

Thermochemistry of Alkaline Earth Silicate and Sub –
Orthosilicate GlassesNektarios K. Nasikas and Alexandra Navrotsky
Peter A. Rock Thermochemistry Laboratory and NEAT
ORU, University of California, Davis
One Shields Ave. Davis, CA, 95616 USA

Recent advancements in instrumentation used in high temperature synthesis have opened new pathways to synthesizing novel glasses [1]. A series of glasses, ranging from diopside ($\text{CaMgSi}_2\text{O}_6$) to monticellite (CaMgSiO_4) compositions and even beyond, reaching more depleted in SiO_2 compositions, in the so called sub-orthosilicate region (< 33.3 mol % SiO_2) have been successfully synthesized by the non-conventional glass forming technique of aerodynamic levitation and CO_2 laser melting that is newly established in our laboratory. For all glasses we measured the drop solution enthalpies (ΔH_{ds}) in molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 974 K in a twin Tian - Calvet microcalorimeter [2, 3]. From these ΔH_{ds} values and by employing appropriate Thermochemical cycles we calculated the formation enthalpies from the oxides at room temperature ($\Delta H_{f,ox}^{0,298K}$) for glasses forming in the $(1 - x)\text{Ca}_{0.5}\text{Mg}_{0.5}\text{O} - x\text{SiO}_2$ system with mole fraction silica, x , between 0.30 and 0.50. The $\Delta H_{f,ox}^{0,298K}$ values become increasingly exothermic as the SiO_2 content decreases and reach a minimum around the monticellite composition ($x = 0.33$). Further lowering of SiO_2 content leads to a small rise in the $\Delta H_{f,ox}^{0,298K}$, indicating diminishing stability. These findings will be compared with enthalpies of formation of analogous glasses in the pseudobinary system enstatite (MgSiO_3) - forsterite (Mg_2SiO_4) thus giving a more complete picture regarding the energetics of glass formation in glasses perceived as poor glass formers and can only be synthesized with non – conventional techniques.

References

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