Thermal and combined high-temperature and high-pressure behavior of a natural intermediate scapolite

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A natural intermediate member of the scapolite solid solution {Me14; chemical formula: (Na1.86Ca1.86K0.23Fe0.01)(Al4.36Si7.64)O24[Cl0.48(CO3)0.48(SO4)0.01]}, with the unusual 4/m space group, has been studied at various temperatures and combined high-T and high-P by means of in situ single-crystal and powder X-ray diffraction, using both conventional and synchrotron X-ray sources. In addition, single-crystal neutron diffraction data were collected at ambient-T and 685 °C. A fit of the experimental V-T data with a thermal equation of state yielded a thermal expansion coefficient at ambient conditions: α25°C = 1/(∂V/∂T)T=25°C = 1.74(3)·10–5 K–1. A comparative analysis of the elastic behavior of scapolite based on this study and previous high-T XRD data suggests that a thorough re-investigation of the different members of the marialite-meleonite solid solution is needed to fully understand the role of crystal chemistry on the thermal behavior of these complex nonbinary solid solutions. The experimental data obtained within the full temperature range of analysis at ambient pressure confirm that the investigated sample always preserves the 4/m space group, and possible implications on the metastability of 4/m intermediate scapolite are discussed. Neutron diffraction data show that no significant Si and Al rearrangement among the T sites occurs between 25 and 685 °C. The combined high-T and high-P data show that at 650 °C and between 10.30(5) and 10.71(5) GPa a phase transition toward a triclinic polymorph occurs, with a positive Clapeyron slope (i.e., dP/dT > 0). A comprehensive description of the atomic-scale structure deformation mechanisms induced by temperature and/or pressure, including those leading to structural instability, is provided based on single-crystal structure refinements.

Keywords: Scapolite, temperature, pressure, phase transition, synchrotron X-ray diffraction, neutron diffraction; Microporous materials: Crystal-chemistry, properties, and utilizations

INTRODUCTION

Scapolites are a group of open-framework aluminosilicates with general formula M4Ti4O12A4, where M are monovalent or divalent cations (usually Na, Ca, and minor K), T are trivalent or tetravalent cations (mostly Al and Si) in tetrahedral coordination, and A are anionic elements or groups such as Cl, CO3, and SO4. Three mineral end-members are recognized: marialite, Na4Al3Si9O24Cl; meionite, Ca4Al6Si6O24CO3; and silvialite, Ca4Al6Si6O24SO4, even though most natural samples possess intermediate compositions (e.g., Seto et al. 2004; Sokolova and Hawthorne 2008; Hawthorne and Sokolova 2008) revealed that natural scapolites follow three different compositional trends along the marialite-meoineite joint, with discontinuities at 3.6 and 4.7 Al atoms per formula units (Teertstra and Sherriff 1997).

A common formalism, widely adopted to refer to a member of the scapolite solid solution, is that of meionite fraction (Shaw 1960a, 1960b): Me% = (ΣM/ΣM + M+2)·100. Due to the complex nature of the chemical substitutions within the solid solution series, this formalism is not accurate but can still be considered valid at a first approximation (Sokolova and Hawthorne 2008) and will be adopted throughout this manuscript.

Besides their complex chemical features, scapolites are characterized by the presence of two crystal-chemistry-controlled polymorphs: phases with a composition closer to the marialite and meionite end-members are usually reported to crystallize in a structure with the 4/m space group, whereas intermediate members show a P42/n symmetry. A detailed discussion on the crystal chemical and structural reasons for the occurrence of the phase transitions between the two polymorphs is presented in Hawthorne and Sokolova (2008).