

Heat capacity of 72SiO₂-9B₂O₃-10Al₂O₃-9MO (M=Mg, Ca, Sr and Ba) glasses and melts

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The isobaric heat capacities (C_p) of 72SiO₂-9B₂O₃-10Al₂O₃-9MO (M=Mg, Ca, Sr and Ba) glasses and melts have been determined from differential scanning calorimetry (DSC) and drop-calorimetry measurements and the compositional dependence of the C_p of alkaline-earth borosilicate melts are examined. The DSC measurements for glasses were performed using Perkin-Elmer Pyris1 between 373 and 913K in step-scan mode. The relative enthalpies of glasses and melts were measured using a bunsen ice calorimeter connected to a vertical quench furnace between 773 and 1873K.

The temperature dependence of heat capacities of glasses is fitted by the Maier-Kelly equation using the C_p data by DSC and relative enthalpies by drop-calorimetry through least squares minimization. Fictive temperatures determined by intersections of the relative enthalpies of glass and melt are between 1080 and 1180K. The glass transition takes place when the heat capacity of glass is 96-98% of the Dulong-Petit limit (3R/g-atom). Configurational heat capacity at glass transition is calculated to be between 3.9 and 5.3 J/K g-atom. This is consistent with those of pyrex and soda-lime-silica glasses reported previously.

The heat capacities of melts obtained from temperature differentiation of relative enthalpies increase in the order of M=Ba (27.9 J/K g-atom) < Ca (28.6) < Sr (28.8) < Mg (29.4). By combining the measured enthalpies with previously reported partial molar heat capacities (C_{p_i}) for silicate melts, the $C_{p_{B_2O_3}}$ in the alkaline-earth aluminoborosilicate melts is calculated to be 121±14 J/K-mol. The derived $C_{p_{B_2O_3}}$ is consistent with heat capacity of pure B₂O₃ liquid. The $C_{p_{B_2O_3}}$ calculated using previously reported enthalpies of alkali borosilicate melts are larger than those of the alkaline-earth aluminoborosilicate melts, suggesting that coordination changes of boron affect the $C_{p_{B_2O_3}}$.