Thermal behavior of polyhalite: A combined high-temperature synchrotron XRD and calorimetric study

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As an accessory mineral in marine evaporites, polyhalite, K$_2$MgCa$_2$(SO$_4$)$_4$·2H$_2$O, coexists with halite (NaCl) in salt formations, which have been considered as potential repositories for permanent storage of high-level nuclear wastes. However, because of the heat generated by radioactive decays in the wastes, polyhalite may dehydrate, and the released water will dissolve its neighboring salt, potentially affecting the repository integrity. Thus, studying the thermal behavior of polyhalite is important. In this work, a polyhalite sample containing a small amount of halite was collected from the Salado formation at the WIPP site in Carlsbad, New Mexico. To characterize its thermal behavior, in situ high-temperature synchrotron X-ray diffraction was conducted from room temperature to 1066 K with the sample powders sealed in a silica-glass capillary. At ~506 K, polyhalite started to decompose into water vapor, anhydrite (CaSO$_4$) and two langbeinite-type phases, K$_2$Ca$_{x}$Mg$_{2-x}$(SO$_4$)$_3$, with different Ca/Mg ratios. XRD peaks of the minor halite disappeared, presumably due to its dissolution by water vapor. With further increasing temperature, the two langbeinite solid solution phases displayed complex variations in crystallinity, composition and their molar ratio and then were combined into the single-phase triple salt, K$_2$CaMg(SO$_4$)$_3$, at ~919 K. Rietveld analyses of the XRD data allowed determination of structural parameters of polyhalite and its decomposed anhydrite and langbeinite phases as a function of temperature. From the results, the thermal expansion coefficients of these phases have been derived, and the structural mechanisms of their thermal behavior been discussed. In addition, to determine stability relations, standard enthalpies of formation of polyhalite from constituent oxides and elements were measured using high-temperature oxide-melt drop-solution calorimetry.