High-pressure phase transformation in LiFeGe$_2$O$_6$ pyroxene

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ABSTRACT

A synthetic pyroxene with composition LiFeGe$_2$O$_6$ and space group $P2_1/c$ at ambient conditions was investigated by single-crystal X-ray diffraction using a diamond anvil cell. The unit-cell parameters and crystal structure were determined at eight different pressures up to 8.7 GPa. Between 4.16 and 4.83 GPa, the sample shows a strongly first-order phase transition as indicated by a drastic drop in $a$, $c$, $\beta$, and unit-cell volume. The transition is marked by the disappearance of $b$-type reflections ($h + k = \text{odd}$) forbidden in a $C$-centered lattice. The volume bulk modulus of the $P2_1/c$ phase is estimated to be 110 GPa as compared to 147 GPa of the $C2/c$ one. The crystal structure evolution as a function of pressure is mainly influenced by the kinking of tetrahedral chains; the A and B non-symmetry equivalent chains of the $P2_1/c$ phase undergo strong deformations up to 4.16 GPa (A chain $\sim$2%, B chain $\sim$5.3%). At the transition, the two chains become symmetry equivalent and the single tetrahedral chain of the $C2/c$ phase shows only minor deformations with pressure ($\sim$1.9%) due to its already strong kinking ($\sim$130°). Such behavior is the main reason for the strong difference in compressibility between the low- and high-symmetry forms.

Keywords: Single-crystal structure analysis, germanates, high-pressure phase transformations, X-ray diffraction

INTRODUCTION

Li-bearing silicate pyroxenes have been recently investigated at high pressure as such phases undergo a $C2/c$–$P2_1/c$ phase transition (e.g., LiAlSi$_2$O$_6$, LiGaSi$_2$O$_6$, LiSiO$_4$, LiFeSiO$_4$; Arlt and Angel 2000; Pommier et al. 2005; Nestola et al. 2008) similar to that observed in clinopyroxenes stable at Earth’s mantle conditions [e.g., (Mg,Ca,Fe)SiO$_3$; Angel et al. 1992; Nestola et al. 2004]. Previous works provided topological models capable of predicting the behavior of pyroxene as a function of pressure, temperature, and composition (Downs 2003; Thompson and Downs 2003). An important difference between Li-bearing and mantle clinopyroxenes concerns the $C2/c$ phases involved in the transformation. Generally, mantle clinopyroxenes showing this transition are $P2_1/c$ at room pressure and transform to $C2/c$ at high pressure, whereas Li-bearing clinopyroxenes are $C2/c$ at room pressure and become $P2_1/c$ at high pressure. One exception is the composition Li$_{0.68}$Mg$_{0.11}$Fe$_{0.16}^{2+}$Fe$_{0.16}^{3+}$Mg$_{0.15}$Si$_2$O$_6$, which maintains the $P2_1/c$ symmetry from ambient conditions up to at least 8 GPa (Gatta et al. 2005).

The $C2/c$ high-pressure phase of mantle clinopyroxenes is structurally distinct from the low-pressure phase typical for Li-bearing clinopyroxenes. It is characterized by a strongly kinked tetrahedral chain. Such structures are denoted as HPC2/c and show kinking angles close to 140° (e.g., Mg$_{1.15}$Ca$_{0.85}$Si$_2$O$_6$, Nestola et al. 2004), whereas the low-pressure $C2/c$ phase is denoted as HTC2/c and shows a much more extended tetrahedral chain [e.g., 170° for LiAlSi$_2$O$_6$ (Arlt and Angel 2000); 179.9° in LiGaSi$_2$O$_6$ (Redhammer and Roth 2004); 180.8° in LiFeSi$_2$O$_6$ (Redhammer et al. 2001)]. To our best knowledge, there is just one published report on the high-pressure crystal structure evolution of the HPC2/c phase, focused on composition Fe$_2$Ge$_6$O$_{18}$ (tetrahedral chain kinking angle at room pressure = 131.1°; Hattori et al. 2000). Considering that the HPC2/c structure should be the stable one at Earth’s mantle conditions, it is important to perform systematic studies to better constrain the behavior of such phases. Moreover, as it is well known that many germanates show phase transformations similar to those of silicates, but at lower pressures (Ross and Navrotsky 1988), germanate clinopyroxenes can be used as structural models for investigating the behavior of mantle clinopyroxenes (e.g., clinoenstatite Mg$_{1.15}$Si$_2$O$_6$). In this work, we synthesized and studied by single-crystal X-ray diffraction in situ at high pressure a sample with composition LiFeGe$_2$O$_6$. This composition was chosen because the complete substitution of Si by Ge and Li for Fe stabilizes the $P2_1/c$ symmetry at room pressure, which enables us to also characterize the $P2_1/c$–HPC2/c phase transition and the crystal structure evolution of the HPC2/c phase.

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