

12.5-3 USE OF THE RIETVELD TECHNIQUE FOR DETERMINING CATION DISTRIBUTIONS. By Anders G. Nord and Theodor Stefanidis*, Section of Mineralogy, Swedish Museum of Natural History, Box 50007, S-104 05 Stockholm 50, and*Dept. of Structural Chemistry, Arrhenius Laboratory, S-106 91 Stockholm, Sweden.

The Rietveld full-profile refinement technique (J. Appl. Cryst. 2, 1969, 65-71), has been used to determine cation distributions among Me^{2+} ions in numerous solid solutions. These investigations have been based on neutron powder diffraction data or photographic X-ray Guinier-Hagg data (cf. Malmros & Thomas, J. Appl. Cryst. 10, 1977, 7-11). The mineral and inorganic oxosalt structures studied are comparatively simple. The refinements include atomic parameters, a scale factor, peak-profile parameters, and unit cell dimensions, which implies 14 parameters to be refined for olivines, 25-32 parameters for farringtonite and sarcopside orthophosphates and $M_2P_4O_{12}$ tetrametaphosphates, and around 45 for grafftonite (cf. Nord & Stefanidis, Mat. Res. Bull. 15, 1980, 1183-1191; Phys. Chem. Min. 10, 1983, 10-15; Nord & Ericsson, Z. Kristallogr. 161, 1982, 209-224; Nord, Mat. Res. Bull. 18, 1983, 765-773).

All iron-containing phases have been checked by means of ^{57}Fe Mössbauer spectroscopy at the University of Uppsala (cf. Annersten, Ericsson & Nord, J. Phys. Chem. Solids, 41, 1980, 1235-1240). The results show that a good estimate of the cation distribution pattern can be obtained with the time-saving Rietveld technique, although the precision is not as good as with single-crystal data; the e.s.d. of the distribution coefficient K_D was usually 5-10 % for the phases studied. The interatomic distances and angles are quite reasonable, which is shown by the good agreement between observed and estimated (calculated) average metal-oxygen distances in the solid solutions.

12.5-4 THE X-RAY RIETVELD SYSTEM XRS-84. By Ch. Baerlocher, Institut für Kristallographie und Petrographie, ETH-Z, 8092 Zürich, Switzerland.

The X-ray Rietveld System is a collection of programs designed to carry out the calculations required to solve and refine crystal structures with the Rietveld technique using x-ray or neutron powder data. It has been successfully used in a number of cases, especially for the refinement of complex zeolite structures (e.g. TPA-ZSM-5 with 181 structural parameters (BAERLOCHER, Proc. 6th intl. Zeolite Conf. (1983), Butterworth, UK)).

XRS-84 is an extended and perfected version of XRS-82 and is based on the X-ray System (Stewart et al., University of Maryland). It includes all the advantages of the latter (e.g. efficiency, binary data file, transportability) as well as all programs relevant to powder structure refinements (e.g. lattice constant determination, Fourier calculation and peak search, bond distance and angle calculation).

The main routine, the whole pattern LS program accepts neutron, strictly monochromatic α_1 and α_1/α_2 x-ray radiation. A "learned" peak shape function, Gaussian or Pearson VII functions can be used to describe a peak. It is simple to add any other desired analytical functions. The background can be refined using different orthogonal polynomials for different regions of the pattern. Other features are: distance and angle constraints as additional observations, mixing of line shapes for different classes of reflections, a variable metric algorithm as an alternative LS procedure, etc.

Examples of its applications will be shown. The system is written in a subset of FORTRAN IV (approx. 50K lines, tested on CDC Cyber and VAX computers and is available on magnetic tape).

12.5-5 RIETVELD REFINEMENT OF SYNCHROTRON X-RAY POWDER DATA: THE STRUCTURE OF Ba_2SrWO_6 . By D. E. Cox, J. B. Hastings, and W. Thomlinson, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

It has recently been demonstrated that the high resolution of powder diffraction data which can be obtained with synchrotron radiation may have important applications to structure analysis by means of Rietveld refinement (Cox, Hastings, Thomlinson, and Prewitt, Nucl. Instr. and Meth. (1983) 208, 573; Hastings, Thomlinson and Cox, J. Appl. Cryst. (1984), in press). This technique has been applied to a refinement of the structure of Ba_2SrWO_6 , which was originally reported to be a moderately distorted form of the cubic $(NH_4)_2FeF_6$ structure (Steward and Rooksby, Acta Cryst. (1951) 4, 503), and subsequently to have a monoclinic cell (Kovba, Lykova and Shevchenko, Russ. J. Inorg. Chem. (1971) 16, 1150).

Synchrotron x-ray data were collected at the Cornell High Energy Synchrotron Source (CHESS) with x-rays of wavelength 1.54 Å from a perfect Si(220) double-crystal monochromator and a modified Philips diffractometer equipped with a perfect Ge(111) analyzing crystal. The observed peaks were intermediate in shape between Gaussian and Lorentzian, and significantly broadened with respect to the instrumental resolution function, with an angle dependence qualitatively consistent with a predominantly Lorentz-like particle size broadening. The effects of this and also strain broadening were taken into account by modifications to the Rietveld program in an intuitively simple way within the framework of the "pseudo-Voigt" approximation (Wertheim, Butler, West, and Buchanan, Rev. Sci. Instr. (1974) 11, 1369; Young and Wiles, J. Appl. Cryst. (1982) 15, 430). With these modifications, Rietveld refinement was satisfactorily accomplished on the basis of a monoclinic cell, space group I2/m, with refined lattice constants $a = 6.10390(6)$ Å, $b = 6.03592(8)$ Å, $c = 8.53814(10)$ Å, $\beta = 90.4325(8)$ deg. A striking feature of this refinement is that the angular variation of the peak halfwidths and the relative contributions of Gaussian and Lorentzian components is described satisfactorily by only two variable parameters, one for the instrumental resolution and the other for the particle size broadening.

The structure may be viewed as a modification of an ideal ordered perovskite-type structure with $Fm\bar{3}m$ symmetry in which there is cooperative tilting of rigid SrO_6 and WO_6 octahedra about a pseudo-cubic [110] axis, very similar to that of $Ba_2Bi^{3+}Bi^{5+}O_6$ (Cox and Sleight, Solid State Commun. (1976) 19, 969; Thornton and Jacobson, Acta Cryst. (1978) B34, 351). Neutron data collected from the same sample confirm this structure.

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