Composition, stability, and structure of a new member of the aenigmatite group, 
\[ Na_2Mg_{4-x}Fe^{3+}_{1-2x}Si_{6+x}O_{20} \] synthesized at 13–14 GPa

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ABSTRACT

A new phase isostructural with the minerals of the aenigmatite group \[ Na_2Mg_{4-x}Fe^{3+}_{1-2x}Si_{6+x}O_{20} \] with \( x = 0.25 - 0.5 \) was synthesized at 13–14 GPa with a split-sphere anvil apparatus (USSA-2000). The structure (for \( x = 0.4 \)) was determined from twinned-crystal X-ray diffraction data. The unit cell is triclinic, \( P\bar{1}, a = 10.328(1), b = 10.724(1), c = 8.805(1) \) Å, \( \alpha = 105.15(1), \beta = 96.85(1), \gamma = 125.47(1)^\circ, V = 719.67(3) \) Å³, \( Z = 2 \), calculated density \( 3.335 \) g/cm³. The twin law, independently determined from electron diffraction and transmission electron microscopy and by inspection of the X-ray data collected with an area detector, relates the twin components by a 180° rotation about [110]*. Due to the coupled substitution, \( 2Fe^{3+} = MgSi \), which introduces octahedral Si, the stability of the phases with the aenigmatite structure apparently expands with increasing pressure. Hence, these phases could play a major role in the transition zone (410–660 km), where the more common minerals they are replacing, olivine and clinopyroxene, reach the limit of their stability. The new evidence for the stability of aenigmatite-like minerals in the deep mantle could have important implications for the origin of the parental magmas producing aenigmatite-bearing and other agpaitic rocks.

INTRODUCTION

Recent advances in seismic tomography provide strong evidence that some or most of the subducted oceanic lithosphere resides in the Earth’s transition zone (e.g., van der Hilst et al. 1991; Fukao et al. 1992). Hence, the complete understanding of the transition-zone mineralogy and chemistry must include information on the stability, crystal chemistry, and structure of the phases present at relevant temperatures and pressures as well as sodium-rich compositions typical for the basaltic portion of the oceanic lithosphere. Previous studies in chemically simpler Na-bearing systems (e.g., Gasparik 1989, 1992, 1996; Litvin and Gasparik 1993; Gasparik et al. 1995) are extended here to Fe-bearing compositions that more closely approach the chemical complexity of the Earth’s mantle. The primary motivation for this study was to test the prediction of Gasparik and Litvin (1997) that jadeitic clinopyroxene would react with forsterite at a pressure between 13 and 13.5 GPa producing clinoenstatite, garnet, and \( Na,Mg,Si,O_3 \) (NMS) (Fig. 1). This reaction should cause a major decrease in the temperatures of the anhydrous mantle solidus in the transition zone due to the relatively low melting temperatures of NMS with respect to other mantle phases. In the course of this experimental investigation, a new Na- and Fe-bearing phase was discovered (Gasparik 1997a), and here we report its structure, chemistry, and stability.

SYNTHESIS TECHNIQUES

Experiments were carried out with a split-sphere anvil apparatus using 10 mm sample assemblies (Gasparik 1989). Lanthanum chromite sleeves were used as the resistance heaters and the samples were enclosed in rhenium capsules. Temperature was measured by a W3%Re vs. W25%Re thermocouple introduced axially and maintained constant during the experiments by a Eurotherm controller. The details of the temperature and pressure calibrations and experimental procedures were given by Gasparik (1989).

Starting materials were mechanical mixtures of high-purity oxides and compounds, including \( MgO \), amorphous \( SiO_2 \), Fe metal and synthetic nepheline (\( NaAlSiO_3 \)), fayalite (\( FeSiO_3 \)), and sodium disilicate (\( Na_2Si_2O_5 \)). The compositions are given in Table 1. The starting materials already loaded in the sample assemblies were dried overnight before the experiments at 100 °C.

After the experiments, the samples still inside the capsules were mounted in epoxy for microprobe analysis. A polished mount contained a lengthwise section of a sample, allowing analysis along the full 200 °C gradient.