

研究论文

稀土高氯酸盐-谷氨酸配合物 $[\text{Pr}_2(L\text{-}\alpha\text{-Glu})_2(\text{ClO}_4)(\text{H}_2\text{O})_7](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ 的低温热容和热化学研究

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摘要 合成了一种稀土高氯酸盐-谷氨酸配合物. 经TG/DTG、化学和元素分析、FTIR及与相关文献对比, 确定其组成为 $[\text{Pr}_2(L\text{-}\alpha\text{-Glu})_2(\text{ClO}_4)(\text{H}_2\text{O})_7](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ , 纯度为99.0%以上. 利用显微熔点仪分析发现其没有熔点. 在78~370 K温区, 用精密绝热量热仪测量其低温热容, 在285~306 K温区发现一明显吸热峰, 归结为固-固相变过程. 通过相变温区三次重复热容测量, 得到相变温度 $T_{\text{tr}}$ 、相变焓 $\Delta_{\text{tr}}H_{\text{m}}$ 和相变熵 $\Delta_{\text{tr}}S_{\text{m}}$ 分别为

(297.158±0.280) K, (12.338±0.016) kJ·mol<sup>-1</sup>和(41.520±0.156) J·K<sup>-1</sup>·mol<sup>-1</sup>.

用最小二乘法将非相变温区的热容对温度进行拟合, 得到了热容随温度变化的两个多项式方程.

用此方程进行数值积分, 得到每隔5 K的舒平热容值和相对于273.15 K的热力学函数值. 根据TG/DTG结果, 推测了该配合物的热分解机理. 依据Hess定律, 选择1 mol·dm<sup>-3</sup>盐酸为量热溶剂, 利用等温环境溶解-反应量热计, 测定了该配合物的标准摩尔生成焓为:  $\Delta_{\text{f}}H_{\text{m}}^0 = -(7223.1 \pm 2.4)$  kJ·mol<sup>-1</sup>.

关键词 [稀土高氯酸盐-谷氨酸配合物](#) [绝热量热法](#) [低温热容](#) [溶解-反应量热法](#) [标准摩尔生成焓](#)

分类号

**Low-temperature Heat Capacities and Thermochemistry of the Complex of Praseodymium Perchlorate with *L*- $\alpha$ -Glutamic Acid:  $[\text{Pr}_2(\text{Glu})_2(\text{ClO}_4)(\text{H}_2\text{O})_7](\text{ClO}_4)_3 \cdot 4\text{H}$**

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**Abstract** A complex of praseodymium perchlorate with *L*- $\alpha$ -glutamic acid,  $[\text{Pr}_2(\text{Glu})_2(\text{ClO}_4)(\text{H}_2\text{O})_7](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ , was synthesized. By chemical analysis, elemental analysis, FTIR, TG/DTG, and comparison with relevant literatures, its chemical composition and structure were established. The purity was found to be >99.0%, without melting point. Low-temperature heat capacities were measured by a precision automated adiabatic calorimeter over the temperature range from 78 to 370 K. An obvious endothermic peak in the heat capacity curve was observed over the temperature region of 285~306 K, which was ascribed to a solid-to-solid phase transition according to the results of TG/DTG analysis and melting point measurement. The temperature  $T_{\text{tr}}$ , the enthalpy  $\Delta_{\text{tr}}H_{\text{m}}$  and the entropy  $\Delta_{\text{tr}}S_{\text{m}}$  of the phase transition for the compound were determined to be: (297.158±0.280) K, (12.338±0.016) kJ·mol<sup>-1</sup> and (41.520±0.156) J·K<sup>-1</sup>·mol<sup>-1</sup>, respectively through three repeated heat capacity measurements in the phase transition region with different amounts of the sample. Two polynomial equations of heat capacities as a function of the temperature in the regions of 78~285 K and 306~370 K were fitted by the least square method, respectively. Based on the two fitted polynomials, the smoothed heat capacities and thermodynamic functions of the complex relative to the standard reference temperature 273.15 K were calculated with the interval of 5 K. The mechanism about thermal decomposition of the complex was deduced on the basis of the TG/DTG analysis. In accordance with Hess law the standard molar enthalpy of formation for the complex was determined as  $\Delta_{\text{f}}H_{\text{m}}^0 = (-7223.1 \pm 2.4)$  kJ·mol<sup>-1</sup>, by application of an isoperibol solution-reaction calorimeter and choice of 1 mol·L<sup>-1</sup> HCl as calorimetric solvent.

**Key words** [rare earth perchlorate salt](#) [L- \$\alpha\$ -glutamic acid](#) [adiabatic calorimetry](#) [low-temperature heat capacity](#) [isoperibol solution-reaction calorimetry](#) [standard molar enthalpy of formation](#)

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