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Electronic transitions of iron in almandine-composition glass to 91 GPa

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Abstract

Valence and spin states of Fe were investigated in a glass of almandine ($Fe_3Al_2Si_3O_{12}$) composition to 91 GPa by X-ray emission spectroscopy and energy- and time-domain synchrotron Mössbauer spectroscopy in the diamond-anvil cell. Changes in optical properties, total spin moment and Mössbauer parameters all occur predominantly between 1 bar and ~30 GPa. Over this pressure range, the glass changes from translucent brown to opaque and black. The total spin moment of the glass derived from X-ray emission spectroscopy decreases by ~20%. The complementary Mössbauer spectroscopy approaches reveal consistent changes in sites corresponding to 80–90% Fe^{2+} and 10–20% Fe^{3+}. The high-spin Fe^{2+} doublet exhibits a continuous decrease in isomer shift and increase in line width and asymmetry. A high-spin Fe^{3+} doublet with quadrupole splitting of ~1.2 mm/s is replaced by a doublet with quadrupole splitting of ~1.9 mm/s, a value higher than all previous measurements of high-spin Fe^{3+} and consistent with low-spin Fe^{3+}. These observations suggest that Fe^{3+} in the glass undergoes a continual transition from a high-spin to a low-spin state between 1 bar and ~30 GPa. Almandine glass is not expected to undergo any abrupt transitions in electronic state at deep mantle pressures.

Keywords: Silicate glass, spin transitions, Mössbauer spectroscopy, nuclear forward scattering, X-ray emission spectroscopy