Equation of state of skiagite-majorite garnet up to 100 GPa

LEYLA ISMAILOVA[1], ANDREY BOBROV[2], MAXIM BYKOV[1], ELENA BYKOVA[1], VALERIO CERANTOLA[1], ILYA KUPENKO[3], CATHERINE MCCAMMON[1], MICHAEL HANFLAND, ALEXANDER CHUMAKOV, NATALIA DUBROVINSKAIA[1] AND LEONID DUBROVINSKY[1]

[1]University of Bayreuth, Bayreuth, Germany
[2]Lomonosov Moscow State University, Moscow, Russia
[3]European Synchrotron Radiation Facility, Grenoble, France

Considering the abundance of garnet in upper mantle and transition zone, information about their behavior under extreme conditions plays an important role in understanding the deep Earth's interior. Because of the compositional complexity of natural garnets, the relationships between the composition of mantle garnets and PT-conditions of their formation are still semi-empirical.Study of garnet containing both di- and trivalent iron (e.g. skiagite) is important to indicate oxygen fugacity models for garnet-bearing assemblages.

Experiments at P=9.5 GPa and T=1100 C were performed on a multi-anvil apparatus at the Bayerisches Geoinstitut (Bayreuth, Germany). The starting material (corresponding to the nominal composition $Fe_3Fe_2Si_3O_{12}$) was a powdered mixture of chemically pure oxides. Single crystal X-ray diffraction data were collected at Swiss-Norwegian beamline (BM01A, ESRF, Grenoble, France). Structure refinement revealed that the octahedral site is fully occupied by Fe and Si atoms yielding the chemical composition $Fe^{2+}_3(Fe^{2+}_{0.234(2)}Fe^{3+}_{1.53(1)}Si_{0.234(2)})Si_3O_{12}$, which is in a good agreement with the results of the electron microprobe analysis.

The high-pressure behaviour of skiagite-majorite garnet was studied at pressures up to 100 GPa using single-crystal synchrotron x-ray diffraction at ID09A at ESRF. When K` is fixed to 4 and V_0 = 1612(1) $Å^3$, the fitting to to a third-order Birch–Murnaghan BM EoS gives the zero-pressure bulk modulus, K_0, of skiagite-majorite garnet 160 (2) GPa. At the pressure range between 50 and 60 GPa the overall unit-cell volume is reduced about 4 % and a collapse of about 7 % of FeO6 is observed. Since octahedral positions are occupied by Fe^{3+} reduced Fe-O distances can be associtated with spin-pairing transitions.

Synchrotron Mössbauer spectroscopy was performed at ID18 at ESRF at a series of pressures between ambient pressure and 60 GPa. The spectra at ambient pressures contains two doublets one doublet has a large center shift (CS) of 1.32(1) mm/s and a large quadrupole splitting (QS) of 3.45(2) mm/s. The other doublet with CS=0.37(1) mm/s and small QS= 0.26(2) mm/s is assigned to ferric iron Fe3+ located in the octahedral position. Up to 50 GPa spectra remain the same and at ~52 GPa QS of Fe^{3+} increases with decreasing CS which is clearly associated with spin pairing transition. Out single crystal x-ray diffraction and mössbauer data are in a good agrement with each other.