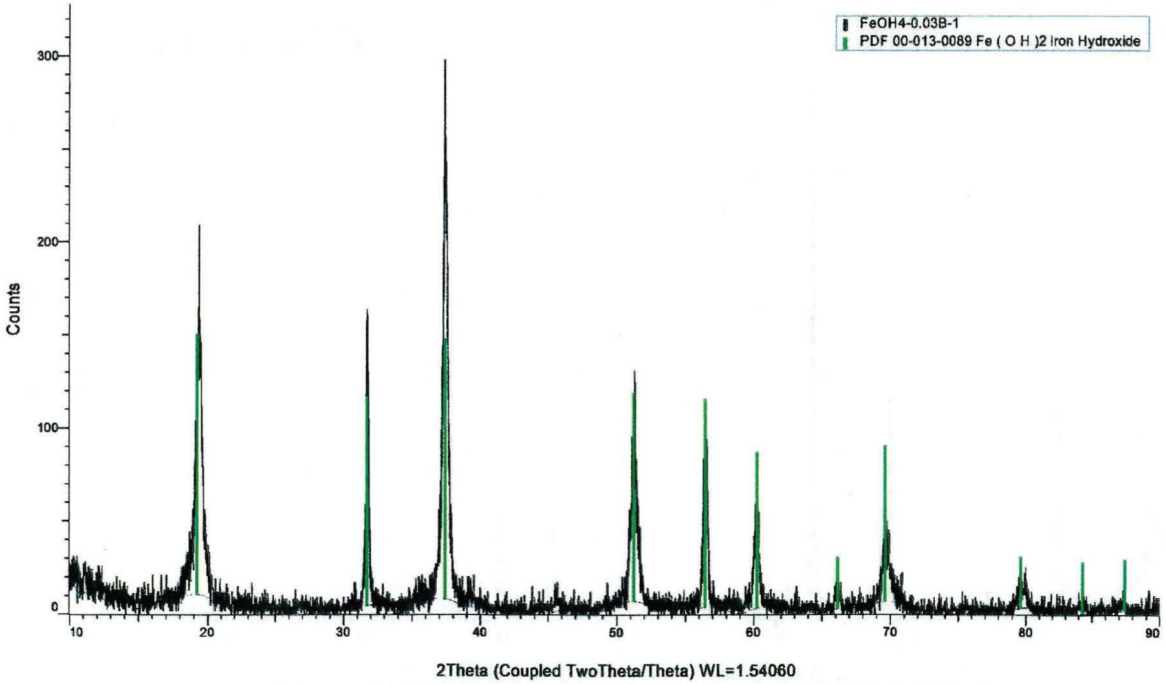



Figure 10 XRD analysis of sample FeB(OH)4-0.03B-1
Source of Figure 10: Scientific Notebook WIPP-Borate-10 Pg. 51

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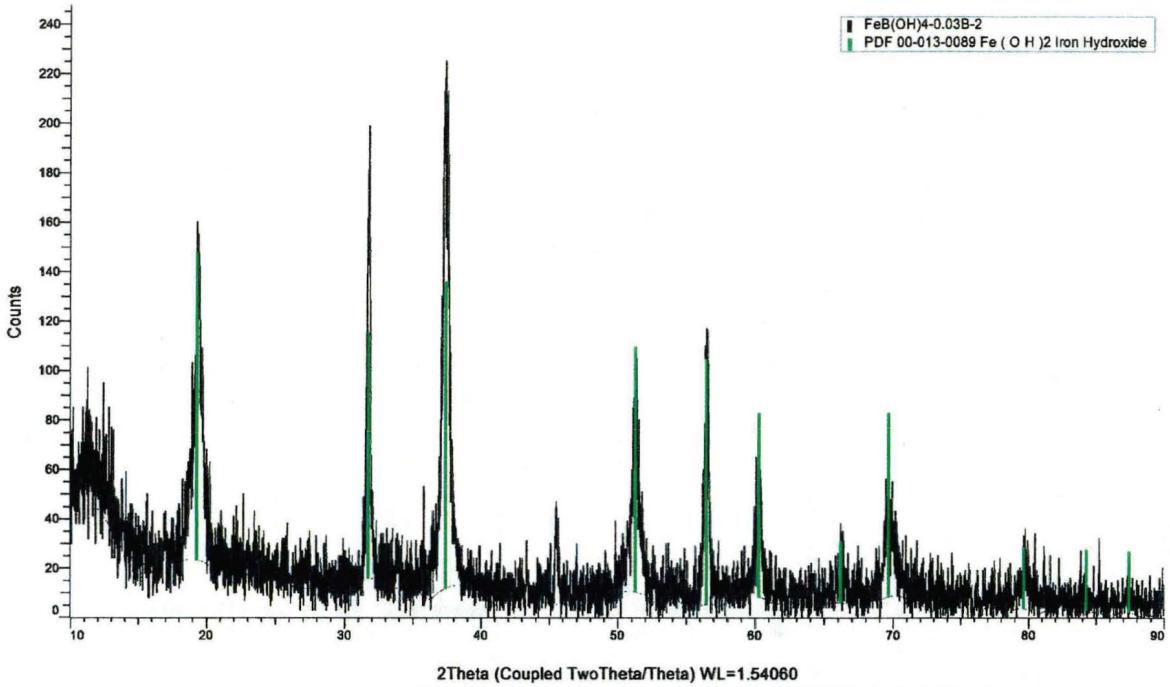



Figure 11 XRD analysis of sample FeB(OH)4-0.03B-2
Source of Figure 11: Scientific Notebook WIPP-Borate-10 Pg. 91

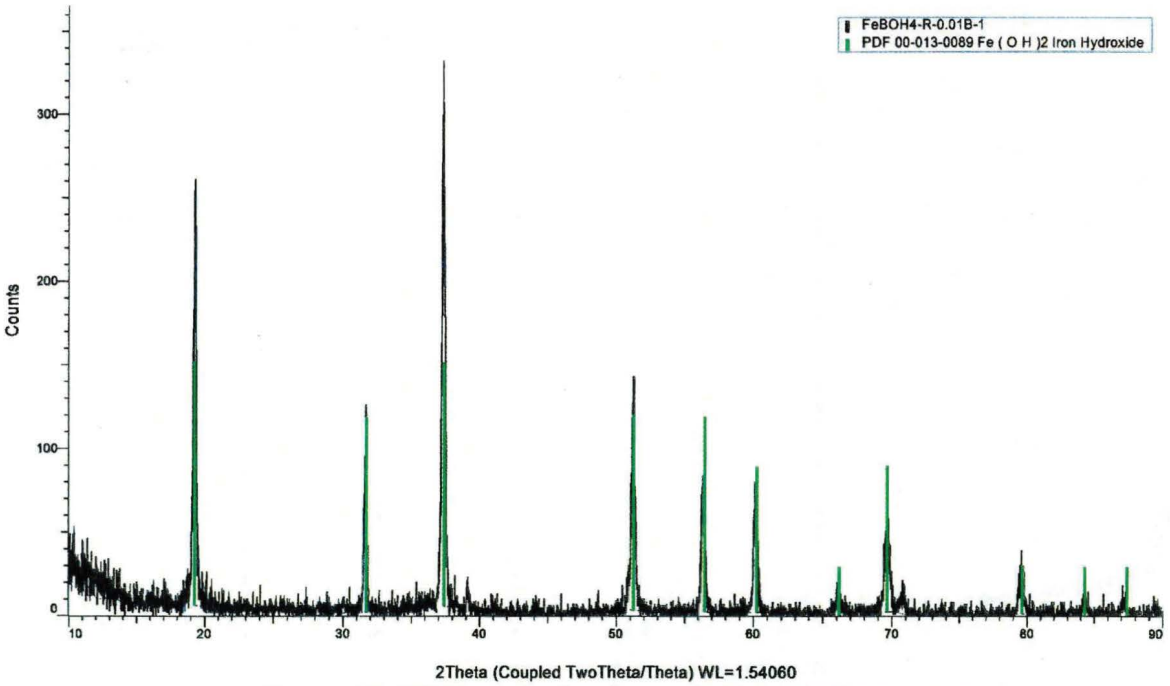



Figure 12 XRD analysis of sample FeB(OH)4 R-0.01B-1
Source of Figure 12: Scientific Notebook WIPP-Borate-10 Pg. 51

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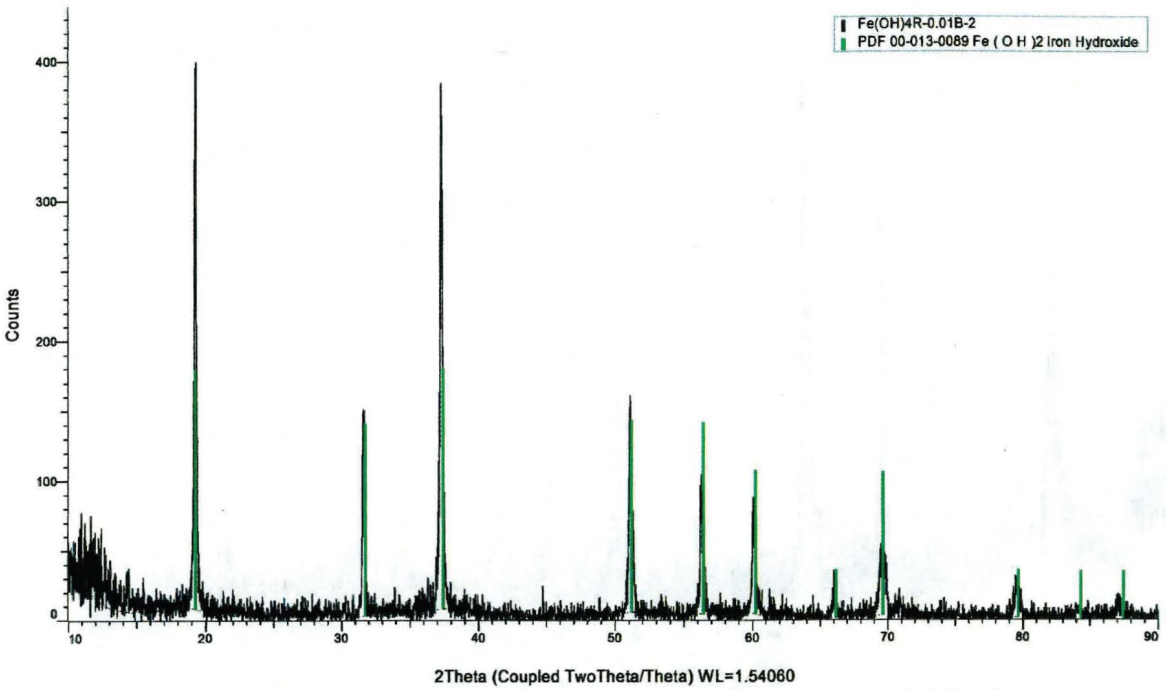



Figure 13 XRD analysis of sample FeB(OH)4 R-0.01B-2
Source of Figure 13: Scientific Notebook WIPP-Borate-10 Pg. 91

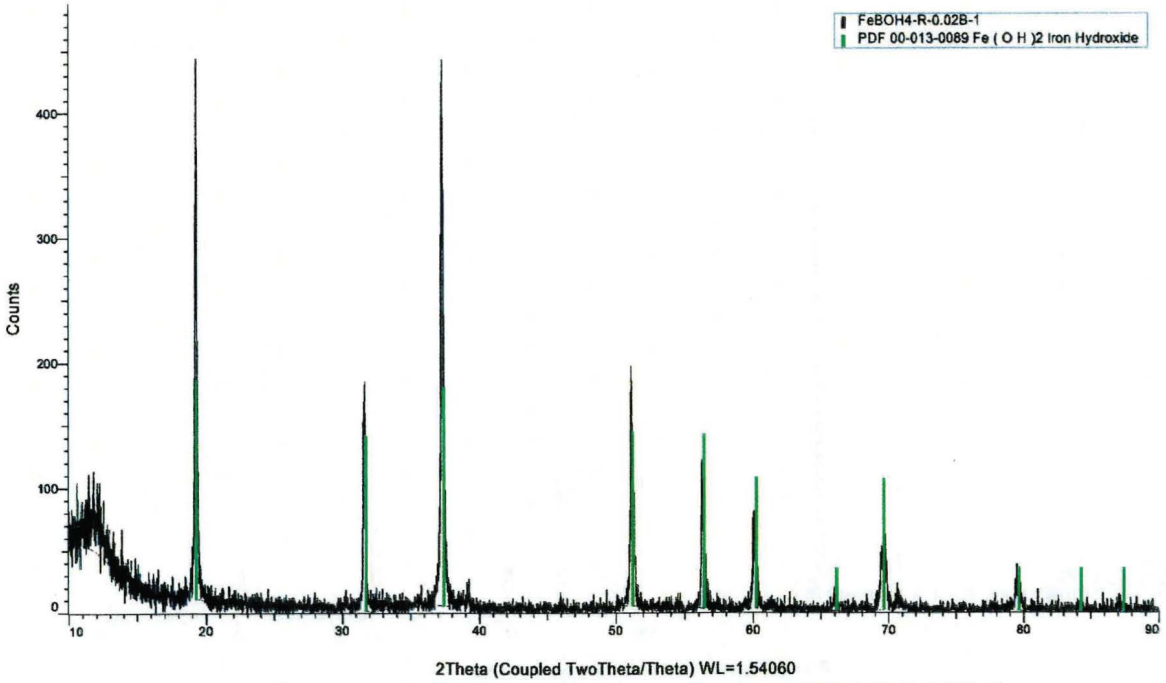



Figure 14 XRD analysis of sample FeB(OH)4 R-0.02B-1
Source of Figure 14: Scientific Notebook WIPP-Borate-10 Pg. 51

Information Only

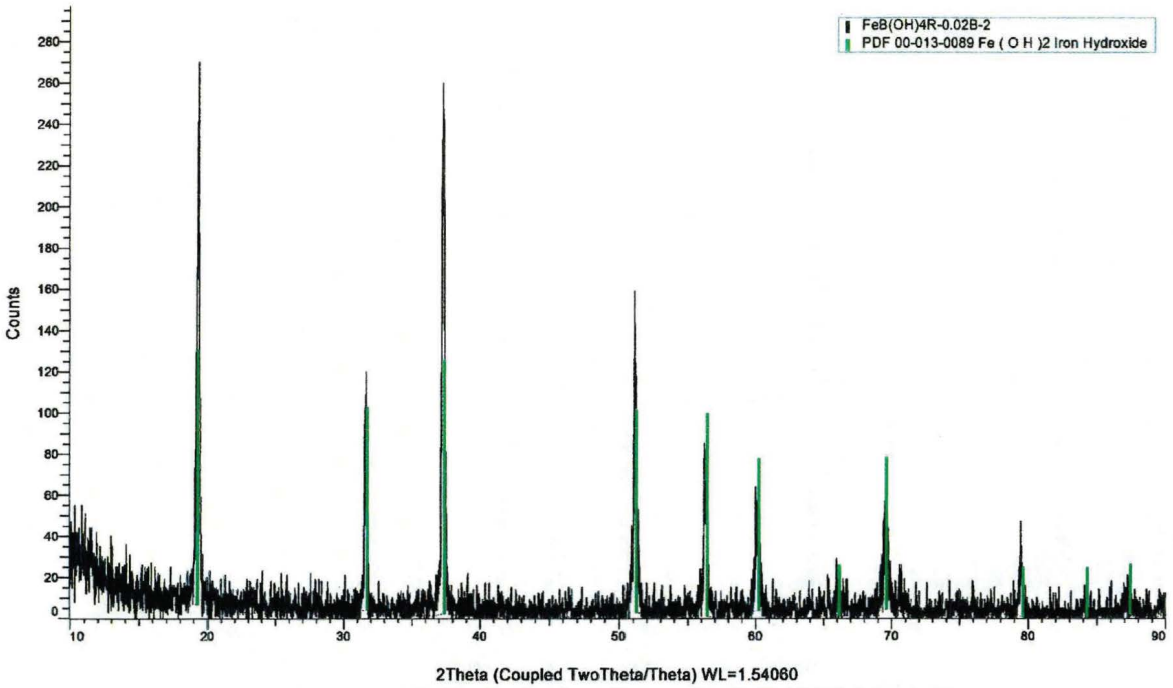



Figure 15 XRD analysis of sample FeB(OH)4 R-0.02R-2
Source of Figure 15: Scientific Notebook WIPP-Borate-10 Pg. 91

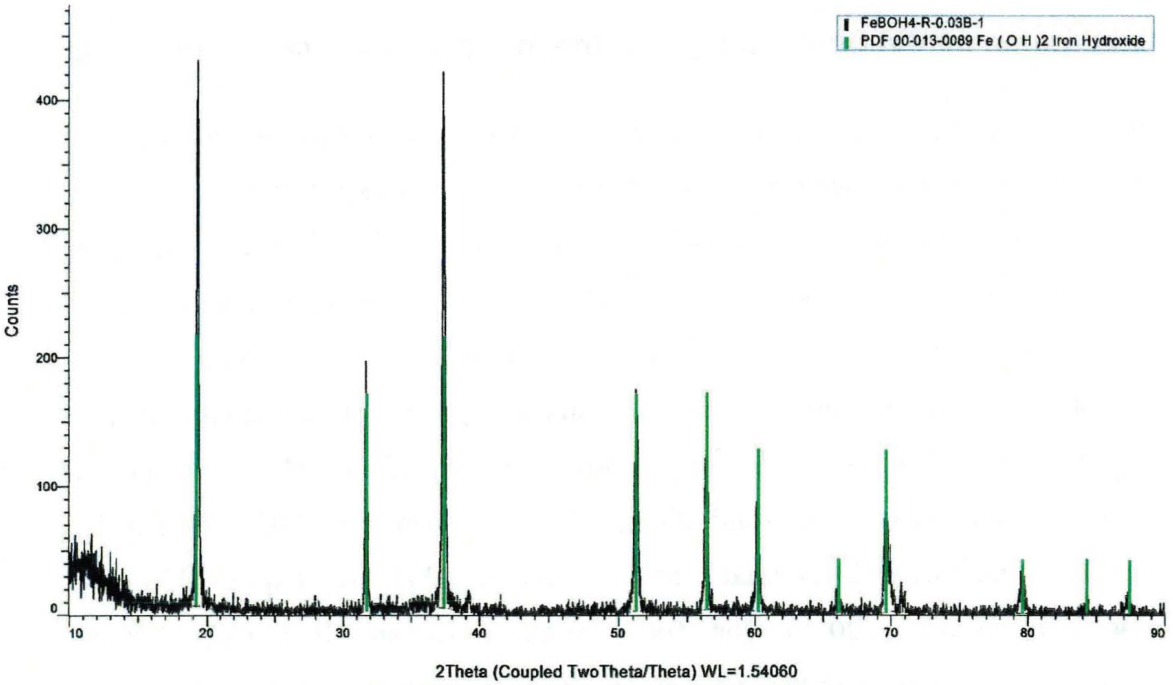



Figure 16 XRD analysis of sample FeB(OH)4 R-0.03B-1
Source of Figure 16: Scientific Notebook WIPP-Borate-10 Pg. 51

Information Only

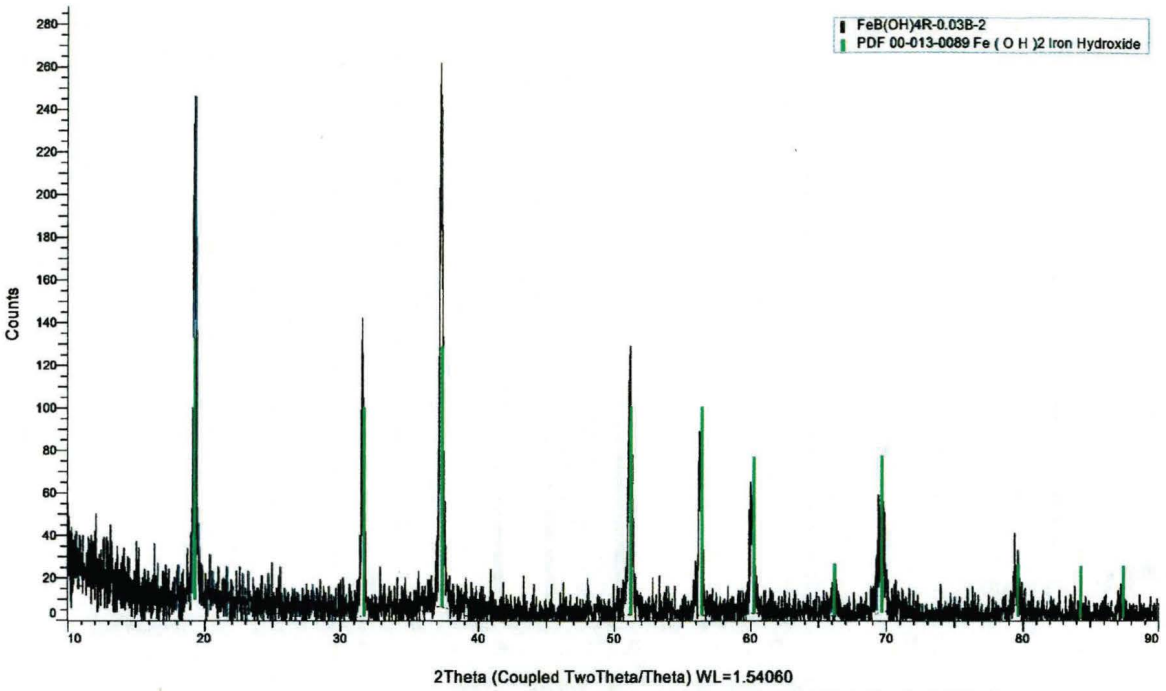



Figure 17 XRD analysis of sample FeB(OH)4 R-0.03B-2
Source of Figure 17: Scientific Notebook WIPP-Borate-10 Pg. 91

### 3.3 Task 3: Experimental Determination of the formation constant of $PbB_4O_7(aq)$

Table 3-4 shows the experimental set-up of the $PbB_4O_7$ experiments. Figures below document the XRD solids characterization for the PbB4O7…ClO4 experiments and PbB4O7…B4O7 experiments respectively. At 3142 days, solid material was collected from the PbB4O7…ClO4 experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solids characterization. At 3127 days, solid material was collected from the PbB4O7…B4O7 experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solids characterization. All the samples from the PbB4O7…ClO4 experiments match with good agreement to the expected solid litharge (PbO) PDF pattern 00-005-056. This is an expected result in that litharge is reported to be stable at high pH (10-12) and low chloride concentration (Regenspurg, S. 2016). The pHs in this experiment are ~10-11 (Xiong, Y. and Kirkes, L. 2017) and the matrix of the experiments are low in chloride. The samples in this set of experiments also contained the solid sodium perchlorate (NaClO4) PDF pattern 00-007-0226, which is an expected result because this is part of the matrix in these experiments. The samples in the PbB4O7…B4O7 experiment all match with good agreement to the expected solid litharge (PbO) PDF pattern 00-005-0561 and the solid laurionite (PbCl(OH)) PDF pattern 04-011-5179.

Information Only

Based on the studies conducted by Ioannidis et al. (2006, 2007) and Sidra et al. (2013), laurionite and its derivatives such as Pb(OH)Br and Pb(OH)I are precipitated from aqueous acidic solutions, and are not normally stable at the pH measured in these experiments (~9). This experimental result may be a good candidate for future research in new experiments, or possibly further analysis by SEM/EDS. The Figures below show the XRD data.

Table 3-4 Preparation of experimental set-ups for investigation of the formation constant of $PbB_4O_7(aq)$.

| Set-up ID | Boron (m) | $NaClO_4$ (m) | PbO (g) | De-gassed DI Water (g) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB4O7-0.1 ClO4-1 | N/A | 0.10 | 2.0003 | 100.0015 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.1 ClO4-2 | N/A | 0.10 | 2.0000 | 100.0006 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.2 ClO4-1 | N/A | 0.20 | 2.0006 | 100.0002 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.2 ClO4-2 | N/A | 0.20 | 2.0003 | 100.0001 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.3 ClO4-1 | N/A | 0.30 | 2.0001 | 100.0013 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.3 ClO4-2 | N/A | 0.30 | 2.0001 | 100.0006 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.4 ClO4-1 | N/A | 0.4 | 2.0004 | 100.0016 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.4 ClO4-2 | N/A | 0.4 | 2.0008 | 100.0014 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.45 ClO4-1 | N/A | 0.45 | 2.0003 | 100.0020 | WIPP-Borate-1 Pg. 20 |
| PbB4O7-0.45 ClO4-2 | N/A | 0.45 | 2.0009 | 100.0009 | WIPP-Borate-1 Pg. 20 |

| Set-up ID | Boron (m) | PbO (g) | De-gassed DI Water (g) | Scientific Notebook Reference |
|---|---|---|---|---|
| PbB4O7-0.1 B4O7-1 | 0.13 | 2.0006 | 100.0024 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.1 B4O7-2 | 0.13 | 2.0001 | 100.0003 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.2 B4O7-1 | 0.27 | 2.0011 | 100.0028 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.2 B4O7-2 | 0.27 | 2.0012 | 100.0040 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.3 B4O7-1 | 0.40 | 2.0001 | 100.0005 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.3 B4O7-2 | 0.40 | 2.0004 | 100.0033 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.4 B4O7-1 | 0.53 | 2.0004 | 100.0004 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.4 B4O7-2 | 0.53 | 2.0008 | 100.0014 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.45 B4O7-1 | 0.60 | 2.0015 | 100.0019 | WIPP-Borate-1 Pg. 21 |
| PbB4O7-0.45 B4O7-2 | 0.60 | 2.0003 | 100.0030 | WIPP-Borate-1 Pg. 21 |

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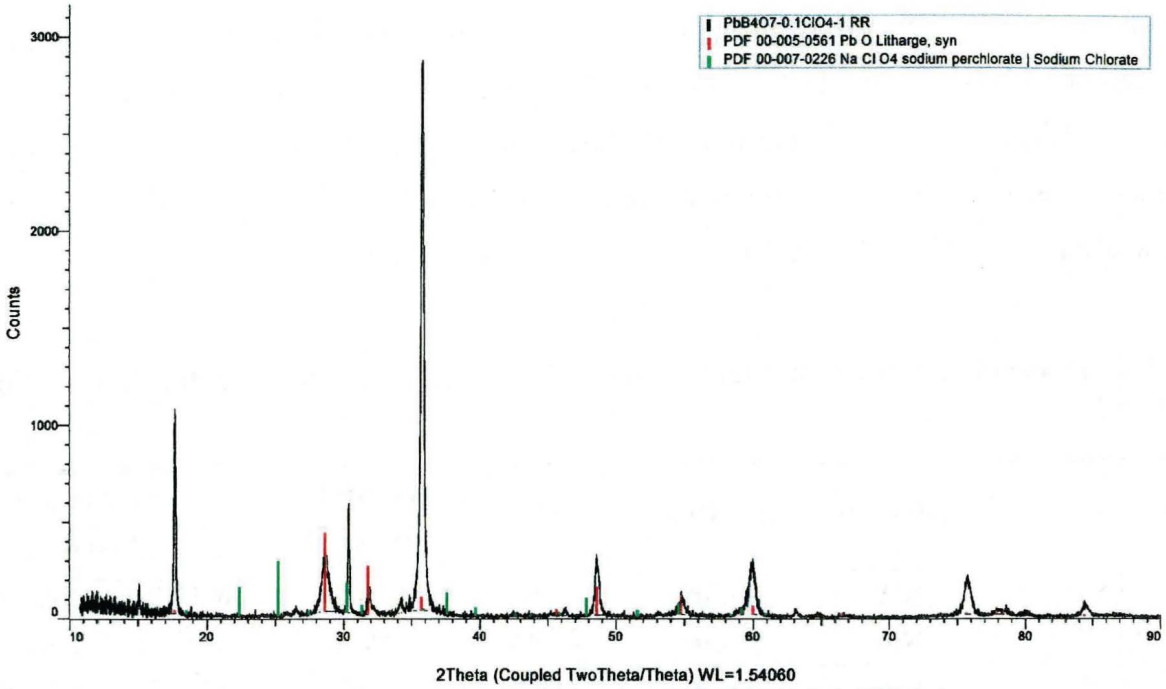



Figure 18 XRD analysis of PbB4O7-0.1 ClO4-1
Source of Figure 18: Scientific Notebook WIPP-Borate-10 Pg. 90

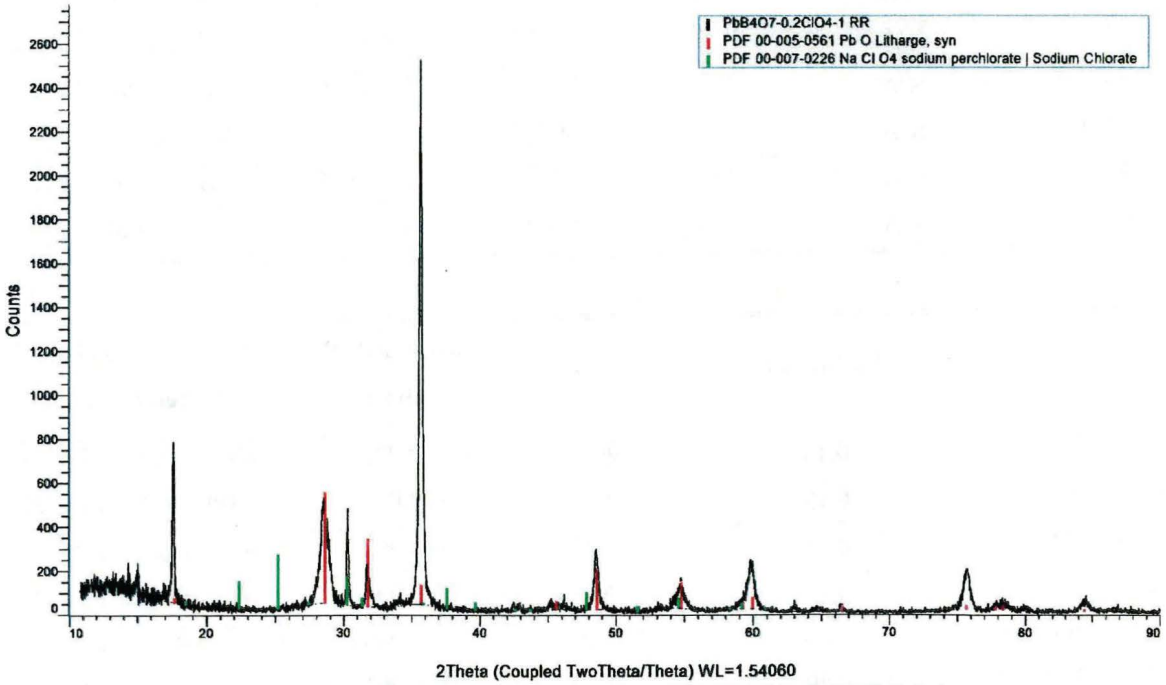



Figure 19 XRD analysis of PbB4O7-0.2 ClO4-1
Source of Figure 19: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

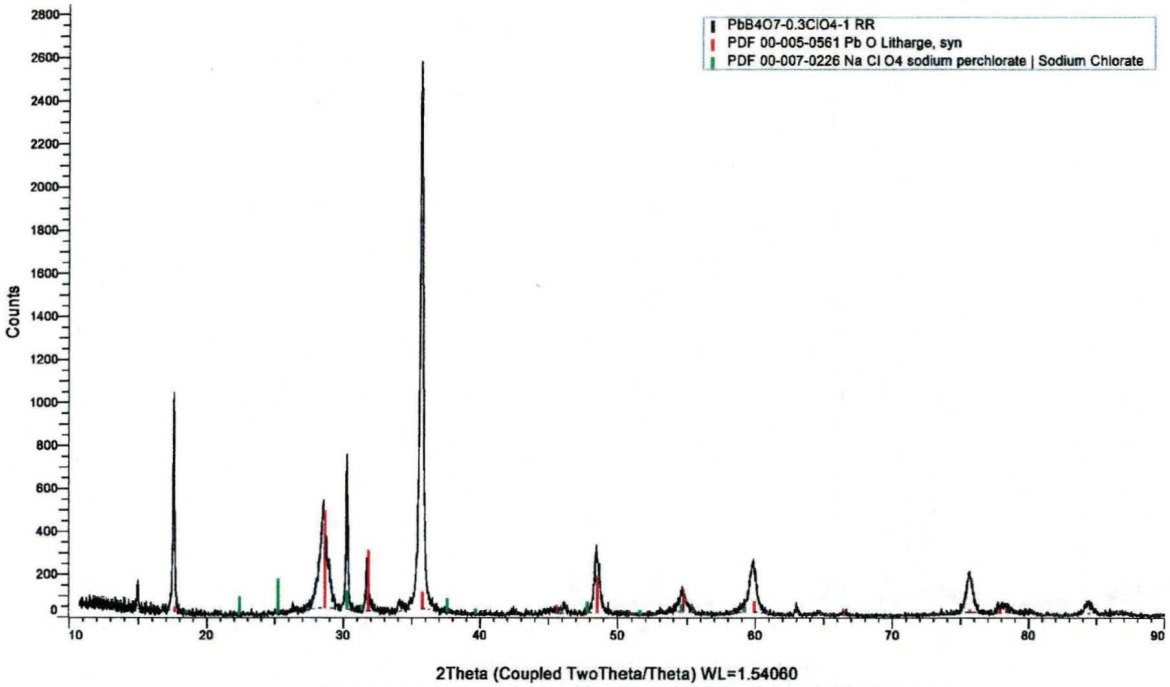



Figure 20 XRD analysis of PbB4O7-0.3 ClO4-1
Source of Figure 20: Scientific Notebook WIPP-Borate-10 Pg. 90

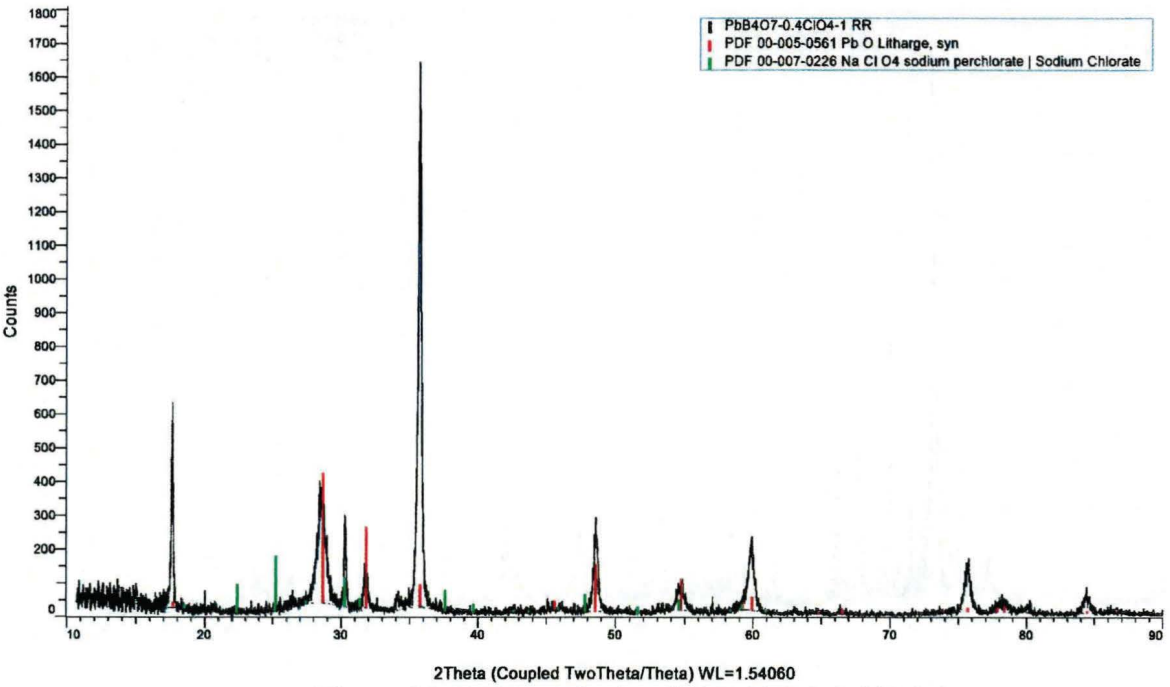



Figure 21 XRD analysis of PbB4O7-0.4 ClO4-1
Source of Figure 21: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

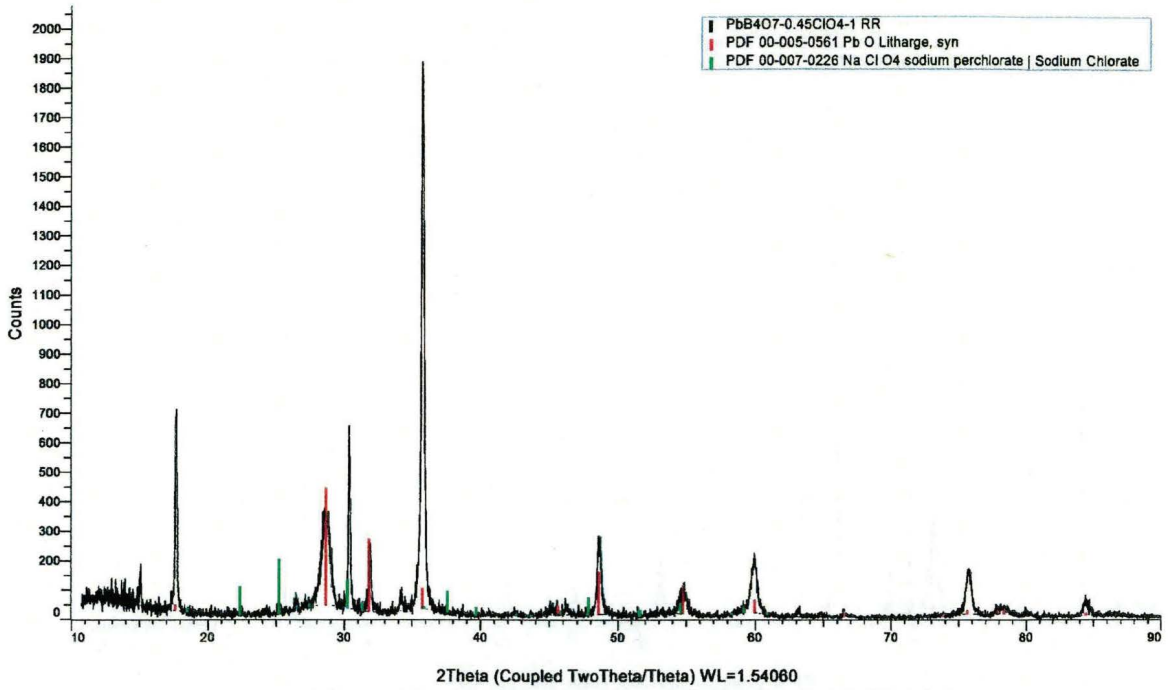



Figure 22 XRD analysis of PbB4O7-0.45 ClO4-1
Source of Figure 22: Scientific Notebook WIPP-Borate-10 Pg. 90

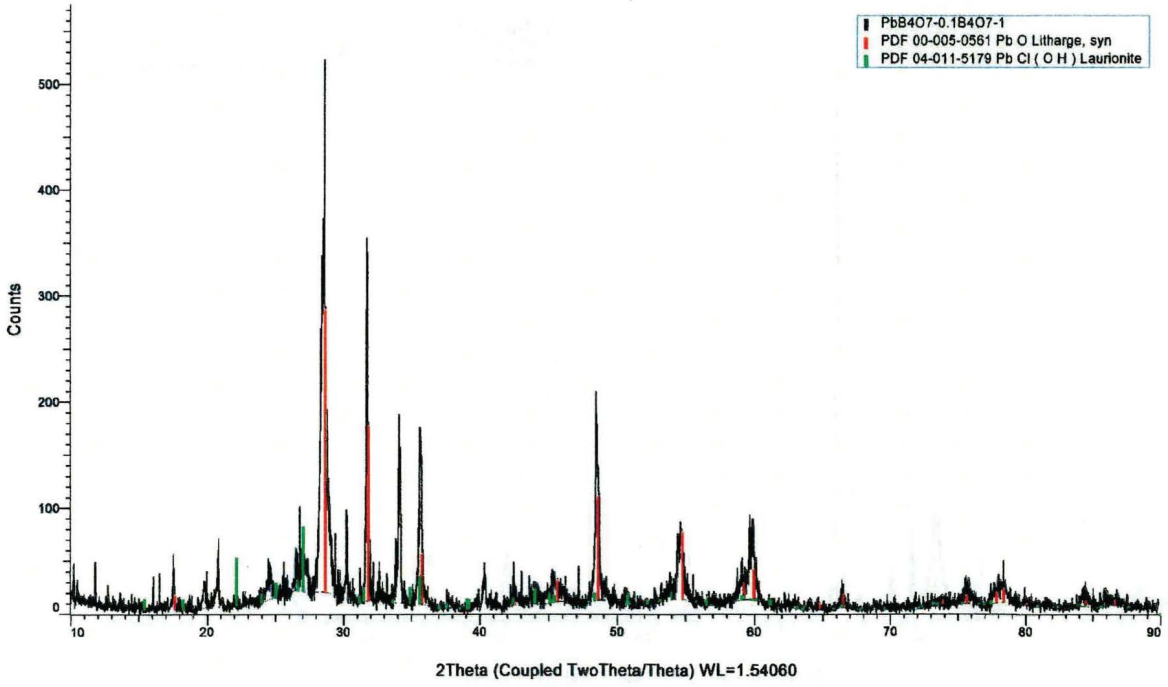



Figure 23 XRD analysis of PbB4O7-0.1 B4O7-1
Source of Figure 23: Scientific Notebook WIPP-Borate-10 Pg. 92

Information Only

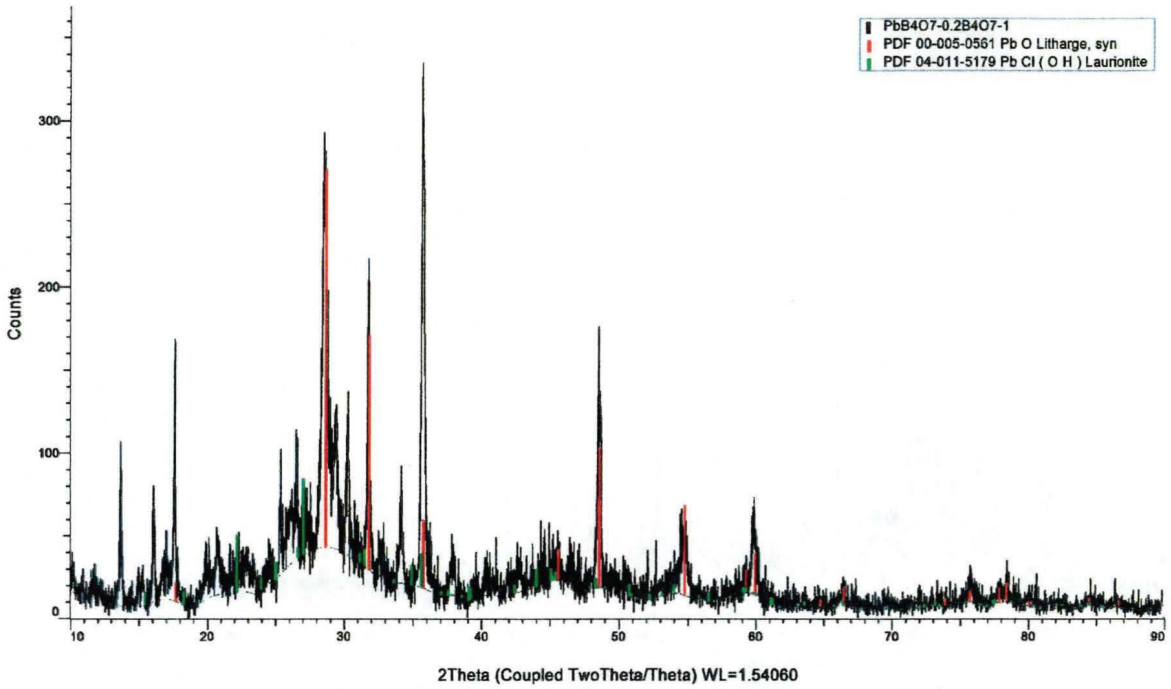



Figure 24 XRD analysis of PbB4O7-0.2 B4O7-1
Source of Figure 24: Scientific Notebook WIPP-Borate-10 Pg. 92

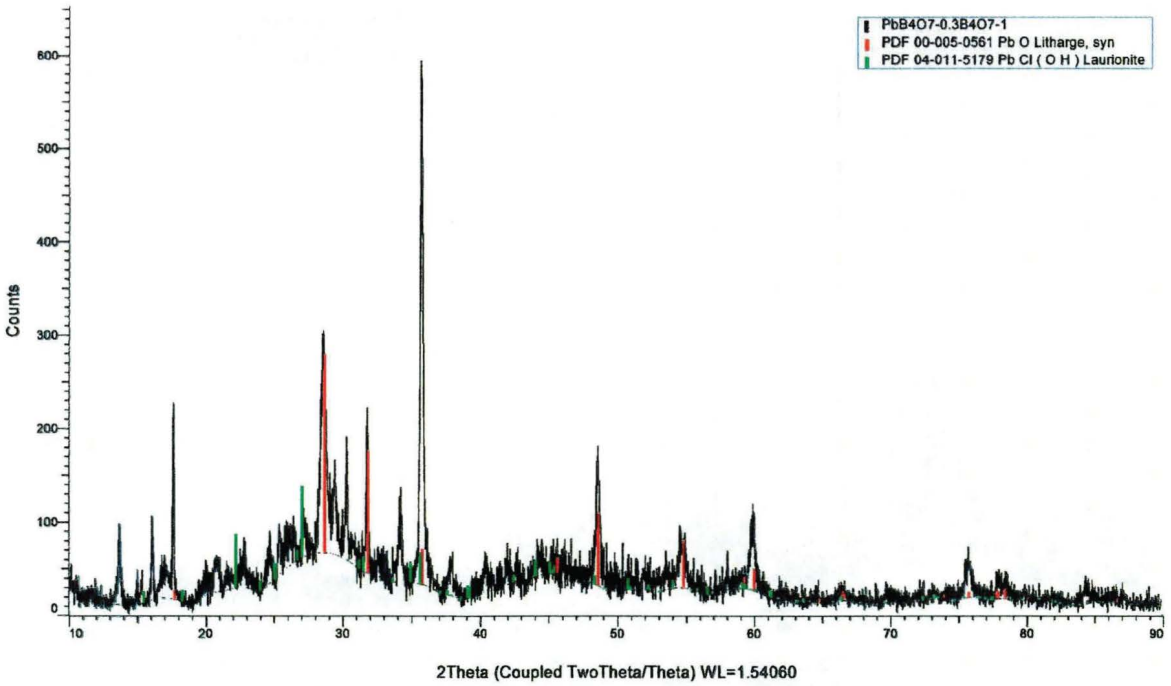



Figure 25 XRD analysis of PbB4O7-0.3 B4O7-1
Source of Figure 25: Scientific Notebook WIPP-Borate-10 Pg. 92

Information Only

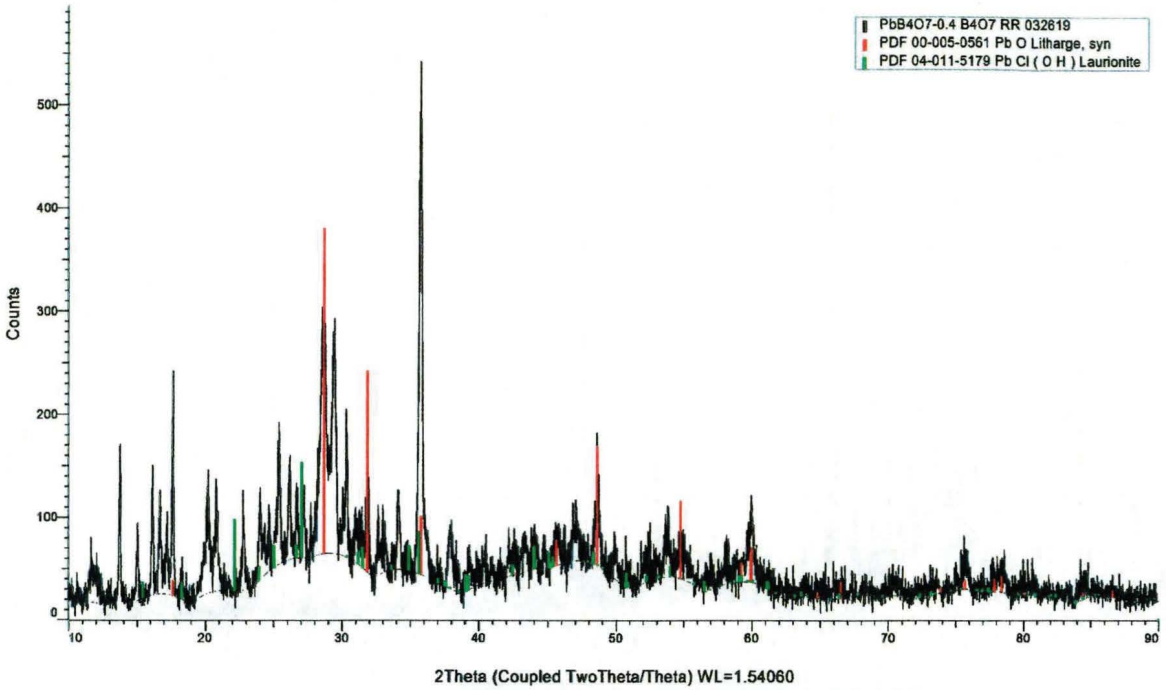



Figure 26 XRD analysis of PbB4O7-0.4 B4O7-1
Source of Figure 26: Scientific Notebook WIPP-Borate-10 Pg. 92

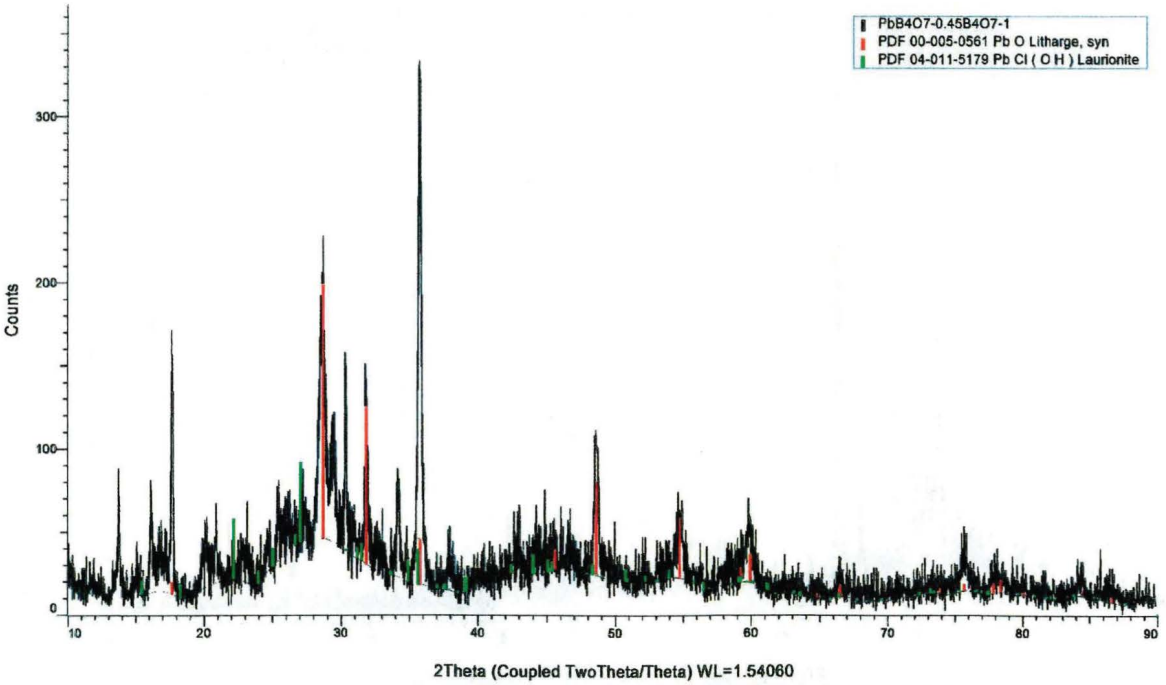



Figure 27 XRD analysis of PbB4O7-0.45 B4O7-1
Source of Figure 27: Scientific Notebook WIPP-Borate-10 Pg. 92

Information Only

## 3.4 Task 4: Experimental Determination of Pitzer Interaction Parameters Relevant to the WIPP Brines

### 3.4.1 $PbB(OH)_4^+$—$Cl^-$ Interactions

Table 3-5 shows the experimental set-up of the $PbB(OH)_4^+$-$Cl^-$ experiment. The figures below document the XRD solids characterization of samples in the $PbB(OH)_4^+$-$Cl^-$ experiment. At the termination time of 3156 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Samples PbB(OH)4-0.01Cl-1 and PbB(OH)4-0.1Cl-1 were comprised of solids blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193 and lead oxide (PbO) PDF pattern 00-005-0561 and lead boron oxide ($Pb_6B_{10}O_{21}$) PDF pattern 04-011-1619. Samples PbB(OH)4-1.0Cl-1, PbB(OH)4-2.0Cl-1, PbB(OH)4-3.0-1 and PbB(OH)4-4.0-1 were comprised primarily of blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193 and litharge (PbO) PDF pattern 00-005-0561. Sample PbB(OH)4-5.0Cl-1 was comprised of blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193, litharge (PbO) PDF pattern 00-005-0561 and laurionite (PbCl(OH)) PDF pattern 04-011-5179. Based on the investigations conducted by Ioannidis et al. (2006, 2007) and Sidra et al. (2013), laurionite should not be stable at the pH measured in these experiments (~11) when the experiments sampled for solution chemistry (Xiong, Y. and Kirkes, L. 2017). Therefore, new experiments including sampling for solution chemistry are needed to corroborate. This experimental result may be a good candidate for future research in new experiments. The figures below show the XRD data.

Table 3-5 Preparation of experimental set-ups for investigation of $PbB(OH)_4^+$—$Cl^-$ Interactions.

| Set-up ID | NaCl (m) | PbO (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB(OH)4-0.01Cl- 1 | 0.010 | 2.0019 | 98.0192 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-0.01Cl- 2 | 0.010 | 2.0065 | 98.0193 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-0.1Cl- 1 | 0.10 | 2.0023 | 98.0028 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-0.1Cl- 2 | 0.10 | 2.0047 | 98.0193 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-1.0Cl- 1 | 1.0 | 2.0045 | 98.0153 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-1.0Cl- 2 | 1.0 | 2.0020 | 98.0215 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-2.0Cl- 1 | 2.0 | 2.0017 | 98.0034 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-2.0Cl- 2 | 2.0 | 2.0092 | 98.0114 | 0.0010 | WIPP-Borate-1 Pg. 8 |

Information Only

| Set-up ID | NaCl (m) | PbO (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB(OH)4-3.0Cl- 1 | 3.0 | 2.0013 | 98.0004 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-3.0Cl- 2 | 3.0 | 2.0021 | 98.0064 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-4.0Cl- 1 | 4.0 | 2.0018 | 98.0112 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-4.0Cl- 2 | 4.0 | 2.0040 | 97.9996 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-5.0Cl- 1 | 5.0 | 1.9999 | 98.0090 | 0.0010 | WIPP-Borate-1 Pg. 8 |
| PbB(OH)4-5.0Cl- 2 | 5.0 | 2.0006 | 98.1948 | 0.0010 | WIPP-Borate-1 Pg. 8 |

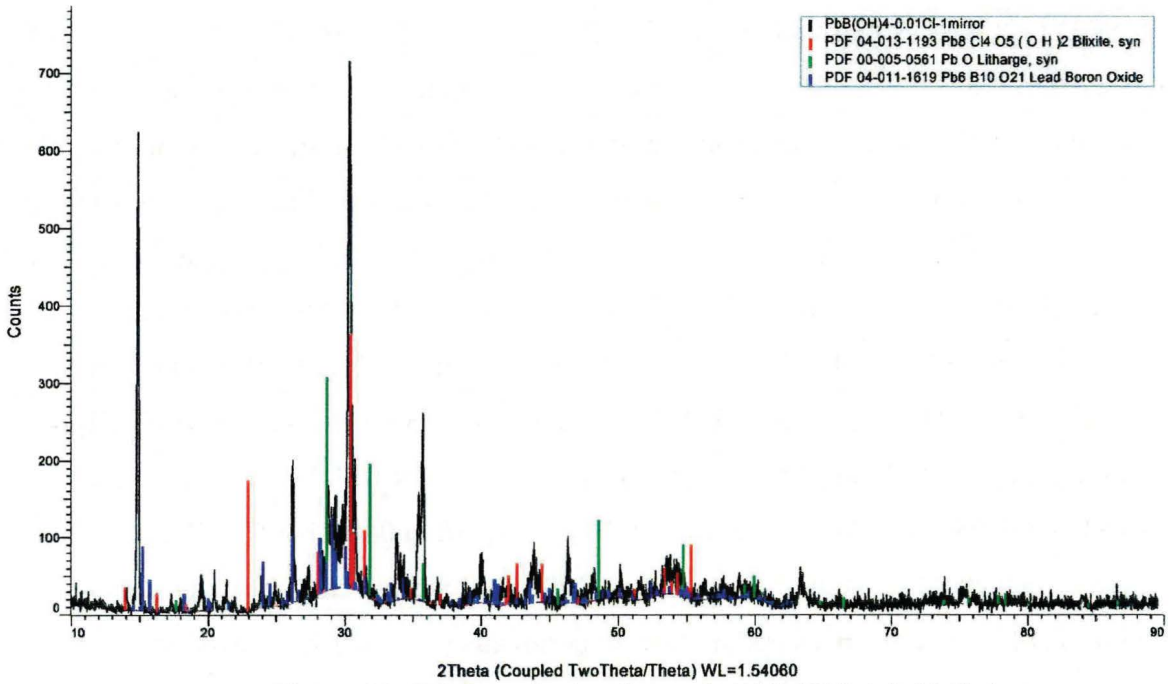



Figure 28 XRD analysis of sample PbB(OH)4-0.01Cl-1
Source of Figure 28: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

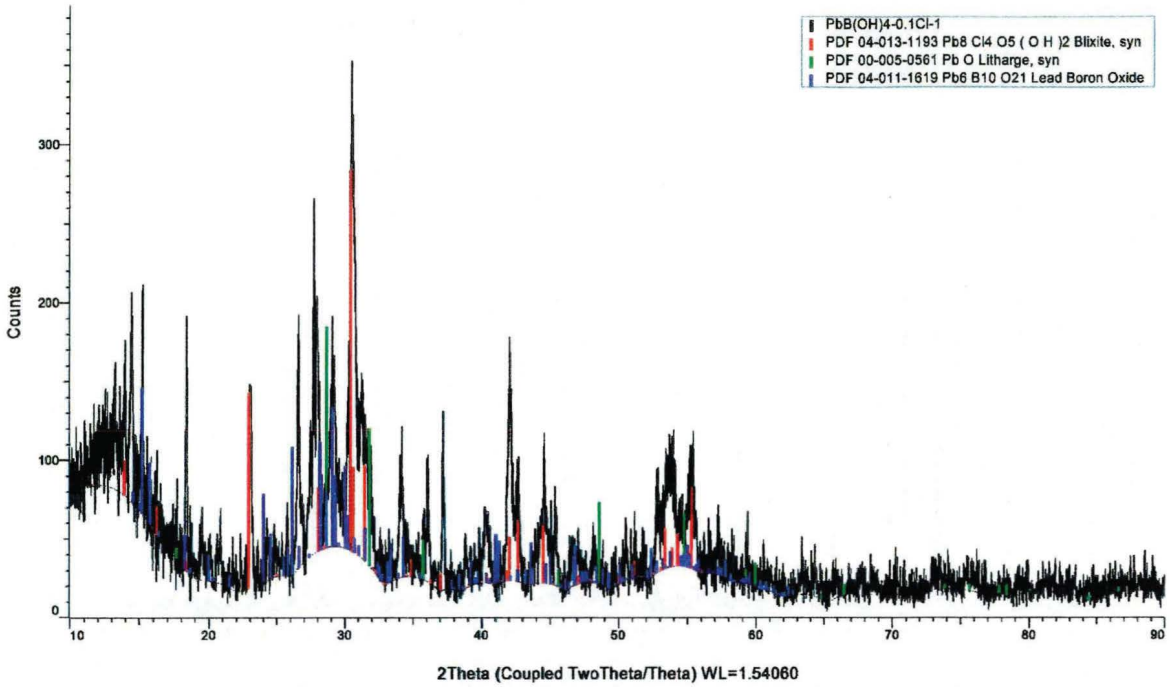



Figure 29 XRD analysis of sample PbB(OH)4-0.1Cl-1
Source of Figure 29: Scientific Notebook WIPP-Borate-10 Pg. 90

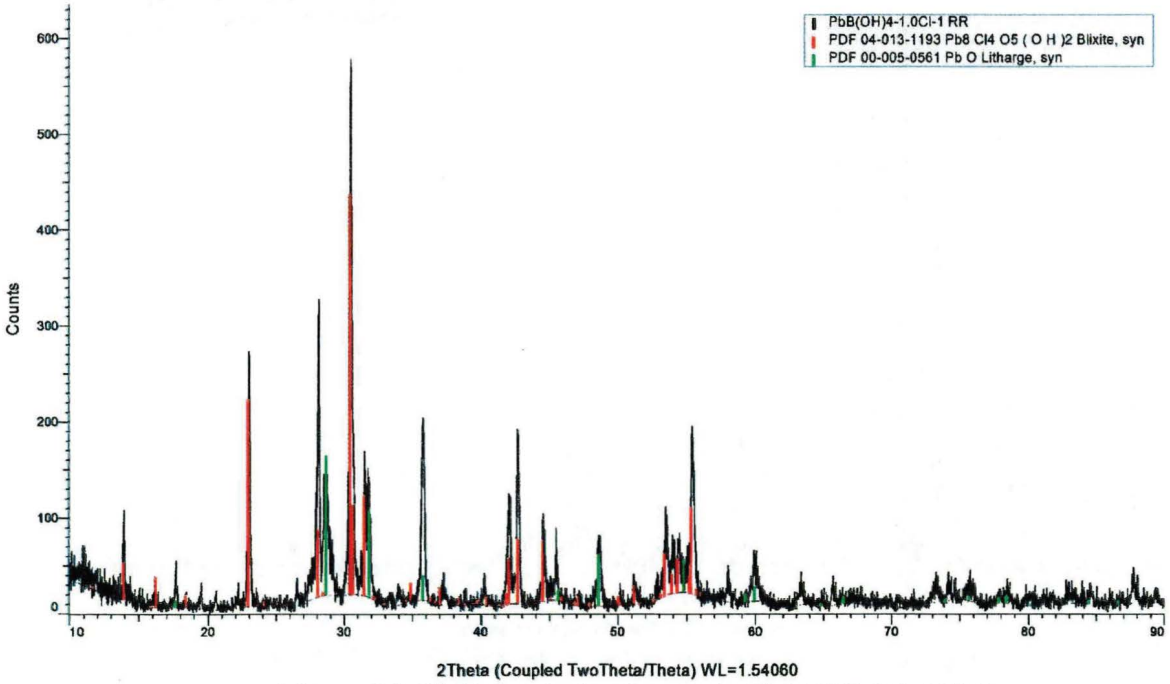



Figure 30 XRD analysis of sample PbB(OH)4-1.0Cl-1
Source of Figure 30: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

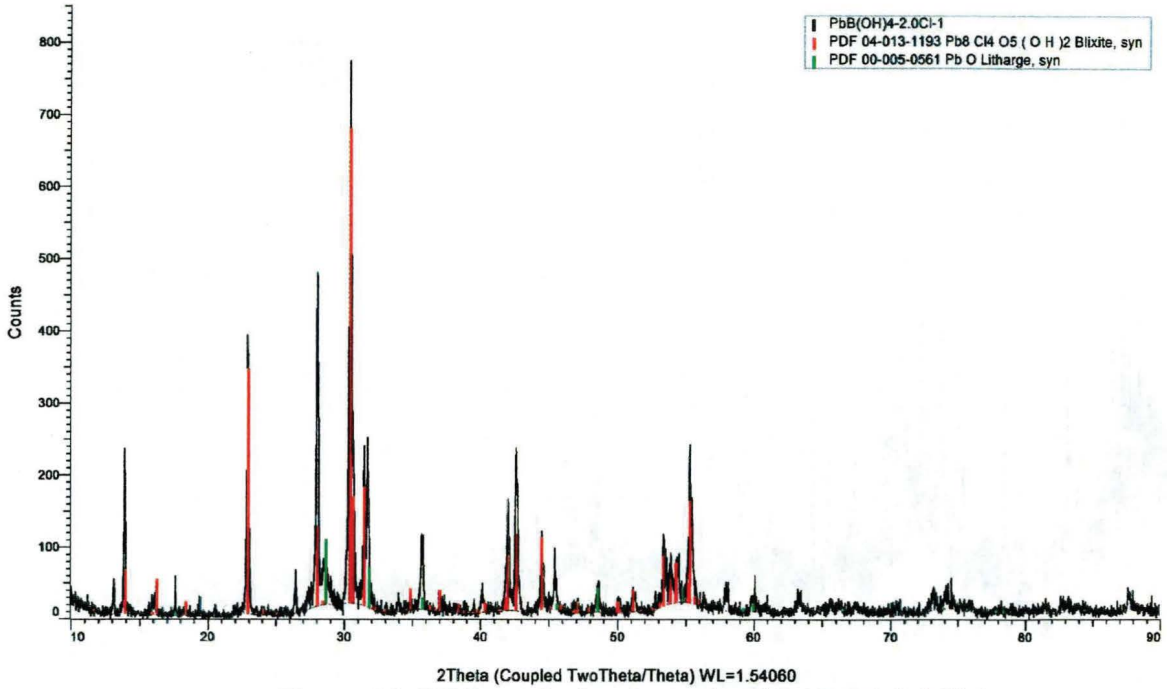



Figure 31 XRD analysis of sample PbB(OH)4-2.0Cl-1
Source of Figure 31: Scientific Notebook WIPP-Borate-10 Pg. 90

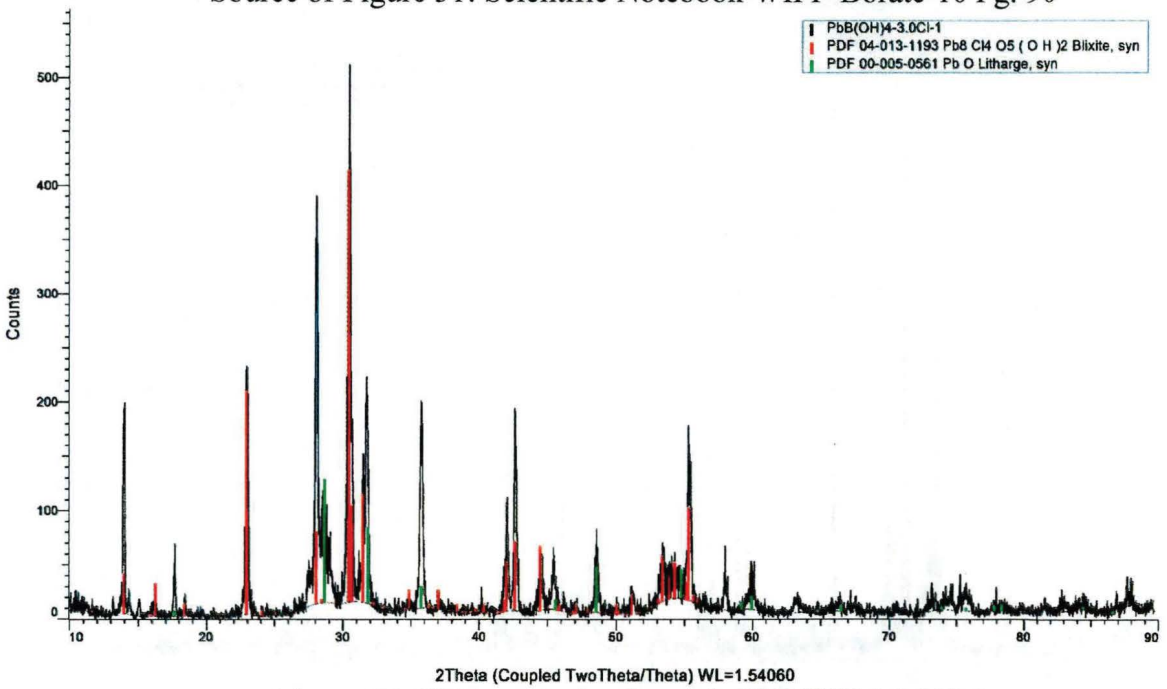



Figure 32 XRD analysis of sample PbB(OH)4-3.0Cl-1
Source of Figure 32: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

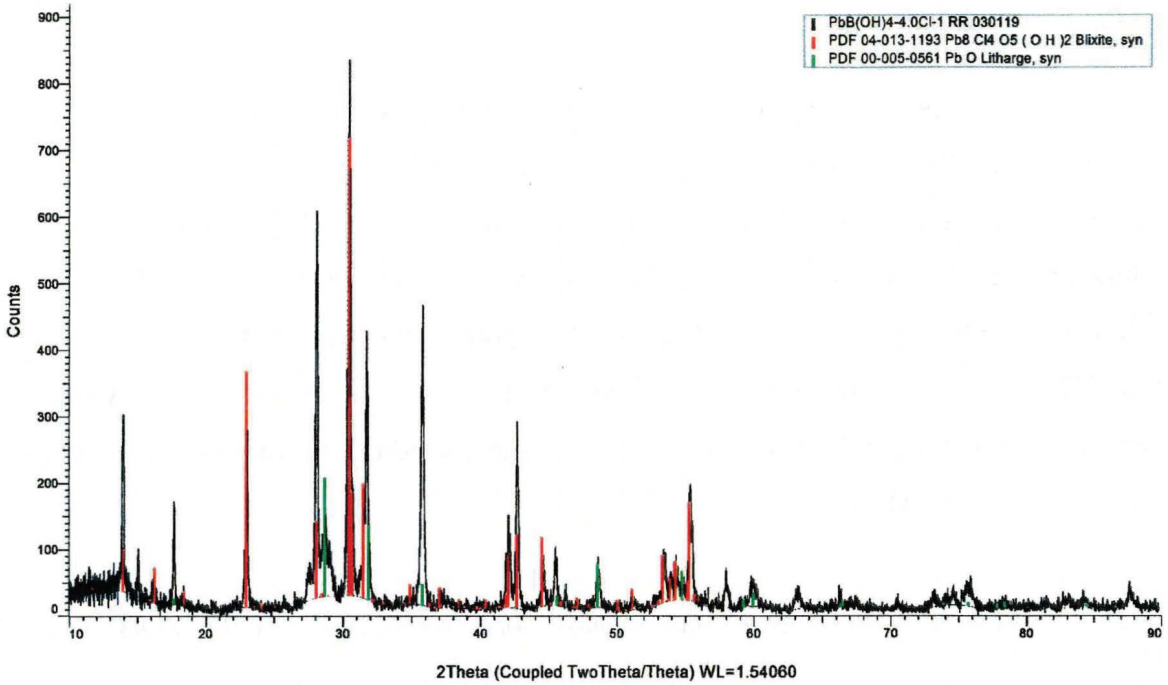



Figure 33 XRD analysis of sample PbB(OH)4-4.0Cl-1
Source of Figure 33: Scientific Notebook WIPP-Borate-10 Pg. 90

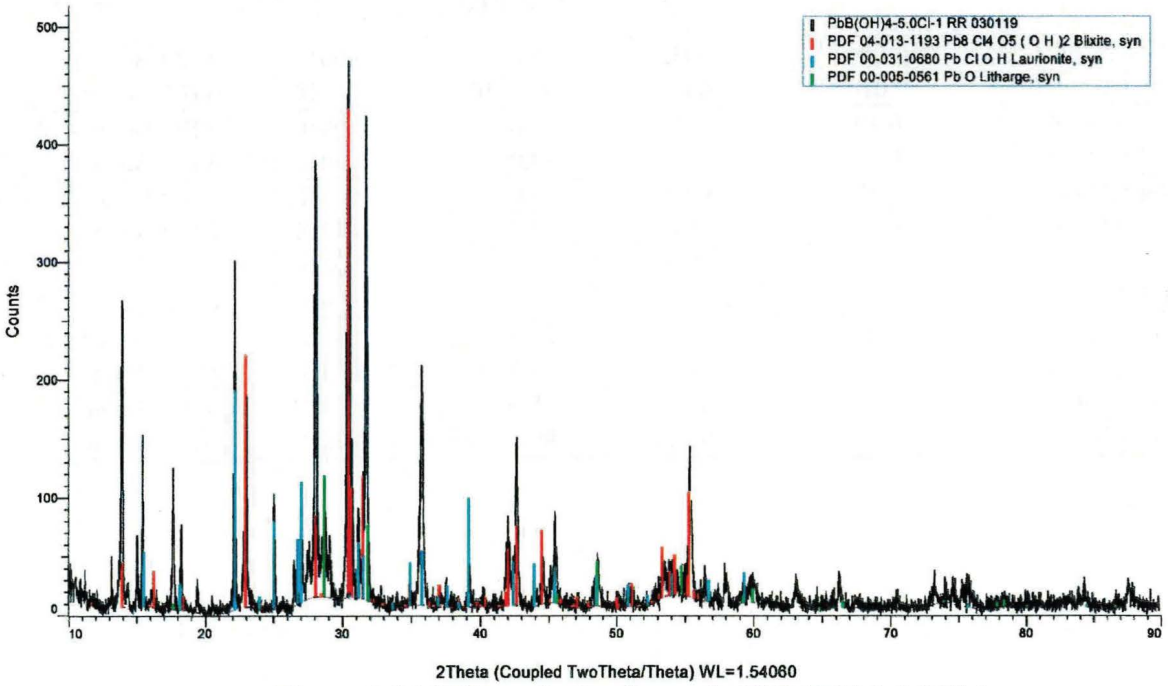



Figure 34 XRD analysis of sample PbB(OH)4-5.0Cl-1
Source of Figure 34: Scientific Notebook WIPP-Borate-10 Pg. 90

Information Only

### 3.4.2 $PbB(OH)_4^+$—$SO_4^{2-}$ Interactions

Table 3-6 shows the experimental set-up of the $PbB(OH)_4^+$-$SO_4^{2-}$ experiments. The figures below, document the XRD analyses. At 2940 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed by XRD. Samples in this system show litharge (PbO) PDF pattern 00-005-0561 as the predominant solid. Lead oxide sulfate ($Pb_5(SO_4)O_4$) PDF pattern 04-015-1561 and lead borate hydroxide hydrate ($Pb_5B_3O_8(OH)_3 \cdot H_2O$) PDF pattern 00-052-1259 were also found to be present in these systems. Further characterization through SEM/EDS needs to be completed to confirm this result. The figures below show the XRD data.

Table 3-6 Preparation of experimental set-ups for investigation of $PbB(OH)_4^+$–$SO_4^{2-}$ Interactions.

| Set-up ID | $Na_2SO_4$ (m) | PbO (g) | De-gassed DI Water (g) | $H_3BO_3$(m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB(OH)4-0.01SO4- 1 | 0.010 | 1.9955 | 98.0032 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-0.01SO4- 2 | 0.010 | 2.0013 | 98.0110 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-0.1SO4- 1 | 0.10 | 2.0033 | 98.0066 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-0.1SO4- 2 | 0.10 | 2.0034 | 98.0067 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-0.5SO4- 1 | 0.50 | 1.9988 | 98.0010 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-0.5SO4- 2 | 0.50 | 2.0081 | 98.0018 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.0SO4- 1 | 1.0 | 2.0038 | 98.0054 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.0SO4- 2 | 1.0 | 2.0037 | 98.0082 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.5SO4- 1 | 1.5 | 2.0046 | 98.0175 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.5SO4- 2 | 1.5 | 2.0010 | 98.0049 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.8SO4- 1 | 1.8 | 2.0069 | 98.0061 | 0.0010 | WIPP-Borate-1 Pg. 9 |
| PbB(OH)4-1.8SO4- 2 | 1.8 | 2.0072 | 98.0013 | 0.0010 | WIPP-Borate-1 Pg. 9 |

Information Only

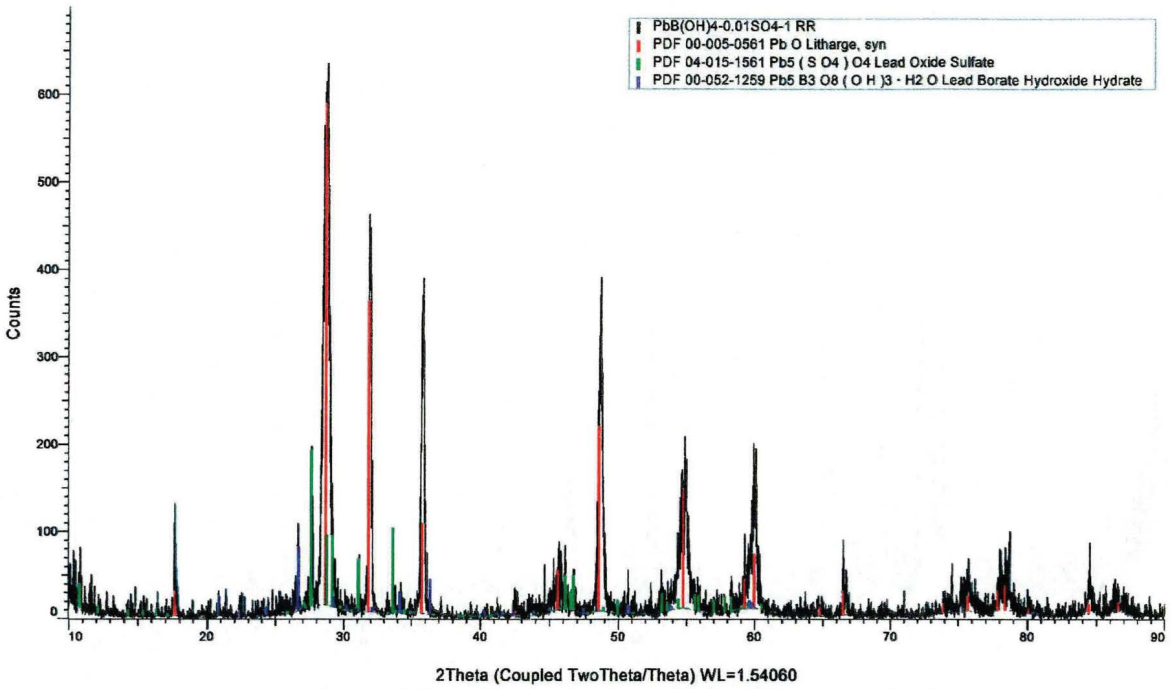



Figure 35 XRD analysis of PbB(OH)4-0.01SO4-1
Source of Figure 35: Scientific Notebook WIPP-Borate-10 Pg. 85

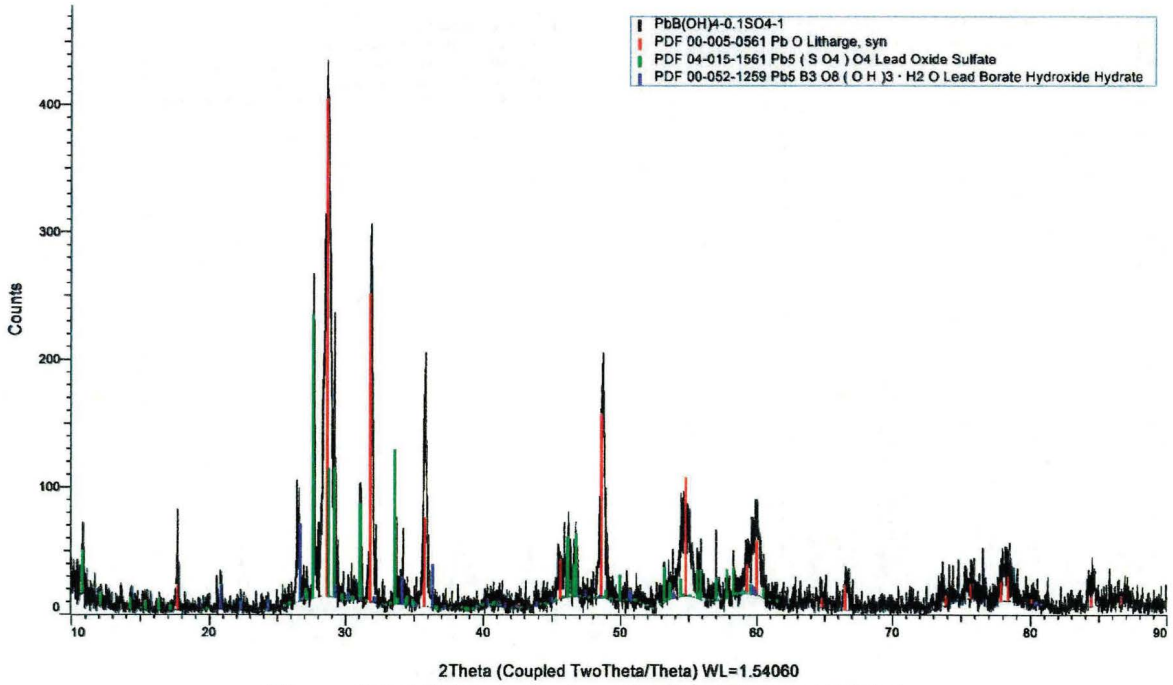



Figure 36 XRD analysis of PbB(OH)4-0.1SO4-1
Source of Figure 36: Scientific Notebook WIPP-Borate-10 Pg. 85

Information Only

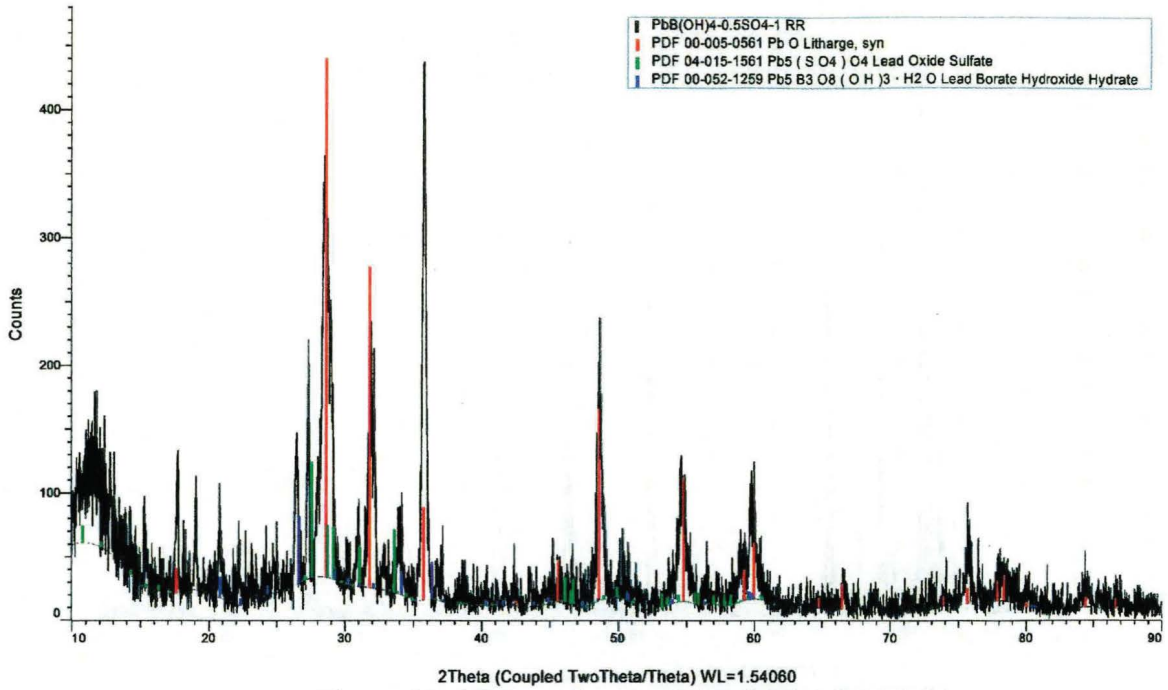



Figure 37 XRD analysis of PbB(OH)4-0.5SO4-1
Source of Figure 37: Scientific Notebook WIPP-Borate-10 Pg. 85

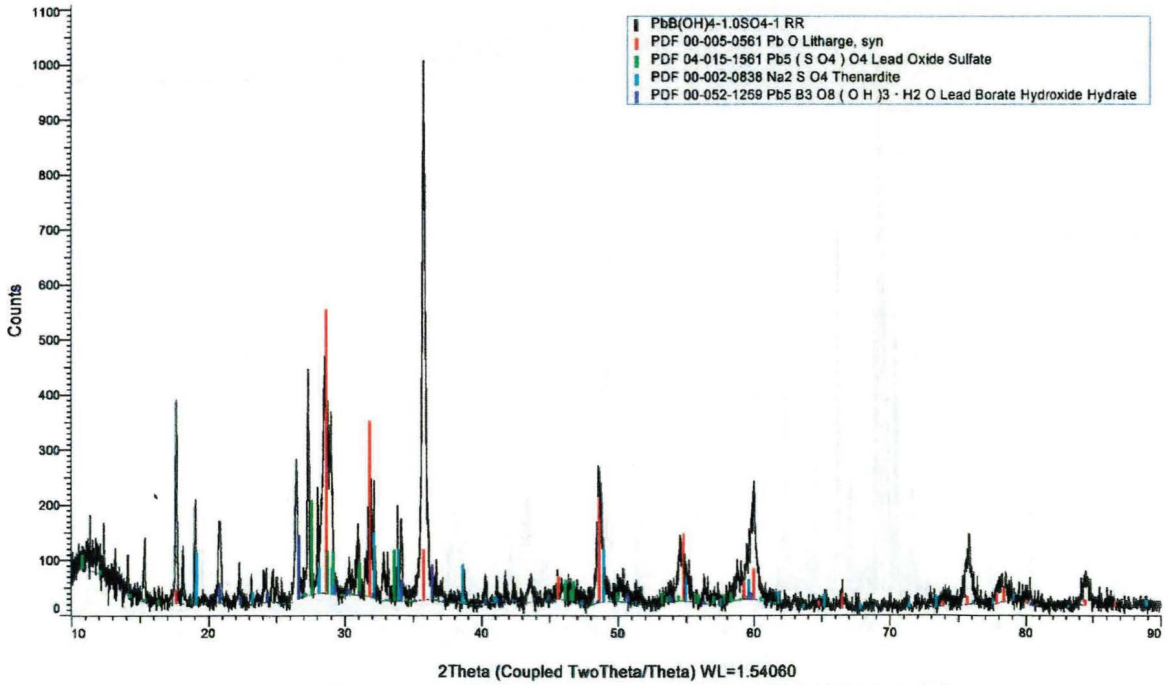



Figure 38 XRD analysis of PbB(OH)4-1.0SO4-1
Source of Figure 38: Scientific Notebook WIPP-Borate-10 Pg. 85

Information Only

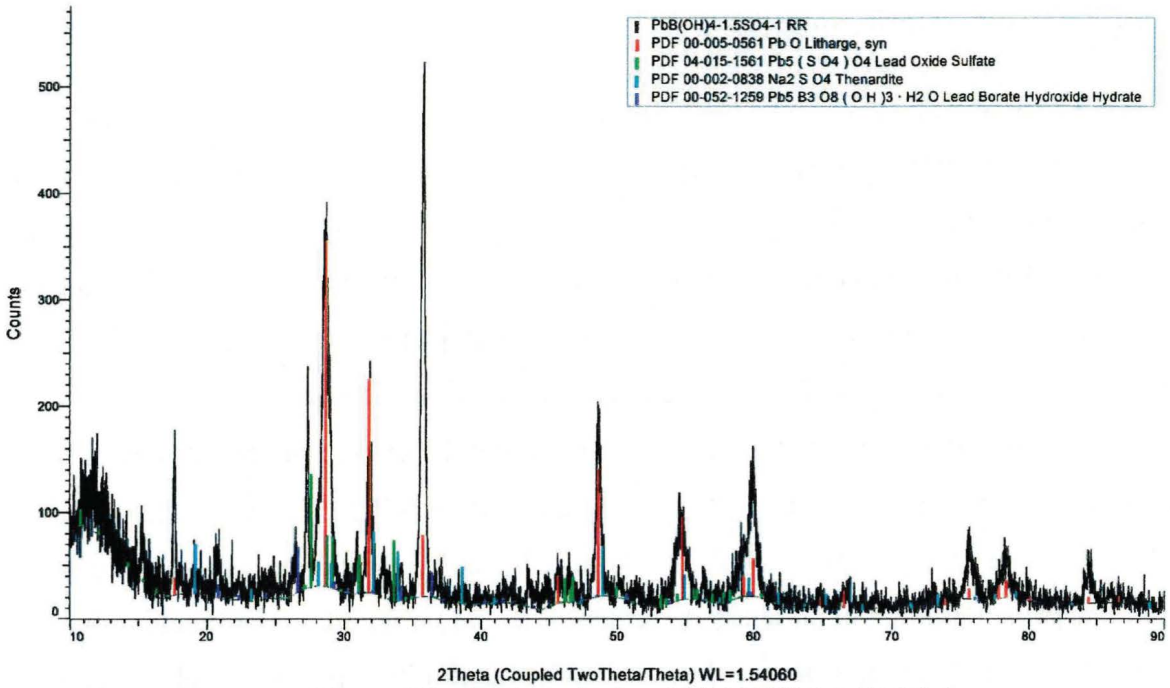



Figure 39 XRD analysis of PbB(OH)4-1.5SO4-1
Source of Figure 39: Scientific Notebook WIPP-Borate-10 Pg. 85

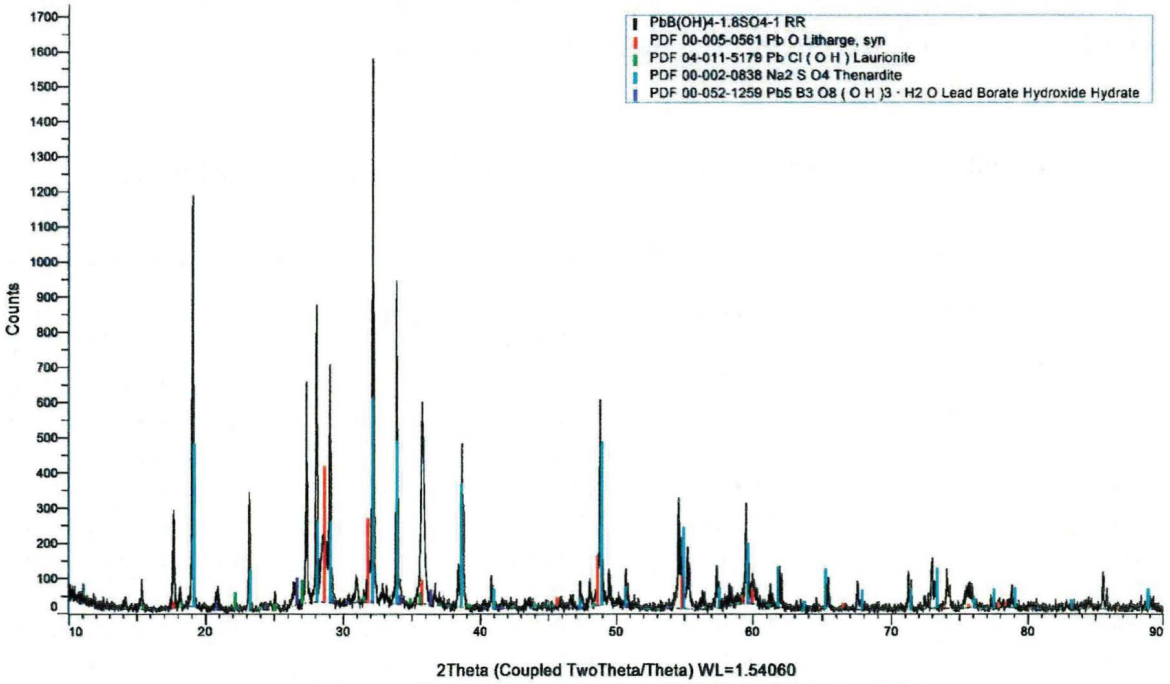



Figure 40 XRD analysis of PbB(OH)4-1.8SO4-1
Source of Figure 40: Scientific Notebook WIPP-Borate-10 Pg. 85

Information Only

### 3.4.3 $Pb[B(OH)_4]_3^-$—$Na^+$ Interactions

Table 3-7 shows the experimental set-up of the $Pb[B(OH)_4]_3^-$ experiments. The figures below document the XRD solids characterization results from those experiments. At 2952 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Samples PbB3-0.01Na-1, PbB3-0.1Na-1 and PbB3-1.0 Na-1 show varying amounts of litharge (PbO) PDF pattern 00-005-0561, blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193 and lead borate hydroxide hydrate ($Pb_5B_3O_8(OH)_3 \cdot H_2O$) PDF pattern 00-052-1259. The rest of the samples in the set show an additional presence of laurionite (PbCl(OH)) PDF pattern 04-011-5179. Based on the studies conducted by Ioannidis et al. (2006, 2007) and Sidra et al. (2013), laurionite should not be stable at the alkaline pH's measured in these experiments (>8 to ~11) when the experiments sampled for solution chemistry (Xiong, Y. and Kirkes, L. 2017). Laurionite is primarily stable at pH values less than 8. This experimental result may be a good candidate for future research in new experiments in which solution chemistry in equilibrium with laurionite will be investigated, or possibly further analysis by SEM/EDS. The figures below show the XRD data.

Table 3-7 Preparation of experimental set-ups for investigation of $Pb[B(OH)_4]_3^-$—$Na^+$ Interactions.

| Set-up ID | NaCl (m) | PbO (g) | De-gassed DI Water (g) | $H_3BO_3$(m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB3- 0.01 Na-1 | 0.010 | 2.0129 | 94.0113 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 0.01 Na-2 | 0.010 | 2.0365 | 94.0036 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 0.1 Na-1 | 0.10 | 2.0045 | 94.0093 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 0.1 Na-2 | 0.10 | 2.0372 | 94.0094 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 1.0 Na-1 | 1.0 | 2.0303 | 94.0072 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 1.0 Na-2 | 1.0 | 2.0133 | 94.0089 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 2.0 Na-1 | 2.1 | 2.0117 | 94.0056 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 2.0 Na-2 | 2.1 | 2.0130 | 94.0010 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 3.0 Na-1 | 3.2 | 2.0057 | 94.0223 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 3.0 Na-2 | 3.2 | 2.0043 | 94.0157 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 4.0 Na-1 | 4.4 | 2.0029 | 94.0101 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 4.0 Na-2 | 4.4 | 2.0047 | 94.0072 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 5.0 Na-1 | 5.0 | 2.0130 | 94.0011 | 0.03 | WIPP-Borate-1 Pg. 10 |
| PbB3- 5.0 Na-2 | 5.0 | 2.0114 | 94.0072 | 0.03 | WIPP-Borate-1 Pg. 10 |

Information Only

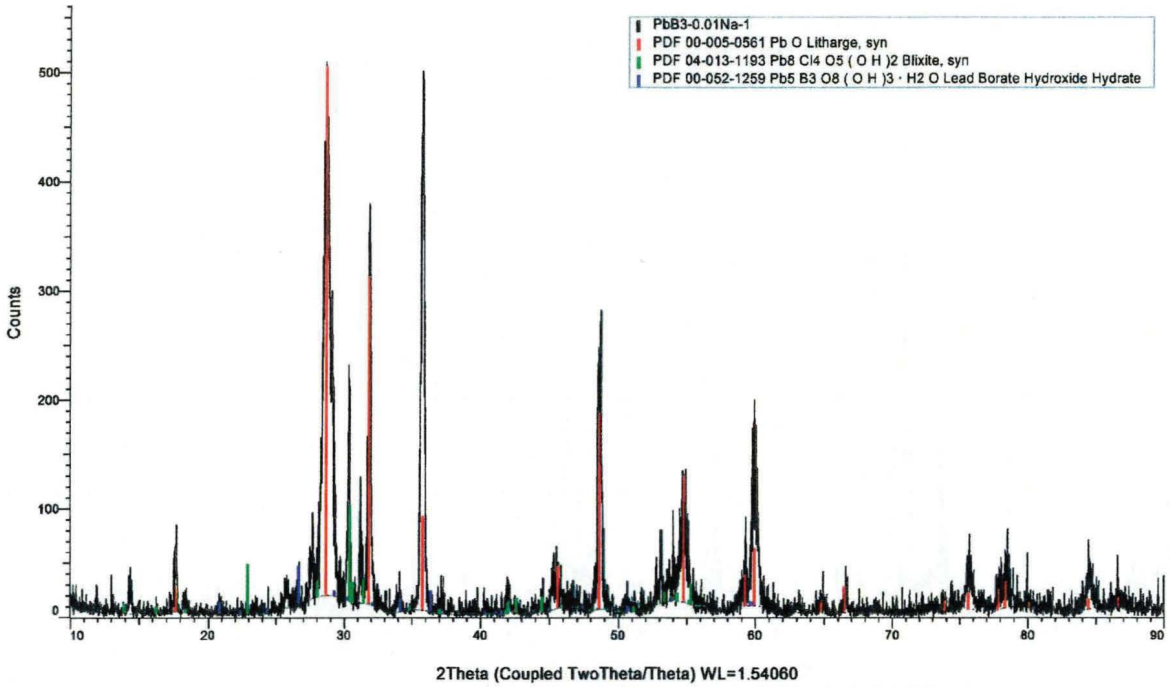



Figure 41 XRD analysis of sample PbB3-0.01 Na-1
Source of Figure 41: Scientific Notebook WIPP-Borate-10 Pg. 86

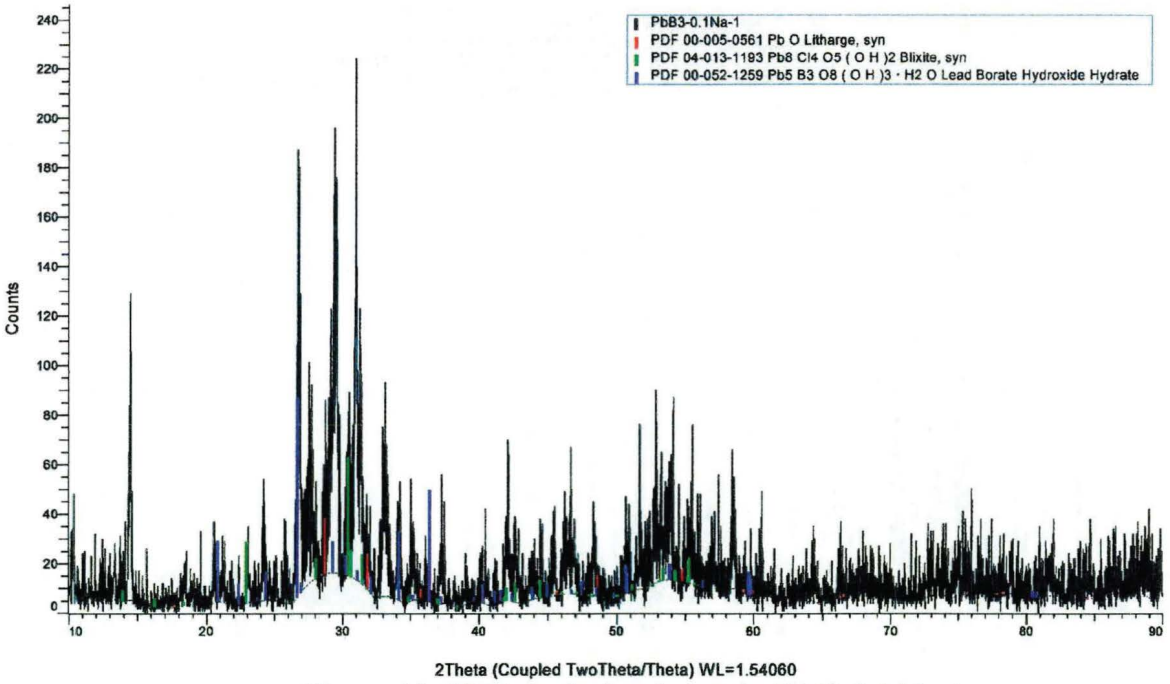



Figure 42 XRD analysis of sample PbB3-0.1 Na-1
Source of Figure 42: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

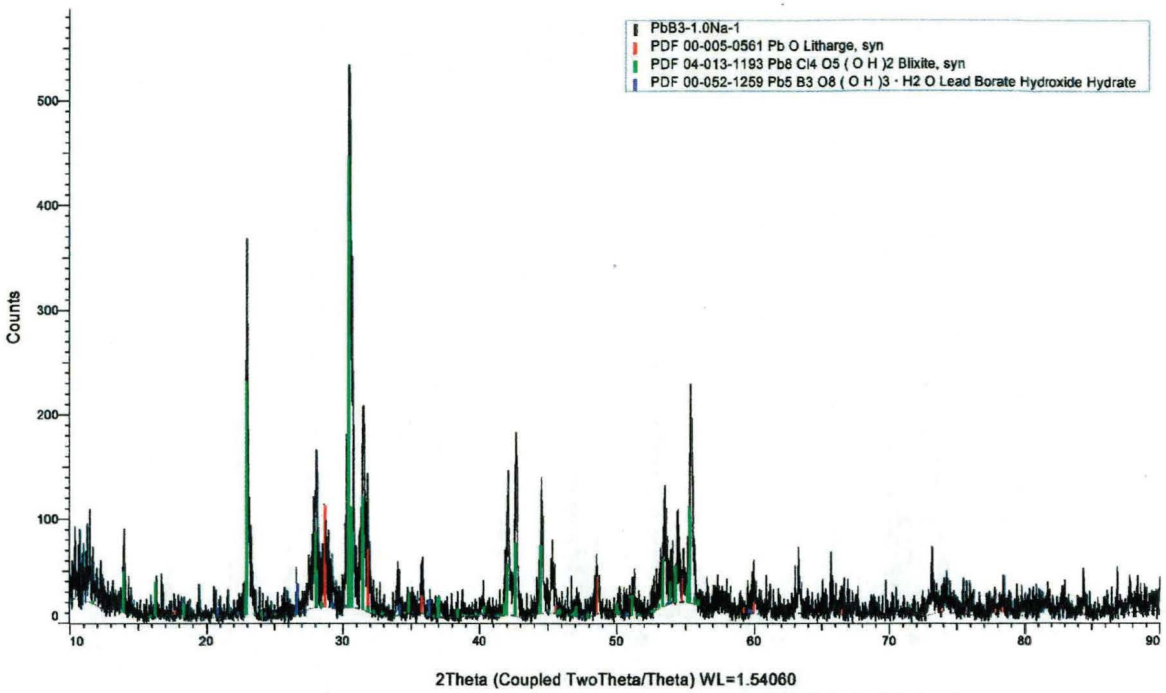



Figure 43 XRD analysis of sample PbB3-1.0 Na-1
Source of Figure 43: Scientific Notebook WIPP-Borate-10 Pg. 86

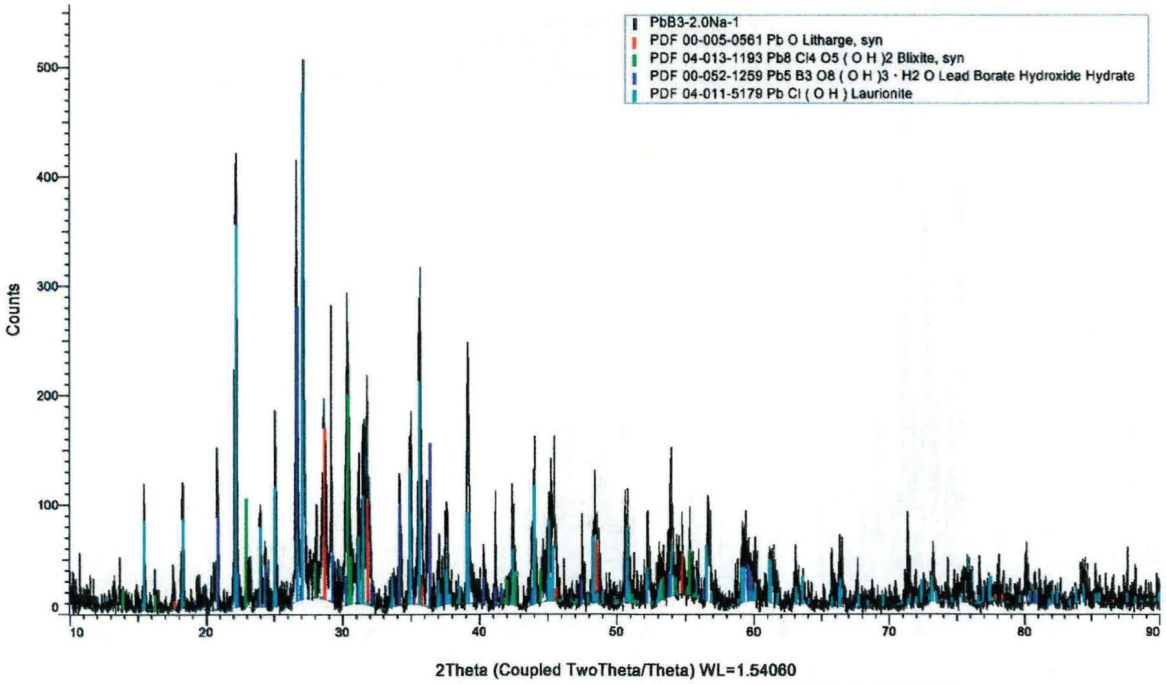



Figure 44 XRD analysis of sample PbB3-2.0 Na-1
Source of Figure 44: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

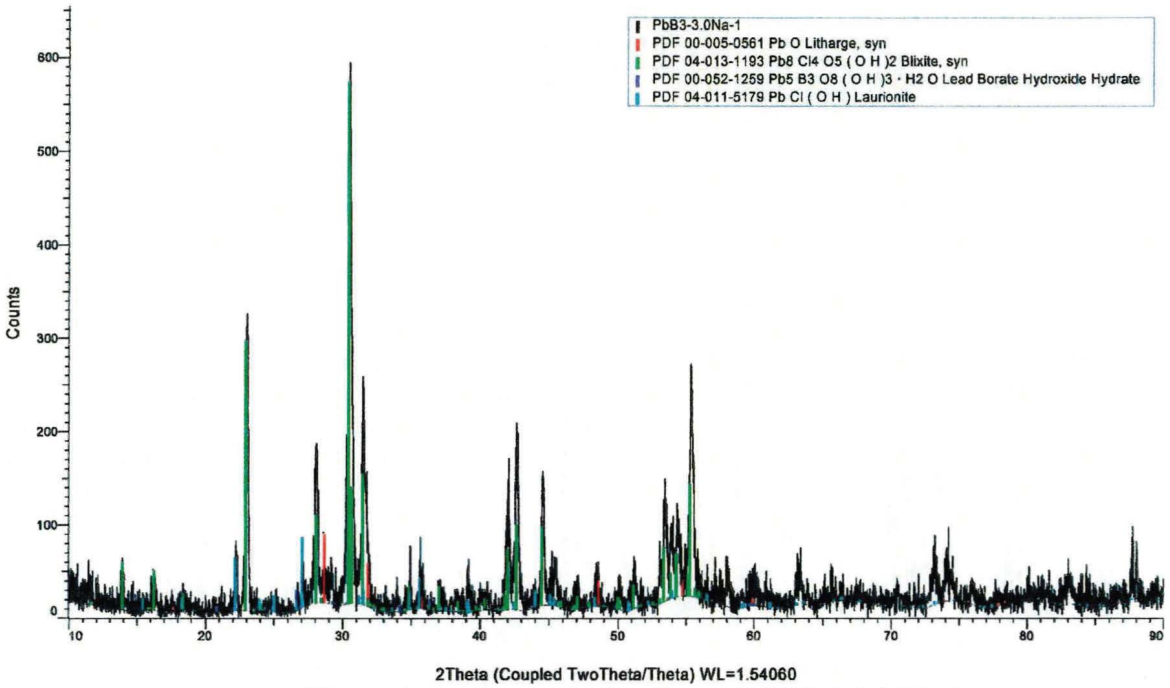



Figure 45 XRD analysis of sample PbB3-3.0 Na-1
Source of Figure 45: Scientific Notebook WIPP-Borate-10 Pg. 86

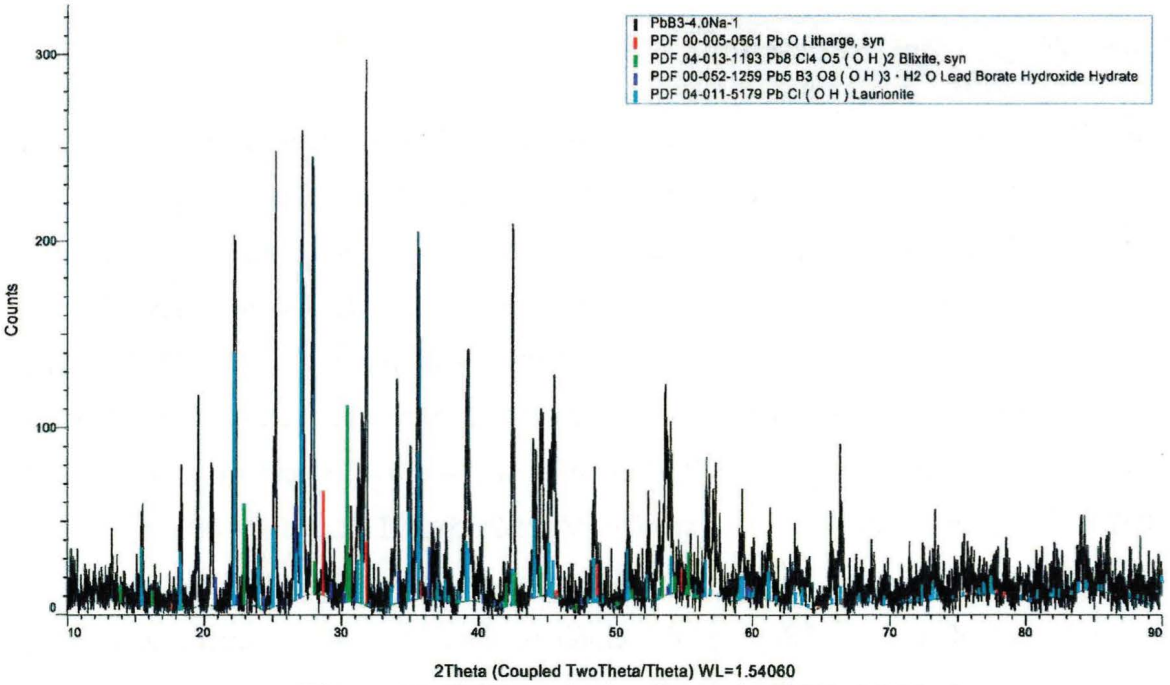



Figure 46 XRD analysis of sample PbB3-4.0 Na-1
Source of Figure 46: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

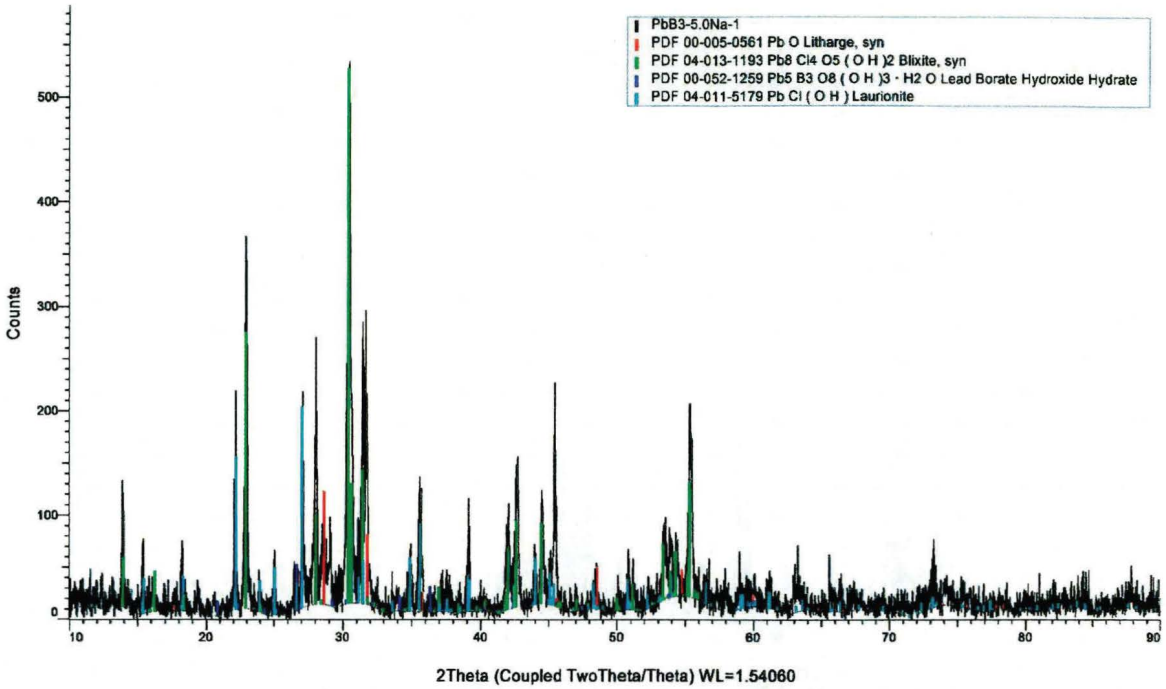



Figure 47 XRD analysis of sample PbB3-5.0 Na-1
Source of Figure 47: Scientific Notebook WIPP-Borate-10 Pg. 86

### 3.4.4 $Pb[B(OH)_4]_3^-$—$Mg^{2+}$ Interactions

Table 3-8 shows the experimental set-ups of the Pb[B(OH)4]3- experiments. The figures below document the XRD solids characterization of these experiments. At 2944 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Sample PbB3-0.01Mg-1 shows an XRD characterization of litharge (PbO) PDF pattern 00-005-0561 and blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193. All other samples show a solid system containing, litharge (PbO) PDF pattern 00-005-0561, blixite ($Pb_8Cl_4O_5(OH)_2$) PDF pattern 04-013-1193, and laurionite (PbCl(OH)) PDF pattern 04-011-5179 and suanite (Mg2B2O5) PDF pattern 04-009-2452. It is important to note that this was a very mixed solid system and many of the PDF patterns match with varying degrees of accuracy. Some peaks remain unidentified in these patterns and in order to verify what solids are present and in what concentrations, an alternate instrument technique would need to be employed. The figures below show the XRD data.

Information Only

Table 3-8 Preparation of experimental set-ups for investigation of $Pb[B(OH)_4]_3^-$—$Mg^{2+}$ Interactions.

| Set-up ID | PbO (g) | $MgCl_2$ (m) | mL of $MgCl_2$ Solution | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB3- 0.01 Mg-1 | 2.0011 | 0.010 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 0.01 Mg-2 | 2.0198 | 0.010 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 0.1 Mg-1 | 2.0123 | 0.10 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 0.1 Mg-2 | 2.0160 | 0.10 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 1.0 Mg-1 | 2.0156 | 1.0 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 1.0 Mg-2 | 2.0221 | 1.0 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 1.5 Mg-1 | 2.0027 | 1.5 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 1.5 Mg-2 | 2.0153 | 1.5 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 2.0 Mg-1 | 2.0009 | 2.0 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 2.0 Mg-2 | 2.0118 | 2.0 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 2.5 Mg-1 | 2.0117 | 2.5 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |
| PbB3- 2.5 Mg-2 | 2.0296 | 2.5 | 100 | 0.03 | WIPP-Borate-1 Pg. 11 |

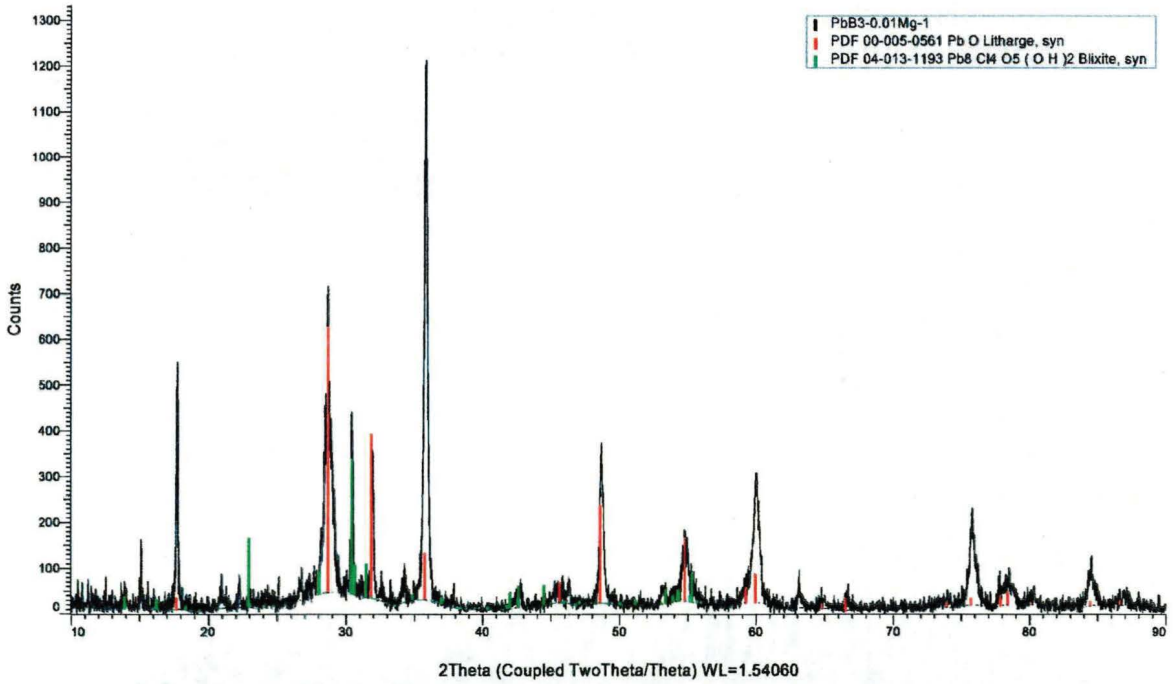



Figure 48 XRD analysis of sample PbB3-0.01 Mg-1
Source of Figure 48: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

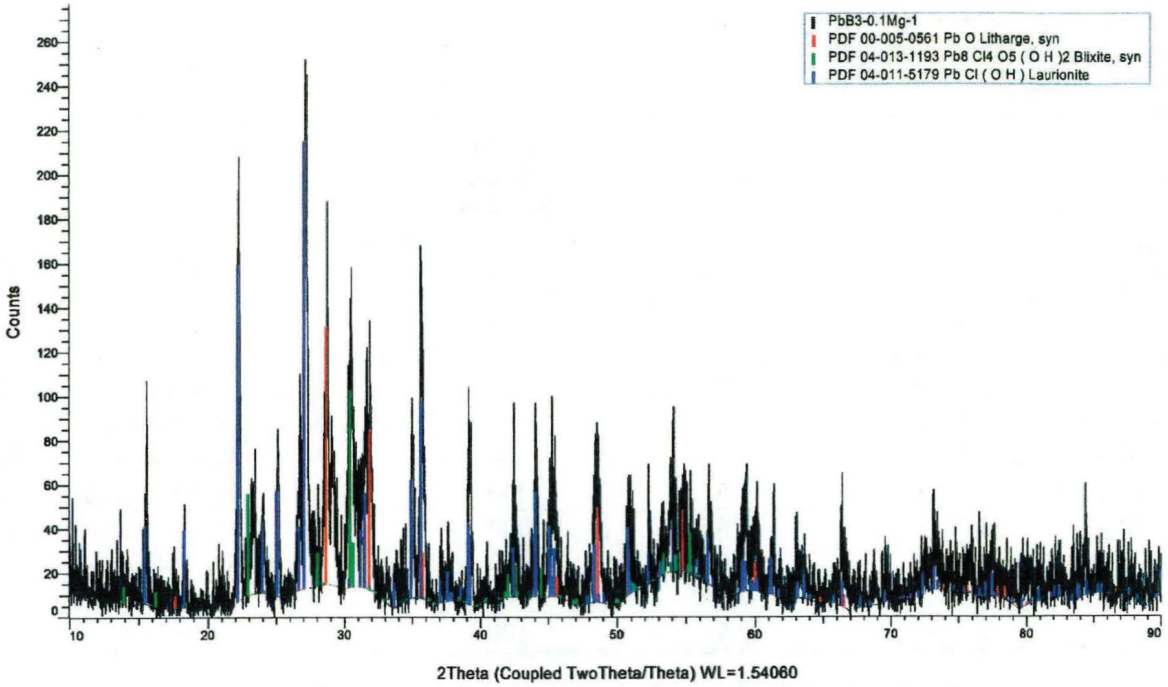



Figure 49 XRD analysis of sample PbB3-0.1 Mg-1
Source of Figure 49: Scientific Notebook WIPP-Borate-10 Pg. 86

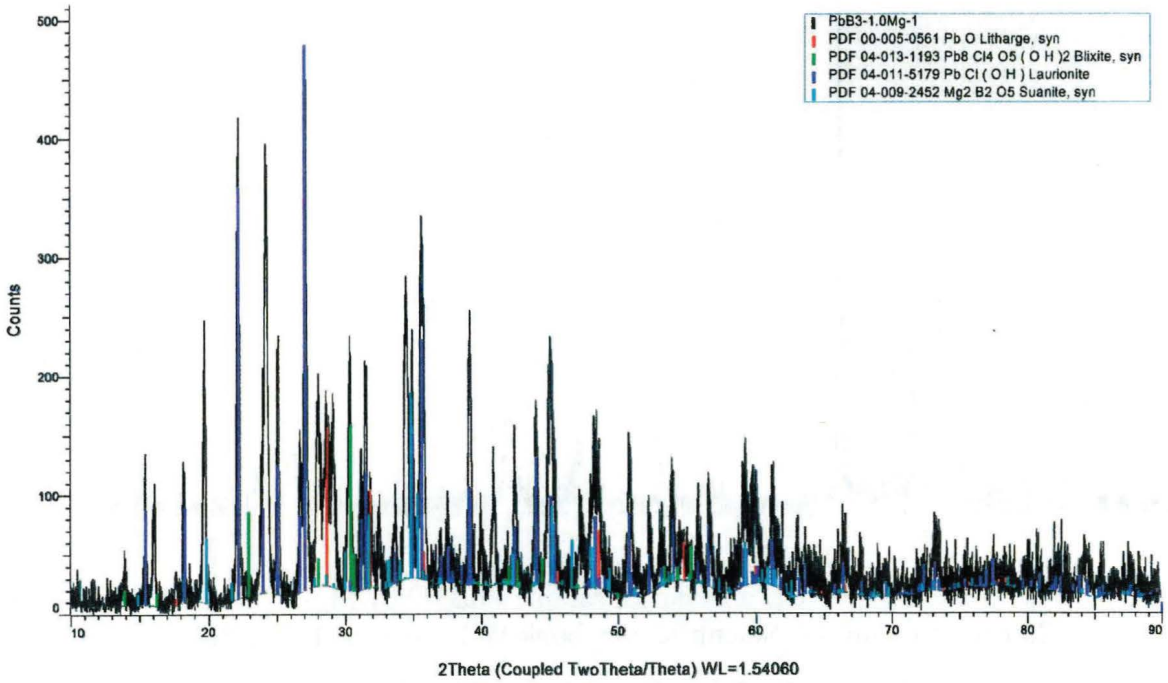



Figure 50 XRD analysis of sample PbB3-1.0 Mg-1
Source of Figure 50: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

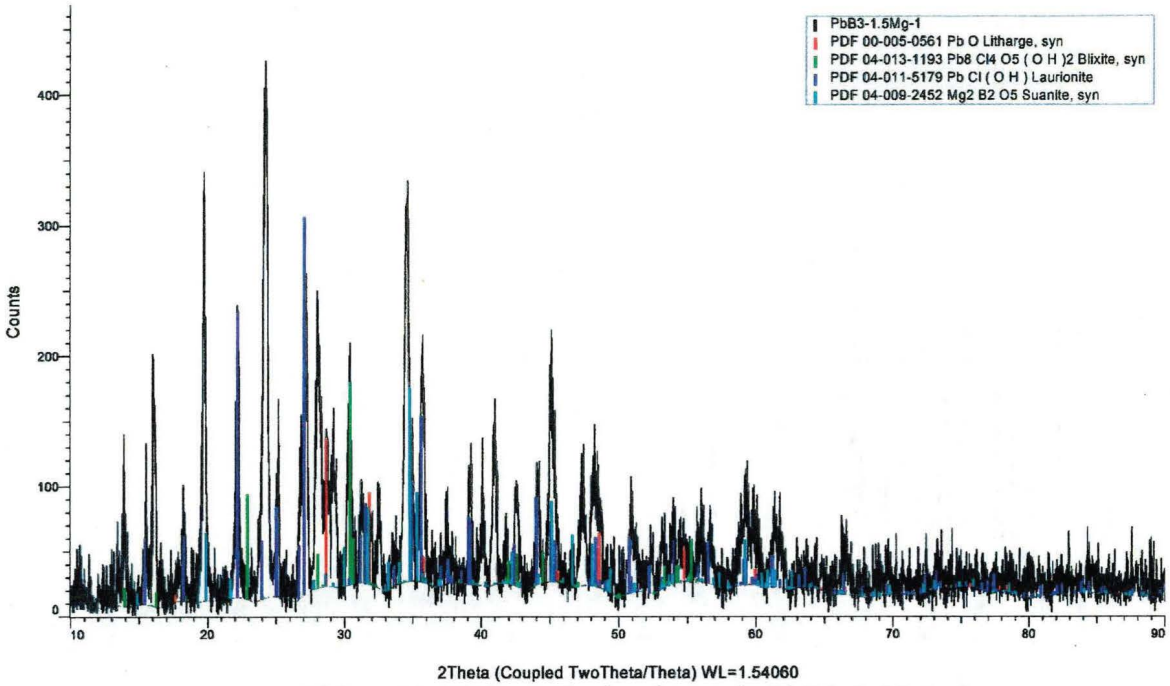



Figure 51 XRD analysis of sample PbB3-1.5 Mg-1
Source of Figure 51: Scientific Notebook WIPP-Borate-10 Pg. 86

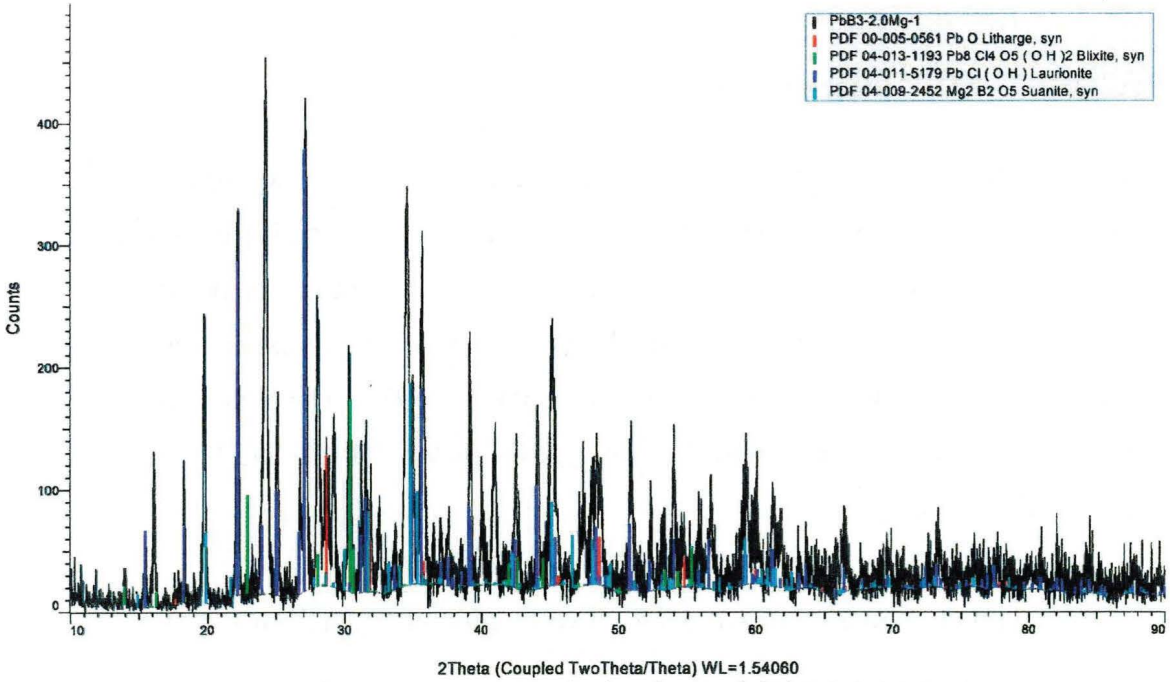



Figure 52 XRD analysis of sample PbB3-2.0 Mg-1
Source of Figure 52: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

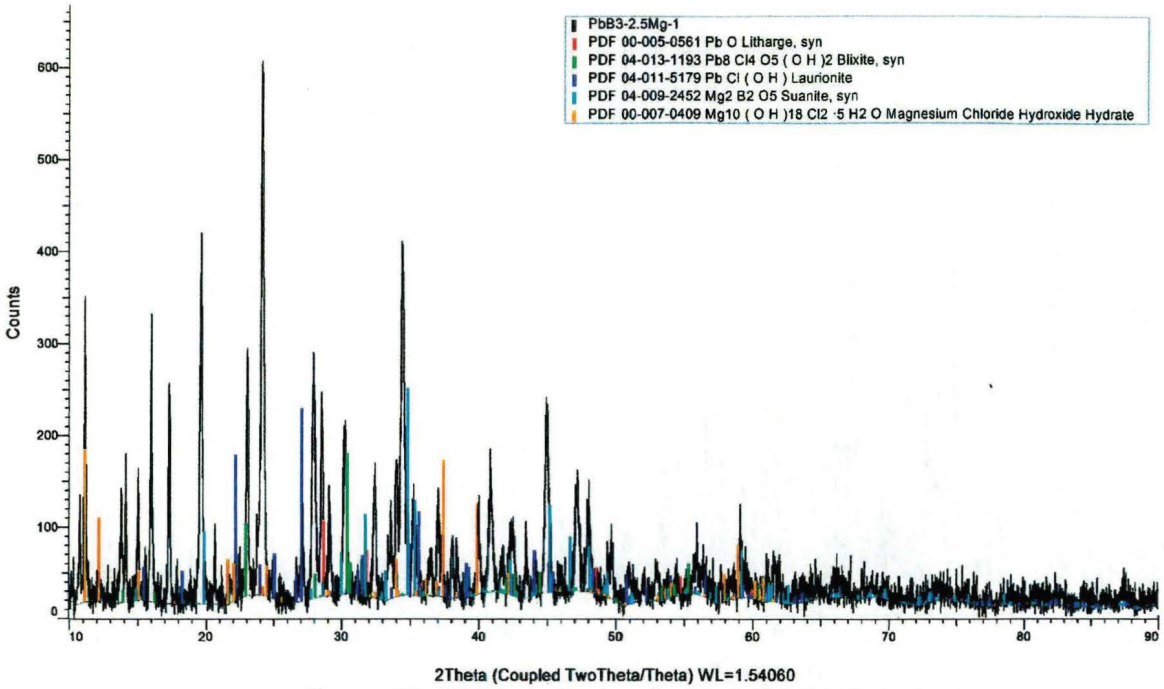



Figure 53 XRD analysis of sample PbB3-2.5 Mg-1
Source of Figure 53: Scientific Notebook WIPP-Borate-10 Pg. 86

### 3.4.5 $MgB(OH)_4^+$—$SO_4^{2-}$ Interactions

Table 3-9 shows the experimental set-ups for the $MgB(OH)_4^+$-$SO_4^{2-}$ experiments. Figures 54-59 document the XRD solids characterization for the experiments. At 2575 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. All of the samples in this experiment match with good agreement to brucite ($Mg(OH)_2$) PDF pattern 04-011-5938. The higher concentration samples also show the matrix of thenardite ($Na_2(SO_4)$) PDF pattern 04-010-2457. The figures below show the XRD data.

Table 3-9 Preparation of experimental set-ups for investigation of $MgB(OH)_4^+$—$SO_4^{2-}$ Interactions.

| Set-up ID | $Na_2SO_4$ (m) | $Mg(OH)_2$ (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| MgB(OH)4 - 0.01 SO4-1 | 0.010 | 2.0008 | 98.0151 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 0.01 SO4-2 | 0.010 | 2.0000 | 98.0066 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 0.1 SO4-1 | 0.10 | 2.0004 | 98.0175 | 0.0010 | WIPP-Borate-1 Pg. 13 |

Information Only

| Set-up ID | $Na_2SO_4$ (m) | $Mg(OH)_2$ (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| MgB(OH)4 - 0.1 SO4-2 | 0.10 | 2.0003 | 98.0225 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 0.5 SO4-1 | 0.50 | 2.0007 | 98.0191 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 0.5 SO4-2 | 0.50 | 2.0000 | 98.0006 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.0 SO4-1 | 1.0 | 2.0000 | 98.0002 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.0 SO4-2 | 1.0 | 2.0000 | 98.0107 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.5 SO4-1 | 1.5 | 2.0007 | 98.0041 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.5 SO4-2 | 1.5 | 2.0007 | 98.0042 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.8 SO4-1 | 1.8 | 2.0008 | 98.0018 | 0.0010 | WIPP-Borate-1 Pg. 13 |
| MgB(OH)4 - 1.8 SO4-2 | 1.8 | 2.0001 | 98.0021 | 0.0010 | WIPP-Borate-1 Pg. 13 |

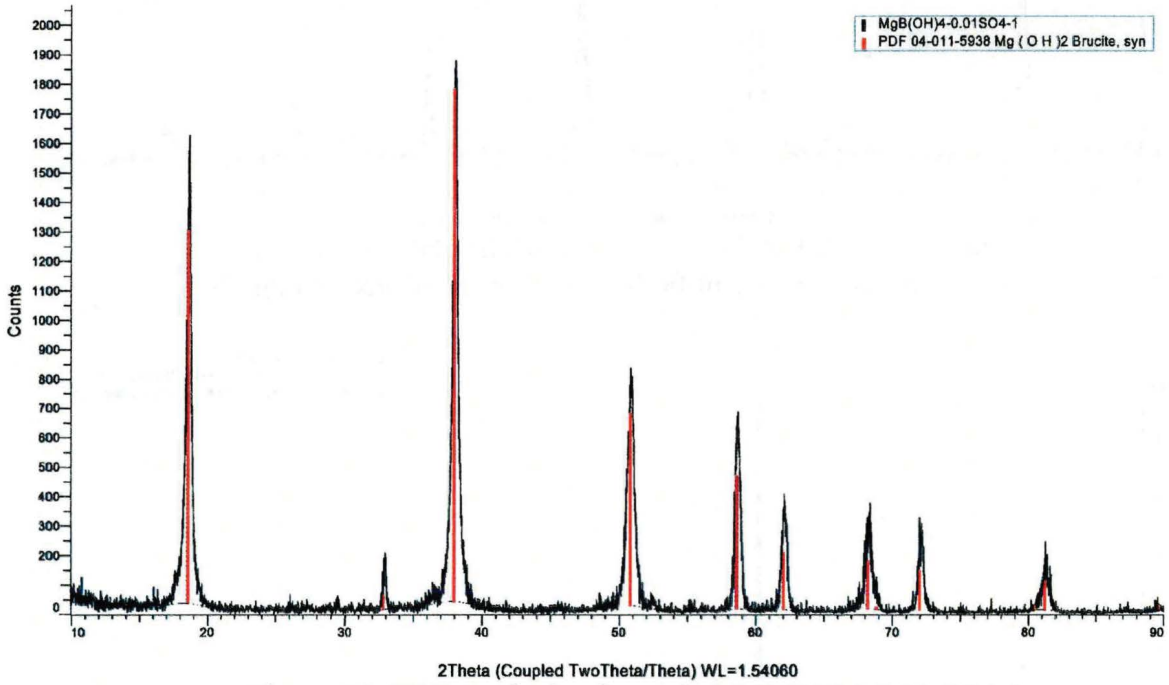



Figure 54 XRD analysis of sample MgB(OH)4-0.01 SO4-1
Source of Figure 54: Scientific Notebook WIPP-Borate-10 Pg. 78

Information Only

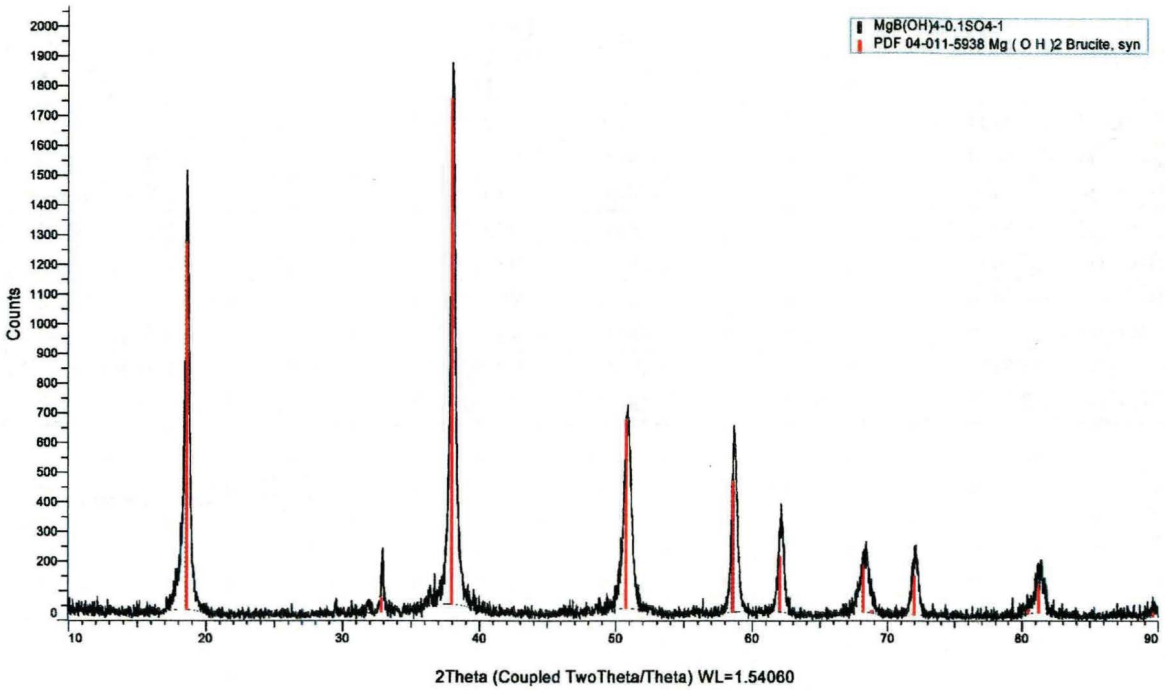



Figure 55 XRD analysis of sample MgB(OH)4-0.1 SO4-1
Source of Figure 55: Scientific Notebook WIPP-Borate-10 Pg. 79

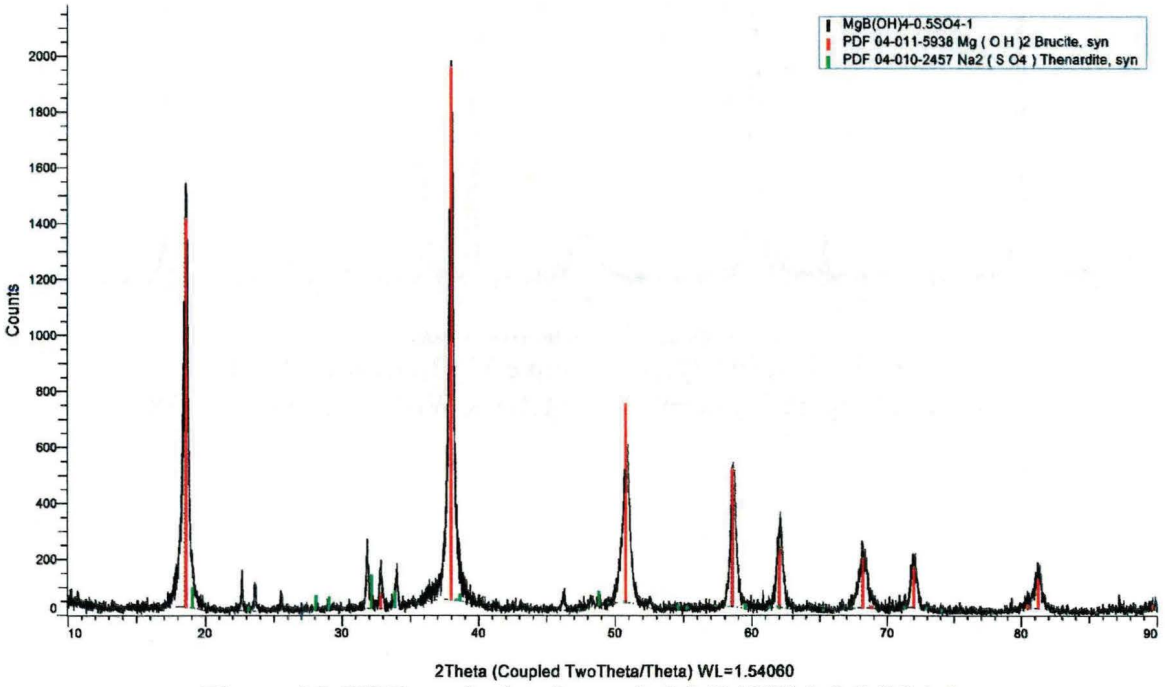



Figure 56 XRD analysis of sample MgB(OH)4-0.5 SO4-1
Source of Figure 56: Scientific Notebook WIPP-Borate-10 Pg. 80

Information Only

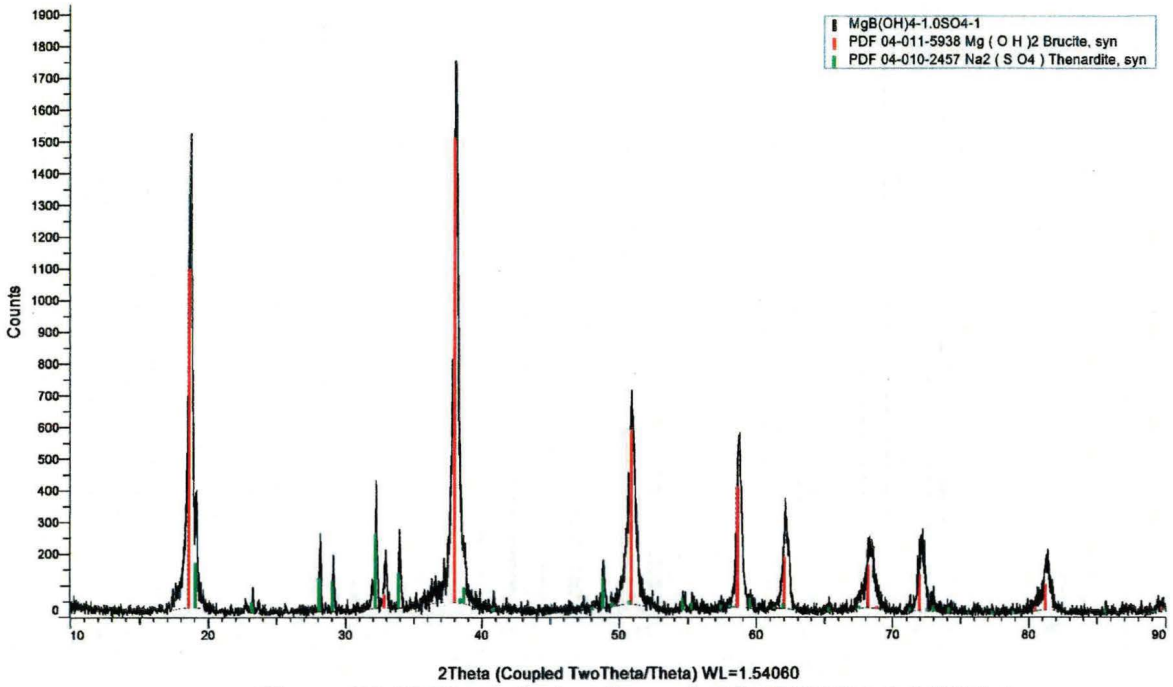



Figure 57 XRD analysis of sample MgB(OH)4-1.0 SO4-1
Source of Figure 57: Scientific Notebook WIPP-Borate-10 Pg. 81

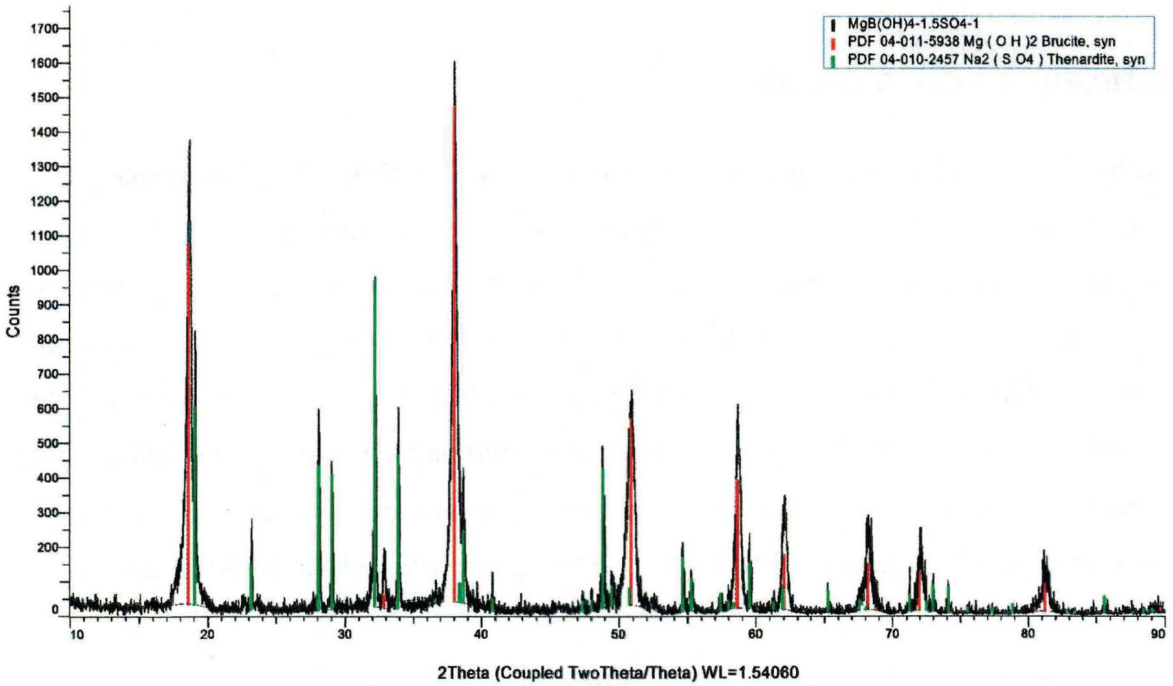



Figure 58 XRD analysis of sample MgB(OH)4-1.5 SO4-1
Source of Figure 58: Scientific Notebook WIPP-Borate-10 Pg. 82

Information Only

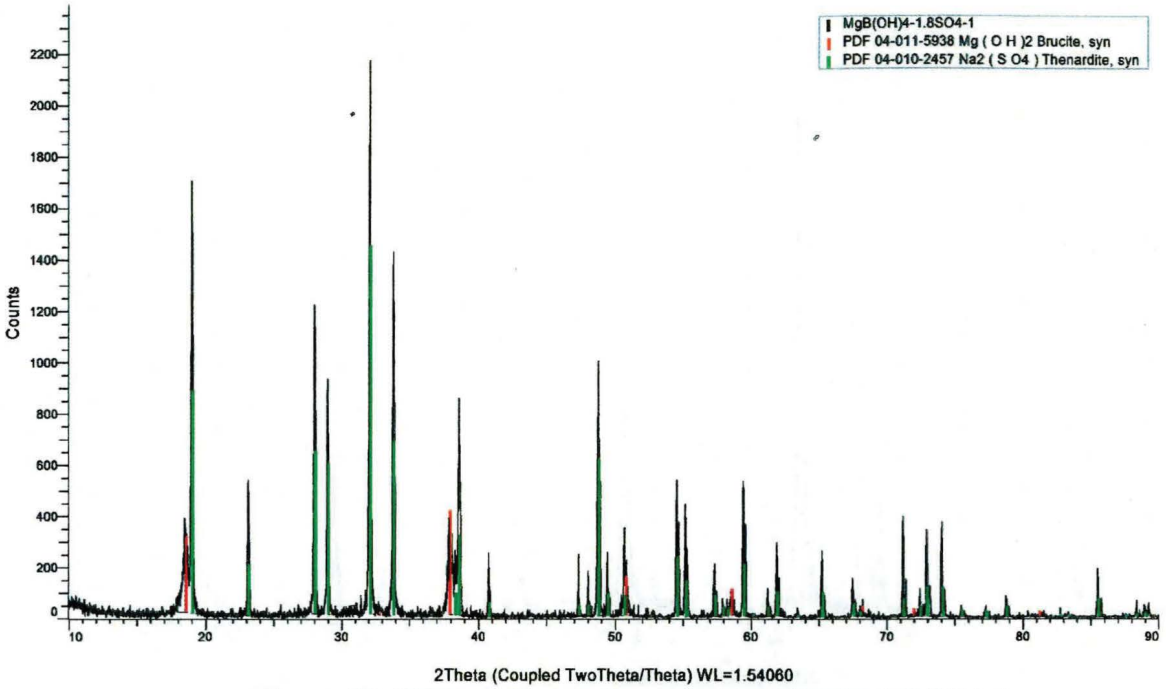



Figure 59 XRD analysis of sample MgB(OH)4-1.8 SO4-1
Source of Figure 59: Scientific Notebook WIPP-Borate-10 Pg. 83

### 3.4.6 $CaB(OH)_4^+$—$SO_4^{2-}$ Interactions

Table 3-10 describes the experimental set-ups for the $CaB(OH)_4^+$-$SO_4^{2-}$ experiments. Figures 60-65 document the XRD solids characterization of the experiments. At 2868 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Sample CaB(OH)4-0.01 SO4-1 matches with good agreement with portlandite ($Ca(OH)_2$) PDF pattern 01-078-0315. All of the other samples in this experiment show a mixed solid system containing portlandite and gypsum ($CaSO_4 \cdot 2H_2O$) PDF pattern 00-033-0311. The higher concentration samples also begin to show the matrix thenardite ($Na_2(SO_4)$) PDF pattern 04-010-2457. The figures below show the XRD data.

Table 3-10 Preparation of experimental set-ups for investigation of $CaB(OH)_4^+$—$SO_4^{2-}$ Interactions.

| Set-up ID | $Na_2SO_4$ (m) | $Ca(OH)_2$ (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| CaB(OH)4-0.01 SO4- 1 | 0.010 | 2.0006 | 98.0066 | 0.0010 | WIPP-Borate-1 Pg. 14 |

Information Only

| Set-up ID | $Na_2SO_4$ (m) | $Ca(OH)_2$ (g) | De-gassed DI Water (g) | $H_3BO_3$ (m) | Scientific Notebook Reference |
|---|---|---|---|---|---|
| CaB(OH)4-0.01 SO4- 2 | 0.010 | 2.0009 | 98.0012 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-0.1 SO4- 1 | 0.10 | 2.0007 | 98.0111 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-0.1 SO4- 2 | 0.10 | 2.0008 | 98.0096 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-0.5 SO4- 1 | 0.50 | 2.0000 | 98.0022 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-0.5 SO4- 2 | 0.50 | 2.0009 | 98.0040 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.0 SO4- 1 | 1.0 | 2.0000 | 98.0065 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.0 SO4- 2 | 1.0 | 2.0006 | 98.0095 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.5SO4- 1 | 1.5 | 2.0008 | 98.0004 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.5SO4- 2 | 1.5 | 2.0003 | 98.0097 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.8SO4- 1 | 1.8 | 2.0000 | 98.0096 | 0.0010 | WIPP-Borate-1 Pg. 14 |
| CaB(OH)4-1.8SO4- 2 | 1.8 | 2.0007 | 98.0111 | 0.0010 | WIPP-Borate-1 Pg. 14 |

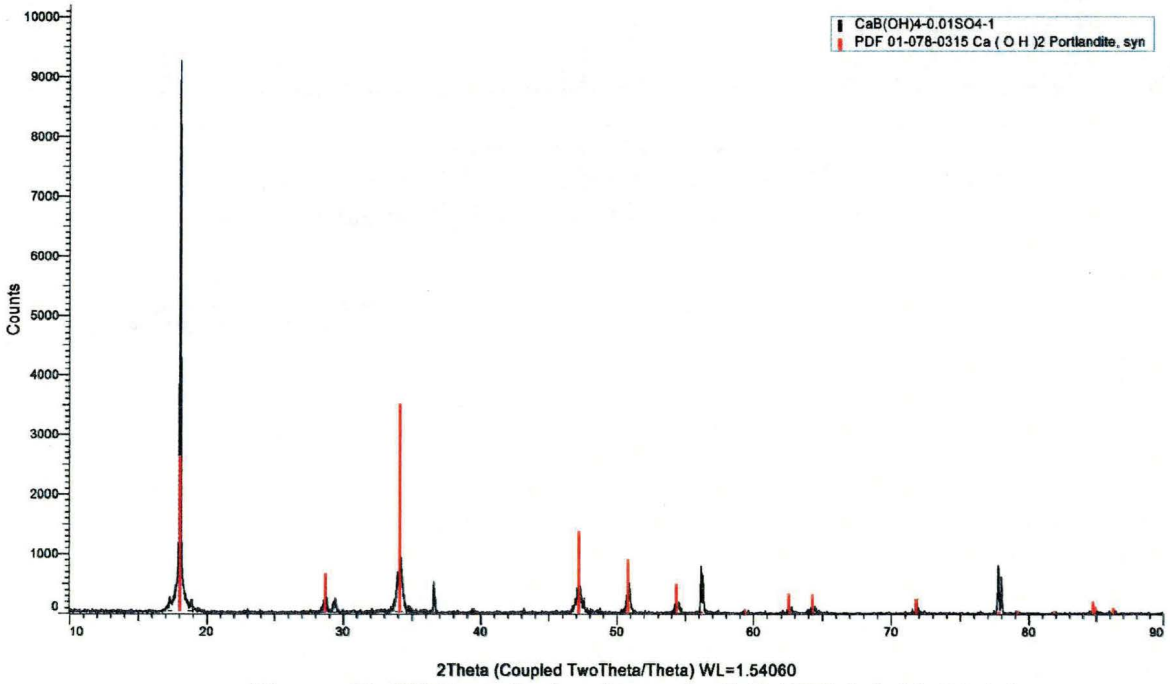



Figure 60 XRD analysis of sample CaB(OH)4-0.01 SO4-1
Source of Figure 60: Scientific Notebook WIPP-Borate-10 Pg. 66

Information Only

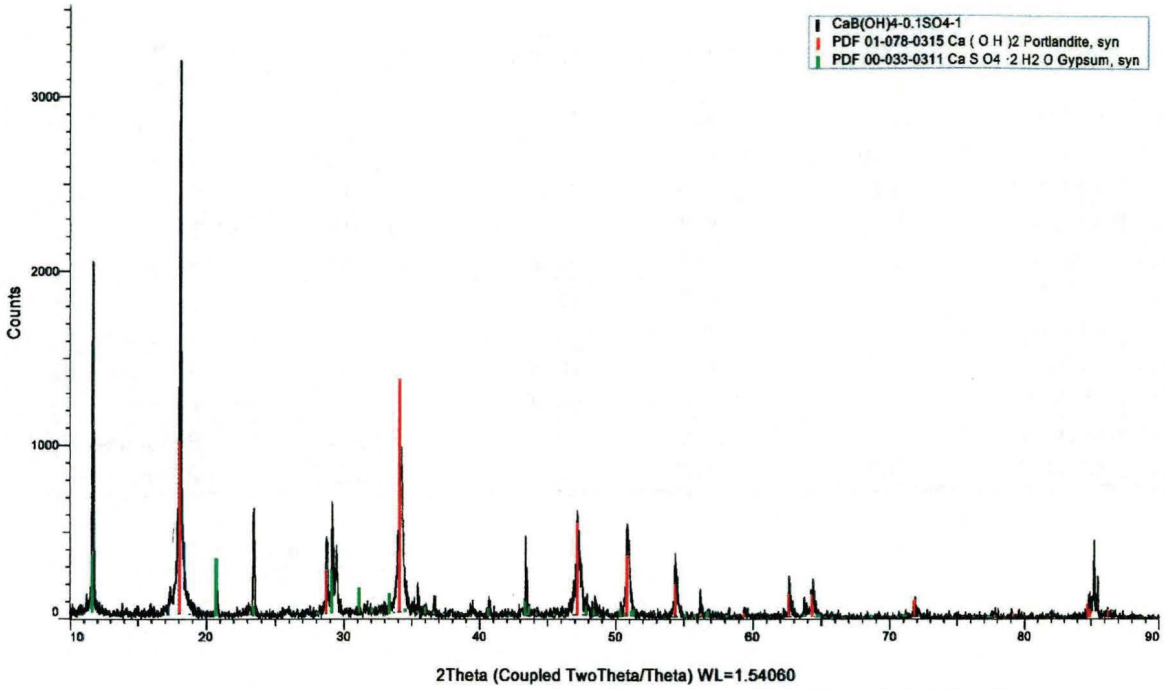



Figure 61 XRD analysis of sample CaB(OH)4-0.1 SO4-1
Source of Figure 61: Scientific Notebook WIPP-Borate-10 Pg. 67

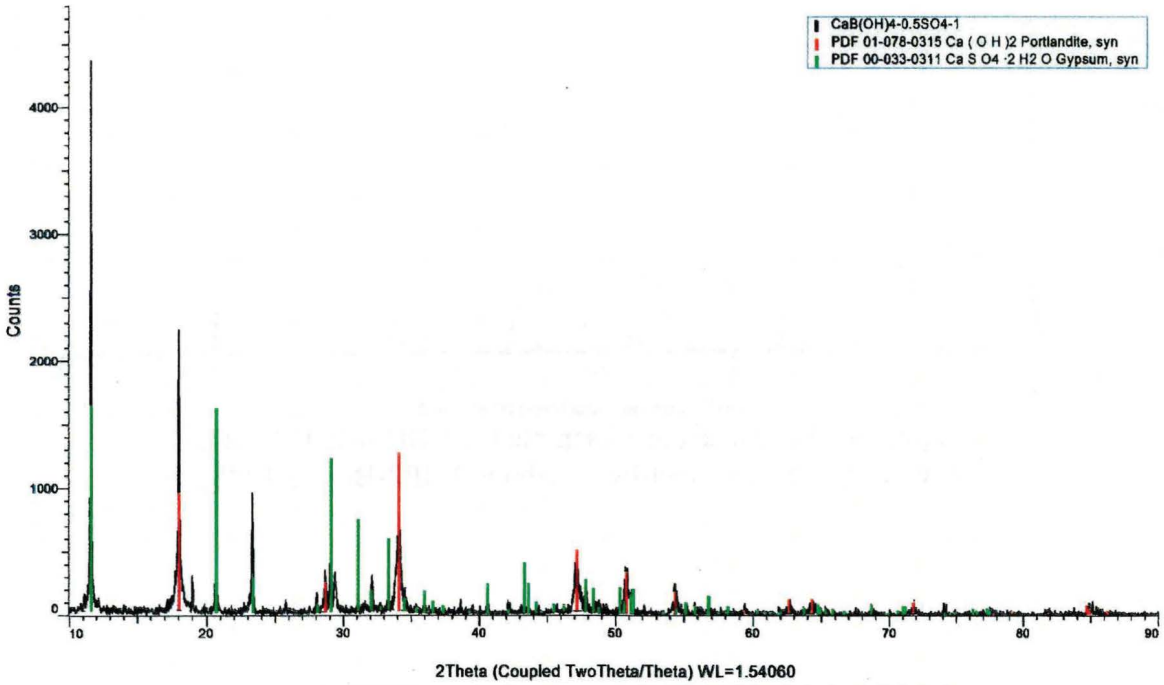



Figure 62 XRD analysis of sample CaB(OH)4-0.5 SO4-1
Source of Figure 62: Scientific Notebook WIPP-Borate-10 Pg. 68

Information Only

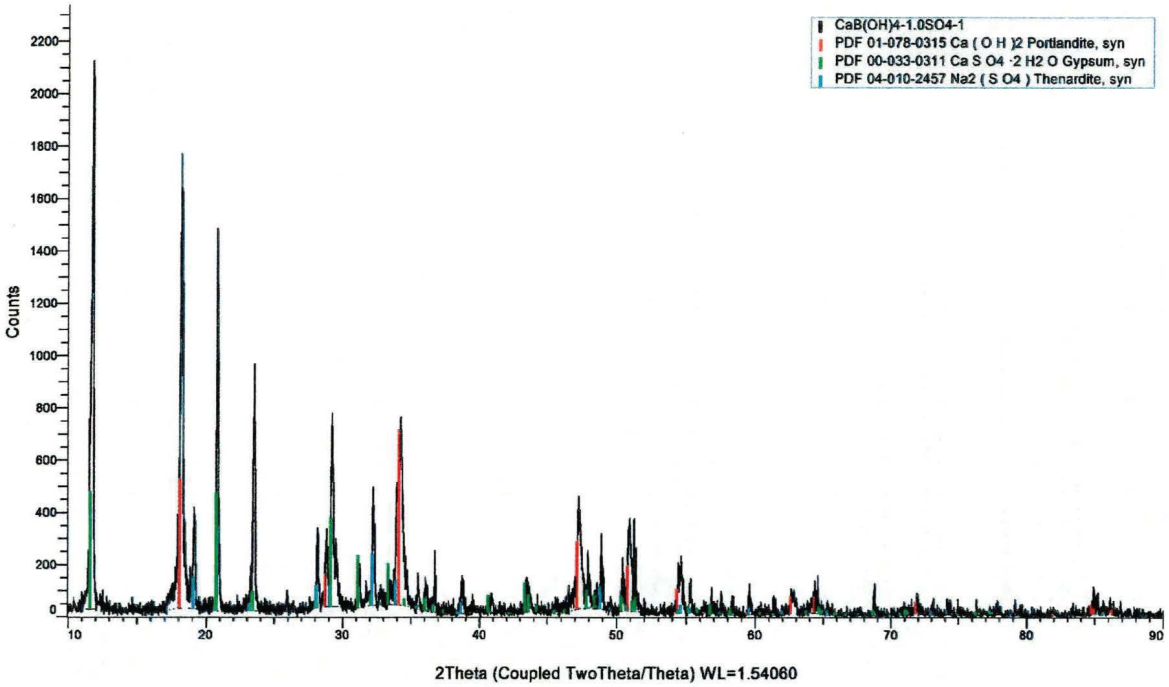



Figure 63 XRD analysis of sample CaB(OH)4-1.0 SO4-1
Source of Figure 63: Scientific Notebook WIPP-Borate-10 Pg. 69

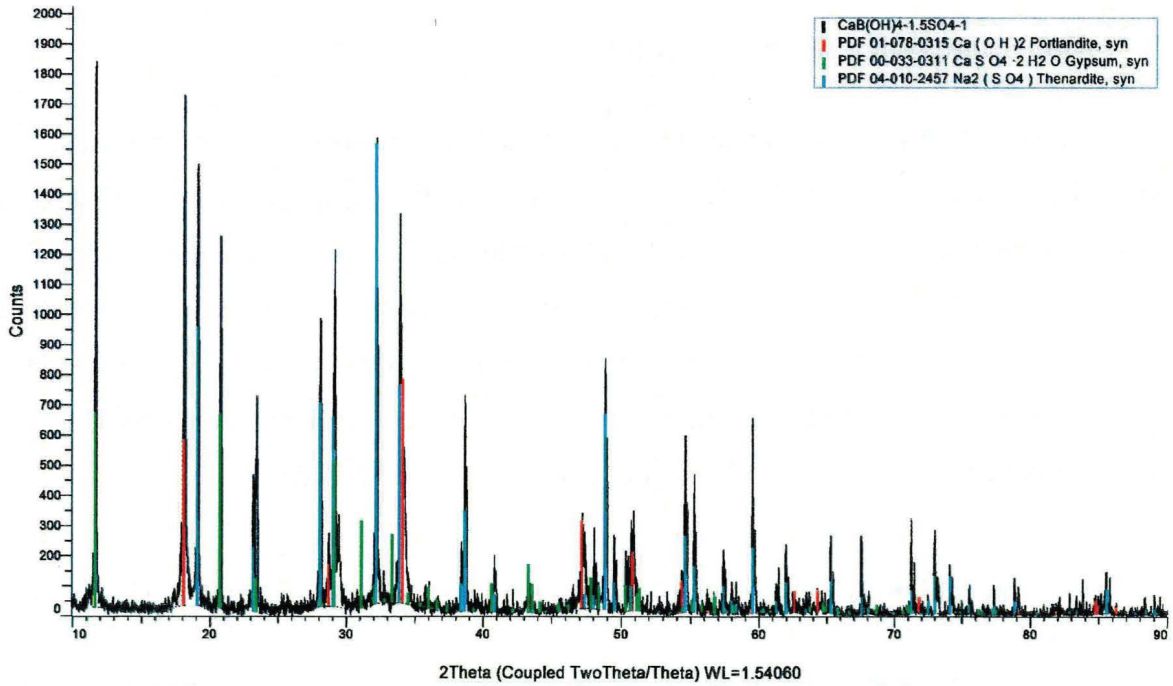



Figure 64 XRD analysis of sample CaB(OH)4-1.5 SO4-1
Source of Figure 64: Scientific Notebook WIPP-Borate-10 Pg. 70

Information Only

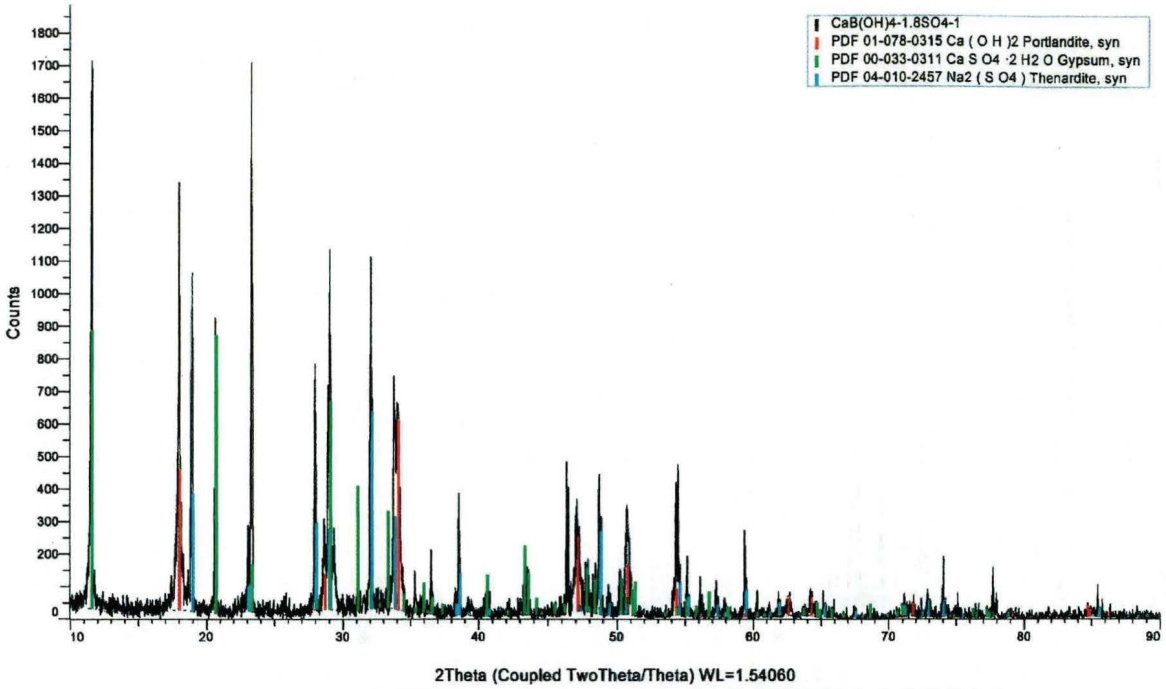



Figure 65 XRD analysis of sample CaB(OH)4-1.8 SO4-1
Source of Figure 65: Scientific Notebook WIPP-Borate-10 Pg. 71

### 3.4.7 $NaB(OH)_4(aq)$—$Na^+/Cl^-$ Interactions

Table 3-11 shows the experimental set-ups of the NaB(OH)4-Na+/Cl- experiments. The figures below document the XRD solids characterization of the experiments. At 3143 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. All of the samples in this experiment matched with good agreement to borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) PDF pattern 04-012-8356. Samples Na2B4O7-NaCl 4.0-1 and Na2B4O7-NaCl 5.0-1 also contained the matrix peaks for halite (NaCl) PDF pattern 00-005-0628. The figures below show the XRD data.

Table 3-11 Preparation of experimental set-ups for investigation of $NaB(OH)_4(aq)$—$Na^+/Cl^-$ Interactions.

| Set-up ID | $Na_2B_4O_7.10\ H_2O$ (g) | NaCl (m) | mL of NaCl Solution | Scientific Notebook Reference |
|---|---|---|---|---|
| Na2B4O7-NaCl-0.01-1 | 5.0024+5.0009* | 0.010 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-0.01-2 | 5.0057+4.9989* | 0.010 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-0.1-1 | 5.0031+4.9992* | 0.10 | 100 | WIPP-Borate-1 Pg. 4 |

Information Only

| Set-up ID | $Na_2B_4O_7.10\ H_2O$ (g) | NaCl (m) | mL of NaCl Solution | Scientific Notebook Reference |
|---|---|---|---|---|
| Na2B4O7-NaCl-0.1-2 | 5.0064+5.0007* | 0.10 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-1.0-1 | 5.0005 | 1.0 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-1.0-2 | 5.0098 | 1.0 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-2.0-1 | 5.0094 | 2.1 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-2.0-2 | 5.0066 | 2.1 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-3.0-1 | 5.0073 | 3.2 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-3.0-2 | 5.0053 | 3.2 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-3.0-1R | 5.0099 | 3.2 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-4.0-1 | 5.0011 | 4.4 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-4.0-2 | 5.0097 | 4.4 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-5.0-1 | 5.0086 | 5.0 | 100 | WIPP-Borate-1 Pg. 4 |
| Na2B4O7-NaCl-5.0-2 | 5.0092 | 5.0 | 100 | WIPP-Borate-1 Pg. 4 |

*In these experiments, there were still small amounts of the solubility-controlling phase present, but additional amounts of $Na_2B_4O_7 \cdot 10\ H_2O$ grams added for these experiments, see WIPP-Borate-3 Pg. 39.

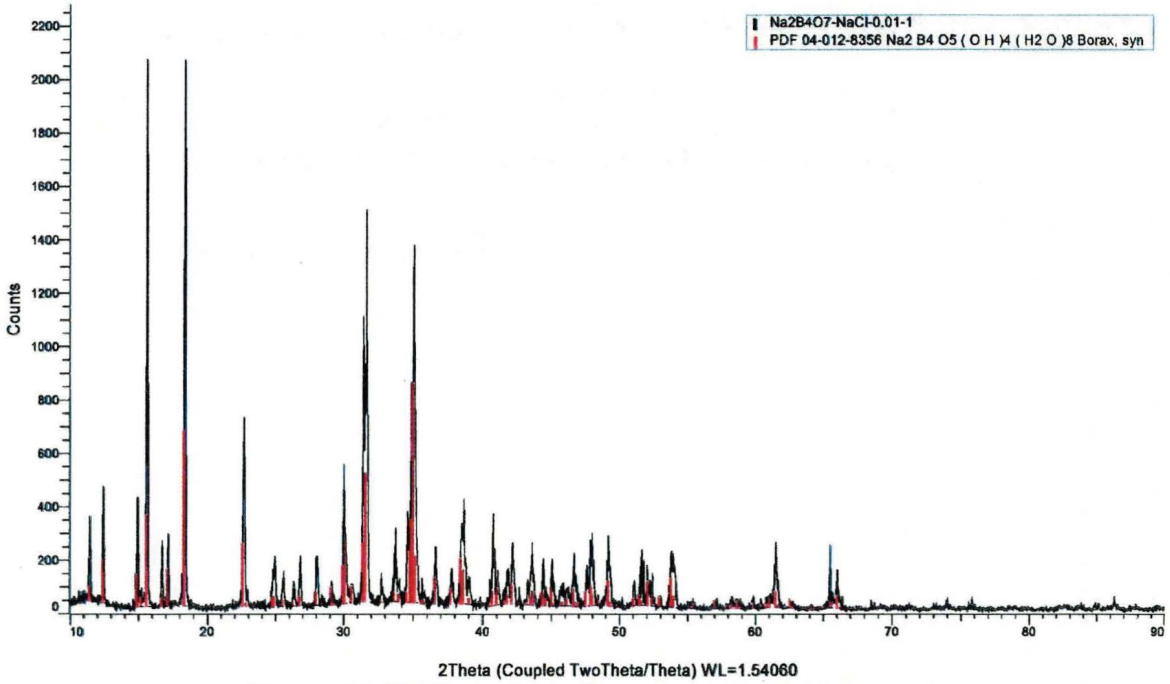



Figure 66 XRD analysis for sample Na2B4O7-NaCl-0.01-1
Source of Figure 66: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

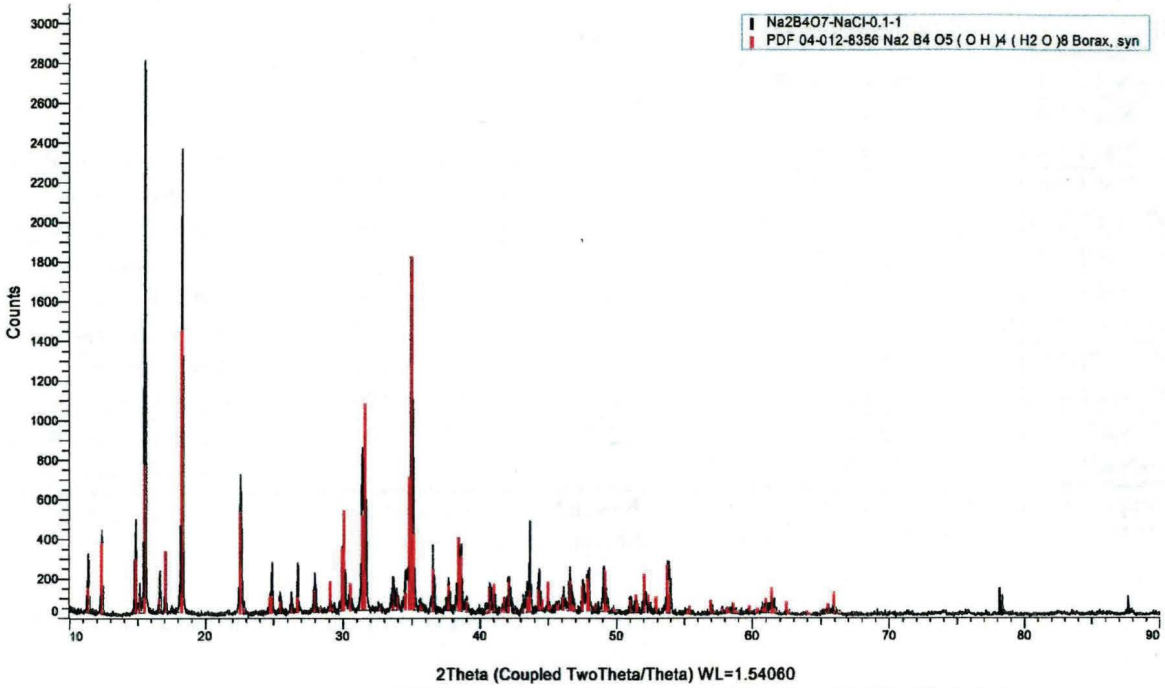



Figure 67 XRD analysis for sample Na2B4O7-NaCl-0.1-1
Source of Figure 67: Scientific Notebook WIPP-Borate-10 Pg. 87

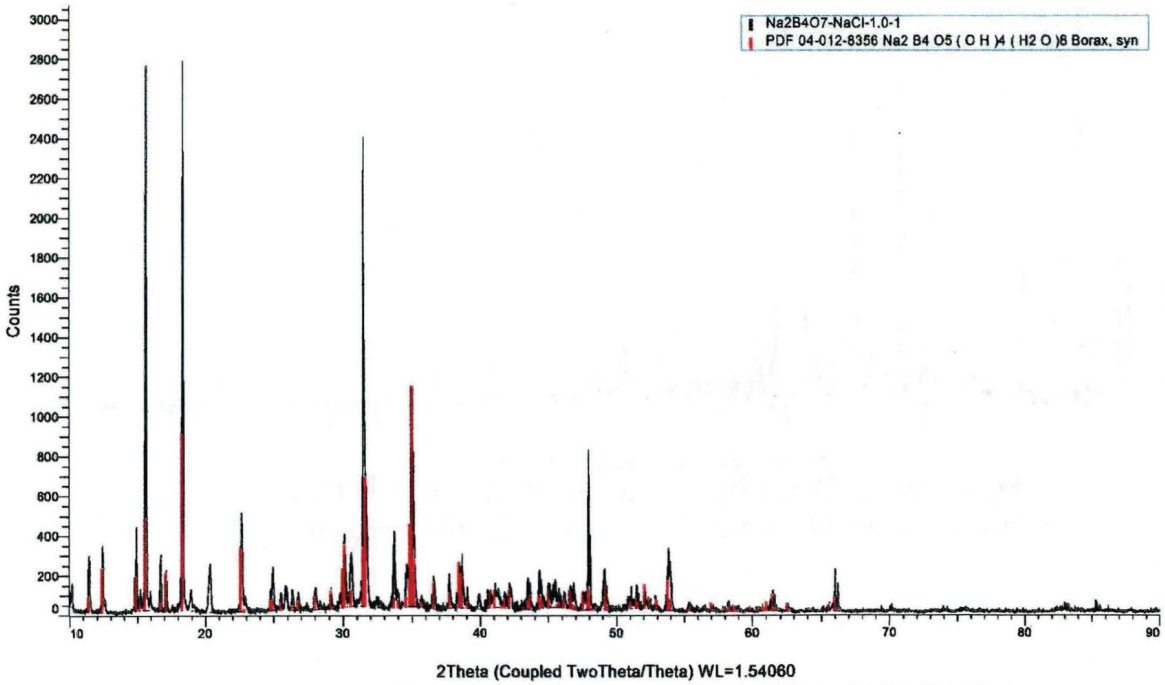



Figure 68 XRD analysis for sample Na2B4O7-NaCl-1.0-1
Source of Figure 68: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

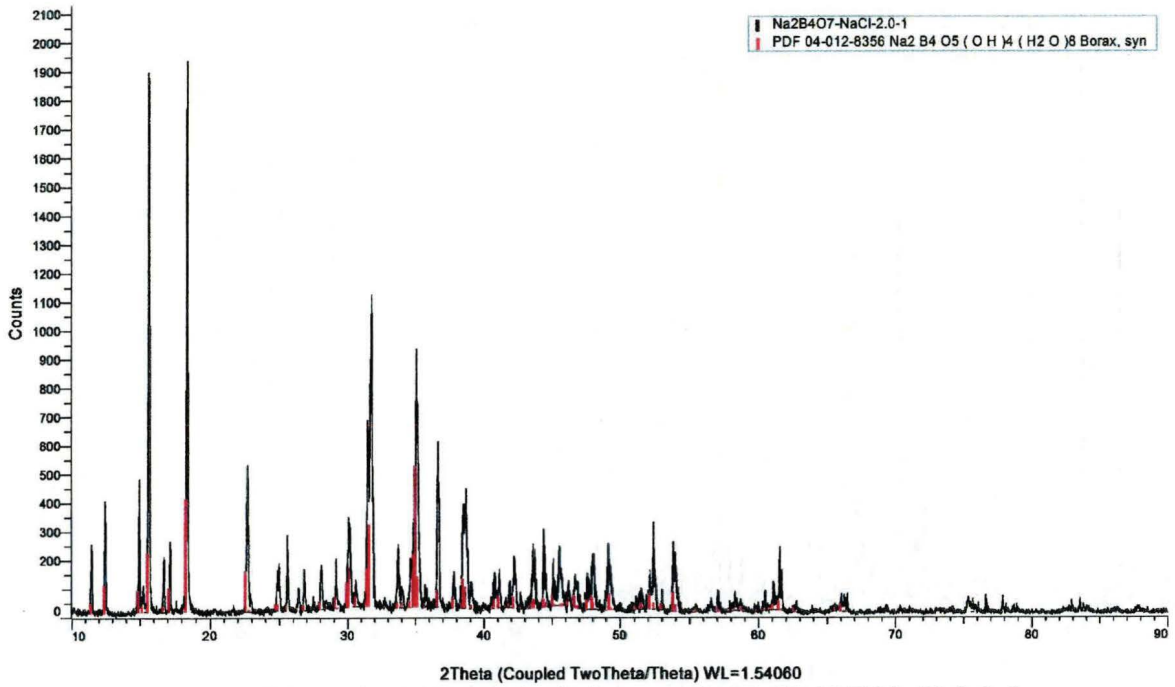



Figure 69 XRD analysis for sample Na2B4O7-NaCl-2.0-1
Source of Figure 69: Scientific Notebook WIPP-Borate-10 Pg. 87

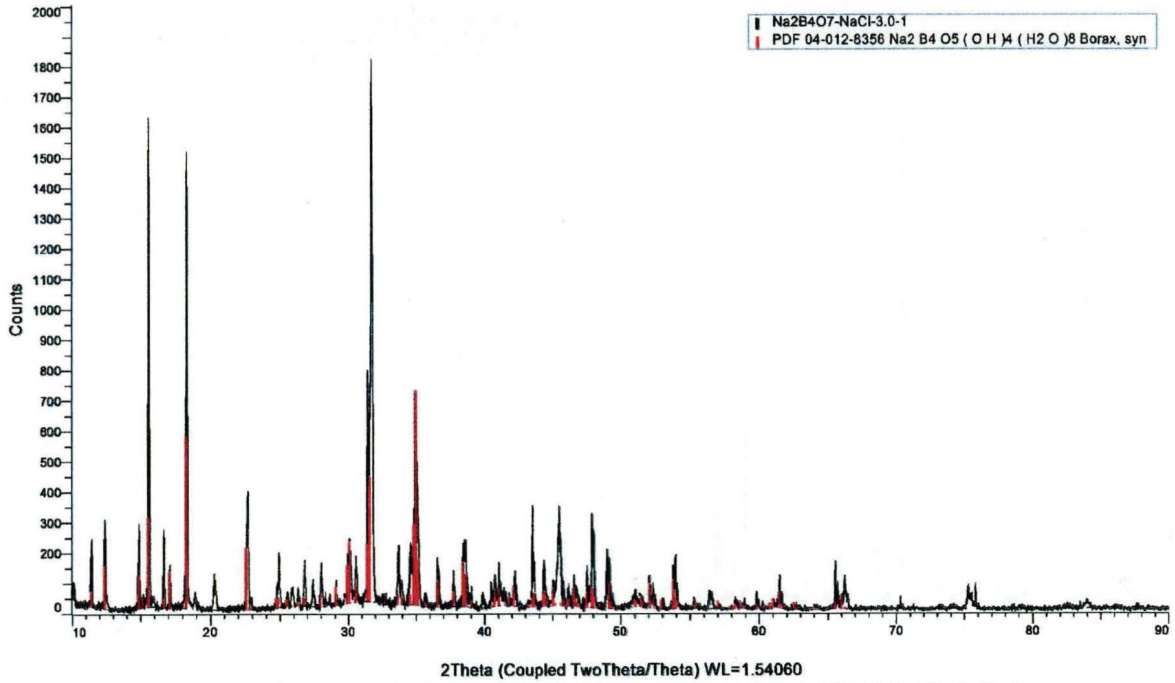



Figure 70 XRD analysis for sample Na2B4O7-NaCl-3.0-1
Source of Figure 70: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

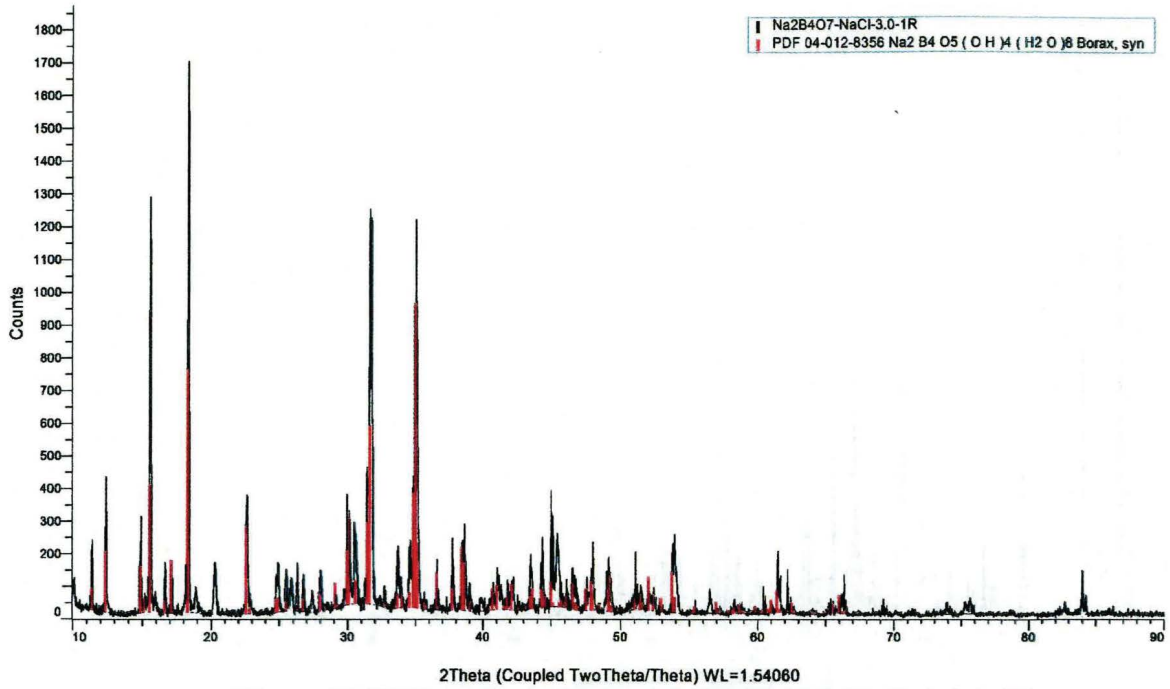



Figure 71 XRD analysis for sample Na2B4O7-NaCl-3.0-1 (R)
Source of Figure 71: Scientific Notebook WIPP-Borate-10 Pg. 87

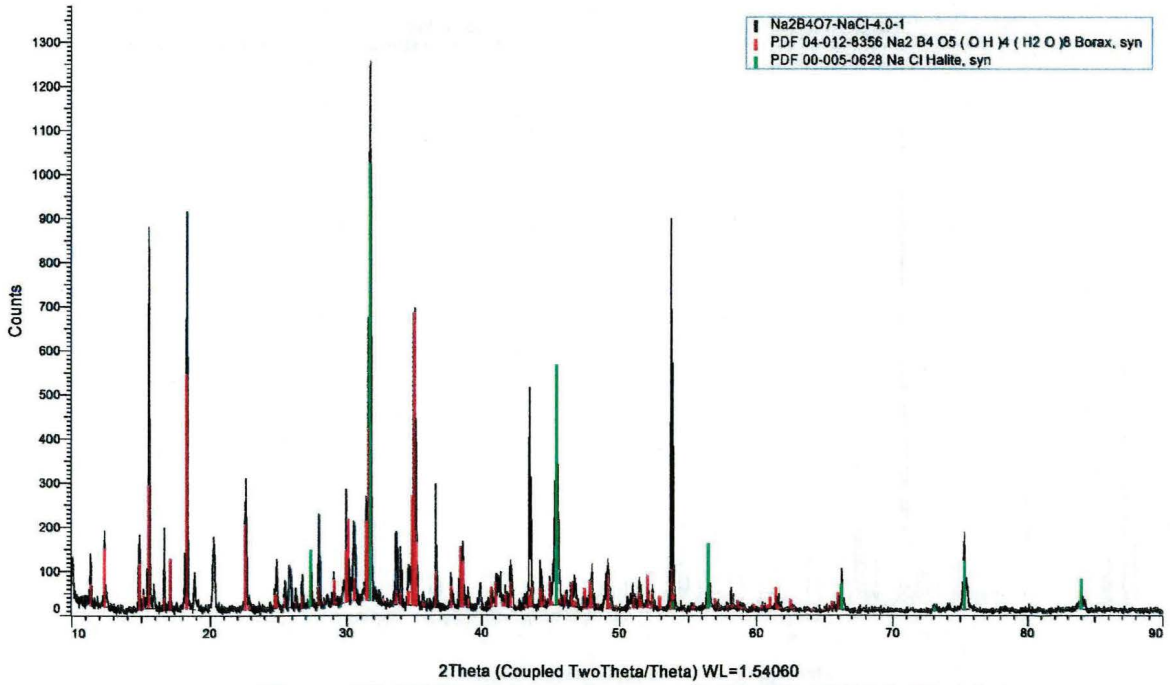



Figure 72 XRD analysis for sample Na2B4O7-NaCl-4.0-1
Source of Figure 72: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

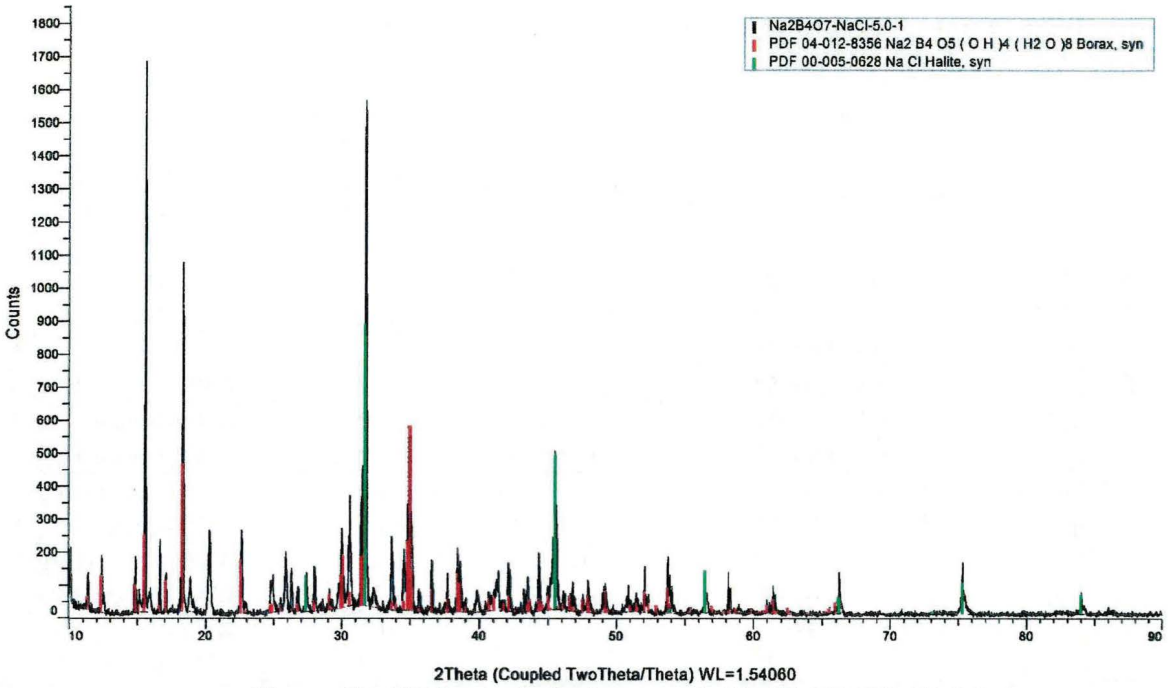



Figure 73 XRD analysis for sample Na2B4O7-NaCl-5.0-1
Source of Figure 73: Scientific Notebook WIPP-Borate-10 Pg. 87

### 3.4.8 $NaB(OH)_4$(aq)—$Mg^{2+}/Cl^-$ Interactions

Table 3-12 shows the experimental set-ups for the $NaB(OH)_4$-$Mg^{2+}/Cl^-$ experiments. Figures 74-79 show the XRD solids characterization of the experiments. At 3145 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Sample Na2B4O7-0.01 Mg-1 matched with good agreement to borax ($Na_2B_4O_5(OH)_4{\cdot}8H_2O$) PDF pattern 04-012-8356. Sample Na2B4O7-0.1 Mg-1 matched with good agreement to borax ($Na_2B_4O_5(OH)_4{\cdot}8H_2O$) PDF pattern 04-012-8356 and sodium borate hydrate ($Na_2B_6O_{10}{\cdot}4H_2O$) PDF pattern 00-024-1057. All other samples in the set matched to these two minerals, in addition to ezcurrite ($Na_4B_{10}O_{17}{\cdot}7H_2O$) PDF pattern 00-011-0257, magnesium borate hydroxide hydrate ($MgB_3O_3(OH)_5{\cdot}6H_2O$) PDF pattern 00-049-0837 and bischofite ($MgCl_2{\cdot}6H_2O$) PDF pattern 00-025-0515. It is important to note that this was a very mixed solid system and many of the PDF patterns match with varying degrees of accuracy. Some peaks remain unidentified in these patterns and in order to verify what solids are present and in what concentrations, an alternate instrument technique, such as SEM/EDS, would need to be employed. The Figures below show the XRD data.

Information Only

Table 3-12 Preparation of experimental set-ups for investigation of $NaB(OH)_4(aq)$—$Mg^{2+}/Cl^-$ Interactions.

| Set-up ID | $Na_2B_4O_7.10\ H_2O$ (g) | $MgCl_2$ (m) | mL of $MgCl_2$ Solution | Scientific Notebook Reference |
|---|---|---|---|---|
| Na2B4O7-0.01Mg-1 | 5.0047+5.0012* | 0.01 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-0.01Mg-2 | 5.0099+5.0011* | 0.01 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-0.1Mg-1 | 5.0089+4.9996* | 0.1 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-0.1Mg-2 | 5.0098+4.9988* | 0.1 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-1.0Mg-1 | 5.0012+5.0001* | 1.0 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-1.0Mg-2 | 5.0067+4.9989* | 1.0 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-1.5Mg-1 | 5.0085+5.0010* | 1.5 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-1.5Mg-2 | 5.0027+5.0012* | 1.5 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-2.0Mg-1 | 5.0008+5.0009* | 2.0 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-2.0Mg-2 | 5.0028+5.0006* | 2.0 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-2.5Mg-1 | 5.0043+4.9997* | 2.5 | 100 | WIPP-Borate-1 Pg. 5 |
| Na2B4O7-2.5Mg-2 | 5.0032+5.0012* | 2.5 | 100 | WIPP-Borate-1 Pg. 5 |

*Additional amounts of $Na_2B_4O_7$•10 $H_2O$ grams was added WIPP-Borate-3 Pg. 39.

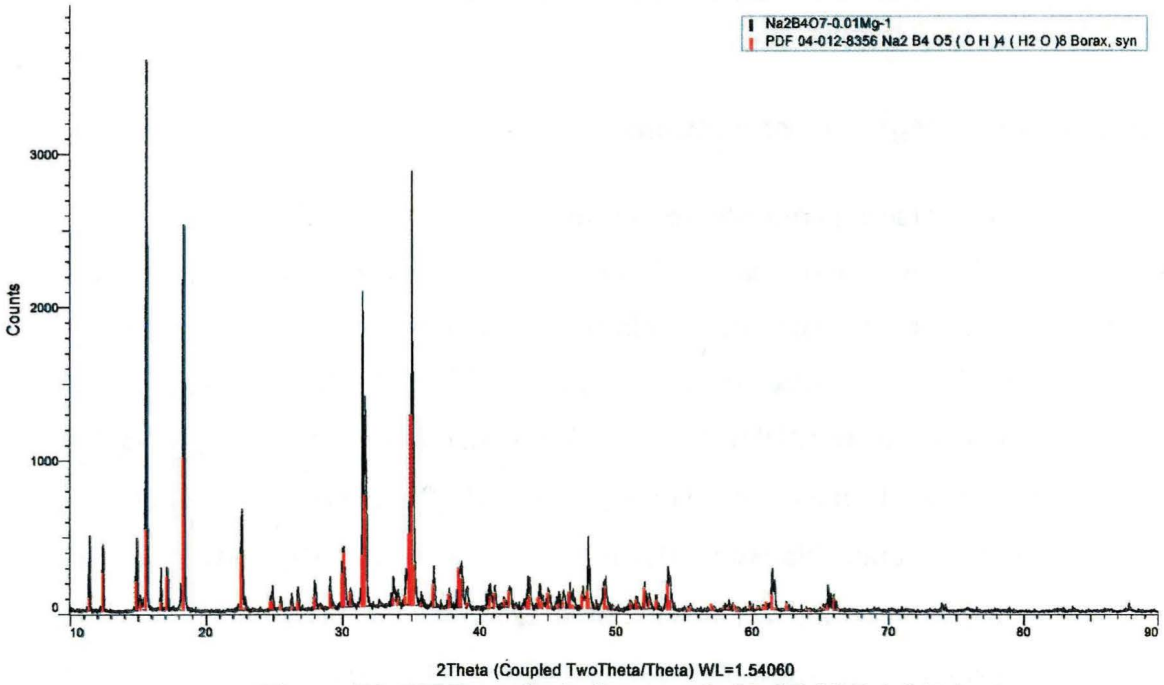



Figure 74 XRD analysis for sample Na2B4O7-0.01Mg-1
Source of Figure 74: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

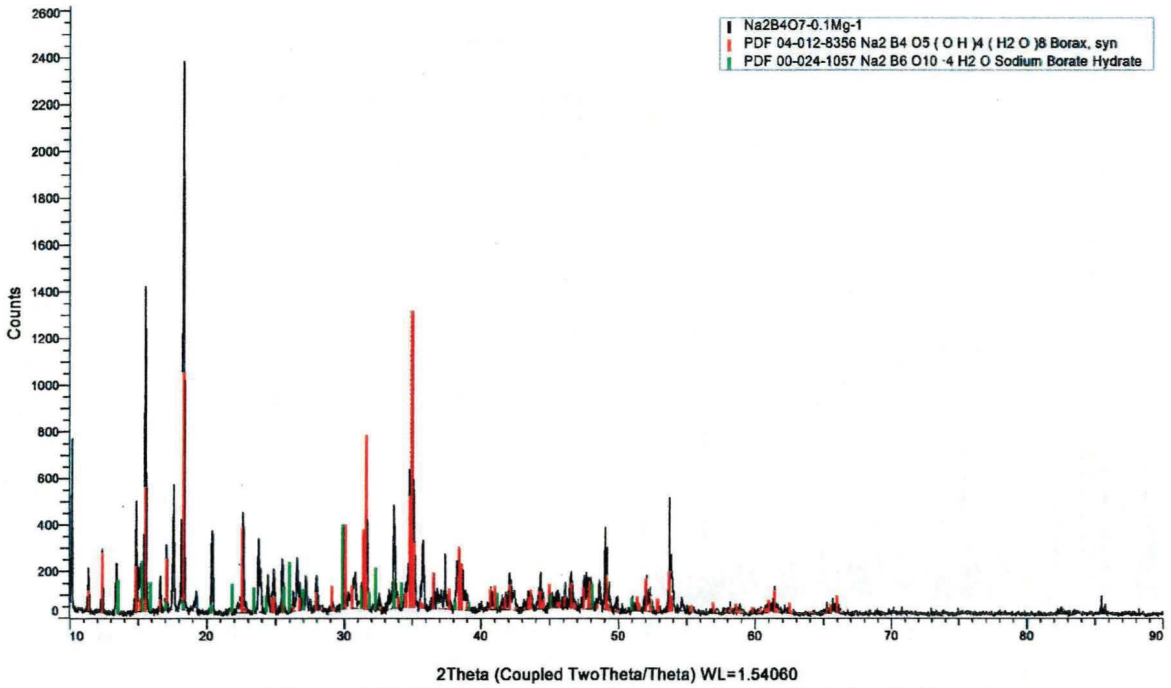



Figure 75 XRD analysis for sample Na2B4O7-0.1Mg-1
Source of Figure 75: Scientific Notebook WIPP-Borate-10 Pg. 89

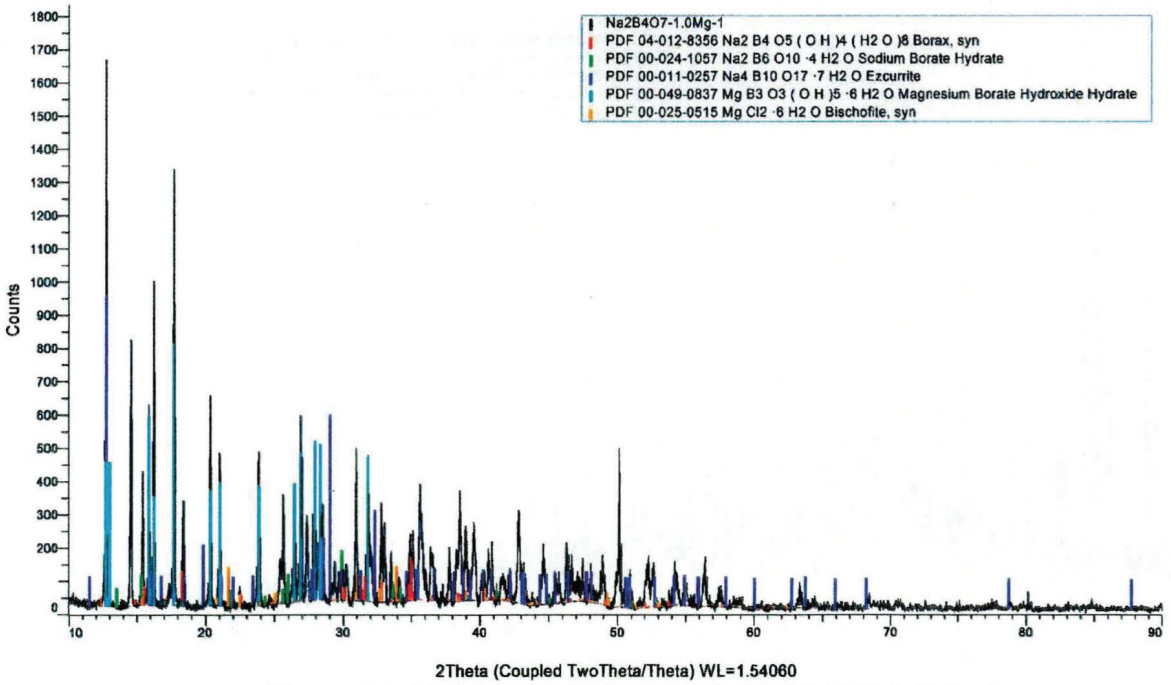



Figure 76 XRD analysis for sample Na2B4O7-1.0Mg-1
Source of Figure 76: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

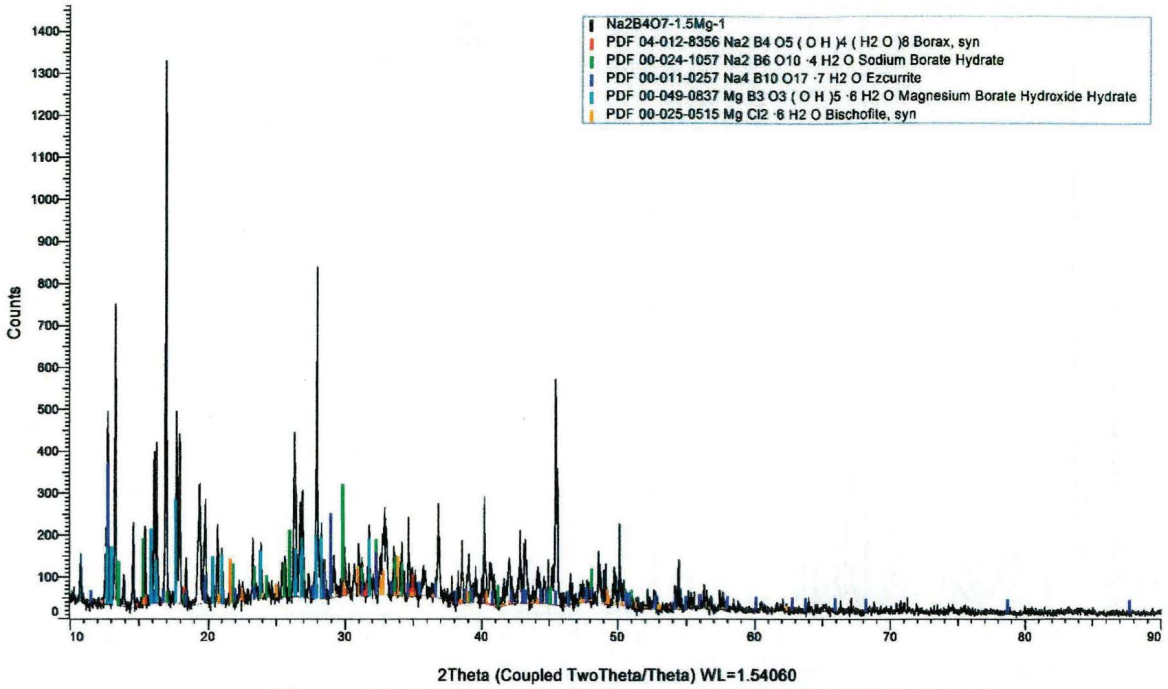



Figure 77 XRD analysis for sample Na2B4O7-1.5Mg-1
Source of Figure 77: Scientific Notebook WIPP-Borate-10 Pg. 89

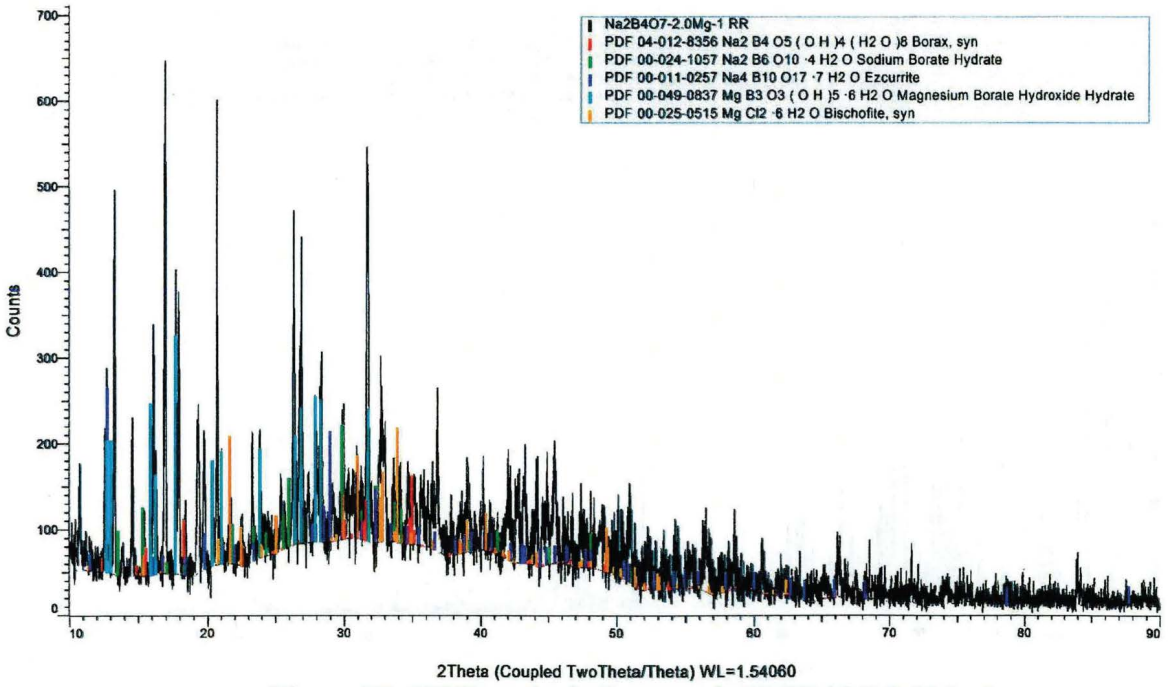



Figure 78 XRD analysis for sample Na2B4O7-2.0Mg-1
Source of Figure 78: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

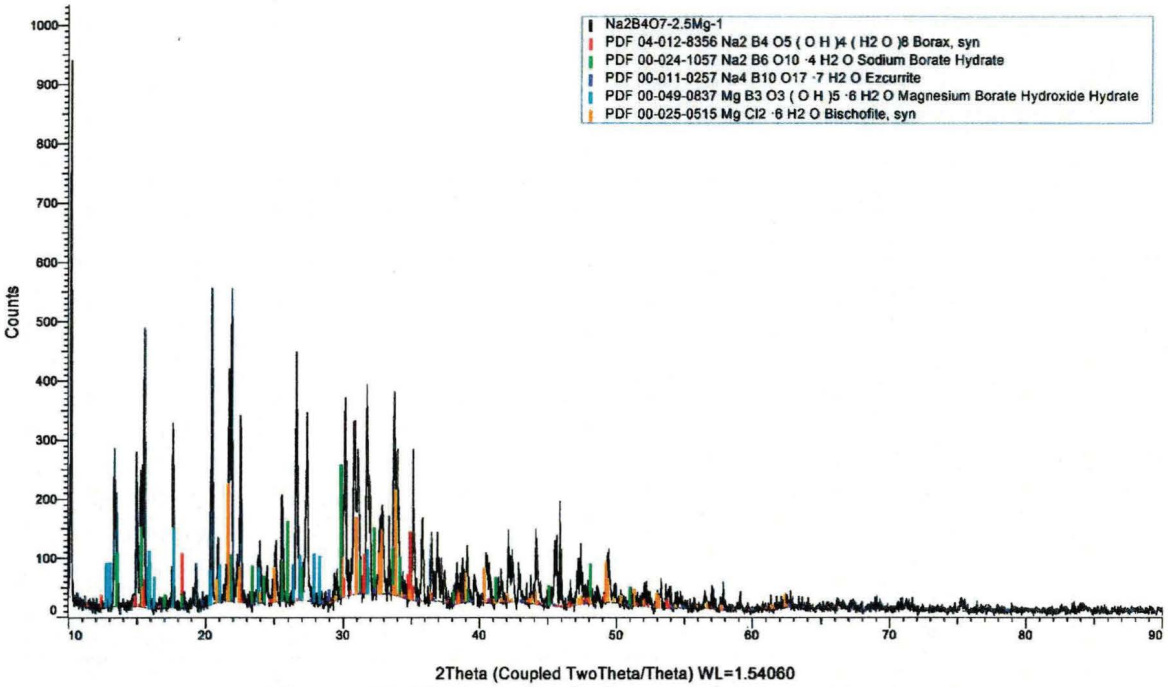



Figure 79 XRD analysis for sample Na2B4O7-2.5Mg-1
Source of Figure 79: Scientific Notebook WIPP-Borate-10 Pg. 89

### 3.4.9 $NaB(OH)_4(aq)$—$Mg^{2+}$—$Na^+$ Interactions

Table 3-13 shows the experimental set-ups for the $NaB(OH)_4(aq)$—$Mg^{2+}$—$Na^+$ experiments. The figures below document the XRD solids characterization of these experiments. At 2804 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Sample Na2B4O7-MgCl2-A-1 matches with good agreement to borax ($Na_2B4O_5(OH)_4{\cdot}8H_2O$) PDF pattern 04-012-8356. All other samples show varying amounts of solids including: borax ($Na_2B4O_5(OH)_4{\cdot}8H_2O$) PDF pattern 04-012-8356, sodium borate hydrate ($Na_2B_6O_{10}{\cdot}4H_2O$) PDF pattern 00-024-1057, inderite ($MgB_3O_3(OH)_5{\cdot}5H_2O$) PDF pattern 04-011-2718 and magnesium borate hydroxide hydrate ($MgB_3O_3(OH)_5{\cdot}6H_2O$) PDF pattern 00-049-0837. The figures below show the XRD data.

Information Only

Table 3-13 Preparation of experimental set-ups for investigation of $NaB(OH)_4(aq)$—$Mg^{2+}$—$Na^+$ Interactions.

| Set-up ID | $Na_2B_4O_7$•10 $H_2O$ (g) | $MgCl_2$ (m) | NaCl (m) | mL of Solution | Scientific Notebook Reference |
|---|---|---|---|---|---|
| Na2B4O7-MgCl2 A-1 | 5.0048+4.9990* | 0.500 | 5.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 A-2 | 5.0091+5.0003* | 0.500 | 5.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 B-1 | 5.0018+5.0011* | 0.800 | 3.5 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 B-2 | 5.0029+5.0008* | 0.800 | 3.5 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 C-1 | 5.0088+4.9996* | 1.25 | 3.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 C-2 | 5.0037+4.9998* | 1.25 | 3.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 D-1 | 5.0082+5.0006* | 1.50 | 2.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 D-2 | 5.0017+5.0009* | 1.50 | 2.0 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 E-1 | 5.0055+4.9994* | 1.75 | 1.5 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 E-2 | 5.0063+4.9991* | 1.75 | 1.5 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 F-1 | 5.0083+4.9997* | 2.00 | 0.50 | 100 | WIPP-Borate-1 Pg. 6 |
| Na2B4O7-MgCl2 F-2 | 5.0057+5.0007* | 2.00 | 0.50 | 100 | WIPP-Borate-1 Pg. 6 |

*Additional amounts of $Na_2B_4O_7$•$10H_2O$ grams added WIPP-Borate-3 Pg. 40.

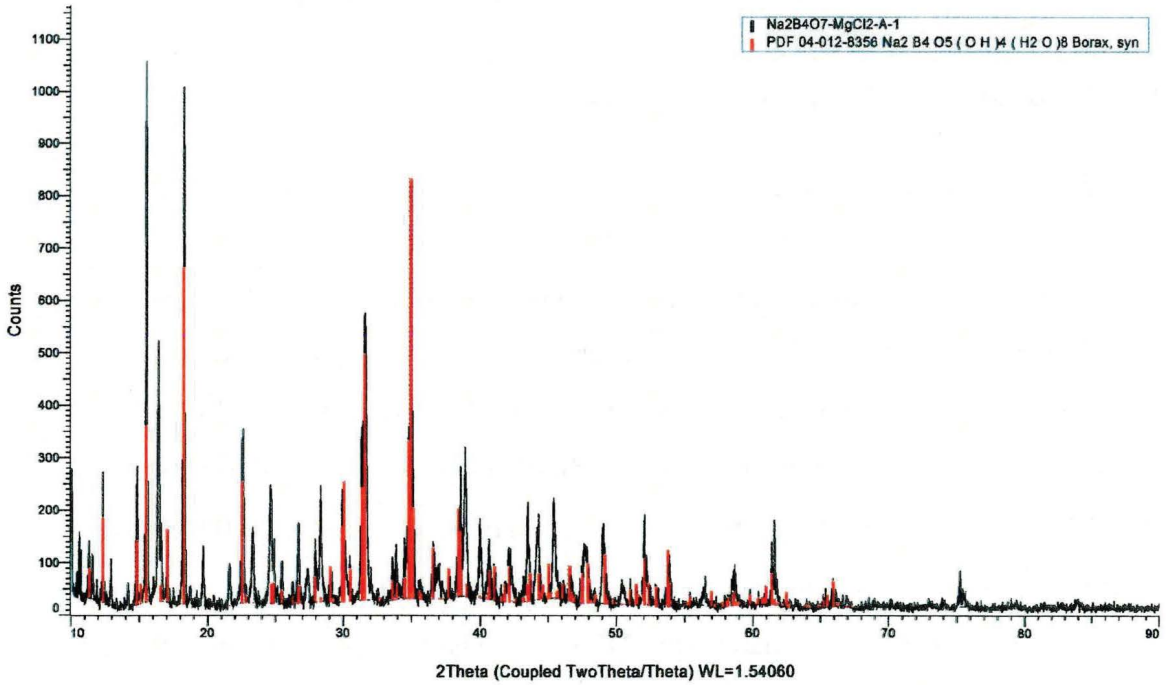



Figure 80 XRD analysis for sample Na2B4O7-MgCl2 A-1
Source of Figure 80: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

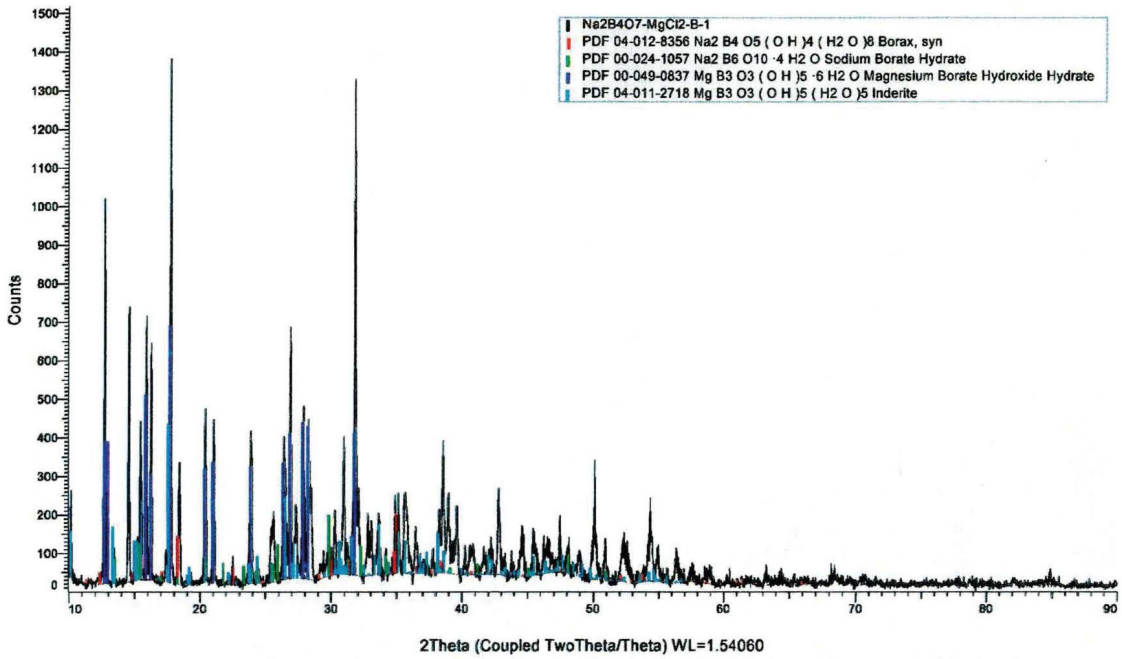



Figure 81 XRD analysis for sample Na2B4O7-MgCl2-B-1
Source of Figure 81: Scientific Notebook WIPP-Borate-10 Pg. 89

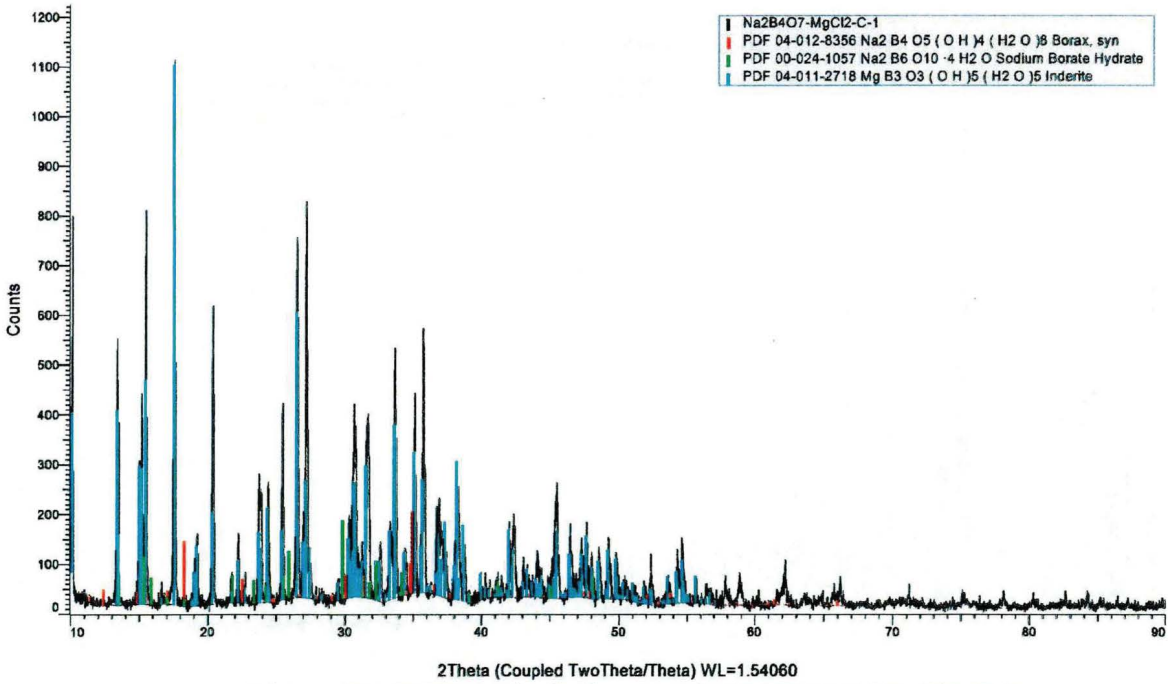



Figure 82 XRD analysis for sample Na2B4O7-MgCl2-C-1
Source of Figure 82: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

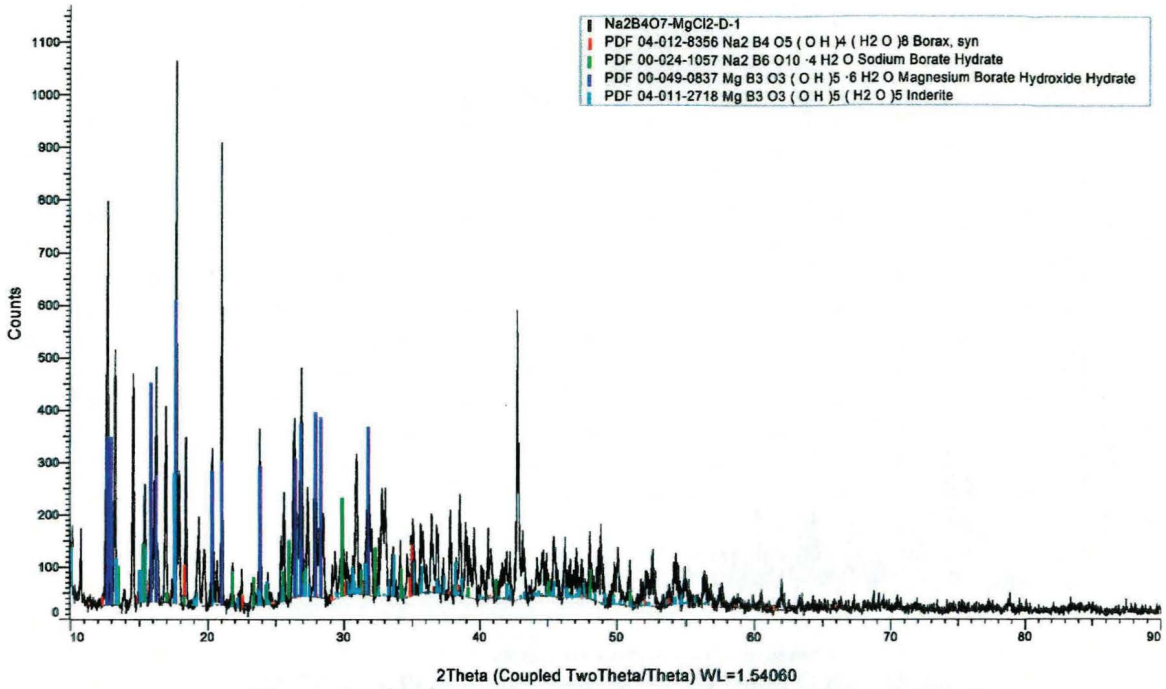



Figure 83 XRD analysis for sample Na2B4O7-MgCl2-D-1
Source of Figure 83: Scientific Notebook WIPP-Borate-10 Pg. 89

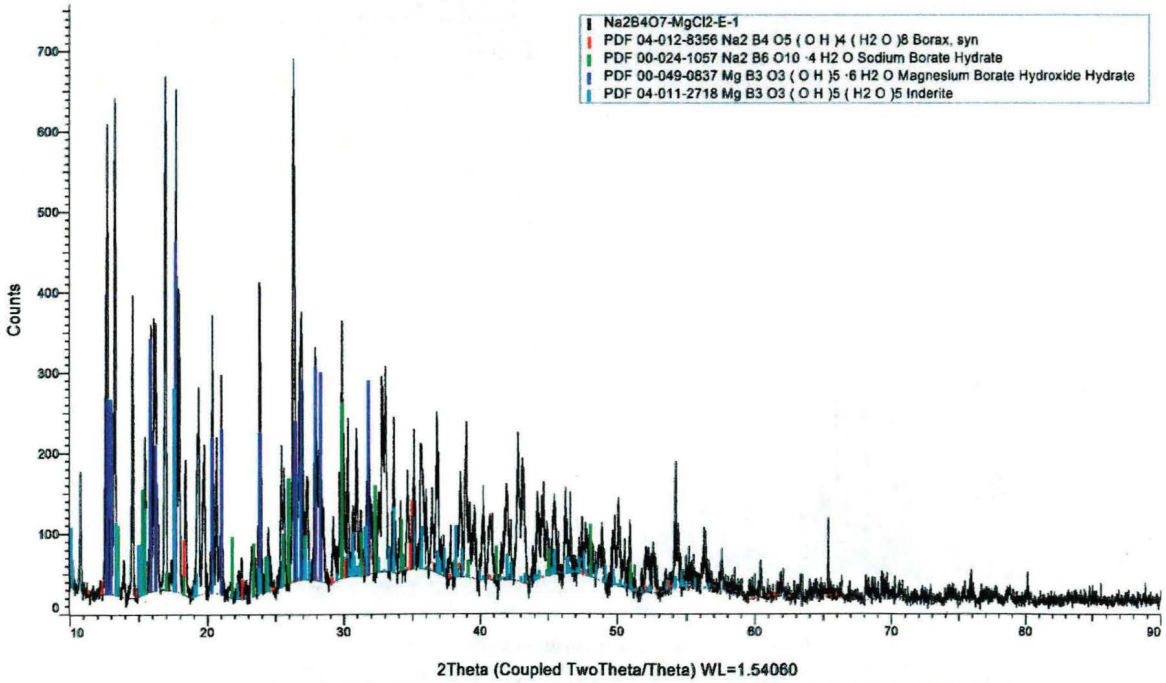



Figure 84 XRD analysis for sample Na2B4O7-MgCl2-E-1
Source of Figure 84: Scientific Notebook WIPP-Borate-10 Pg. 89

Information Only

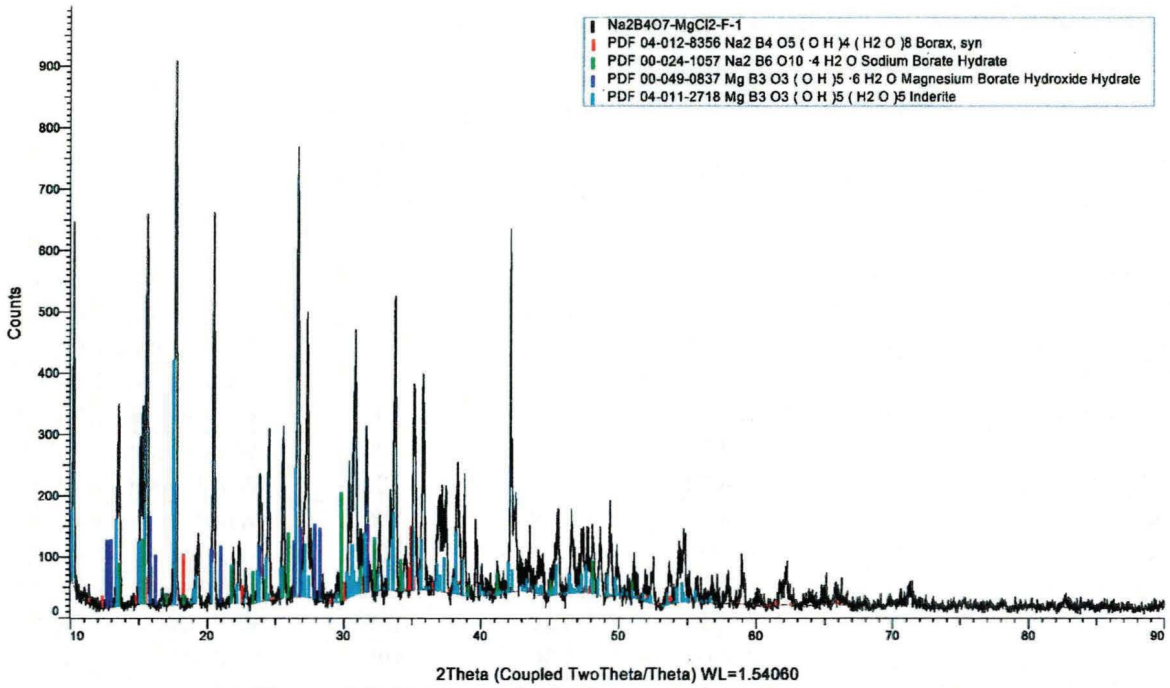



Figure 85 XRD analysis for sample Na2B4O7-MgCl2-F-1
Source of Figure 85: Scientific Notebook WIPP-Borate-10 Pg. 89

### 3.4.10 $PbB_4O_7$(aq)—$Na^+/Cl^-$ Interactions

Table 3-14 shows the experimental set-ups of the $PbB_4O_7$(aq)—$Na^+/Cl^-$ experiments. Figures 86-92 document the XRD solids characterization of the experiments. At 2900 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Samples PbB4(AQ)-0.01 Na-1, PbB4(AQ)-0.1 Na-1 and PbB4(AQ)-1.0 Na-1 show a mixed solid system containing varying amounts of litharge (PbO) PDF pattern 00-005-0561, laurionite (Pb(OH)Cl) PDF pattern 00-052-0289 and lead borate hydrate ($PbB_4O_7 \cdot 3H_2O$) PDF pattern 00-028-0523. All other samples in the experiment match with good agreement to laurionite (Pb(OH)Cl) PDF pattern 00-052-0289. In addition, lead metaborate monohydrate ($PbB_2O_4 \cdot H_2O$) could be present in those experiments. However, metaborate monohydrate is not present in the PDF4+ 2019 database, but it is in the NIST database. Since the PDF4+ 2019 database is utilized for the Search/Match of these experiments, this phase could be missed. The Figures below show the XRD data.

Information Only

Table 3-14 Preparation of experimental set-ups for investigation of $PbB_4O_7(aq)$—$Na^+/Cl^-$ Interactions.

| Set-up ID | NaCl (m) | PbO (g) | $H_3BO_3$ (m) | mL of De-gassed DI Water | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB4 (AQ)- 0.01 Na-1 | 0.010 | 2.0007 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 0.01 Na-2 | 0.010 | 2.0005 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 0.1 Na-1 | 0.10 | 2.0001 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 0.1 Na-2 | 0.10 | 2.0009 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 1.0 Na-1 | 1.0 | 2.0004 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 1.0 Na-2 | 1.0 | 2.0012 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 2.0 Na-1 | 2.1 | 2.0001 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 2.0 Na-2 | 2.1 | 2.0002 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 3.0 Na-1 | 3.2 | 2.0005 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 3.0 Na-2 | 3.2 | 2.0000 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 4.0 Na-1 | 4.4 | 2.0002 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 4.0 Na-2 | 4.4 | 2.0012 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 5.0 Na-1 | 5.0 | 2.0000 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |
| PbB4 (AQ)- 5.0 Na-2 | 5.0 | 2.0010 | 0.30 | 100 | WIPP-Borate-1 Pg. 15 |

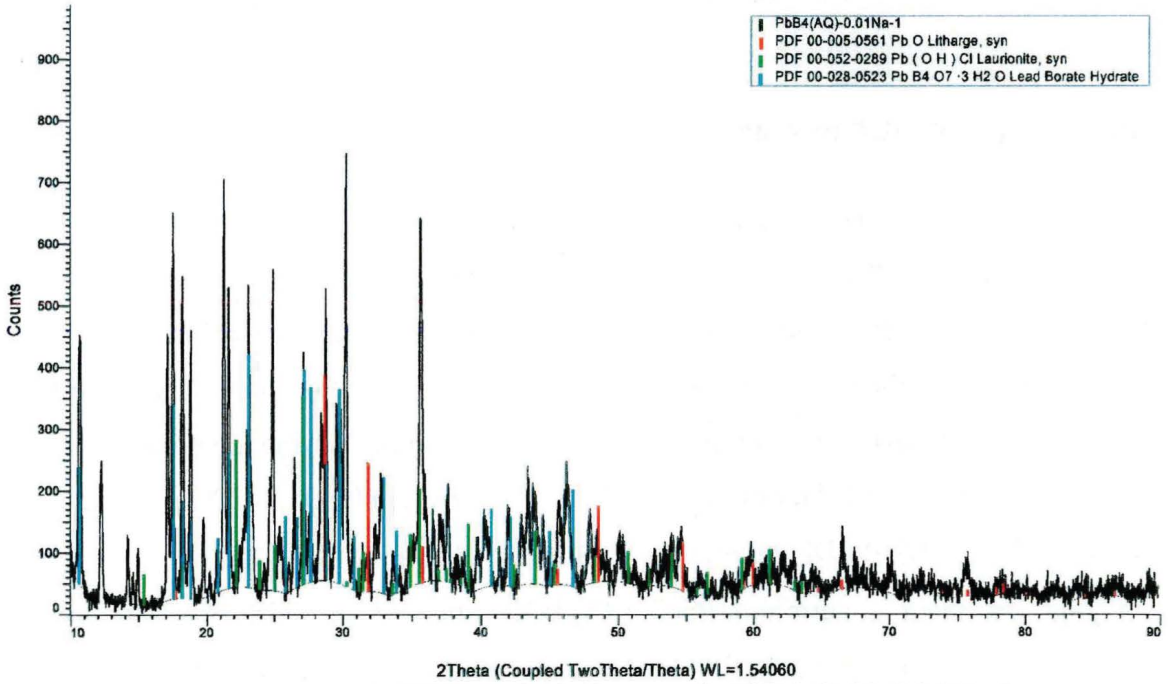



Figure 86 XRD analysis for sample PbB4-(AQ)-0.01Na-1
Source of Figure 86: Scientific Notebook WIPP-Borate-10 Pg. 84

Information Only

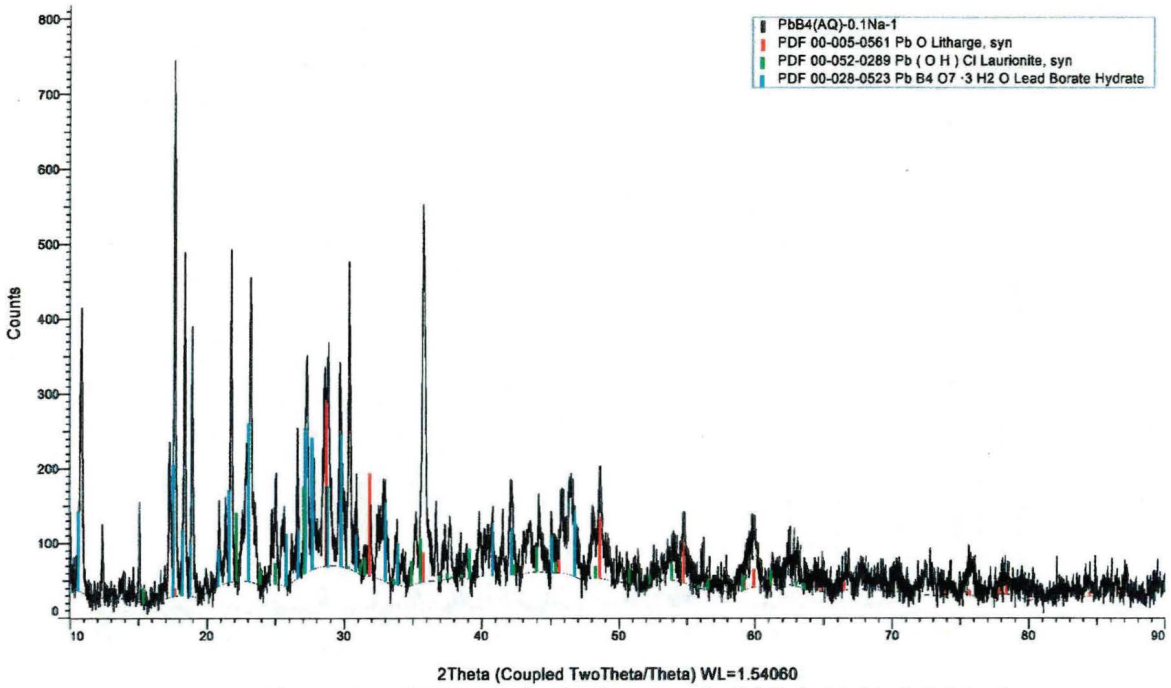



Figure 87 XRD analysis for sample PbB4-(AQ)-0.1 Na-1
Source of Figure 87: Scientific Notebook WIPP-Borate-10 Pg. 84

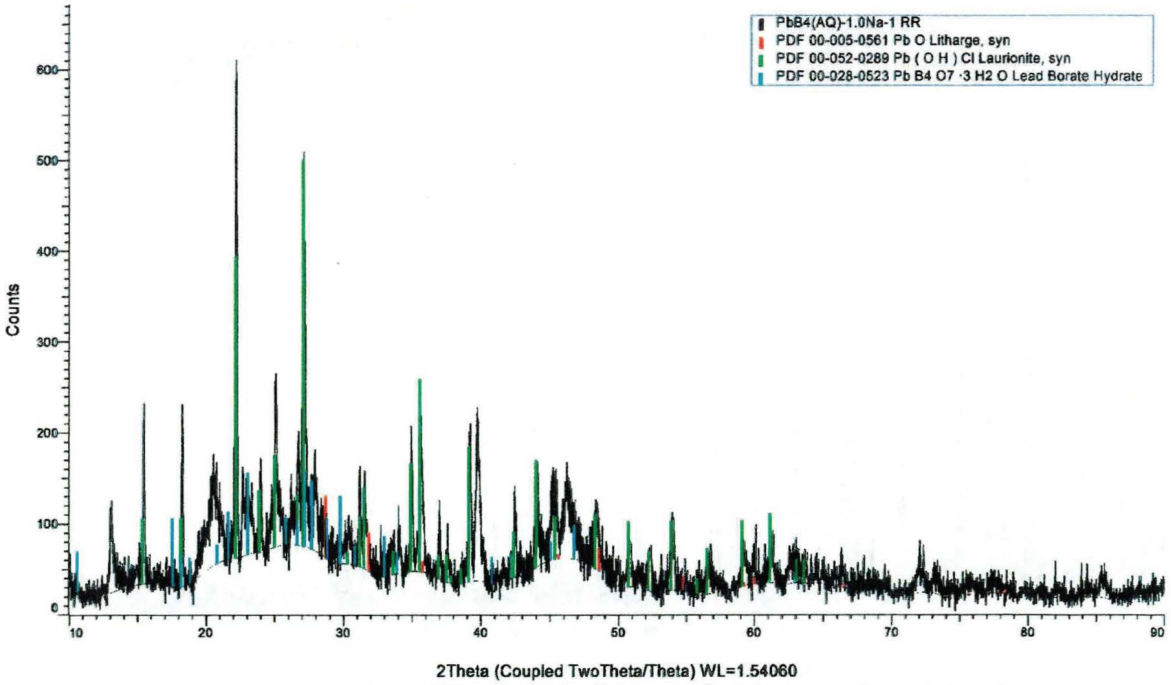



Figure 88 XRD analysis for sample PbB4-(AQ)-1.0 Na-1
Source of Figure 88: Scientific Notebook WIPP-Borate-10 Pg. 92

Information Only

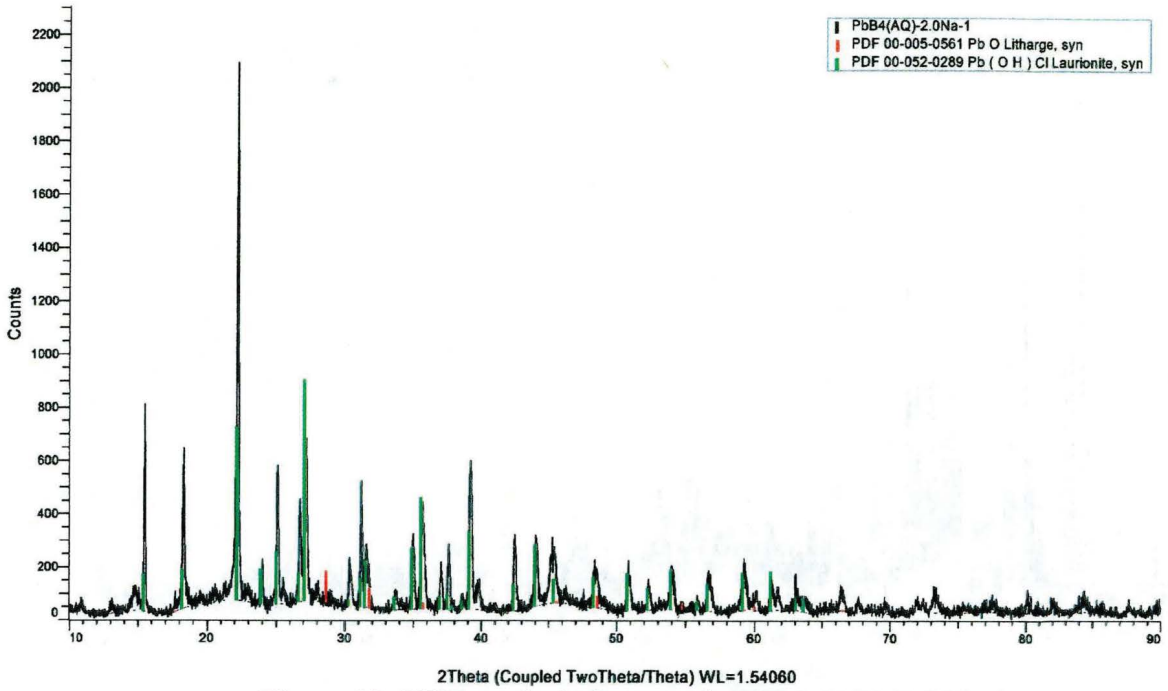



Figure 89 XRD analysis for sample PbB4-(AQ)-2.0 Na-1
Source of Figure 89: Scientific Notebook WIPP-Borate-10 Pg. 84

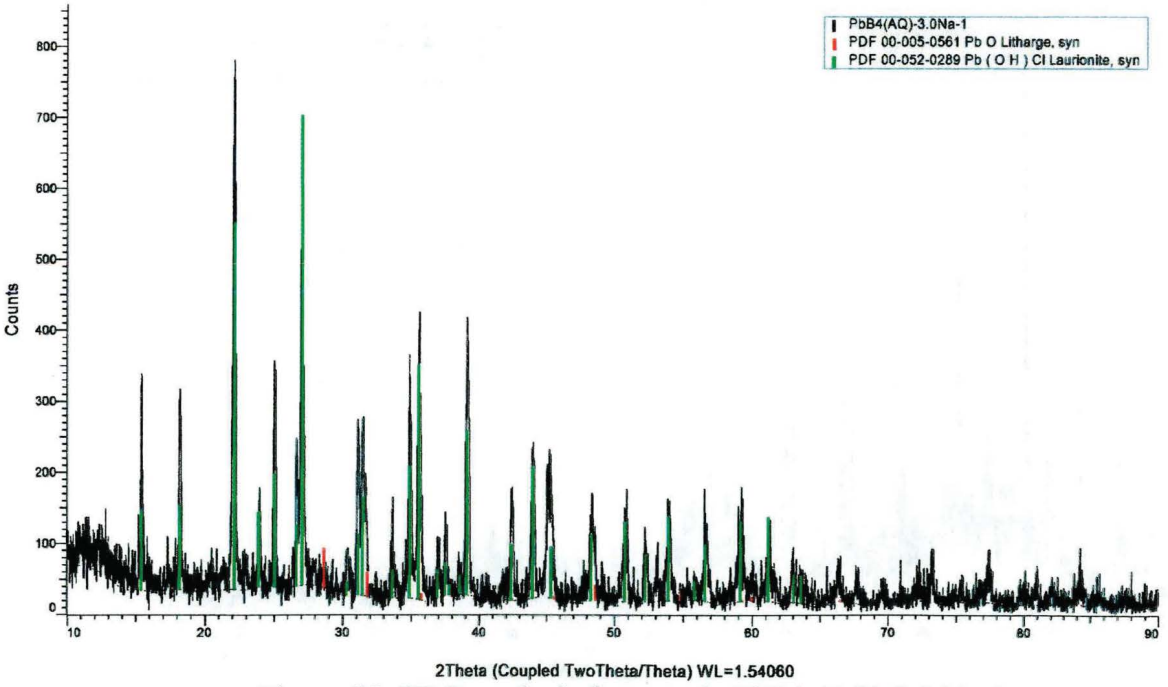



Figure 90 XRD analysis for sample PbB4-(AQ)-3.0 Na-1
Source of Figure 90: Scientific Notebook WIPP-Borate-10 Pg. 84

Information Only

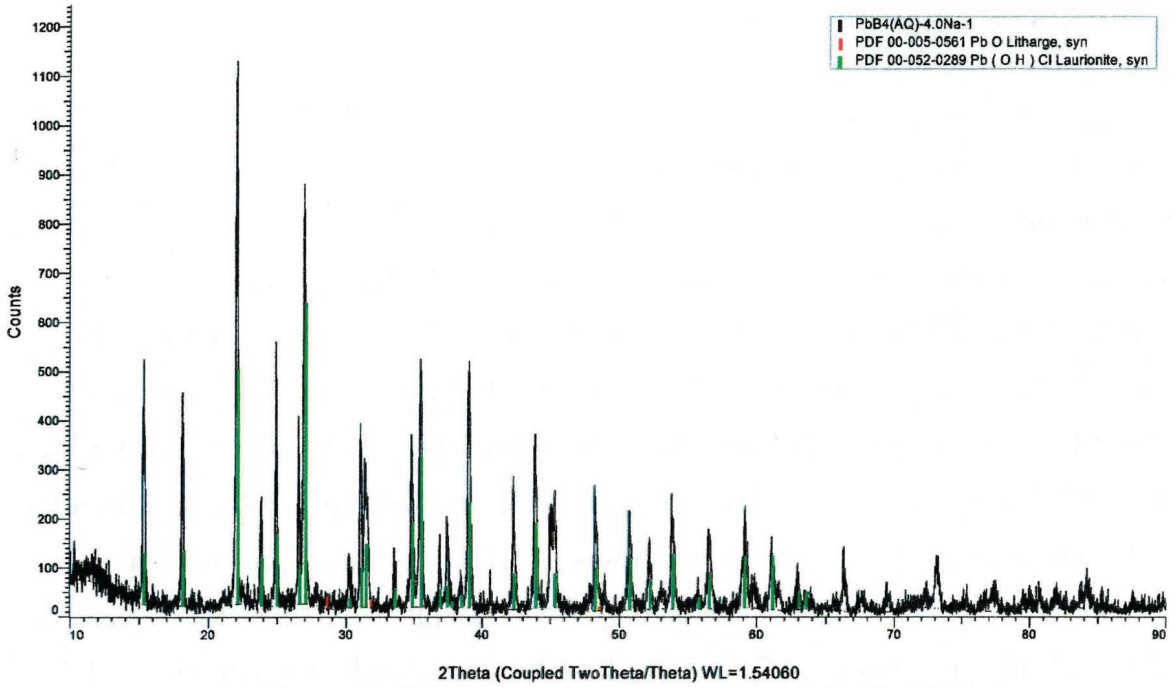



Figure 91 XRD analysis for sample PbB4-(AQ)-4.0 Na-1
Source of Figure 91: Scientific Notebook WIPP-Borate-10 Pg. 84

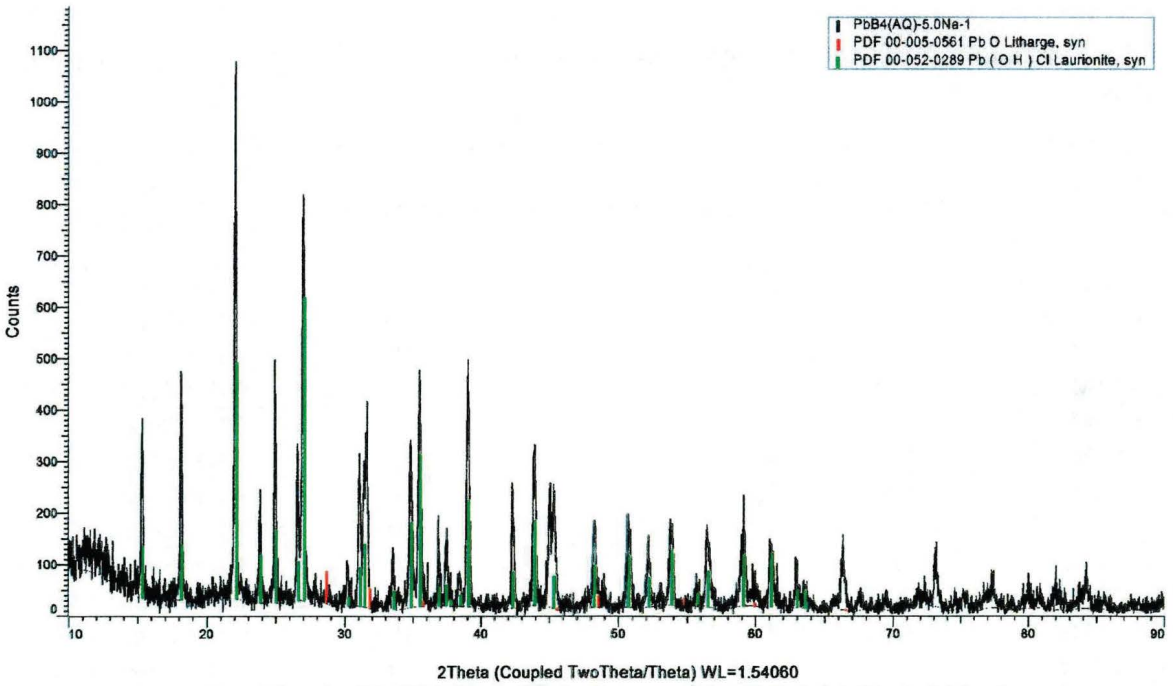



Figure 92 XRD analysis for sample PbB4-(AQ)-5.0 Na-1
Source of Figure 92: Scientific Notebook WIPP-Borate-10 Pg. 84

Information Only

### 3.4.11 $PbB_4O_7$(aq)—$Mg^{2+}$/$Cl^-$ Interactions

Table 3-15 shows the experimental set-ups for the $PbB_4O_7$(aq)—$Mg^{2+}$/$Cl^-$ experiments. Figures 93-98 document the XRD solids characterization of those experiments. At 2944 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. Samples PbB4(AQ)-0.01 Mg-1, PbB4(AQ)-0.1 Mg-1 and PbB4(AQ)-2.5 Mg-1 show a mixed solid system containing litharge (PbO) PDF pattern 00-005-0561, laurionite (Pb(OH)Cl) PDF pattern 00-052-0289 and lead borate hydrate ($PbB_4O_7 \cdot 3H_2O$) PDF pattern 00-028-0523. Samples PbB4(AQ)-1.0 Mg-1, PbB4(AQ)-1.5 Mg-1 and PbB4(AQ)-2.0 Mg-1 match with good agreement to laurionite (Pb(OH)Cl) PDF pattern 00-052-0289. In addition, lead metaborate monohydrate ($PbB_2O_4 \cdot H_2O$) could be present in those experiments. However, metaborate monohydrate is not present in the PDF4+ 2019 database, but it is in the NIST database. Since the PDF4+ 2019 database is utilized for Search/Match of these experiments, this phase could be missed. The figures below show the XRD data.

Table 3-15 Preparation of experimental set-ups for investigation of $PbB_4O_7$(aq)—$Mg^{2+}$/$Cl^-$ Interactions.

| Set-up ID | PbO (g) | $H_3BO_3$ (m) | $MgCl_2$ (m) | mL of Solution | Scientific Notebook Reference |
|---|---|---|---|---|---|
| PbB4(AQ)-0.01Mg- 1 | 2.0004 | 0.30 | 0.01 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-0.01Mg- 2 | 2.0006 | 0.30 | 0.01 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-0.1Mg- 1 | 2.0006 | 0.30 | 0.1 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-0.1Mg- 2 | 2.0006 | 0.30 | 0.1 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-1.0Mg- 1 | 2.0001 | 0.30 | 1.0 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-1.0Mg- 2 | 2.0000 | 0.30 | 1.0 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-1.5Mg- 1 | 2.0001 | 0.30 | 1.5 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-1.5Mg- 2 | 2.0000 | 0.30 | 1.5 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-2.0Mg- 1 | 2.0002 | 0.30 | 2.0 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-2.0Mg- 2 | 2.0009 | 0.30 | 2.0 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-2.5Mg- 1 | 2.0000 | 0.30 | 2.5 | 100 | WIPP-Borate-1 Pg. 16 |
| PbB4(AQ)-2.5Mg- 2 | 2.0000 | 0.30 | 2.5 | 100 | WIPP-Borate-1 Pg. 16 |

Information Only

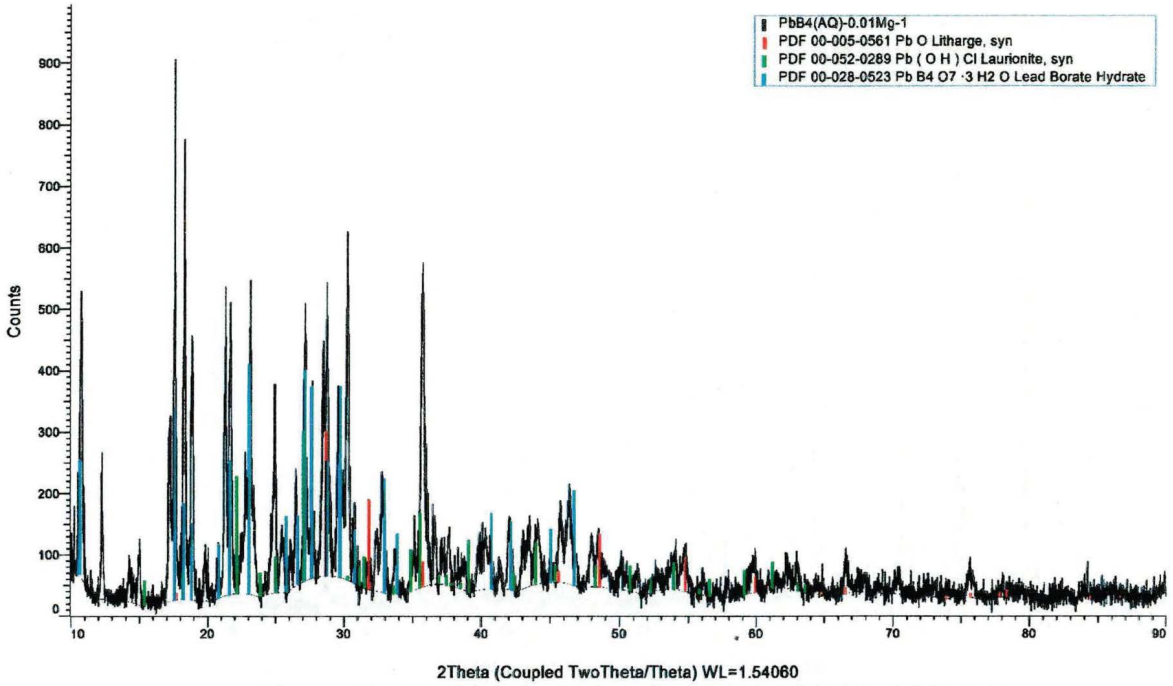



Figure 93 XRD analysis for sample PbB4(AQ)-0.01Mg-1
Source of Figure 93: Scientific Notebook WIPP-Borate-10 Pg. 87

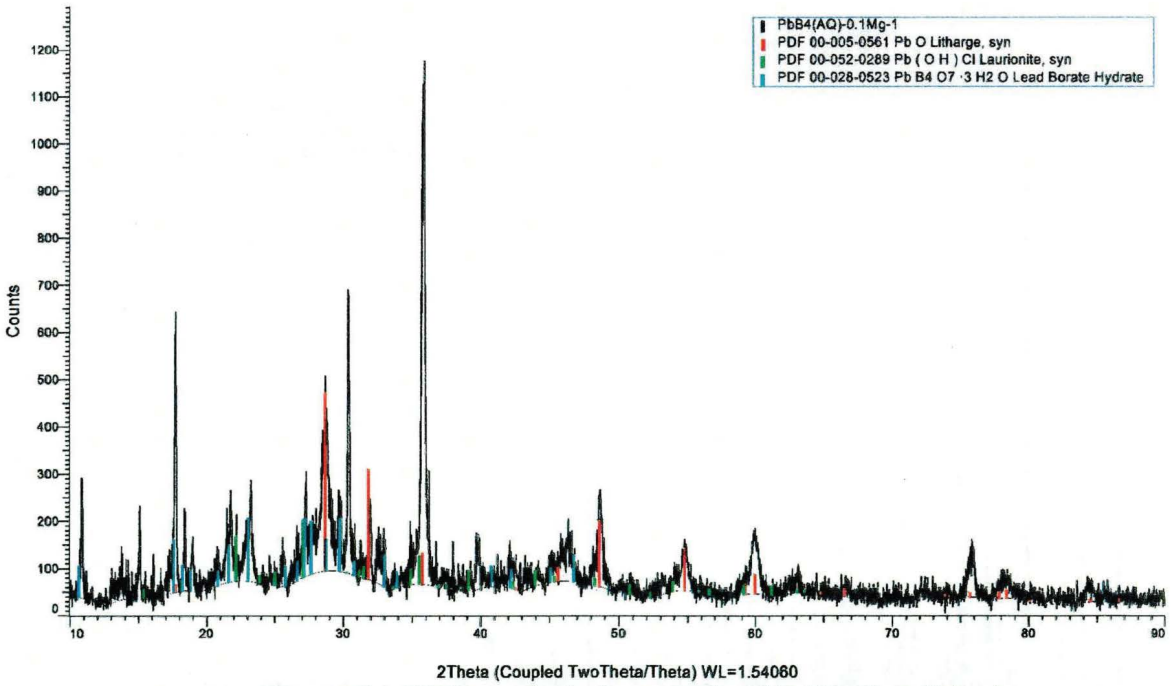



Figure 94 XRD analysis for sample PbB4(AQ)-0.1Mg-1
Source of Figure 94: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

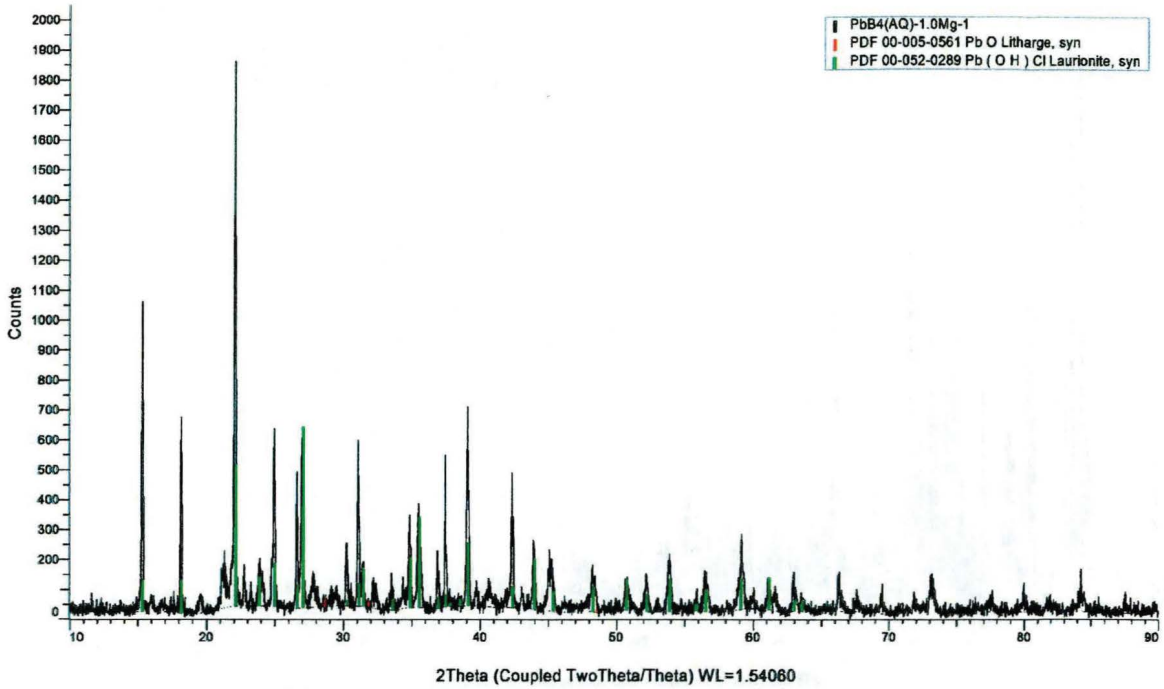



Figure 95 XRD analysis for sample PbB4(AQ)-1.0Mg-1
Source of Figure 95: Scientific Notebook WIPP-Borate-10 Pg. 87

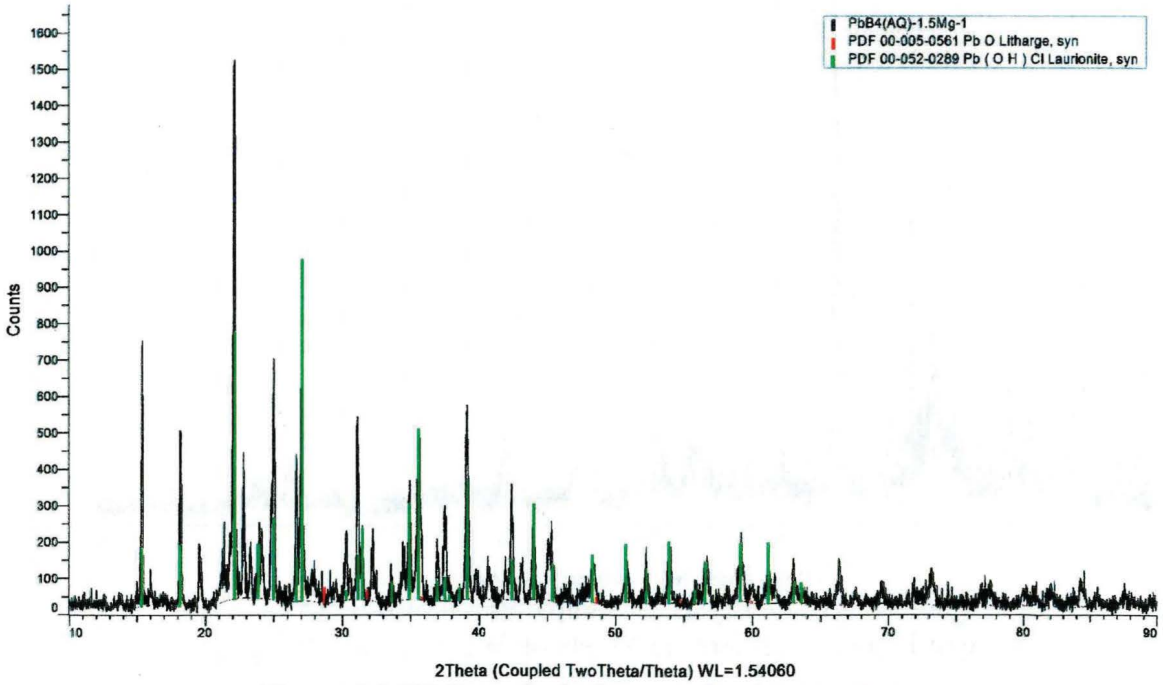



Figure 96 XRD analysis for sample PbB4(AQ)-1.5 Mg-1
Source of Figure 96: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

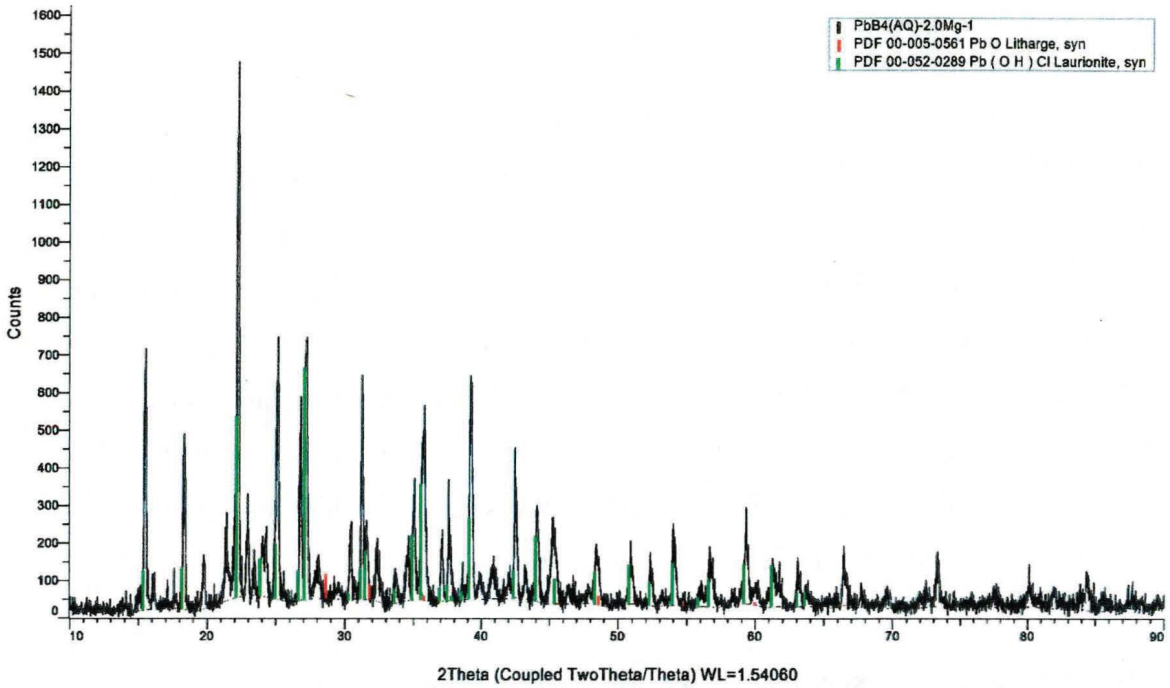



Figure 97 XRD analysis for sample PbB4(AQ)-2.0 Mg-1
Source of Figure 97: Scientific Notebook WIPP-Borate-10 Pg. 87

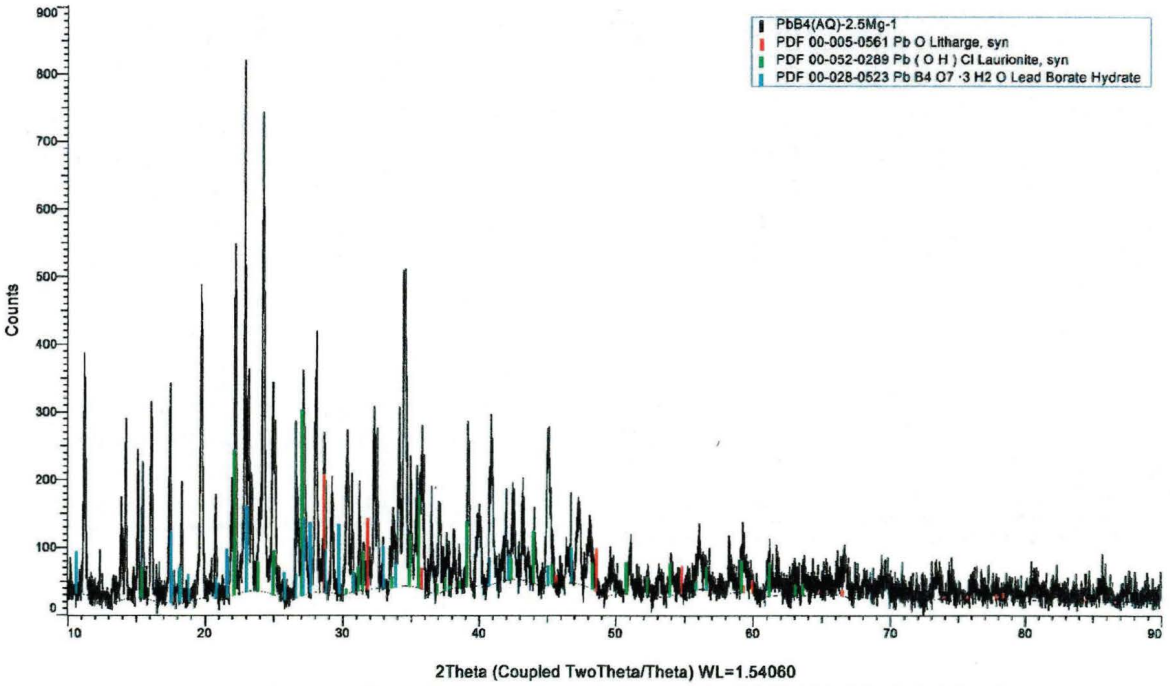



Figure 98 XRD analysis for sample PbB4(AQ)-2.5 Mg-1
Source of Figure 98: Scientific Notebook WIPP-Borate-10 Pg. 87

Information Only

### 3.4.12 $PbB_4O_7(aq)$—$Mg^{2+}$—$Na^+$ Interactions

Table 3-16 shows the experimental set-ups for the $PbB_4O_7(aq)$—$Mg^{2+}$—$Na^+$ experiments. Figures 99-104 document the XRD solids characterization of the experiments. At 2624 days, solid material was collected from the experiments, allowed to dry, ground into a fine powder and analyzed on the XRD for solid characterization. All of the samples in this experiment matched with good agreement to laurionite (Pb(OH)Cl) PDF pattern 00-052-0289. In addition, lead metaborate monohydrate ($PbB_2O_4 \cdot H_2O$) could be present in those experiments. However, metaborate monohydrate is not present in the PDF4+ 2019 database, but it is in the NIST database. Since the PDF4+ 2019 database is used for the Search/Match of these experiments, this phase could be missed. The figures below show the XRD data.

Table 3-16 Preparation of experimental set-ups for investigation of $PbB_4O_7(aq)$—$Mg^{2+}$—$Na^+$ Interactions.

| Set-up ID | PbO (g) | $H_3BO_3$ (m) | $MgCl_2$ (m) | NaCl (m) | mL of Solution | Scientific Notebook Reference |
|---|---|---|---|---|---|---|
| PbB4 (AQ) MgCl2 A-1 | 2.0000 | 0.30 | 0.500 | 5.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 A-2 | 2.0012 | 0.30 | 0.500 | 5.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 B-1 | 2.0001 | 0.30 | 0.800 | 3.5 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 B-2 | 2.0008 | 0.30 | 0.800 | 3.5 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 C-1 | 2.0009 | 0.30 | 1.25 | 3.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 C-2 | 2.0000 | 0.30 | 1.25 | 3.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 D-1 | 2.0000 | 0.30 | 1.50 | 2.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 D-2 | 2.0008 | 0.30 | 1.50 | 2.0 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 E-1 | 2.0000 | 0.30 | 1.75 | 1.50 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 E-2 | 2.0007 | 0.30 | 1.75 | 1.50 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 F-1 | 2.0007 | 0.30 | 2.00 | 0.50 | 100 | WIPP-Borate-1 Pg. 19 |
| PbB4 (AQ) MgCl2 F-2 | 2.0011 | 0.30 | 2.00 | 0.50 | 100 | WIPP-Borate-1 Pg. 19 |

* Amounts of 1.8478 grams of $H_3BO_3$ were added on 6/2/11, see WIPP-Borate-1 Pg. 19.

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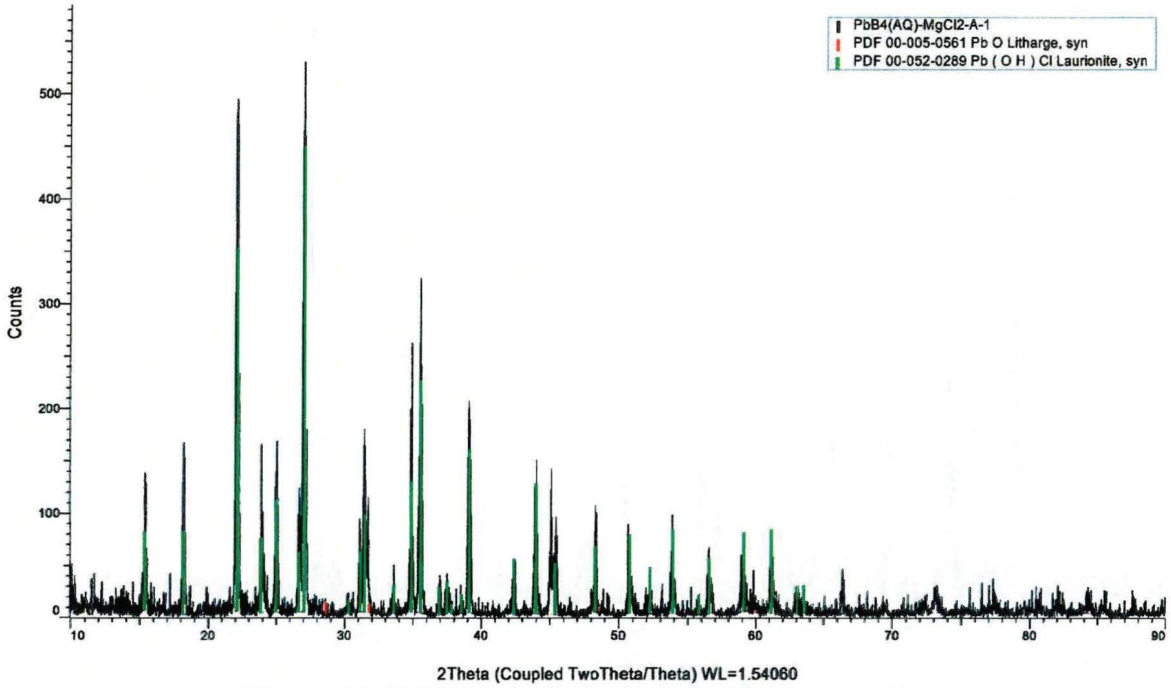



Figure 99 XRD analysis for sample PbB4(AQ)-MgCl2 A-1
Source of Figure 99: Scientific Notebook WIPP-Borate-10 Pg. 86

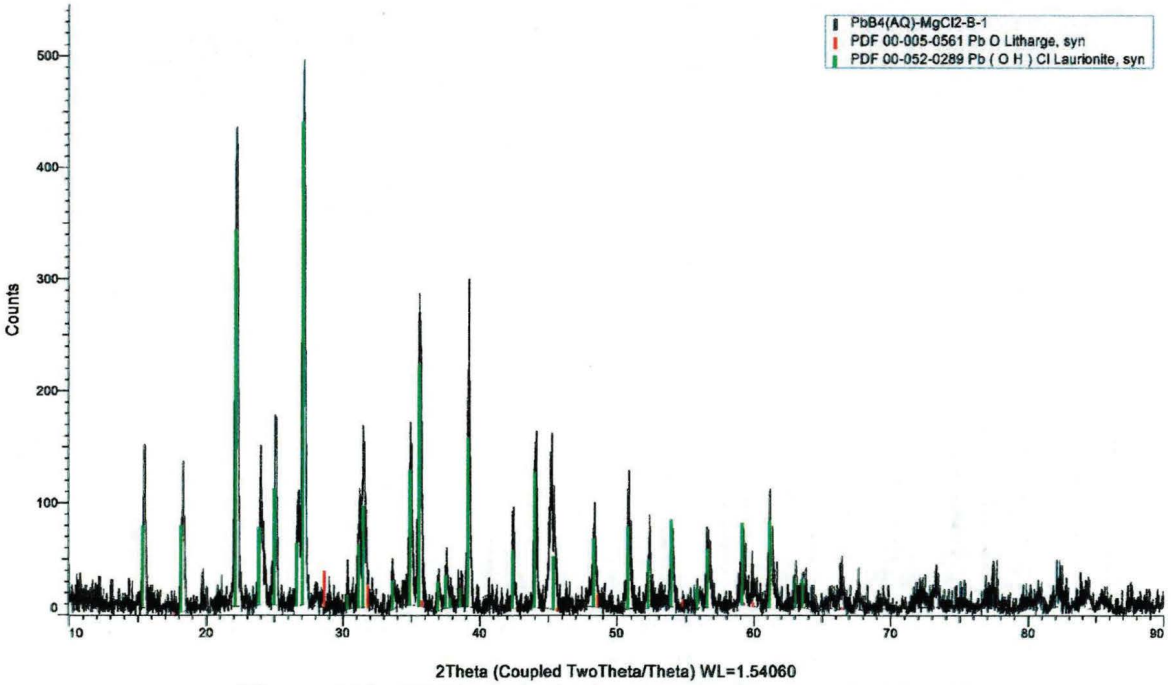



Figure 100 XRD analysis for sample PbB4(AQ)-MgCl2 B-1
Source of Figure 100: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

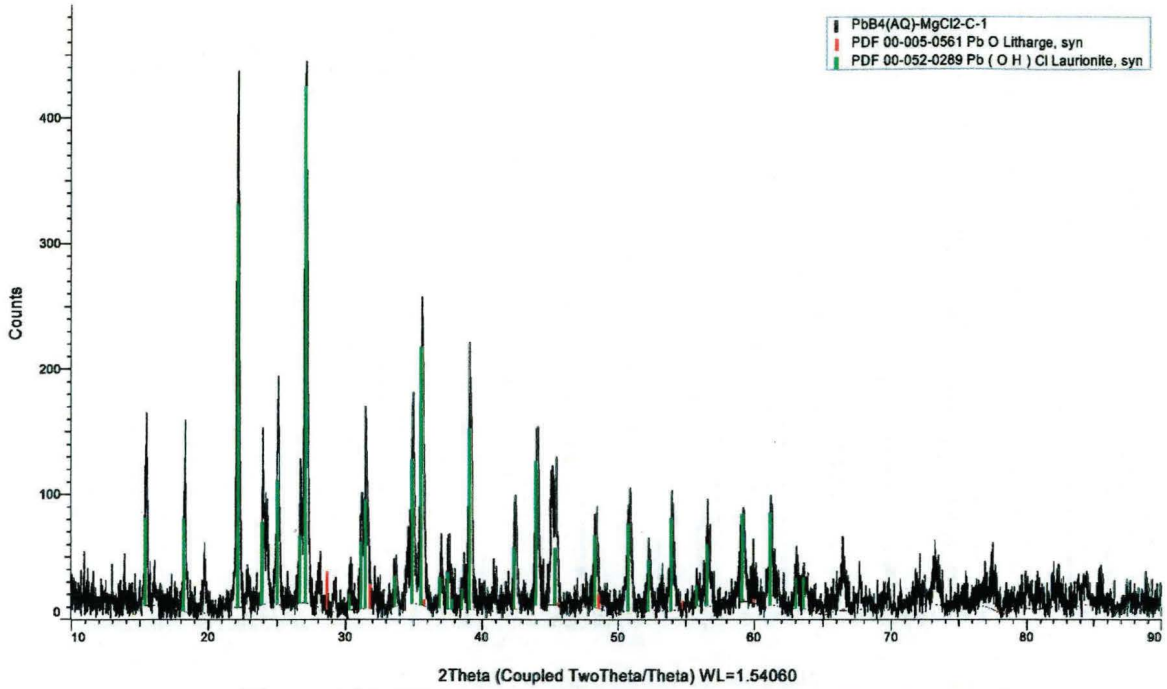



Figure 101 XRD analysis for sample PbB4(AQ)-MgCl2 C-1
Source of Figure 101: Scientific Notebook WIPP-Borate-10 Pg. 86

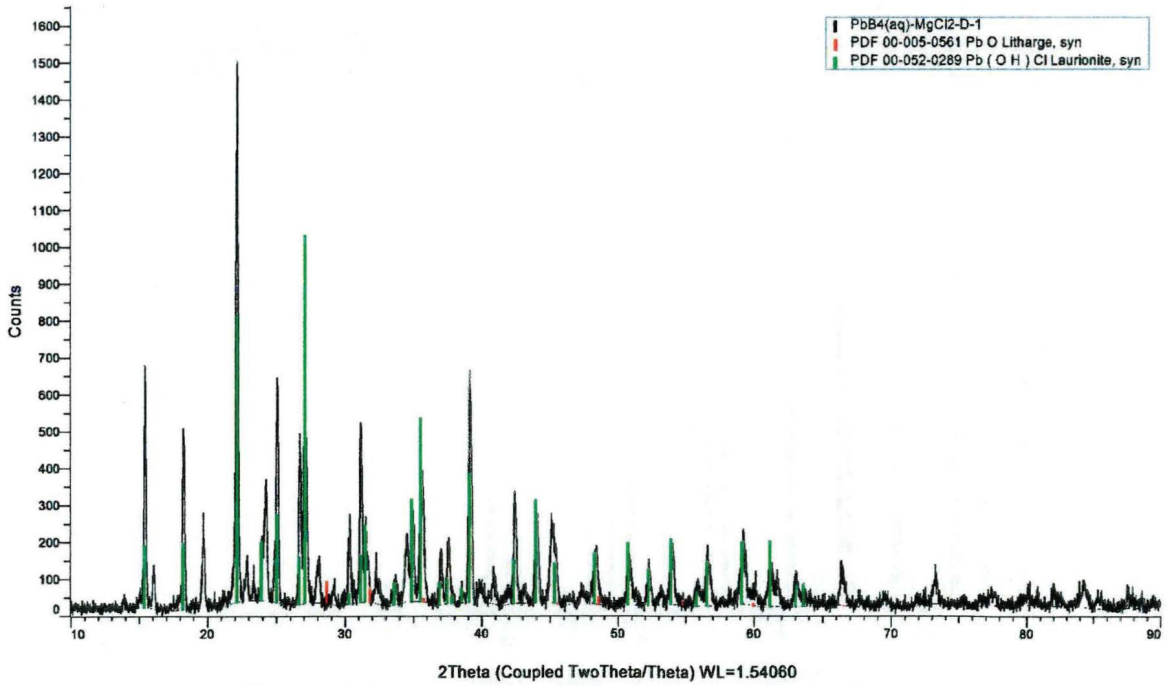



Figure 102 XRD analysis for sample PbB4(AQ)-MgCl2 D-1
Source of Figure 102: Scientific Notebook WIPP-Borate-10 Pg. 86

Information Only

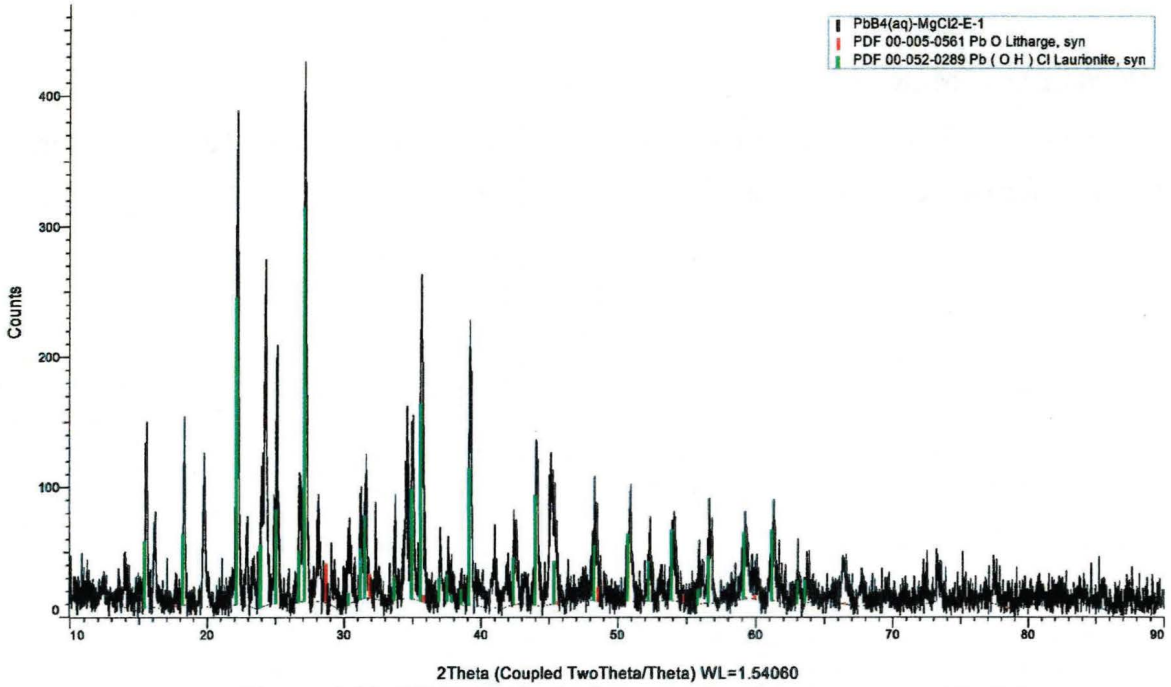



Figure 103 XRD analysis for sample PbB4(AQ)-MgCl2 E-1
Source of Figure 103: Scientific Notebook WIPP-Borate-10 Pg. 86

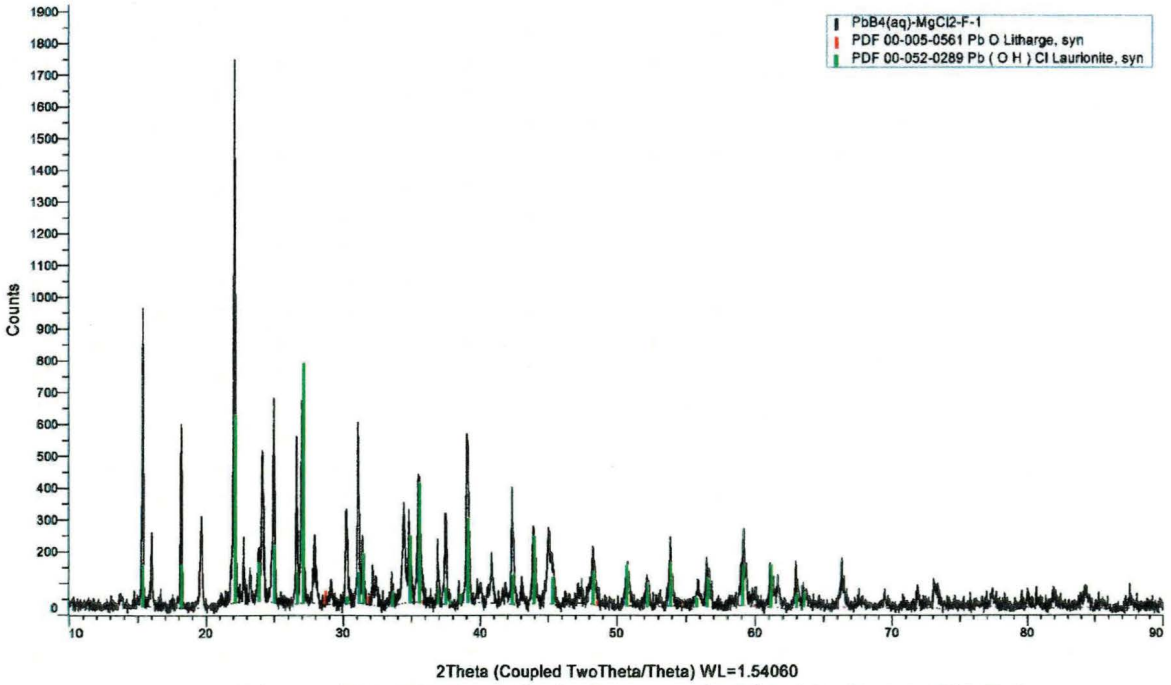



Figure 104 XRD analysis for sample PbB4(AQ)-MgCl2 F-1
Source of Figure 104: Scientific Notebook WIPP-Borate-10 Pg. 86

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## 4 ACKNOWLEDGEMENTS

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## 6 APPENDIX A

| Mineral Name | Formula | PDF pattern ID | Quality Mark |
|---|---|---|---|
| aksaite | (MgB6O10·5H2O) | PDF 00-015-0564 | Indexed |
| bischofite | (MgCl2·6H2O) | PDF 00-025-0515 | Star |
| blixite | (Pb8Cl4O5(OH)2) | PDF 04-013-1193 | Star |
| boracite | (Mg3B7O13Cl) | PDF 00-005-0710 | Blank |
| boracite | (Mg3B7O13Cl) | PDF 04-007-8460 | Blank |
| borax | (Na2[B4O5(OH)4]·8H2O) | PDF 04-012-8356 | Star |
| brucite | (Mg(OH)2) | PDF 04-011-5938 | Star |
| ezcurrite | (Na4B10O17·7H2O) | PDF 00-011-0257 | low-precision |
| gypsum | (CaSO4·2H2O) | PDF 00-033-0311 | Star |
| halite | (NaCl) | PDF 00-005-0626 | Star |
| halite | (NaCl) | PDF 00-005-0628 | Star |
| inderite | (MgB3O3(OH)5·5H2O) | PDF 04-011-2718 | Indexed |
| inyoite | (CaB3O3(OH)5·4H2O) | PDF 00-006-0361 | Indexed |
| iron chloride hydroxide | (Fe2Cl(OH)3) | PDF 00-034-0199 | Star |
| iron hydroxide | (Fe(OH)2) | PDF 00-013-0089 | Blank |
| kurnakovite | (Mg2B6O11·15H2O) | PDF 00-024-0700 | low-precision |
| laurionite | (PbCl(OH)) | PDF 04-011-5179 | Star |
| laurionite | (Pb(OH)Cl) | PDF 00-052-0289 | Indexed |
| lead borate hydrate | (PbB4O7·3H2O) | PDF 00-028-0523 | low-precision |
| lead borate hydroxide hydrate | (Pb5B3O8(OH)3·H2O) | PDF 00-052-1259 | Blank |
| lead boron oxide | (Pb6B10O21) | PDF 04-011-1619 | Indexed |
| lead oxide sulfate | (Pb5(SO4)O4) | PDF 04-015-1561 | Blank |
| litharage | (PbO) | PDF 00-005-0561 | Indexed |
| magnesium borate hydroxide | (MgB3O3(OH)5·6H2O) | PDF 00-049-0837 | Blank |
| magnesum chloride hydrate | (MgCl2·2H2O) | PDF 00-053-0259 | Calculated |
| portlandite | (Ca(OH)2) | PDF 01-078-0315 | Star |
| sodium borate hydrate | (Na2B6O10·4H2O) | PDF 00-024-1057 | low-precision |
| sodium perchlorate | (NaClO4) | PDF 00-007-0226 | Indexed |
| suanite | (Mg2B2O5) | PDF 04-009-2452 | Star |
| thenardite | (Na2(SO4)) | PDF 04-010-2457 | Star |
| ulexite | (NaCaB5O9·8H2O) | PDF 00-012-0419 | Indexed |

**Quality Mark Significance**

- Star (Well Characterized chemically and crystallographyically, No unindexed lines
- Indexed (Well Characterized chemically, No unindexed strong lines
- Blank (Does not meet the criteria for Star or Indexed
- Calculated (author calculated d values)
- Low precision (poorly characterized, with editorial comment explaining the reason)

Information Only