

12.5-14 CRYSTAL STRUCTURE DETERMINATION OF BARIUM PLUTONATE BY NEUTRON DIFFRACTION. By Allen C. Larson, Gary G. Christoph, P. Gary Eller, John D. Purson, John D. Zahrt, R. A. Penneman and Gary H. Rinehart, Los Alamos National Laboratory, University of California, Los Alamos, NM 87545 (USA)

The three dimensional crystal structure of barium plutonate, $BaPuO_3$, has been determined by Rietvelt refinement of time-of-flight neutron powder diffraction data using the newly developed Generalized Crystal Structure Analysis System (GSAS). Data were collected at the Los Alamos Neutron Scattering Center (LANSCE) using the NPD diffractometer. Three banks of detectors centered at $\pm 150^\circ$ and 90° two theta were used in the refinement. D-spacing ranges were 0.35 to 1.41 Å for the two 150° banks and 0.83 to 1.60 Å for the 90° bank. The maximum number of reflections contributing to one profile point was 564. Final profile R-factors were 0.0301, 0.0255 and 0.0250 and final weighted profile R-factors were 0.0221, 0.0214 and 0.0277. Crystal data: Pbnm, $a = 6.2198(21)$, $b = 6.1938(22)$ and $c = 8.7447(31)$ Å, $Z = 4$, Integrated reflection $R = 0.021$ for all of the reflection in the three profiles.

The structure is a distorted perovskite structure ($GdFeO_3$ type) which contains nearly regular PuO_6 octahedra with Pu-O distances of 2.2307(8), 2.2301(13) and 2.2229(14) Å and cis O-Pu-O angles of $90.41(3)^\circ$, $90.46(8)^\circ$ and $90.70(7)^\circ$. The observed Pu-O distances and the deviations from the idealized cubic perovskite structure are in excellent accord with expectations based on crystal chemical models.

12.6-2 NUMERICAL APPROXIMATION TO HIGH RESOLUTION TIME-OF-FLIGHT NEUTRON POWDER DIFFRACTION PROFILES. Robert B. Von Dreele, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

Very high resolution time-of-flight neutron powder diffractometers require an accurate mathematical description of the powder line profile which includes functions characteristic of the source physics, instrumental broadening, and sample broadening. The best representation is a function developed by Ikeda & Carpenter (1985) convoluted with Gaussian and Lorentzian functions. As yet the full convolution is unknown and thus approximations have been developed. One is to use a pseudo-Voigt (David, 1986, 1987) approximation but the resulting function involves complex numbers and is computationally expensive. To overcome these shortcomings, this work reports a Gaussian integration for the convolution which is computationally fast and matches the pseudo-Voigt calculation for moderate Lorentzian broadening.

Ikeda, S. & Carpenter, J. M. (1985). Nucl. Inst. and Meth., A239, 536-544.
David, W.I.F. (1986). J. Appl. Cryst., 19, 63-64.
David, W.I.F. (1987). private communication.

12.6-1 PROFILE FITTING PROCEDURES IN THE X-RAY LINE BROADENING ANALYSIS OF POLYCRYSTALLINE MATERIALS. By A. Benedetti, S. Enzo and G. Fagherazzi, Dipartimento di Chimica-Fisica, Università di Venezia, Italy;

The advantages of using profile fitting procedures for X-ray line broadening analysis have recently been pointed out and applied to several cases. It is also possible to analyse peaks which are blurred within envelopes of unwanted peaks. After correction for the $K\alpha_1\alpha_2$ doublet the $K\alpha_1$ peaks can be parameterized by means of suitable symmetrical functions such as Pearson VII, Voigt and pseudo-Voigt. Owing to instrumental aberrations, asymmetry is generally present, especially in the narrow peak profiles occurring below diffraction angles of about 40° in 2θ . In particular, the following problems will be discussed in the practical cases investigated here (supported metal catalysts, metallic oxides such as ZrO_2 , polymers):

- i) peak asymmetry due to instrumental causes and its parameterization (asymmetry due to structural causes is excluded from the present analysis);
- ii) acquisition of representative parameters, free from instrumental broadening, in terms of Voigt, pseudo-Voigt or Pearson VII functions;
- iii) Fourier transform of the best-fitted profiles corrected for the instrumental line broadening; application of Warren-Averbach and related methods operating on the Fourier coefficients in order to determine crystallite size and lattice distortions;
- iv) comparison of the results obtained by the different procedures employed.

12.6-3 DIFFERENCE METHODS IN QUALITATIVE AND QUANTITATIVE POWDER DIFFRACTION ANALYSIS I.G. Wood, Soils and Plant Nutrition Department, Rothamsted Experimental Station, Harpenden, Herts, England

The sensitivity and accuracy of X-ray powder diffraction analysis may often be enhanced by difference methods, which compare diffraction patterns collected from samples that have been altered either chemically or physically. These methods are particularly useful in analyses of complex systems such as soil clays. Indeed, they have been used for many years in clay mineralogy to distinguish structurally similar minerals by their responses to heating, solvation with ethylene glycol etc. Other treatments include size fractionation, alteration of preferred orientation and chemical dissolution of one or more of the components present. Recently, it was shown that difference methods can be combined with least-squares profile refinement techniques to produce accurate quantitative analyses of iron oxides in soil clays containing as little as 1% of these minerals (Brown, G. and Wood, I.G. (1985); Clay Minerals 20, 15-27). Further developments of this work will be described, including an extension of the method to determination of the degree of Al for Fe substitution in the iron oxides (via the cell parameters) and their "particle sizes" (via the widths of the diffraction maxima).

An alternative means of producing differences patterns is to use more than one wavelength, so as to exploit anomalous scattering effects. This method has the advantage that it requires only a single, chemically untreated, specimen. Although it is perhaps best suited to use with synchrotron sources it is also feasible in a conventional laboratory, particularly when the compounds studied contain transition metals (Wood, I.G., Nicholls, L. and Brown, G. (1986); J. Appl. Cryst. 19, 364-71). Applications of this technique to soil clay analysis will also be presented.