Synthetic and natural Fe-Mg chloritoid: structural, spectroscopic and thermodynamic studies

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Abstract: Fe-Mg bearing chloritoids were synthesized at 18-35 kbar and 590-720°C in a piston cylinder apparatus under the fO2 defined by the Fe/FeO buffer (IW). We investigated the synthetic crystals by electron microprobe, X-ray powder diffraction, high-resolution transmission electron microscopy, Mössbauer spectroscopy and diffuse reflectance spectroscopy in the UV-NIR (30000-6000 cm⁻¹). Structural studies reveal that the high-pressure chloritoids crystallize in the triclinic space group \( \text{C}_1 \). The molar volume of the chloritoid solid solutions depends linearly on composition. The crystal lattices are nearly perfect with almost no defects, while some of the triclinic chloritoids may contain minor amounts of monoclinc intergrowths. Mössbauer spectroscopy shows that in the synthetic chloritoids a small amount of \( \text{Fe}^{3+} \) is incorporated as \( \text{Fe}^{3+} \). This result is consistent with estimates from electron microprobe analyses and the results of diffuse reflectance spectroscopy. The diffuse reflectance spectra exhibit a broad band at about 15000 cm⁻¹ caused by \( \text{Fe}^{3+} \text{Fe}^{3+} \) charge transfer and two small crystal-field bands at about 11000 and 8200 cm⁻¹ due to \( \text{Fe}^{2+} \) in the strongly distorted M1B octahedron (Håhlenius et al., 1981). The crystal-field effect on \( \Delta \text{CFSE}^\text{excess} \) of \( \text{Fe}^{2+} \) in chloritoid was determined by an analysis of the crystal-field spectra. \( \Delta \text{CFSE}^\text{excess} \) is negative within the whole Fe-Mg chloritoid solid-solution series. It is larger in the Fe-rich than in the Mg-rich part of the system, which indicates a non-ideal, asymmetrical mixing behaviour of Fe-Mg chloritoid.

Key-words: Fe-Mg chloritoid, syntheses, Mössbauer spectroscopy, electron microprobe, diffuse reflectance spectroscopy, crystal-field spectra, \( \Delta \text{CFSE}^\text{excess} \).

Introduction

Chloritoid is a characteristic mineral of low-temperature metapelites. It is an orthosilicate with the general formula \((\text{Fe}^{2+}, \text{Mg}, \text{Mn}^{2+})_2(\text{Al}, \text{Fe}^{3+})\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_4\). Although the most common chloritoids are Fe-rich, an increasing number of Mg-rich chloritoids have been found in the last decade indicating that there is a complete solid-solution series: \((\text{Fe}^{2+}, \text{Mg}_{1-x})_2\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_4\) (Chopin et al., 1992). Fe-rich chloritoid is characteristically found in rocks of low grade, whereas magnesiochloritoid is a key-mineral in high-pressure pelitic blueschists (Chopin, 1983). Although a lot of work has been done to gain insight into the structure, stability and crystal chemistry of chloritoids there are many open questions. Some of them are summarized below:

i) Polymorphism versus polytypism: The most abundant chloritoids occur in two modifications: a monoclinic one, space group \( C2/c \) and a triclinic one, space group \( C1 \) (Hanscom, 1975 and 1980; Jefferson & Thomas, 1978). The last mentioned authors investigated natural chloritoids by high-resolution electron microscopy in combination with X-ray precession photographs. They sug-