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$^{VIII}(Mg,Fe)_{0.85}{}^{VI}(Mg,Fe)_4{}^{IV}(Fe,Ge)_3O_{12}$: A new tetragonal phase and its comparison with garnet

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ABSTRACT

Tetragonal $Mg_{2.12}Fe_{3.17}Ge_{2.56}O_{12}$ is a new germanate forming at 1 atm pressure in the MgO-Fe_2O_3-GeO_2 system. It is an analogue of the high-pressure silicate mineral TAPP occurring as inclusions in diamonds of lower-mantle origin. Its crystal structure was determined by X-ray diffraction using single-crystals grown from a potassium molybdate flux. It crystallizes in the $I\bar{4}2d$ space group with a = 6.8153(4) Å, c = 18.669(2) Å, Z = 4. The refinement of its cation distribution, $^{VIII}(Mg_{0.52}Fe_{0.33})^{VI}(Mg_{1.60}Fe_{2.40})^{IV}(Ge_{2.56}Fe_{0.44})O_{12}$, shows the presence of a partially filled (85%) dodecahedral site characterized by an unusual geometry with two very different bond lengths [2.169 Å (×4) and 2.609 Å (×4)]. The structure determinations of the Ca^{2+}- and Y^{3+}-substituted phases show that the larger cations are completely partitioned in the dodecahedral site, increasing its occupancy slightly (up to 92% in the case of Ca^{2+}).

Cubic $Mg_{2.35}Y_{2.00}Fe_{0.97}Ge_{2.59}O_{12}$ is a new garnet phase forming at 1 atm pressure in the MgO-Y_2O_3-Fe_2O_3-GeO_2 system. Its crystal structure and cation distribution were also determined by single-crystal X-ray diffraction: $^{VIII}(MgY_2)^{VI}(Mg_{1.35}Fe_{0.56})^{IV}(Ge_{2.59}Fe_{0.41})O_{12}$, $Ia\bar{3}d$ space group, a = 12.232(1) Å, Z = 8. In spite of similarities in their chemical compositions, the tetragonal and garnet phases are structurally distinct, with different ratios of dodecahedral to octahedral sites, viz., $^{VIII}A^{VI}B_4{}^{IV}T_3O_{12}$ and $^{VIII}A_3{}^{VI}B_2{}^{IV}T_3O_{12}$ respectively. As a consequence, the tetragonal phase forms in systems containing smaller cations, such as Mg^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, whereas larger cations, such as Y^{3+}, show a strong preference for the garnet phase.