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Thermodynamic characterization of synthetic lead-arsenate apatites with different halogen substitutions

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Abstract

Thermodynamic parameters have been measured for synthetic analogs of the mimetite-group minerals $Pb_5(AsO_4)_3X$ (X = OH, Cl, Br, I) belonging to the apatite supergroup. Phases precipitated from aqueous solutions under ambient conditions with well characterized structures and compositions were studied. For each phase, dissolution enthalpy was experimentally determined by oxide melt drop solution calorimetry in a molten solvent of sodium molybdate ($3Na_2O{\cdot}4MoO_3$) at 976 K. The enthalpy of formation from the elements $\Delta H^\circ_{f,el}$ was calculated using thermochemical cycles and was −3030.6 ± 11.5, −3026.6 ± 15.8, −2967.6 ± 25.0, and −2993.1 ± 12.2 kJ/mol for $Pb_{5.00}(AsO_4)_{3.00}OH_{0.86}(CO_3)_{0.07}$, $Pb_{5.00}(AsO_4)_{3.00}Cl_{0.80}(CO_3)_{0.10}$, $Pb_{5.00}(AsO_4)_{3.00}Br_{0.80}(CO_3)_{0.10}$, and $Pb_{5.00}(AsO_4)_{3.00}I_{0.45}OH_{0.35}(CO_3)_{0.10}$, respectively. These $\Delta H^\circ_{f,el}$ values exhibit typical trends for apatites: they increased (were less negative) with the increasing molar mass and ionic radius of X and decreased with the electronegativity and ionization energy of X. The compilation and comparison of data for Ca-, Pb-, P-, and As-apatites revealed correlations indicating that thermodynamic enthalpic stability is largely influenced by chemical factors (e.g., differences in electronegativities of the elements, ionization energy, or ionic characteristics of the bonds) and to a lesser extent by physical and geometric parameters in the crystal structure related to the mass and size of the X anion. Using the correlations, it was possible to estimate the value of hitherto unknown $\Delta H^\circ_{f,el}$ for $Pb_5(AsO_4)_3F$, −3144.3 ± 66.5 kJ/mol. The observed relationships apply to the entire apatite supergroup and can be used to predict the values of $\Delta H^\circ_{f,el}$ for phases that have not been studied experimentally. The new data on environmentally significant phases will contribute to the modeling of mineral-water interactions, particularly for potential use in the remediation of soils and wastes contaminated with Pb and As and in the immobilization of radioactive waste containing I-129.

Keywords: Lead apatite, lead arsenates, calorimetry, enthalpy, mimetite, iodoapatites