American Mineralogist, Volume 91, pages 97–103, 2006

Phase transitions and volumetric properties of cryolite, Na_3AlF_6: Differential thermal analysis to 100 MPa

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ABSTRACT

Cryolite, Na_3AlF_6, is the most abundant aluminofluoride mineral in highly evolved felsic suites and their pegmatites, but its phase transitions and thermodynamic properties at elevated pressures are unknown. We used a simple modification of the TZM pressure vessel to perform differential thermal analysis of cryolite at high pressures. Temperatures of the α-β transition are as follows: 559.30 ± 0.23 °C (1 atm), 562.10 ± 0.28 °C (47 MPa), and 567.33 ± 0.23 °C (101 MPa). Cryolite melting temperatures increase as follows: 1011.4 ± 0.2 °C (1 atm), 1019.2 ± 0.4 °C (50 MPa), and 1028.7 ± 0.4 °C (100 MPa). Both pressure-temperature relationships are linear: $(dT/dp)_{\alpha\text{-}\beta} = 78.4 \pm 8.4$ °C/GPa and $(dT/dp)_m = 174 \pm 12$ °C/GPa. Application of the Clapeyron relationship leads to the following volumetric changes: $\Delta V_{\alpha-\beta} = 0.089 \pm 0.019$ J/(mol·bar) and $\Delta V_m = 1.49 \pm 0.12$ J/(mol·bar). Despite the significant self-dissociation in the cryolite liquid, melting sensu stricto (without dissociation) dominates the heat and volumetric changes during melting in comparable amounts: 83.3 ± 6.7 % ΔH_m and 68 ± 15 % ΔV_m and suggests that the degree of dissociation has no significant effect on the $(dT/dp)_m$. Evaluation of previous and current volumetric data for cryolite polymorphs leads to $V_{\beta,1284} = 8.49 \pm 0.17$ J/(mol·bar); coefficients for the volumetric thermal expansion in the form of the third-order polynomial equation are: $V_{298} = 7.080 \pm 0.012$ J/(mol·bar), $a_1 = (1.39 \pm 0.20)\cdot10^{-4}$ K^{-1}, $a_2 = (-2.15 \pm 0.51)\cdot10^{-7}$ K^{-2}, and $a_3 = (2.68 \pm 0.34)\cdot10^{-10}$ K^{-3}. The total $(dT/dp)_m$ of cryolite is very similar to that of villiaumite (NaF), whereas $\Delta V_m/V_{\beta,1284}$ of cryolite is smaller than for other alkali halides (NaF, NaCl).

Keywords: DTA, TGA, cryolite, phase transition, thermodynamics