Structural effects of pressure on monoclinic chlorite: A single-crystal study

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ABSTRACT

A single-crystal X-ray diffraction study in a diamond anvil cell up to 5.41 GPa was carried out on a clinochlore [monoclinic polytype IIb-2, S.G. C2/m, (Mg9.09Fe2+0.02Mn0.02Ti0.01Cr0.02Al1.80)Σ8O20(OH)16] from Val Malenco, Italy. The bulk modulus of monoclinic clinochlore calculated by fitting unit-cell volumes and pressures to a third-order Birch-Murnaghan Equation of State (EoS), is K0 = 71(9) GPa with K′ = 8(5). Axial compressibility values were β0ab = 3.8(1), β0ac = 3.6(1), and β0bc = 5.4(5) × 10−3 GPa−1, showing that axial anisotropy is much less than that found for other phyllosilicates. Compressibility data are in fair agreement with literature data, which are based on powder neutron and synchrotron diffraction methods. Results were compared with the behavior of the triclinic polytype of similar composition and coexisting in the same rock. Symmetry has little overall influence on compressibility, but compared with the triclinic polytype of similar composition and coexisting in the same hand specimen, the monoclinic polytype is slightly less rigid. Comparison of structural refinements at different pressures showed that structural deformations mainly affect the interlayer region, where hydrogen bonds are important for the structural properties of the phase. The mean decrease in OH-O distances was about 9% in the pressure range 0–5 GPa. Structural behavior was very similar to that found for the triclinic polytype.

Although energy differences between polytypes are relatively small, their compressional behavior may have implications in terms of relative stability. A computation of molar volume applying an isothermal EoS shows that the triclinic polytype is lower in volume up to 0.9 GPa, above which the volume of the monoclinic phase is smaller. This fact gives information on the relative stability of the two polytypes and a possible explanation for the greater abundance of the triclinic polytype in low to medium-P environments, as is commonly observed in nature.

Keywords: Chlorite, high pressure, polytypism, equation of state

INTRODUCTION

Chlorite is a widespread family of di- and trioctahedral layer silicates. The structure of trioctahedral chlorite consists of talc-type, negatively charged T-O-T layers with ideal composition (R2+,R3+)Σ2(OH)2 alternating with positively charged brucite-type octahedral interlayer sheets with ideal composition (R2+,R3+)Σ2(OH)6 (Bailey 1988). Electrostatic interactions and a system of hydrogen bonding between the T-O-T layer and the brucite-like sheet contribute to the stability of the structure. Different ways of positioning the T-O-T layer on the interlayer sheet create a large number of regular-stacking polytypes (Bailey 1988). The triclinic Ilb-4 polytype, with symmetry C1, and the monoclinic Ilb-2 polytype, with symmetry C2/m, are the most abundant regular-stacking one-layer chlorites occurring in nature. The monoclinic structure was described by Zheng and Bailey (1988), Rule and Bailey (1987), and Joswig and Fuess (1989). Chlorite is among the hydrous phases that may play an important role in upper mantle mass transport and melting processes. In view of its role as a water carrier in subducting slabs, knowledge of the stability field of this hydrous phase may be obtained by studying its compressibility and the dependence of its crystal structure on pressure.

No high-pressure, single-crystal study has yet been carried out on monoclinic chlorite, the only determination being that on a triclinic polytype (Zanazzi et al. 2006). The aim of the present work on good-quality single-crystal samples is: (1) to investigate the nature of pressure-induced deformation on the atomic arrangement, with particular attention to H-bond system changes in the interlayer region; (2) to compare high-pressure behavior with that of the triclinic polytype coexisting in a rock from Val Malenco (Zanazzi et al. 2006); and (3) to examine how pressure can influence their relative stability, using the opportunity offered by the rock from Val Malenco in which the two polytypes with similar compositions crystallized coevally under the same P-T conditions.

EXPERIMENTAL METHODS

A natural clinochlore from Alpe Raguzzolo, Val Malenco (Eastern Central Alps, Italy), kindly supplied by the Mineralogy Museum, University of Florence (no. 13087/626), was selected for high-pressure X-ray diffraction experiments. According to Müntener et al. (2000), the assemblage olivine + tremolite + chlorite + talc formed in the second stage of the retrograde metamorphism of the Malenco peridotite, during later hydration of ultramafic rocks. Estimated metamorphic conditions were 0.9 ± 0.1 GPa and 600 ± 50 °C. The sample consists of green platy...