Geometric crystal chemical models for structural analysis of micas and their stacking polytypes

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ABSTRACT

A sequence of progressively more realistic geometric crystal chemical models for TOT layers in mica is developed, starting from the usual main uniform distortions (octahedral flattening, tetrahedral rotation, octahedral counter-rotation) toward additional features as they are shown to be required. These additional features include tetrahedral basal flattening and apical bond adjustment, geometric meso-octahedral sheets (having unequal M1 and M2/M3 site bond lengths), and geometric hetero-octahedral sheets (having equal M1, M2, and M3 site bond lengths) and is described using a minimal number of independent crystal chemical parameters: octahedral, tetrahedral basal, tetrahedral apical, and interlayer metal-anion bond lengths, and flattening angles of octahedral and tetrahedral sheets. The monoclinic lattice parameters (a, b, c, and β) and the tetrahedral rotation angle (α) follow from these assumed parameters. These models are designed to allow analyses (that are reported elsewhere) of both structural and lattice-parameter refinement data in terms of deviations from various predictions based on specified sets of crystal chemical assumptions. Fractional atomic coordinates are derived in terms of the atomic positions for the 1M unit cell of C2/m symmetry. These coordinates allow a structural analysis of diffraction data for different stacking polytype structures using the same 1M-type TOT layer as a modular unit.

INTRODUCTION

The ultimate crystal chemical model of a mica would predict exactly the atomic coordinates of all atoms in the unit cell, given the stoichiometry and degree and type of any chemical order. The large chemical variability of the octahedral, tetrahedral, and interlayer sites complicates the modelling of the crystal structure of a mica, as does the inherent misfit between octahedral and tetrahedral sheets. Because the apical oxygen atoms are shared between tetrahedral and octahedral sheets, various structural distortions are required to ensure lateral matching of these two types of sheets. Moreover, the crystallographically distinct cationic sites may be occupied by different ion populations either in an ordered or a disordered way, Al³⁺ and Fe³⁺ (and Ti⁴⁺?) may populate both octahedral and tetrahedral sites, and Fe and Mn may be present in different oxidation states (Fe²⁺ and Fe⁶⁺; Mn²⁺ and Mn⁴⁺). To account for this complexity, an approach based on a simple conceptual framework is desirable.

Micas are divided into three families based on the refinements of site-specific occupancies (i.e., mean electron counts) for the three possible unit cell octahedral sites (Durovič 1994; Nespolo and Durovič 2002; Ferraris and Ivaldi 2002): (1) homo-octahedral micas have an octahedral sheet of layer symmetry H(3)1m, where all three octahedral sites M1, M2, and M3 are occupied by the same kind of crystallochemical entity (i.e., by the same the kind of ion or by the same statistical average of different kinds of ions including vacancies); (2) meso-octahedral micas have an octahedral sheet of layer symmetry PH(3)1m, where two of the octahedral sites are occupied by the same kind of crystallochemical entity and the third by a different one; and (3) hetero-octahedral micas have an octahedral sheet of layer symmetry P(3)12, where each of the three octahedral sites is occupied by a different crystallochemical entity [layer symmetry notation after Dornberger-Schiff (1959), as cited by Nespolo et al. (1999)]. On the other hand, Weiss et al. (1985, 1992) identified three octahedral sheet types based on the values of the average octahedral cation-anion bond lengths <M1-O>, <M2-O>, and <M3-O>: type-I, <M1-O> = <M2-O> = <M3-O>; type-II, any two are equal and the third is different; and type-III, the three average octahedral site bond lengths are different.

The above situation is complicated because sometimes, in a given refinement of a given sample, the average electron densities of two distinct octahedral sites are different but there is no significant difference between the average bond lengths of these two sites, or vice versa (e.g., see Weiss et al. 1992; Brigatti and Guggenheim 2002; Nespolo and Durovič 2002). To take this situation into account, the following terminology is used in this paper. We here use the terms geometric homo-octahedral, geometric meso-octahedral, and geometric hetero-octahedral to refer to each of the three octahedral sheet types I, II, and III described by Weiss et al. (1992), respectively. Note that the latter classification is based on the average bond lengths obtained.