



Enthalpies of formation of polyhalite: A mineral relevant to salt repository



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ABSTRACT

Polyhalite is an important coexisting mineral with halite in salt repositories for nuclear waste disposal, such as Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. The thermal stability of this mineral is a key knowledge in evaluating the integrity of a salt repository in the long term, as water may release due to thermal decomposition of polyhalite. Previous studies on structural evolution of polyhalite at elevated temperatures laid the basis for detailed calorimetric measurements. Using high-temperature oxide-melt drop-solution calorimetry at 975 K with sodium molybdate as the solvent, we have determined the standard enthalpies of formation from constituent sulfates ($\Delta H_{f,\text{sul}}^\circ$), oxides ($\Delta H_{f,\text{ox}}^\circ$) and elements ($\Delta H_{f,\text{ele}}^\circ$) of a polyhalite sample with the composition of $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 1.95\text{H}_2\text{O}$ from the Salado formation at the WIPP site. The obtained results are: $\Delta H_{f,\text{sul}}^\circ = -152.5 \pm 5.3$ kJ/mol, $\Delta H_{f,\text{ox}}^\circ = -1926.1 \pm 10.5$ kJ/mol, and $\Delta H_{f,\text{ele}}^\circ = -6301.2 \pm 9.9$ kJ/mol. Furthermore, based on the estimated formation entropies of polyhalite, its standard Gibbs free energy of formation has been derived to be in the range of -5715.3 ± 9.9 kJ/mol to -5739.3 ± 9.9 kJ/mol. These determined thermodynamic properties provide fundamental parameters for modeling the stability behavior of polyhalite in salt repositories.

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1. Introduction

Salt formation can potentially serve as a geological repository for storing used nuclear fuel and high level waste. It has several advantages in hosting radioactive waste such as impermeability, self-sealing, and good thermal conductivity [1]. The Waste Isolation Pilot Plant (WIPP) located in Carlsbad, New Mexico, is one such salt repository. Polyhalite [ideal composition: $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$], as one of the hydrous minerals coexisting with halite in evaporates [2], is an important minor component in salt formations such as WIPP [3,4]. Heat accumulating in the site due to radioactive decay of the stored nuclear waste [5–7] may decompose the hydrous phases, as shown by their thermal decomposition experiments [3,8–10]. The thermal behavior of polyhalite indicates its decomposition in the temperature range of ~500–650 K with the release of water and the formation of anhydrous langbeinite solid solutions [9]. However, despite the extensive thermal analyses of polyhalite, there is little knowledge about its fundamental thermodynamic properties such as the standard enthalpies and Gibbs free energies of formation [4,9,11–14]. In this study, we collected a natural polyhalite sample with the composition $\text{K}_2\text{Ca}_2\text{Mg}$

$(\text{SO}_4)_4 \cdot 1.95\text{H}_2\text{O}$ from the Salado formation at the WIPP site [9] and conducted high-temperature oxide-melt drop-calorimetric measurements on the sample to derive its enthalpies of formation from constituent sulfates, oxides and elements. Based on the estimated formation entropies of polyhalite from literature, its standard Gibbs free energies of formation have also been derived. In addition to its nuclear waste disposal relevance, polyhalite has commercial applications as organic fertilizers [15], since it contains important nutrient elements, K, Ca and Mg, in a form without the presence of chlorides. Knowledge about the thermodynamic properties of polyhalite may also help develop more effective strategies for its agricultural utilization.

2. Experimental methods

2.1. Materials and sample characterization

A polyhalite sample in the form of a fine-grained massive chunk was collected from the Salado formation at the WIPP site. Its detailed description can be found in our recent structural study of this sample using high-temperature synchrotron X-ray diffraction (XRD) [9]. The composition of the polyhalite sample was determined by electron probe microanalysis (EPMA) (Cameca SX100 electron microprobe with an accelerating voltage of

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15 keV and a beam current of 20 nA), and its homogeneity was confirmed with elemental mapping. More specifically, the contents of K, Mg, Ca and S were measured by wavelength dispersive spectroscopy with KAlSi_3O_8 , MgO and CaSO_4 (for both Ca and S) as the standards, respectively. Oxygen was not directly measured, and the chemical formula was calculated assuming an oxygen stoichiometry. In addition, to derive the standard enthalpies of formation of polyhalite, two standard samples, MgSO_4 and CaSO_4 , were obtained by heating $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ chemicals (Alfa Aesar, analytical grade), respectively, at ~ 773 K in a furnace overnight.

2.2. Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed simultaneously by heating ~ 20 mg of the polyhalite sample in a flowing argon atmosphere (40 mL/min) to 1073 K with a rate of 3 K/min in a Netzsch 449 simultaneous thermal analyzer instrument. Detailed procedures have been described previously [16].

2.3. High-temperature oxide-melt drop-solution calorimetry

High-temperature oxide-melt drop-solution calorimetric measurements were conducted using a Calvet-type Setaram Alexsys-800 twin microcalorimeter at Los Alamos National Laboratory [17]. Powdered samples were hand-pressed into small pellets of ~ 5 mg in mass. Each pellet was dropped from room temperature into molten solvent [~ 20 g of sodium molybdate ($3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$)] in a Pt crucible at 975 K. The sodium molybdate solvent was prepared from a mixture of sodium molybdate dihydrate (ACS reagent grade, EMD) and molybdenum trioxide (ACS reagent grade, J.T. Baker) in a weight ratio of 100:19.83. The calorimeter was calibrated using the heat contents of ~ 5 mg $\alpha\text{-Al}_2\text{O}_3$ (Sigma-Aldrich, 99.9%) pellets [18]. Flushing O_2 gas at ~ 50 mL/min through the calorimeter chamber assisted in maintaining a constant gas environment above the solvent [19]. Dissolution of oxides, hydrates and sulfates were previously demonstrated in this solvent [16,20–22]. Upon rapid and complete dissolution of the sample, the enthalpy of drop solution, ΔH_{ds} , was obtained. Finally, using appropriate thermochemical cycles, the enthalpies of formation of polyhalite from constituent sulfates ($\Delta H_{\text{f,sul}}^\circ$), oxides ($\Delta H_{\text{f,ox}}^\circ$), and elements ($\Delta H_{\text{f,ele}}^\circ$), were calculated.

3. Results and discussion

The homogeneity and stoichiometry of the polyhalite sample were analyzed by EPMA (Fig. 1; Table 1). As shown in Table 1, the determined K: Ca: Mg: S ratio is 2.06: 2.12: 1.07: 4, which is close to the ideal stoichiometry of K: Ca: Mg: S = 2: 2: 1: 4. Given the uncertainties associated with EPMA analysis, we assume the sample adopts this ideal stoichiometry for later thermochemical calculations (The small compositional deviations would not significantly affect the calorimetric results).

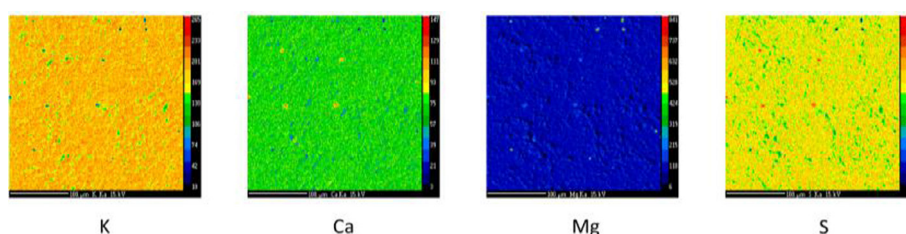
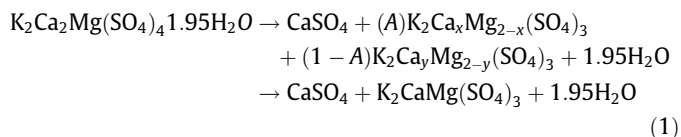


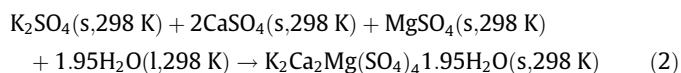
Fig. 1. EPMA elemental maps of the polyhalite sample (from left to right: K, Ca, Mg and S).

Stepwise decomposition and recombination of polyhalite were observed by *in situ* high-temperature synchrotron XRD measurements [9]:



Instead of directly forming the triple salt [$\text{K}_2\text{CaMg}(\text{SO}_4)_3$] via dehydration, polyhalite first decomposed into two langbeinite solid solutions phases [$\text{K}_2\text{Ca}_x\text{Mg}_{2-x}(\text{SO}_4)_3$] and [$\text{K}_2\text{Ca}_y\text{Mg}_{2-y}(\text{SO}_4)_3$], and these two phases were then combined into the triple salt at higher temperatures. This stepwise thermal behavior was reflected in TGA and DSC curves. As shown in Fig. 2, there was no further weight loss when the temperature was above ~ 650 K (the TGA curve), implying completion of the dehydration at this temperature. Thus, the water content of the polyhalite sample was determined to be 1.95 (± 0.02) mole per formula unit based on the mass change due to the removal of the water. This water is an integral part of the polyhalite structure and serves as a stabilizing species for polyhalite, as reflected by the large endothermic DSC peak associated with the dehydration process [Fig. 2, peak (1)]. On further heating, although there was no additional weight loss, there appeared to be an exothermic DSC peak in the temperature range of ~ 650 – 750 K [Fig. 2, peak (2)] and another smaller endothermic peak around ~ 875 K. These thermal effects are probably associated with the complex structural behavior displayed by the two langbeinite solid solution phases formed upon polyhalite dehydration, as revealed by our high-temperature synchrotron XRD experiments [9].

The enthalpy of drop solution, ΔH_{ds} , of the polyhalite sample in molten sodium molybdate at 975 K was measured to be 704.53 ± 4.72 kJ/mol (the average of seven measurements, Table 2). To derive the enthalpy of formation of polyhalite from its constituent sulfates, we also determined the ΔH_{ds} values of CaSO_4 and MgSO_4 standards. Sample pellets of both standard phases were dropped into the calorimeter at the same condition as for polyhalite. ΔH_{ds} values of CaSO_4 and MgSO_4 were determined to be 110.0 ± 0.4 kJ/mol (the average of four measurements, Table 2) and 44.1 ± 1.3 kJ/mol (the average of three measurements, Table 2), respectively. ΔH_{ds} of K_2SO_4 in molten $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ at 975 K was previously measured to be 153.4 ± 1.8 kJ/mol [20]. The formation reaction of polyhalite from its constituent sulfates is written as:



Using appropriate thermochemical cycles (Table 2), the enthalpy of reaction (2), $\Delta H_{\text{f,sul}}^\circ$, is derived to be -152.5 ± 5.3 kJ/mol. This large negative value suggests that polyhalite is stable in enthalpy relative to its constituent sulfates plus water at standard conditions. However, since this reaction involves the incorporation of liquid water into the polyhalite structure, the entropy of

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