Analysis of Unknown and Disordered Crystal Structures from X-Ray Powder Diffraction Data

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Recent advances in the field of crystal-structure analysis from XRPD data have enabled us to investigate complex structures, including positional disordering of atoms and orientational disordering of atomic groups. The initial structural models may be determined by, for example, direct methods. The structural parameters are subsequently refined using the Rietveld method. In order to disclose the structural details that had not been introduced into the structural models, the combined use of a maximum-entropy method (MEM) and a MEM-based pattern fitting (MPF) method is employed. The Rietveld and MEM analyses are insufficient to readily determine a charge density because the observed structure factors, $F_{o}(\text{Rietveld})$, are biased toward the structural model. The subsequent MPF method reduces the bias as much as possible. Thus, the MEM and MPF analyses are alternately repeated until the reliability indices no longer decrease.

We have successfully determined the highly disordered crystal structures of Ca$_7$ZrAl$_6$O$_{18}$, (Ba$_{0.6}$Sr$_{0.4}$)Al$_2$O$_4$, (Ba$_{0.65}$Ca$_{0.35}$)$_2$SiO$_4$ and (Ba$_{0.24}$Ca$_{0.76}$)$_2$SiO$_4$ from XRPD data. The crystal structures were expressed by the split-atom models, in which the Ca/Sr/Ba atoms and (Al/Si)O$_4$ tetrahedra were, respectively, positionally and orientationally disordered. The three-dimensional electron density distributions were finally determined by the MPF method, which were satisfactorily expressed by the corresponding split-atom models.

In the system Al-Si-O-C, we have discovered and structurally characterized two types of new oxycarbides; (Al$_{18-x}$Si$_x$)(O$_y$C$_{14-y}$) ($x \sim 1.2$ and $y \sim 3.0$) and (Al$_{5-x}$Si$_x$)(O$_y$C$_{4-y}$) ($x \sim 0.6$ and $y \sim 1.0$). These crystal structures were expressed by the split-atom models showing positional disordering of Al/Si sites. Each of these disordered structures can be regarded as a statistical average of the two twin-related structural configurations with the low-symmetry subgroup. The twin-related domain structures were actually observed using TEM.