The crystal structure and cation ordering of Phase-X-(K_{1-x-n})_2(Mg_{1-n}[Al,Cr]_n)_2Si_2O_7H_2x:
A potential K- and H-bearing phase in the mantle*

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ABSTRACT

Phase-X, a potassium di-magnesium acid disilicate, is a high-pressure synthetic compound—a potential K-bearing silicate in the mantle—with space group P63cm (no. 185), a = 5.028(2) Å, c = 13.216(3) Å, V = 289.34 Å³, Z = 2. The structure has been determined with 1521 CCD measured intensities and refined by the least-square method to R = 0.0187. The structure is built up of octahedral MgO sheets and layers containing disilicate groups, SiO_7, (with distinct Si1 and Si2 tetrahedra linked by the apical O2 atom) alternating along the c axis. The octahedral sheet is based on a hexagonal closest-packed array of two layers of non-equivalent O atoms, O1 and O3; two-thirds of all edge-sharing M octahedra are filled. Within the framework of the SiO_7 groups are channel structures parallel to [100], [010], and [110] that contain K atoms disordered in the middle of a large trigonal cavity (the A site). The FTIR spectrum in the OH stretching region shows a sharp peak at 3602 cm⁻¹ due to OH⁻ ordered in one anion site; the position of hydrogen, which operates in a charge-balancing substitution for the partial occupancy of the A site (K_{1-x}H_x)³⁻ ↔ H_{[1-x]}^{+}, is undetermined. Densification in phase-X is affected by the greater compression of the empty octahedra in the octahedral layer and by constraining the trigonal A cavity containing the K atom to the size of the SiO_7-disilicate group. This dense packing contributes to the relatively high zero-pressure calculated density of 3.38 g/cm³.

INTRODUCTION

Potassium plays an important role in the Earth as a result of its involvement in differentiation, its preferred partitioning into partial melts, and its contribution to the heat budget of the Earth by means of radioactive decay of ⁴⁰K. More recently, it has also been found to be influential in melting of the Earth’s mantle because the phases in which it is commonly hosted (e.g., phlogopite and amphibole) are key to dehydration melting. Thus, determination of phases that are potential sinks for potassium at high pressure is likewise important. The K-bearing phases stable at high pressure include phlogopite, sandine, K-cynmite (e.g., Fasshauer et al. 1997; Thompson et al. 1998), KK-richeriterite (e.g., Ulmer and Konzett 1999; Konzett and Fei 2000), K-hollandite (Yamada et al. 1984; Schmidt 1996; Irifune et al. 1994) and K-rich clinopyroxene (see Harlow 1997); several of these are hydrous as well. Phase-X was discovered in synthesis products in various studies (Trønnes 1990; Harlow 1997; Luth 1997; Inoue et al. 1998; Ulmer and Konzett 1999; Konzett and Fei 2000) at a range of conditions from T = 1150–1400 °C and P = 9–17 GPa, which makes it a potential host for K and H2O at mantle conditions. Measured compositions of phase-X are high in K2O (10–15 wt%) and MgO (26–39 wt%) and low in Al2O3 (e.g., Konzett and Fei 2000), although no systematic studies of compositional range have yet been undertaken. With the interpreted ideal stoichiometry of Konzett and Fei (2000), K_{9.5}Mg_{2.5}Si_2O_7H, it can incorporate a significant amount of hydrogen, which as H2O ranges from 1.8–4.2 wt%. Because phase-X contains much larger amounts of potassium and water than coexisting phases in experimental products (e.g., diopside, garnet, and olivine), its abundance may be critical to the total amount of K and H2O in a mantle assemblage. Consequently, we have determined the crystal structure to learn the K sitting, the nature of the hydrous component as well as the general topology.

EXPERIMENTAL METHODS

Phase-X in the present study was produced at P = 9 GPa and T = 1300 °C from a mixture of natural diopside (CaMgSi2O6; with trace Al and Fe), synthetic kosmochlor (NaCrSi2O6), SiO2, and K2CO3·H2O (approximate molar ratio 0.85:0.09:0.06:1), about 10 mg in total, sealed in a platinum capsule and placed in a multianvil device as experiment GG307 (see Harlow 1997 for synthesis details; note the pressure cited here reflects a newer calibration). Phase-X formed a thin layer (<100 μm thick) between clinopyroxene and quenched melt in the experiment. The crystals extracted from the experiment were embedded in epoxy and polished for electron microprobe analysis performed using a five-spectrometer Cameca SX100 electron microprobe. Standard compounds were natural diopside for Ca, Mg and Si, orthoclase for K and Al, MgCr2O4 for Cr, and jadeite for Na.