Ab initio thermodynamic and thermophysical properties of sapphirine end-members in the join $Mg_4Al_8Si_2O_{20}$-$Mg_3Al_{10}SiO_{20}$

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ABSTRACT

Using the hybrid B3LYP density functional method, we computed the ab initio thermodynamic and thermophysical properties of two sapphirine end-members, $Mg_4Al_8Si_2O_{20}$ (sapphirine-442) and $Mg_3Al_{10}SiO_{20}$ (sapphirine-351), in the join $Mg_3(Mg_{1-X}Al_X)Al_8(Al_XSi_{1-X})SiO_{20}$ with $X = 0$–1. Static and vibrational calculations performed in the framework of the quasi-harmonic approximation allowed to define the equation of state (EOS), elastic constant tensor, seismic velocities, IR spectra, mode Grüneisen parameters, and thermodynamic properties of both sapphirine end-members. A modified Kieffer's model was adopted to evaluate the optic and acoustic mode contributions to thermodynamic functions stemming from ab initio phonon frequencies and directionally averaged seismic velocities, respectively. The extrinsic stability and liquidus phase relations of sapphirine were investigated in the model system MgO-Al_2O_3-SiO_2 (MAS) at different pressure conditions by coupling first-principles calculations with the hybrid polymeric approach (HPA) for multicomponent liquids and minimizing the Gibbs free energy of liquid and solid phases through the convex-hull analysis of equipotential surfaces. According to our thermodynamic modeling, sapphirine turns out to have a small field of primary crystallization in the MAS ternary diagram at 1-bar pressure, which becomes larger due to pressure effects up to 10 kbar, then progressively shrinks and disappears above 21 kbar.

Keywords: Sapphirine, thermodynamic properties, ab initio calculations, elasticity, equation of state, liquidus phase relations