Cr-rich phases in the MgO-SiO_2-Cr_2O_3 system at 10-25 GPa: composition, solid solutions, and structural features

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High-pressure phase relations in the MgO-SiO_2-Cr_2O_3 system are important in the study of mantle mineralogy. There are two major high-pressure garnet end-members in the lowermost upper mantle: knorringite ($Mg_3Cr_2Si_3O_{12}$, *Knr*) and majorite ($Mg_4Si_4O_{12}$, *Maj*). With increasing pressure, the phase assemblages include Cr-rich phases: ilmenite, perovskite and $MgCr_2O_4$ with calcium-titanate structure. Experiments were aimed on the study of the phase relations in the MgO-SiO_2-Cr_2O_3 system at 10-25 GPa and 1600ºC, as well as conditions of the formation, structural peculiarities, and compositional changes of Cr-rich phases with pressure using a Kawai-type multi-anvil apparatus.

We investigated the full range of starting compositions, which allowed us to synthesize different Cr-rich phases with a wide compositional range. The main phases obtained in experiments were: *Knr*-*Maj* garnet, pyroxene, eskolaite, Cr-ilmenite (Cr-*Ilm*), Cr-perovskite (Cr-*Pv*), $MgCr_2O_4$ with calcium-titanate structure, and stishovite.

Single-crystal X-ray diffraction studies were carried out to determine the symmetry and study the structural peculiarities of the synthesized Cr-rich phases. All garnets synthesized at 10-21 GPa are characterized by a silicon surplus over 3.0 a.p.f.u. and high chromium content (up to 90 mol. % *Knr*). Cr is incorporated in garnet via the scheme: $Mg^{2+}+Si^{4+}=2Cr^{3+}$. All garnets have cubic symmetry (space group *Ia*-3*d*) and the lattice parameter linearly increases with increasing the *Knr* content. Cr-*Ilm* has the chemical composition of $(Mg_{1-x}Cr_x)(Si_{1-x}Cr_x)O_3$ (with x = 0.015, 0.023 and 0.038) and trigonal symmetry. Compared with $MgSiO_3$-*Ilm*, the occurrence of Cr leads to a general expansion of the unit cell (*a* from 4.7284(4) to 4.7380(1) and *c* from 13.5591(16) to 13.5611(2) Å). Perovskites synthesized at pressures above 20 GPa have a composition of $(Mg_{1-x}Cr_x)(Si_{1-x}Cr_x)O_3$ with x=0-0.07, orthorhombic symmetry (space group *Pbnm*) and the following lattice parameters for x=0.07: a = 4.8213(5), b = 4.9368(6), c = 6.9132(8) Å. For both Cr-minerals (Cr-*Ilm* and Cr-*Pv*), chromium was found to substitute for both Mg and Si, according to the reaction $Mg^{2+}+Si^{4+}=2Cr^{3+}$.

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