Poster

The effect of iron on high-pressure behavior and phase transition in srebrodolskite-brownmillerite ($CaFeO_{2.5}$-$CaAlO_{2.5}$)

M. Merlini[1], B. Chrappan Soldavini[1], D. Comboni[1], V. Kahlenberg[2], M. Hanfland[3]

[1]Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Via Botticelli 23, Milano, Italy, [2]Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020, Innsbruck, Austria, [3]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS40220,38043 Grenoble, Cedex 9, France

marco.merlini@unimi.it

Srebrodolskite ($CaFeO_{2.5}$) and brownmillerite ($CaFeAlO_{2.5}$) are interesting minerals found in both natural occurrences and synthetic forms within industrial contexts such as slags and cements. These compounds exhibit a unique oxygen-deficient perovskite structure characterized by ordered vacancies, notably differing from the primitive perovskite aristotype in the local environments of Fe and Al ions, present both in [6] and [4] coordination. Crystallographically, the stoichiometric vacancies facilitate the formation of various superstructures, leading to complex behaviors influenced by temperature and the emergence of incommensurate structures.

Beyond their crystallographic interest, these minerals serve as valuable models for exploring the role of vacancies in Earth's mantle perovskite, offering insights into the complex crystal chemistry of bridgmanite ($MgSiO_3$) and davemaoite ($CaSiO_3$) under lower mantle conditions.

Here, we present high-pressure single crystal diffraction studies on synthetic end-members $CaFeO_{2.5}$ and $CaAlO_{2.5}$ to provide a comprehensive understanding of the system. The synthetic materials were prepared via high-temperature flux method crystallization.

The compressibility of the Al-end member exhibits no discontinuities within the investigated pressure range (0-40 GPa), with a detailed analysis of both bulk and local compressibility provided. Conversely, the Fe-end member displays a significant discontinuity, evidenced by a 5% volume reduction at 20 GPa and a phase transition from the orthorhombic srebrodolskite structure to primitive perovskite (fig. 1). Structure determination and refinement at both low and high pressures reveal substantial Fe-O shrinking in octahedral sites, consistent with the expected distances for high-spin Fe states at low pressure and low-spin states at high pressure (above 20 GPa). These findings underscore the pivotal role of iron in driving the phase transition and confirm the possibility of trivalent Fe in mantle perovskite adopting a low-spin state when situated in octahedral sites, at significantly low pressures.

The phase transition upon decompression exhibits significant hysteresis.

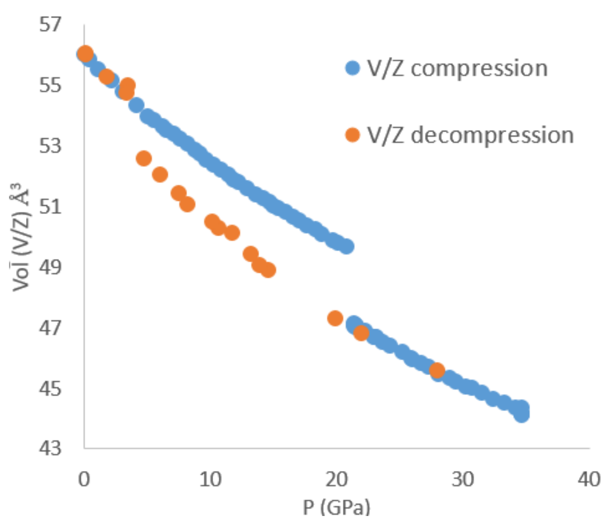

Figure 1. Unit cell normalized volume for srebrodolskite ($CaFeO_{2.5}$) as function of pressure, showing the first order phase transition at 20 GPa.