Review
QUALITY EXPERIMENTAL AND CALCULATED POWDER X-RAY DIFFRACTION

REFERENCE PATTERNS

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INTRODUCTION

For several years we have prepared and submitted a variety of quality powder x-ray diffraction patterns to the International Centre for Diffraction Data (ICDD) for inclusion as reference standards in their Powder Diffraction File (PDF).¹ Patterns submitted and/or currently under development include metal hydrides (inorganics), flavanoids and related compounds (organics), organic compounds involved in pollution (e.g., dioxins), explosives (organics and metal organics) and glass-ceramic phases (inorganics).

As a general procedure we have attempted to obtain the best possible experimental pattern, via automated diffractometric step-scans, from the substance in question with attention being given to specimen preparation, mounting, thickness, transparency and purity. When the structure has been known by whatever means the powder pattern has also been calculated from its lattice and atomic positional parameters and a reconciliation sought between the two patterns. The experimental pattern is indexed, and the unit cell lattice parameter(s) are determined via a least squares "best fit" of the interplanar spacings derived from the peak positions. A figure of merit is computed for the pattern to assess the peak discrimination and positional quality of the pattern. Finally, the data for the analyzed experimental pattern is assembled in PDF format and submitted to the ICDD.

EXPERIMENTAL AND CALCULATED PATTERNS

An attempt was made to obtain a pure, well crystallized sample of the substance under consideration. In general, it is much easier to obtain pure samples than well crystallized ones because purity is usually a concern of the synthesizing scientist, while crystallinity is not unless there is an evident need for it.

Diffraction specimens of the samples were of two types. Reactive and/or radioactive substances were placed in special diffraction cells² that had flat polycrystalline beryllium windows for entry of the incident beam onto and exit of the diffracted x-ray beams from the specimen as it underwent its characterizing diffraction. Air-stable samples were free-fall sprinkled onto double-sticky tape fastened to plain glass microscope slides for diffraction mounts. External standards were used with specimens contained in the Be-window cells, while internal standards were used with those mounted on microscope slides. In both cases the standard utilized was NBS Si (No. 640a).

Diffraction data collection was by means of automated step-scans. The instrument employed for this work was a Rigaku automated, horizontal, wide angle diffractometer equipped with a 12 kW rotating anode x-ray generator. Initial scans were performed with the generator operating at 40 kV and 80 mA for a copper anode. A 1° dispersion slit, a 0.15 mm (~0.05°) receiving slit and a 1° scatter slit collectively defined the x-ray beams. A Ni foil filter sat astride the diffracted beam to eliminate the Cu K_β radiation. The scans were performed in 0.05° steps with 0.4 sec. counts per step. The instrumental and step-scan parameters were adjusted as warranted by the quality of the pattern obtained vs the pattern quality desired. Maximum

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operating levels for the x-ray generator are 60 kV and 200 mA, while step-scan increments can be reduced to 0.001° , and data collection times can be increased several orders of magnitude if desired. The patterns under discussion have undergone this initial step-scan level of data collection and are in various stages of further experimental scrutiny as this article is written.

Pattern analysis was by means of Mound DEC PDP-11/44 computer software, viz., SPECLOT³ for display, peak location (peak maximum or peak centroid algorithms) and calculated pattern overlay, and LATTICE⁴ for peak indexing and least squares lattice pattern determination.

Powder diffraction patterns were calculated by POWD⁵ and stored in a Mound local reference computer file as sets of d-space, I_{rel} pairs for "stick-figure" overlay comparison with experimental patterns. To perform such calculations input lattice and atomic positional parameters are required. When the structure had been solved the known structural parameters were used for input. On one occasion single crystal intensity data was converted to polycrystalline intensity data for comparative purposes.

SOME EXAMPLES

I. BETA-URANIUM HYDRIDE

Beta-uranium hydride, $\beta\text{-UH}_3$, is one form of a metal hydride of considerable interest for hydrogen storage applications. It crystallizes in the primitive cubic space group $\text{Pm}\bar{3}\text{n}$, O_h^3 (No. 223) with eight formula units in a unit cell of $6.6444\text{\AA}$ edge. There are two types of U's in the structure, one occupying (2a) positions and the other (6c) positions. The H's are in (24k) positions. Rundle obtained the U positions via powder x-ray diffraction⁶ and the H positions via powder neutron diffraction (of the deuteride)⁷. Accurate lattice parameters of both the α - and β - forms of UH_3 , UD_3 and UT_3 were determined by Q. Johnson, *et al*⁸. A recent neutron diffraction study of $\beta\text{-UD}_3$ and $\beta\text{-UH}_3$ was made by Bartscher *et al*⁹. There is a PDF pattern (No. 12-436) for this phase, but it has only ten visually estimated lines with d-spacings given to but two decimal places.

Through the good offices of M. C. Nichols of Sandia National Laboratories, Livermore, we obtained a well-annealed sample of $\beta\text{-UH}_3$ that had been prepared at Lawrence Livermore National Laboratory. A specimen of it was placed in a Be-window cell for collection of diffraction data. A comparative powder pattern was calculated using input lattice parameters from Johnson, *et al*⁸, and atomic positions from Bartscher, *et al*⁹. From the obviously high quality pattern obtained, 30 peaks (of which eleven displayed distinct $K_{\alpha\text{I}}$, $K_{\alpha\text{II}}$ pairs) were detectable above background. All were satisfactorily indexed, and a cubic lattice parameter of $6.6431(3)\text{\AA}$ was derived from them. The Smith-Snyder figure of merit¹⁰ obtained for this pattern was 25.6. A comparison of the experimental pattern with the calculated pattern overlaid is shown in Figure 1. Interfering lines from the containing cell's face plate are indicated by adjacent asterisks.

Figure 1

COMPARISON OF EXPERIMENTAL AND CALCULATED BETA-UH3 PATTERNS

1-2017

2θ

II. ALPHA-BARIUM TRITIDE

Alpha-barium tritide, α -BaT₂, is the room temperature form of the radioactive isotopic variety of barium hydride. It crystallizes¹¹ in the primitive orthorhombic space group Pbnm, D_{2h}¹⁶ (No. 62) with four formula units in the cell having lattice parameters of $a_0=7.829$, $b_0=6.788$, $c_0=4.167$ Å. All atoms are in (4c) special positions. There is only one type of Ba in the structure, but there are two types of H's (T's). Each type of atom has two variable positional parameters for a total of six in the structure.

Zintl and Harder¹¹ synthesized and performed both mono- and polycrystalline x-ray diffraction analyses on the isomorphous alkaline earth hydrides, CaH₂, SrH₂ and BaH₂. They determined the structure type for all of them, via the SrH₂ case, from Weissenberg photographic data, finding the metals to be nearly hexagonally close packed. The H's were then placed in plausible interstices of the metal array. Their Debye-Scherrer powder x-ray pattern for BaH₂ is included in the PDF as No. 28-137. No powder XRD data for BaT₂ is found there or in other scientific literature.

For our experimental pattern we used a powder sample synthesized by D. R. Grove at Mound. The diffraction specimen was contained in a Be-window cell for the automated diffractometric step-scan. A comparative pattern was calculated, using the BaH₂ lattice parameters and the SrH₂ atomic positional parameters from Zintl and Harder

Twenty-five peaks were read and indexed (eight overlaps). Of these 22 were included in the least squares' lattice parameter determination which found $a_0=6.790(2)$, $b_0=7.820(4)$ and $c_0=4.161(2)$ Å. A figure of merit⁹ of 18.5 was found for the experimental pattern. The overlay of the calculated BaH₂ pattern onto the experimental BaT₂ pattern (Fig. 2) indicates their agreement. Again, interfering cell face-plate lines are identified by adjacent asterisk

Figure 2.

III. ALPHA-LITHIUM DISILICATE

Alpha-lithium disilicate, α -Li₂Si₂O₅, is the room temperature form of a common phase in the Li₂O-SiO₂ glass-ceramic system. It crystallizes¹² in the primitive monoclinic space group Cc, C_s⁴ (No.9) and is pseudo-orthorhombic, since its beta- angle is approximately 90°. Four formula units are contained in its monoclinic cell having parameters of $a_0=5.82$, $b_0=14.66$, $c_0=4.79$ Å and $\beta=90^\circ$. There are nine atoms in the asymmetric unit, viz., two Li's, two Si's and five O's, all in (4a) positions. Thus there are 27 variable parameters for the structure.

Kracek¹³ first thoroughly explored the phase relationships in the Li₂O-Si₂O system, and

COMPARISON OF EXPERIMENTAL AND CALCULATED BaT2 PATTERNS

Donnay and Donnay¹⁴ studied the habits of the alkali silicates. Liebau¹² determined the crystal structure of α - $\text{Li}_2\text{Si}_2\text{O}_5$ from single crystal data, and Glasser¹⁵ described an experimental procedure for crystallizing alpha-lithium disilicate from Li_2O , SiO_2 glasses. The PDF contains a pattern for α - $\text{Li}_2\text{Si}_2\text{O}_5$ (No. 17-447), but the relative intensities of its three strongest lines [viz., (130), (040) and (111)] never agreed with those of experimental patterns that we obtained during glass-ceramic investigations.

A sample of α - $\text{Li}_2\text{Si}_2\text{O}_5$ was carefully prepared by D. P. Kramer at Mound by a modification of Glasser's method¹⁵. When finely pulverized and dusted through a sieve onto a patch of double-sticky tape affixed to a plain glass microscope slide it yielded a diffraction pattern having much better intensity agreement with our previously obtained experimental patterns as well as with a pattern calculated from Liebau's structure¹². For d-spacing determination in the experimental pattern no background subtraction was employed, but for the I_{Rel} evaluation a polynomial fit of the background was utilized. Twenty-nine peaks were observed and indexed in this pattern, and 23 of those were included in the least squares' parameter determination that found monoclinic cell edges of $a_0=5.823(3)$, $b_0=14.665(6)$ and $c_0=4.775(2)$ Å, and $\beta=90^\circ$. The Smith-Snyder figure of merit¹⁰ for the first 29 lines of this pattern was approximately 30. Figure 3 presents a comparison of the entire experimental α - $\text{Li}_2\text{Si}_2\text{O}_5$ with the entire PDF pattern, while Fig.4 displays contrasting overlays of PDF No.14-447 and our calculated pattern on the (130), (040) and (111) triplet of the experimental pattern. Since in the POWD calculation⁴ random orientation of the crystallites was forced, we believe that the PDF reference pattern has preferred orientation and that our experimental pattern is a viable candidate for its replacement in the PDF. Mention was made in most of the background publications of a strong propensity for preferred orientation in powdered samples of this phase.

Figure 3

Figures 4a and b

COMPARISON OF EXPERIMENTAL α -L12S1205 PATTERN WITH PDF# 17-447

17- 447

COMPARISON OF EXPERIMENTAL α -Li₂Si₂O₅ PATTERN WITH PDF# 17-447

COMPARISON OF EXPERIMENTAL AND CALCULATED α -Li₂Si₂O₅ PATTERNS

IV. 2,2',4,4',6,6'-HEXANITROAZOBENZENE-III

2,2',4,4',6,6'-hexanitroazobenzene-III (HNAB-III), is one of five known forms of an important secondary explosive. The crystal structures of HNAB-I and HNAB-II have been solved from single crystal x-ray diffraction data¹⁶, but though a set of single crystal intensity data has been collected, a solution of its structure has not yet been achieved. However, its space group is known¹⁷ to be end-centered orthorhombic $C222_1$, D_2^5 (No. 20), with lattice parameters of $a_0=15.281$, $b_0=40.925$, $c_0=5.486$ Å. Its density has been measured as 1.751 g/cm³.

In order to obtain an experimental pattern of HNAB-III we prepared as thick a specimen as would adhere to a double-sticky tape patch fastened to a plain glass microscope slide. The sample used for this work was prepared at Mound by D. W. Firsich and was carefully pulverized with a mortar and pestle to a fine powder. A thinner specimen was also prepared of this same finely ground sample because we had suspected possible specimen transparency difficulties with this low atomic number compound. The thick specimen exhibited 25 easily observable and indexable peaks. Fifteen of these reflections were included in a least squares' lattice parameter determination that yielded orthorhombic cell edges of $a_0=15.365(2)$, $b_0=41.370(4)$ and $c_0=5.4955(2)$ Å. The single crystal intensities were converted to powder intensities for comparison with the experimental pattern. The calculated pattern contained 149 reflections with relative intensities of one or greater, so no figure of merit has yet been computed for the experimental pattern. Instead we are currently performing higher power, longer count, finer step scans in an effort to bring more of the weaker peaks up from the background level. Figure 5a reveals the good agreement between the thick specimen and the calculated (overlaid) patterns, while Fig. 5b indicates that the thin specimen did, indeed, experience transparency and, perhaps, preferred orientation problems.

Figures 5a and 5b

W05858 HNAB-III THICK, GROUND SPECIMEN

1-2824

W05867 HNAB-III THIN, GROUND SPECIMEN

CONTINUING AND PROJECTED WORK

These four diffraction patterns are nearing a stage of development where they can be submitted to the ICDD for consideration for inclusion in the PDF as new or replacement reference patterns. We are also developing patterns from numerous other explosives and pyrotechnics, flavanoids and various isotopic varieties of BaT_2 , UH_3 and other metal hydrides. In addition a new, improved cell, featuring an off-reflection cut single crystal of Be for a specimen face plate, is in an advanced stage of development. Initial experiments with it have indicated that a near zero diffraction background is obtainable, auguring well for obtaining diffraction patterns of much improved quality for air-sensitive and radioactive substances.

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