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Thermochemistry of stuffed quartz-derivative phases along the join $LiAlSiO_4$-SiO_2

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ABSTRACT

Enthalpies of drop-solution ($\Delta H_{drop\text{-}soln}$) of a suite of stuffed quartz-derivative phases with the composition $Li_{1-x}Al_{1-x}Si_{1+x}O_4$ ($0 \le x \le 1$) have been measured in molten $2PbO \cdot B_2O_3$ at 974 K. Substitution of Si^{4+} for $Li^{+}+Al^{3+}$ results in more exothermic enthalpies of drop-solution, which is consistent with behavior seen in other crystalline and glassy aluminosilicates. Al/Si ordering serves to stabilize these phases, and long-range ordering for compositions with x approximately <0.3 can be discerned in both calorimetric data and in structural data obtained by electron and synchrotron X-ray diffraction (XRD). In contrast, a structural but not an energetic discontinuity is apparent at $x \cong 0.65$, which corresponds to a compositionally induced α-β quartz transition with a small enthalpy of transformation.

An enthalpy for the Al/Si order-disorder reaction in β-eucryptite was measured as 25.9 ± 2.6 kJ/mol. Standard molar enthalpies of formation of the stuffed quartz-derivative phases from constituent oxides ($\Delta H^0_{f,ox}$) and elements ($\Delta H^0_{f,el}$) at 298 K also are presented. $\Delta H^0_{f,ox}$ = –69.78 ± 1.38 kJ/mol and $\Delta H^0_{f,el}$ = –2117.84 ± 2.50 kJ/mol for β-eucryptite, which are in good agreement with results previously determined by HF solution calorimetry at 346.7 K (Barany and Adami 1966). The enthalpies of formation of other compositions are reported for the first time.