Todorokite [(Na, Ca, K)\(_{12.5-3}\)]\(\cdot\)\(3.2\)H\(_2\)O is thought to be one of the major Mn oxide phases in ocean Mn nodules, and is also of interest because it exhibits zeolite-like cation exchange behavior. Todorokite typically occurs as poorly crystalline masses, therefore it has not been possible to study its structure with single crystal diffraction methods. 

Recent advances in both the experimental and computational aspects of powder diffraction have brought the technique to the point where the ab initio determination of crystal structures from powder data \([\text{J. Appl. Cryst. (1981), 14, 357-361}]\) has further been extended to the characterization of multicomponent ceramic materials. For this purpose, the procedure is improved in some respects: 1) automatic peak shift correction in refining unit cell parameters of the sample containing an internal standard material, 2) remodeling of angular dependent peak asymmetry and intensity decaying rate of the diffraction profile in order to avoid the parameter divergence in the LS, 3) introduction of the overall scale factors, which can be refined instead of individual integrated intensities. Refined unit cell parameters are accurate to about \(10^{-3} - 10^{-4}\) Å. The WPPF technique can extract the maximum information from the whole powder data, and can obtain a much higher accuracy compared to the conventional profile fitting technique, particularly to analyze a minor phase in the mixture. The WPPF is carried out for the quantitative analysis and unit cell measurement of \(\text{NaPO}_3\) stabilized \(\text{ZrO}_2\) polymorphs, of which analyses hitherto have been abandoned due to the complexity of the pattern. Other examples will also be presented.


The procedure of whole-powder-pattern fitting (WPPF) without reference to a structural model, first proposed by Pawley for use with neutron powder data \([\text{J. Appl. Cryst. (1981), 14, 357-361}]\) and then applied to X-ray powder diffraction data \([H. Toraya, J. Appl. Cryst. (1986), 19, 440-447]\), has further been extended to the characterization of multicomponent ceramic materials. For this purpose, the procedure is improved in some respects: 1) automatic peak shift correction in refining unit cell parameters of the sample containing an internal standard material, 2) remodeling of angular dependent peak asymmetry and intensity decaying rate of the diffraction profile in order to avoid the parameter divergence in the LS, 3) introduction of the overall scale factors, which can be refined instead of individual integrated intensities. Refined unit cell parameters are accurate to about \(10^{-3} - 10^{-4}\) Å. The WPPF technique can extract the maximum information from the whole powder data, and can obtain a much higher accuracy compared to the conventional profile fitting technique, particularly to analyze a minor phase in the mixture. The WPPF is carried out for the quantitative analysis and unit cell measurement of \(\text{NaPO}_3\) stabilized \(\text{ZrO}_2\) polymorphs, of which analyses hitherto have been abandoned due to the complexity of the pattern. Other examples will also be presented.


Recent advances in both the experimental and computational aspects of powder diffraction have brought the technique to the point where the ab initio determination of crystal structures from powder data is becoming routine. The general approach, involving indexing of the pattern, assignment of space group, and solution of the structure by Patterson or direct methods, has been described by Christensen \(\text{et al.} (1985), 38, 499-505\), and the feasibility has been demonstrated using ultra high resolution neutron and synchrotron X-ray data \([\text{Cheetham} \text{ et al., Nature, 1986, 322, 46-48; Attfield et al., Nature, 1986, 322, 620-622}]\).

The results of two synchrotron X-ray studies will be presented. The structure determination of \(\alpha\)-CrPO\(_4\) (Imma; \(a=10.406, b=12.889, c=6.299\) Å) will be described and the results will be compared with a refinement of powder neutron diffraction data collected on the same sample. The structure consists of an infinite network of linked CrO\(_4\) octahedra and PO\(_4\) tetrahedra. An interesting feature is the sharing of a common edge between CrO\(_4\) and PO\(_4\) units, both of which are distorted, resulting in a short non-bonding Cr-P distance of 2.65Å and an O-O contact of 3.33Å. The solution of the structure of a new phase MnPO\(_4\)\(\cdot\)\(H_2\)O \((\text{C2/c; } a=6.912, b=7.470, c=7.375\) Å, \(\beta=112.3^\circ)\) will also be discussed, including the location of the hydrogen atoms. The structure comprises a network of vertex-sharing MnO\(_6\) octahedra and PO\(_4\) tetrahedra, the former distorted by the Jahn-Teller mechanism. The water molecules are located in small channels running parallel to the c axis.