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# Low-temperature calorimetric and magnetic data for natural end-members of the axinite group

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## Abstract

The low-temperature heat capacities of natural near end-member minerals (about 95 mol%, except tinzenite of about 34 mol% on average) of the axinite group, previously characterized in detail by means of powder and single-crystal X-ray diffraction, electron microprobe, and Mössbauer spectroscopy, were measured by heat-pulse calorimetry using the Physical Properties Measurement System (Quantum Design) at temperatures between 5(2) and 300 K. From these data, the following entropy values [in J/(mol·K)] of the natural samples at 298.15 K were derived: $S_{298,\text{magnesioaxinite}} = 696.3 \pm 1.1$, $S_{298,\text{ferroaxinite}} = 743.5 \pm 3.5$, $S_{298,\text{manganaxinite}} = 737.5 \pm 2.6$, and $S_{298,\text{tinzenite}} = 758.1 \pm 2.8$. For the end-member compositions, the corrected heat capacities at 298.15 K and standard third-law entropies of the axinites are [all in J/(mol·K)]:

$C_{P\text{magnesioaxinite}}^{\circ} = 827.5 \pm 1.5$ and $S_{\text{magnesioaxinite}}^{\circ} = 693.7 \pm 1.1$,
$C_{P\text{ferroaxinite}}^{\circ} = 841.8 \pm 3.3$ and $S_{\text{ferroaxinite}}^{\circ} = 749.6 \pm 3.5$,
$C_{P\text{manganaxinite}}^{\circ} = 849.1 \pm 2.5$ and $S_{\text{manganaxinite}}^{\circ} = 737.8 \pm 2.6$, and
$C_{P\text{tinzenite}}^{\circ} = 841.6 \pm 2.6$, $S_{\text{tinzenite}}^{\circ} = 754.0 \pm 2.8$.

The standard entropies of manganaxinite and tinzenite include contributions of 1.9 and 4.3 J/(mol·K) for the range 0–5 K evaluated based on a Schottky anomaly fitted to the low-$T$ $C_P$ values of these axinites. The lowest measured heat capacities of ferroaxinite indicate that a lambda-type $C_P$ anomaly should exist between 0 and 2 K. Its likely contribution to the standard entropy was estimated as ~5.2 J/(mol·K). A low-temperature $C_P$ anomaly below 15 K for ferroaxinite is well-explained by ferromagnetic ordering, whereas for manganaxinite by uncompensated antiferromagnetic ordering, and for tinzenite by pure antiferromagnetic ordering.

**Keywords:** Axinite group minerals, chemical composition, heat capacity, heat-pulse calorimetry, magnetic ordering, low-temperature anomaly