

phase-pure V₆O₁₃. Our efforts here focus specifically on this problem, and subsequently on achieving controlled *chemical* lithium insertion. Phase-pure V₆O₁₃ has also been incorporated into thin-film polymer batteries, which were then cycled to facilitate *in situ* X-ray diffraction studies (transmission mode) of the corresponding *electrochemical* lithium insertion process. Structural rearrangements involved in both insertion processes are analyzed carefully and compared; observations are also made regarding the reversibility of these processes.

20.02 – Multiphase Analysis

DS-20.02.01 RECENT DEVELOPMENTS IN THE COMPUTER SEARCH/MATCHING OF MULTI-PHASE MATERIALS. By R. Jenkins, International Centre for Diffraction Data, Swarthmore, PA, U.S.A.

While most contemporary methods of qualitative analysis of multi-phase materials are still based on the classic Search/Match/Identify process developed by Hanawalt, Rinn and Frevel in the 1930's, during the past 10 years or so the Personal Computer has made a dramatic impact on the ways in which classical procedures are being implemented.

Modern search/matching procedures can conveniently be broken down into three categories - Manual Methods, Computer-Aided Methods, and Fully Automated Methods. Even where purely manual search/match methods are used, the computer based diffractometer systems still give the potential benefit of high quality d/I data, especially where automated angular and intensity calibration is employed. In the case of computer-aided and fully automated techniques, the additional use of newer data processing techniques including profile fitting, α_2 stripping, etc., have all conspired to provide the diffractonist with accurate, artifact-free data, with which to start the search/ matching process. Finally, the ability to search index files containing physical and experimental data, beyond the traditional d/I list, and the availability of comprehensive sub-file selections, has resulted in robust boolean search algorithms, which give the user great flexibility in setting up search strategies.

As to the implementation of the search/match approach, the use of fast, modern PC's, with integrated CD-ROM storage and powerful windows-based operating systems, has allowed the software developer a degree of flexibility, undreamed of a decade ago.

This paper will discuss recent progress in the use of some of these personal-computer based, data collection, processing and analysis programs, with special emphasis on their use in the analysis of multi-phase materials.

**DS-20.02.02 Search / Match Using Full Trace Scans:
A Strong Improvement over Using d/I Files**

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A table of d/I values in many cases represents, quite adequately, the ideal powder diffraction pattern of a single phase reference material. However, reducing the diffraction pattern of a complex mixture to such a list is more difficult and more questionable for several reasons:

- Determining "real" peaks through any "peak search" algorithm or "profile fitting" technique becomes practically impossible for weak lines of the measured diffractogram. This in turn, can preclude the identification of minor phases.

- Clusters of lines are most likely to be impossible to decompose due to (an inevitable) lack of information on the number, positions, and widths of non-resolved lines.

- The information on line-widths is lost - whereas in fact this is also an attribute of the respective phase.

The DIFFRAC AT search/match uses the full trace scan with subtracted background. Therefore it takes full advantage of all available information - particularly very weak lines, line clusters and the line widths.

Examples will be considered to demonstrate how important these features are for successful and reliable phase identifications.

Compared to traditional d/I tables, the DIFFRAC AT search/match uses much more input data which could be expected to have a severe penalty in speed of the search/match. In fact, due to very highly optimized code, a search employing the current whole ICDD data base (sets 1 - 42: 61,993 reference patterns) takes less than 15 seconds when performed on a i486/50-based PC.

DS-20.02.03 QUANTITATIVE POWDER DIFFRACTION PHASE ANALYSIS - RECENT DEVELOPMENT AND CURRENT STATUS. By J. Fiala¹⁾ and H. Toraya²⁾, ¹⁾Central Research Institute SKODA, Czech Republic, ²⁾Ceramics Research Laboratory, Nagoya Institute of Technology, Japan.

Methods for quantitative phase analysis (QPA) by using X-ray powder diffraction technique are reviewed, and their precision and accuracy are discussed in this paper. A development of experimental design shifted the analysis strategy from few-line measurement to many-lines and even to whole-pattern measurements. Preparation techniques, which can suppress detrimental effects of texture, particle size, inhomogeneity and amorphization, have been developed for powder samples while a serious problem remains for bulk samples. Standard reference materials of known phase composition have been produced. Chemical constraints are used to help with phase abundance analysis. Large scale systematic measurements were undertaken (inter-laboratory tests, reference intensity ratios determinations), and they form a necessary base for a quantitative assessment of the reliability of QPA. The main problem of QPA, which consists in the fact that diffraction intensities are influenced not only by phase composition of the mixture under analysis but also by real structure (and variable crystal structure) of its individual components and of polycrystalline aggregate as a whole, is addressed by simultaneous determination of phase composition, real structure and crystal structure of all constituents. However, correlations existing between the individual parameters enhance uncertainty of their estimates obtained by such a multivariate refinement. Factorial analysis of diffraction patterns of different fractions from the mixture analyzed provides intensity factors which are automatically corrected for the influence of real structure. Some forty years ago, accuracy of the QPA was estimated to (1 - 10)% absolute. The present day rather optimistic estimate, 2% absolute, seems to be limited to favorable cases of powder mixtures of phases, in which the real structure does not affect their diffraction appreciably.

DS-20.02.04 QUANTITATIVE ANALYSIS OF MULTIPHASE MATERIALS USING THE RIETVELD METHOD. By Julius Schneider, Institut für Kristallographie, Universität München, Theresienstraße 41, D-8000 München 2, Germany.

Use of the Rietveld method in quantitative analysis of multiphase mixtures has recently found increasing attention. As compared to conventional discrete-peak methods the consideration of the entire