

High-temperature heat capacity of SiO₂-Al₂O₃-RO (R=Mg, Ca, Sr, Ba) melts

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Heat capacity (C_p) of silicate melts is an important property in consideration of phase equilibria in magmatic system and a numerical simulation of flow and thermal structures in glass melting furnace. Heat capacity of aluminum-free melts can be expressed by an additive function of partial molar heat capacities for components (Richet and Bottinga, 1985). On the other hand, it has been reported that the heat capacities of aluminosilicate melts show complicated dependence on both temperature and composition (Richet and Mysen, 2005). However, they are still poorly understood due to the lack of calorimetric data. This study provides new experimental data for the high-temperature heat capacities of Ca, Sr and Ba-bearing aluminosilicate melts.

Drop calorimetry measurements were performed for 50SiO₂-25Al₂O₃-25CaO (An), 36.5SiO₂-27Al₂O₃-36.5CaO (Ca36.5), 8SiO₂-30Al₂O₃-62CaO (Ca62) and 75SiO₂-12.5Al₂O₃-12.5SrO or 12.5BaO (Sr12.5, Ba12.5) melts between 873K and 1889K using a Bunsen ice calorimeter. Heat capacity of melts was determined from the differential of measured relative enthalpy. The heat capacity of anorthite melt is $1.356+0.0001151T(K)$ (J/K-g), which is consistent with the value reported by Richet and Bottinga (1985). The heat capacities for Ca36.5, Ca62, Sr12.5 and Ba12.5 are 1.532, 1.508, 1.313 and 1.160 (J/K-g), respectively, and they are independent of temperature.

The temperature and compositional dependence of the C_p for SiO₂-Al₂O₃-RO (R=Mg, Ca, Sr, Ba) melts are considered by combining new calorimetric data and literature data by drop calorimetry ($n=11$, Richet and Bottinga, 1984; Courtial and Richet, 1993; Neuville and Richet, 1991; Richet and Neuville, 1992) and by differential scanning calorimetry ($n=22$, Webb, 2008, 2011). The positive temperature dependence is observed in the SiO₂-Al₂O₃-MgO melts as reported by Courtial and Richet (1993). In the system SiO₂-Al₂O₃-CaO, temperature dependence of the C_p is only observed at anorthite composition. The heat capacity of alkaline-earth aluminosilicate melts can be expressed by a symmetric solution model. The derived heat capacity of mixing is negative value in all of the systems. At constant temperature and oxide ratio, the heat capacity decreases with decreasing field strength of alkaline-earth elements (Ba < Sr < Ca < Mg), suggesting that configurational freedom is restricted in the cations with lower field strength due to the charge compensation effect of aluminum. Further experimental data for Sr and Ba-bearing melts are required to generalize temperature dependence of the heat capacity.

Keywords: Silicate melt, Heat capacity, Calorimetry