American Mineralogist, Volume 89, pages 1586–1596, 2004

Calorimetry of liquids in the system Na_2O-Fe_2O_3-SiO_2

TORU SUGAWARA* AND MASAKI AKAOGI

Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

ABSTRACT

Transposed-temperature, drop-calorimetry measurements were performed in the systems Na_2SiO_3-Fe_2O_3-SiO_2 and Na_2SiO_3-$NaFeSi_2O_6$ at 1373 K to investigate thermodynamic properties of Fe^{3+}-bearing silicate liquids. The results confirm previously measured enthalpy of Na_2SiO_3 and SiO_2 melts. No significant heats of mixing were observed in the Na_2SiO_3-SiO_2 liquids or in peralkaline liquids in the system Na_2SiO_3-Fe_2O_3. The enthalpy of mixing of peralkaline liquids in the system Na_2SiO_3-Fe_2O_3-SiO_2 was less than the standard deviation of drop calorimetry (approx. ±10 kJ/mol). From calorimetric data of Na_2SiO_3-Fe_2O_3 liquids extrapolated to hematite composition and published heat capacity, the enthalpy of fusion of hematite is estimated to be 83.3 ± 10.5 kJ/mol at 1373 K and 133.4 ± 10.5 kJ/mol at its melting point 1895 K. The Fe^{3+}/Fe^{2+} ratio of the liquid was estimated from thermodynamic calculations using the fusion enthalpy of hematite and published data of FeO and O_2, and reproduced measured Fe^{3+}/Fe^{2+} ratios in natural silicate liquids and in CaO-Al_2O_3-Fe_2O_3-FeO-SiO_2 liquids. No significant heats of mixing were observed in the Na_2SiO_3-$NaFeSi_2O_6$ liquids. The enthalpy of formation of $NaFeSi_2O_6$ (acmite) at 1bar and 298 K calculated from calorimetric data is –2546.9 ± 17 kJ/mol. The enthalpy and entropy of fusion of acmite are estimated to be 70.5 ± 9.4 kJ/mol and 51.3 ± 6.8 J/K-mol, respectively, at metastable congruent melting point, 1373 K. The entropy of fusion of acmite is similar to that of $NaAlSi_2O_6$ (jadeite), indicating that Fe^{3+} and Al^{3+} have analogous structural roles in pyroxene melts.