

Layer stacking disorder in Mg-Fe chlorites based on powder X-ray diffraction data

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ABSTRACT

The primary aim of this study was the accurate determination of unit-cell parameters and description of disorder in chlorites with semi-random stacking using common X-ray diffraction (XRD) data for bulk powder samples. In the case of ordered chlorite structures, comprehensive crystallographic information can be obtained based on powder XRD data. Problems arise for samples with semi-random stacking, where due to strong broadening of hkl peaks with $k \neq 3n$, the determination of unit-cell parameters is demanding. In this study a complete set of information about the stacking sequences in chlorite structures was determined based on XRD pattern simulation, which included determining a fraction of layers shifted by $\pm 1/3\mathbf{b}$, interstratification with different polytypes and 2:1 layer rotations.

A carefully selected series of pure Mg-Fe tri-trioctahedral chlorites with iron content in the range from 0.1 to 3.9 atoms per half formula unit cell was used in the study. In addition, powder XRD patterns were carefully investigated for the broadening of the odd-number basal reflections to determine interstratification of 14 and 7 Å layers. These type of interstratifications were finally not found in any of the samples. This result was also confirmed by the XRD pattern simulations, assuming interstratification with $R0$ ordering.

Based on $h0l$ XRD reflections, all the studied chlorites were found to be the I**bb** polytype with a monoclinic-shaped unit cell ($\beta \approx 97^\circ$). For three samples, the hkl reflections with $k \neq 3n$ were partially resolvable; therefore, a conventional indexing procedure was applied. Two of the chlorites were found to have a monoclinic cell (with $\alpha, \gamma = 90^\circ$). Nevertheless, among all the samples, the more general triclinic (pseudomonoclinic) crystal system with symmetry $C\bar{1}$ was assumed, to calculate unit-cell parameters using Le Bail fitting.

A detailed study of semi-random stacking sequences shows that simple consideration of the proportion of I**b**-2 and I**b**-4/6 polytypes, assuming equal content of I**b**-4 and I**b**-6, is not sufficient to fully model the stacking structure in chlorites. Several, more general, possible models were therefore considered. In the first approach, a parameter describing a shift into one of the $\pm 1/3\mathbf{b}$ directions (thus, the proportion of I**b**-4 and I**b**-6 polytypes) was refined. In the second approach, for samples with slightly distinguishable hkl reflections with $k \neq 3n$, some kind of segregation of individual polytypes (I**b**-2/4/6) was considered. In the third approach, a model with rotations of 2:1 layers about $0^\circ, 120^\circ, 240^\circ$ was shown to have the lowest number of parameters to be optimized and therefore give the most reliable fits. In all of the studied samples, interstratification of different polytypes was revealed with the fraction of polytypes being different than I**bb** ranging from 5 to 19%, as confirmed by fitting of $h0l$ XRD reflections.

Keywords: Chlorites, polytype interstratification, stacking disorder, powder X-ray diffraction