

Heat capacity of synthetic hydrous Mg-cordierite at low temperatures: Thermodynamic properties and the behavior of the H₂O molecule in selected hydrous micro and nanoporous silicates

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ABSTRACT

The heat capacity, C_p , of a synthetic hydrous cordierite of composition $\text{Mg}_{1.97}\text{Al}_{3.94}\text{Si}_{5.06}\text{O}_{18}\cdot 0.625\text{H}_2\text{O}$ was measured for the first time using precise adiabatic calorimetry in the temperature range from 6 to 300 K. Hydrous Mg-cordierite was obtained by hydrothermal treatment of anhydrous Mg-cordierite (Paukov et al. 2006) at 4 kbar and 600 °C for 24 hours. The synthetic product was characterized using X-ray diffraction and powder IR spectroscopy. Rietveld refinement gives $a = 17.060(2)$ Å, $b = 9.721(1)$ Å, and $c = 9.338(1)$ Å with $V = 1548.7(3)$ Å³ and $\Delta = 0.25$, and the IR spectrum shows only the presence of Class I-Type I H₂O in the channel cavities. Small C_p anomalies were observed at 272.98 ± 0.03 K and 239.43 ± 0.13 K, which are thought to be related to very small amounts of H₂O occurring in tiny fluid inclusions and to surface H₂O, respectively. From the heat-capacity data on hydrous Mg-cordierite, various thermodynamic functions were calculated and are presented in table form. The calculated partial molar entropy for one mole of H₂O in hydrous Mg-cordierite at 298.15 K and 1 bar is 80.5 J/(mol·K). The partial molar volume for H₂O in hydrous Mg-cordierite at 298 K and 1 bar is zero. The C_p results, together with published heat-capacity data on three different zeolites, permit a comparison and analysis of their heat-capacity behavior. The heat-capacity behavior of H₂O molecules in zeolites is more similar to that of ice at $T < 300$ K and not to gaseous H₂O, which can be attributed to the presence of hydrogen-bonded H₂O molecules. In contrast, the heat-capacity behavior for the “quasi-free” H₂O molecule in cordierite is more similar to that of a free H₂O molecule in the gaseous state between approximately 100 and 300 K. At $T < 100$ K, the energies of low-energy modes, especially external H₂O translations, determine heat-capacity behavior. Model heat capacities for H₂O in cordierite were calculated using the Einstein model and using as input data the results from inelastic neutron-scattering measurements on hydrous Mg-cordierite (Winkler and Hennion 1994). Reasonable agreement between experiment and calculations can be achieved using three H₂O translational modes, one of which is hypothetical, and two librational H₂O modes. The experimental spectra do not appear to show all six external H₂O modes and further vibrational spectroscopic study is required to determine their energies. At $T > 300$ K, the heat capacity for H₂O is the smallest in steam with values increasing in hydrous beryl and cordierite, to H₂O in various zeolites, and finally to liquid H₂O. This behavior may reflect the nature of the hydrogen bonding and the energies of internal H₂O stretching modes, which decrease in energy with increasing hydrogen-bonding strength in the various systems.

Keywords: Hydrous Mg-cordierite, heat capacity, adiabatic calorimetry, H₂O molecule, micro and nanoporous silicates