

The effect of Ca substitution on the compressional behavior of enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) up to 10 GPa

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In a recent investigation, new and old compressibility data on orthoenstatite (Oen, orthorhombic *Pbca*) have been reanalysed in order to obtain an accurate equation of state (EoS), whose coefficients are: $K_0 = 105.8(5)$ GPa and $K' = 8.5(3)$ [1]. Oen at high-pressure shows an anomalous structural behavior, with a significant increase of the compressibility of the SiO_4 tetrahedra after 4 GPa[2]. Such behavior, also observed for Opx richer in iron[3], has been attributed to changes in the deformation mechanisms with pressure. Previous spectroscopic studies, moreover, indicated phase transitions between 8 and 10 GPa to a monoclinic symmetry[4,5]. The aim of our work is to determine how the substitution of Ca for Mg into the Oen structure can affect its compressibility and crystal structure deformation at high-pressure. To this end we have studied a synthetic single-crystal of orthoenstatite with composition $\text{Ca}_{0.07}\text{Mg}_{1.93}\text{Si}_2\text{O}_6$ by *in situ* high-pressure X-ray diffraction. Such Ca content is very close to the maximum amount of Ca atom that can be accommodated by the *Pbca* Oen structure.

The experiments were performed using a BGI-type diamond anvil cell. We have measured the unit-cell parameters at 10 different pressures up to about 10.2 GPa. In such pressure range no evidence of a phase transition was found. The *P-V* data have been fitted by a 3rd-order Birch-Murnaghan EoS giving the following coefficients: $V_0 = 838.26(8)\text{\AA}^3$, $K_0 = 110(1)$ GPa, $K' = 6.6(4)$. Several intensity data collections have been performed up to 6.25 GPa. The octahedra M2 and M1 show deformations similar to those of pure Oen.

References

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Cr oxidation state in periclase by XANES spectroscopy

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We examined the oxidation state and local environment of trace amounts of Cr in synthetic periclase by Cr *K*-edge X-ray Absorption Near Edge Structure (XANES). The syntheses were performed in a multi-anvil press. A natural composition, as found in diamonds, was used first: $(\text{Mg}_{0.825}\text{Fe}_{0.160}\text{Ni}_{0.010}\text{Cr}_{0.005})\text{O}$. This material was annealed at 4 and 12 GPa and at two temperatures, 1200 and 1400°C, using a LaCrO_3 furnace. In order to stabilize divalent chromium into periclase, the sample was inserted into an iron capsule to maintain low oxygen fugacities. $(\text{Mg}_{0.98}\text{Cr}_{0.02})\text{O}$ was also synthesized at ~10 GPa using a graphite capsule and a rhenium furnace and this to preserve a minimal oxygen fugacity. Powder XRD confirmed the samples to be made essentially of periclase, and SEM observations showed the presence of metal coexisting with periclase. The intensity of a shoulder on the absorption edge in the XANES spectra, has been used to quantify the ratio $\text{Cr}^{2+}/\text{Cr}^{3+}$ [1]. In addition, the amount of Cr^{2+} and Cr^{3+} has been calculated using a computer algorithm for iterative transformation factor analysis [2]. In all studied samples minor amounts of Cr^{2+} were determined, together with Cr metal and Cr^{3+} . The effect of pressure and of temperature on the ratio $\text{Cr}^{2+}/\text{Cr}^{3+}$ is discussed. Additional theoretical calculations are in progress to determine the Cr local environment.

References

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