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Iron spin state in perovskite structure: Moessbauer spectroscopy, X-ray diffraction spectroscopy and XANES

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According to laboratory measurements as well as geophysical observations the perovskite phase (Fe,Mg)(Si,Al)$O_3$is believed to be one of the major component in the Earth lower mantle. It is known that spin state of iron has direct influence on the physical properties and crystal chemistry of its host phase. At ambient conditions Fe^{2+} is in high-spin state but with pressure spin state of iron could change, that could influence on phase density, electrical resistance, elasticity, thermal conductivity and elements partitioning. Therefore we decided to investigate iron electronic state in (Mg,Fe)(Si,Al)O_3 perovskite structure combining conventional Moessbauer spectroscopy, neutron forward scattering, X-ray diffraction spectroscopy and XANES at pressures up to 110 GPa in temperature range 300-1000K. By Moessbauer spectroscopy we observed changes in the Fe^{2+} behavior at pressures near 30 GPa – the new component with very high quadrupole splitting (about 4 mm/sec) appeared; and the amount of this component increases with pressure. In the same pressure range (25-30 GPa) we observed some changes in elastic properties of the samples. We interpret this changes as continues transition from high-spin state (central shift about 1 mm/sec and quadrupole splitting around 2.5 mm/sec) to the intermediate spin state (central shift is about 1 mm/sec and quadrupole splitting is about 4 mm/sec). Gradual character of this transition does not suppose any abrupt changes in elasticity, thermal and electrical conductivity and element's partitioning in Earth lower mantle due to iron spin transition in perovskite structure. However, physical and chemical properties of iron-bearing silicate perovskite could be affected by spin crossover and any extrapolations of the properties of Fe-free silicate perovskites towards geophysically and geochemically relevant materials at Earth mantle conditions should be made with great caution.