Thermodynamics of synthetic halogenated mimetites

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The structure of apatites, corresponding to the general chemical formula $M_5(AO_4)_3X$, is very flexible and allows for numerous substitutions [1]. The thermodynamic data for As – bearing apatites are still sparse. In this work five analogs of halogenated mimetites $Pb_5(AsO_4)_3X$ (X = F, Cl, Br, I, OH) where synthesized by a wet chemical method and characterized via PXRD, SEM/EDS, FTIR and Raman Spectroscopy. The standard entropies, $S^o_{298.15}$, and the specific heats capacities, $C^o_{p,\ 298.15}$, of the phases in question (Tab. 1) were experimentally derived from low-temperature heat capacity measurements acquired with a Physical Property Measurement System (PPMS) in the temperature range 2 K < T < 300 K [2]. Additionally, differential scanning calorimetry (DSC) measurements with a Perkin Elmer Diamond DSC were performed in the temperature range 273.15 K < T < 473.15 K [3].

Sample	$S^o_{298.15}$ ($J \cdot mol^{-1} \cdot K^{-1}$)	$C^o_{p,\ 298.15}$ ($J \cdot mol^{-1} \cdot K^{-1}$)
$Pb_5(AsO_4)_3F$	573.2 ±4.0	403.4±1.2
$Pb_5(AsO_4)_3Cl$	584.4 ±4.0	413.5±0.94
$Pb_5(AsO_4)_3Br$	590.1 ±4.1	413.0±0.98
$Pb_5(AsO_4)_3I$	608.3 ±4.3	425.3±0.88
$Pb_5(AsO_4)_3OH$	574.9 ±4.0	403.7±1.0

Table 1: Standard entropy and specific heat capacity of halogenated mimetites. Uncertaintity of one SD.

The novelty of the research stems from the fact that for the first time $S^o_{298.15}$ and $C^o_{p,\ 298.15}$ of these apatites were determined experimentally. Linear increase of the $S^o_{298.15}$ values with atomic mass of the halogen is observed ($R^2 > 0.95$). Hydroxyl substituted phase does not follow the trend. These high quality data will be used for further thermodynamic calculations. This work is funded by NCN research grant No. 2017/27/N/ST10/00776.

[1] Elliot (1994) Elsevier, Amsterdam. [2] Dachs & Bertoldi (2005) *Eur. J. Mineral.* **17**, 251-261. [3] Benisek et al. (2012) *Am. Mineral.* **97**, 657-660.