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Estimation of missing third-law standard entropy of apatites using the optimized Volume-based Thermodynamics

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The standard absolute entropies of many minerals and mineral-based inorganic materials are unknown, thereby precluding a complete insight into their thermodynamic stability. This includes many apatites. The Apatite supergroup is one of the largest groups of minerals. Consequently, they are an incomparable testing ground for finding regularities in the variation of their thermodynamic function of state, e.g., standard entropy ($S°$). In the early 2000's Jenkins and Glasser [1] showed that the formula unit volume alone, V_m, can be used to estimate the standard entropy for any inorganic compound.

It was recently indicated that in terms of their thermodynamic properties, the apatite supergroup splits into distinct subgroups (populations) [2]. These subgroups are formed by $Me_{10}(AO_4)_6X_2$ with the same Me^{2+} cations (e.g., Pb^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}) and tetrahedral AO_4^{3-} anions (e.g., A=P, As, V), but with different anions at the X position (e.g., F^-, Cl^-, Br^-, I^-, OH^-). We found strong linear relationships between $S°$ of apatites and their V_m observed within these subgroups. A system of linear relationships (calibrated with existing experimental data) indicating high positive correlations within selected subgroups of apatites is presented in Fig. 1.

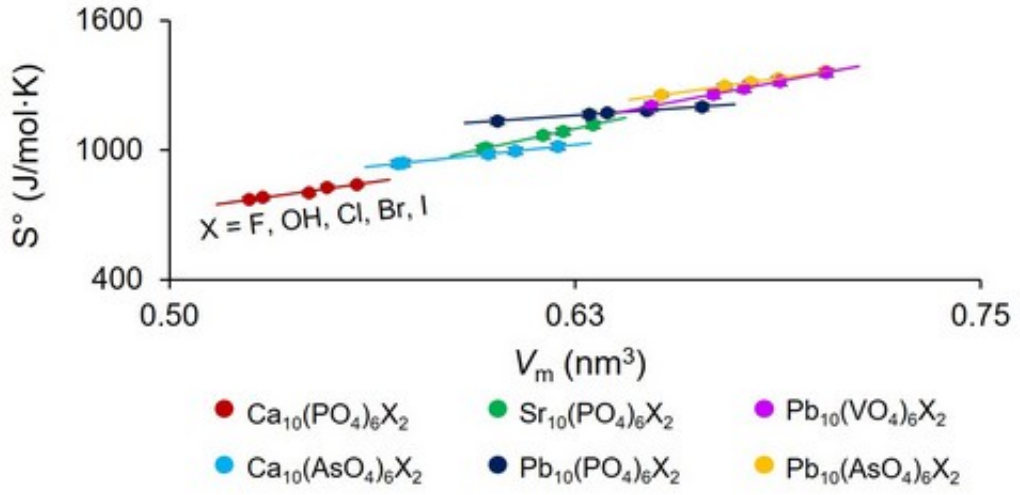

Fig. 1 Standard entropy ($S°$) vs. formula unit volume (V_m)for selected apatite subgroups. Errors bars are within the marker.

Table 1. Selected estimated standard entropies ($S°$) and calculated formation entropies ($\Delta S°_{f, el}$)of iodine apatites.

Apatite	Estimated $S°$ (J/mol·K)	$\Delta S°_{f, el}$ (J/mol·K)
$Ca_{10}(PO_4)_6I_2$	840.7	-2412.8
$Sr_{10}(PO_4)_6I_2$	1117.2	-2264.2
$Pb_{10}(PO_4)_6I_2$	1201.1	-2271.4
$Ca_{10}(AsO_4)_6I_2$	1016.1	-2205.0
$Pb_{10}(AsO_4)_6I_2$	1364.5	-2075.5
$Pb_{10}(VO_4)_6I_2$	1359.6	-2040.0

Using the new estimated with high accuracy $S°$ values, it is possible to calculate the Gibbs energy of formation and plot stability fields for apatites for which this has not been possible so far. Financial support for the research was provided to B.P. by the Polish National Science Centre (NCN) grant No. 2017/27/N/ST10/00776.

References:

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