



Thermodynamic model of the $\text{CaMgSi}_2\text{O}_6$ - KAlSi_2O_6 pyroxene solid solution.

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K-bearing clinopyroxenes (KCPx) with the compositions close to $\text{CaMgSi}_2\text{O}_6$ - KAlSi_2O_6 join are often observed as inclusions in kimberlitic and lamproitic diamonds and in mineral assemblages of some eclogitic and peridotitic xenoliths.

Using static lattice energy calculations based on empirical interatomic potentials and Monte Carlo simulations we modeled thermodynamic mixing properties of the $\text{CaMgSi}_2\text{O}_6$ - KAlSi_2O_6 solid solution in the range of 273–2023 K and constructed the T-X diagram. The simulations predicted complete mixing above 800 K. At lower temperatures the mixing is limited due to the formation of several intermediate compounds. The compound with 50 mol. % of K-jadeite (called K-omphacite) of the space group $P2/b$ is analogous to omphacite in the diopside–jadeite system. However, the cation distribution in this structure is inverted: K and Ca in K-omphacite occupy the sites of Ca and Na, respectively, in omphacite.

Using density functional theory based calculations we estimated the standard enthalpy of formation (-2932.7 kJ/mol), the standard volume (6.479 kJ/mol/bar), and the bulk modulus (145 GPa⁻¹) of K-jadeite. The standard entropy (141.24 J/mol/K) and the thermal expansion coefficient (3.38*10⁻⁵ K⁻¹) of K-jadeite were predicted with the help of force-field lattice dynamics. Both the ab initio and force-field calculations

suggested that the difference in unit-cell volumes in the diopside - K-jadeite system is much smaller than in the diopside – jadeite system. Consequently, the excess enthalpy is much smaller in the diopside - K-jadeite system. The calculated $P - V$ data for diopside and K-jadeite further showed that the volume difference between these end-members decreases with pressure. This suggests that at higher pressures the mixing in the diopside - K-jadeite system will be even closer to ideal. The activity-composition relations in the disordered $C2/c$ phase were approximated with a Redlich-Kister polynomial expression.

From our calculations we conclude that the limited solubility of K-jadeite in natural clinopyroxenes is not caused by immiscibility. More likely, this is a result of a much higher standard enthalpy of K-jadeite with respect to typical K-rich phases, such as sanidine or kalsilite. Using the estimated thermodynamic properties we calculated the isopleths of K-jadeite in clinopyroxene in the assemblages with sanidine + coesite, Si-wadeite + kyanite + stishovite/coesite, and hollandite + stishovite. The calculations suggested that in the presence of sanidine and coesite the mole fraction of K-jadeite in clinopyroxene increases with pressure. However, in the assemblage with hollandite and stishovite the opposite tendency is predicted. In all studied mineral assemblages, the mole fraction of K-jadeite increases with temperature. The opposite tendency is predicted for the assemblage of clinopyroxene with K-rich aluminosilicate melt and coesite.

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