12.5-9 COMBINED REFINEMENT OF SYNCHROTRON AND NEUTRON POWDER DATA FROM THE SUPER-CONDUCTOR $BaPb_{.75}Bi_{.25}O_3$. By J.K. Maichle *, J.P.Jhringer *, W.Prandl *, T.Wroblewski **, A.W. Hewat***
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The Rietveld structure refinement technique has, over the past two decades, proved to be the most important tool for the evaluation of neutron and X-ray powder pattern. However, often it's difficult to find from one data set alone an unambiguous structural model. In $BaPb_{.75}Bi_{.25}O_3$ Cox et al.(Sol. State Comm. 19, 969, (1976)) concluded from neutron powder data a tetragonal structure at room temperature, but high resolution X - ray Guinier diffractometer recordings taken at 300 K exhibited a monoclinic distortion (β=90.089 (2)°). Measurements of 19 reflection groups with synchrotron radiation at an high resolution 3 axis powder diffractometer at HASYLAB/DESY (10 ° < 2θ < 165 ° , λ=1.127 Å) confirmed the monoclinic symmetry. Neutron data collected at instrument D1A at ILL (Grenoble) (0° < 2θ < 130° , λ=1.909 Å°) determined Pm on basis of the known lattice symmetry , with oxygen forming a distorted octahedra network at 308 K . For the evaluation of the different data we created a program in which data sets from the various methods are used in one least squares procedure to fit one structural model appropriate to all data. Free scaling factors and profile parameter for the individual data sets are provided to fit the various primary intensities and instrumental resolutions. Basis of the development was the - Young and Wiles version 3.2 of the Rietveld profile refinement program (J.Appl.Cryst.15,430-438 (1982)) . The new program allowed the structure refinement of $BaPb_{.75}Bi_{.25}O_3$ from 19 reflection groups measured at the DESY synchrotron radiation source , yielding two models for the oxygen positions with space group I2/m and Pm resp. with a=6.07949(5), b=8.58370(4), c=6.10721(3) Å , β=90.0328(7)° at 308 K. Addition of one neutron data set containing the entire diffraction pattern recorded at 308 K° exhibited Pm as correct result with final residuals for the profiles of 1-8 % for the synchrotron data and 4% for the neutron data set. The finding of a monoclinic symmetry at room temperature may have some impact on calculations of the phonon-electron coupling for superconductors with perovskite related structures, because up to now a tetragonal octahedra breathing mode was assumed to reflect the symmetry of a CDW that breaks superconductivity in $BaPb_{1-x}Bi_xO_3$ systems with x>.35.

12.5-10 PHASE RELATIONSHIPS IN SYNROC

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SYNROC is an Australian proposal for the permanent immobilisation of high level nuclear waste. It consists, in principle, of three phases, Hollandite, ($Ba_xAl_{2x}Ti_{8-x}O_{16}$), Zirconolite, (Ca Zr Ti_2O_7) and Perovskite (Ca Ti O_3). All the components of high level waste can enter into solid solutions in one or more of these compounds. Blocks of SYNROC containing waste are prepared, under remote handling conditions, by hot pressing.

A technique was required to

1. Determine the proportions of the three target phases.
2. Determine changes in unit cell dimensions to measure the extent and the solution of waste.
3. Provide information on the homogeneity of solid solution.
4. Provide structural information on the minor, but significant, additional phases produced during hot pressing.

It was an additional requirements that a macroscopic volume (cm^3) should be sampled.

High resolution powder diffraction, using the ISIS spallation neutron source at the Rutherford Laboratory, UK (M.W. Johnson, W.I.F. David and W.T.A. Harrison, RAL 86-068) has been used to obtain data on SYNROC with no waste, with 10% waste, and with 20% waste. High level waste was simulated by the use of non active isotopes.

The data was first smoothed by the maximum entropy deconvolution algorithm (S. Steenstrup, Aust.J. Phys. 1985, 38, 319). The diffraction patterns of the major phases, whose crystal structure are known, were simulated and the pattern indexed. The data corresponding to each of these phases was stripped from the pattern and Rietveld refinement used to determine the concentration and lattice parameters.

Data from the minor phases was isolated for an attempt to find their structures by direct methods (A.K. Cheetham, W.I.F. David, M.M. Eddy, R.J.B. Jackman, M.W. Johnson and C.C. Toradi (Nature 1986, 320, 46).